Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thermochimica Acta 423 (2004) 149–157
thermochimica acta
www.elsevier.com/locate/tca

Correlation of thermal and spectral properties of zinc(II) complexes of pyridinecarboxylic acids with their crystal structures

Zuzana Vargová [a,*], Vladimír Zeleòák [a], Ivana Císaøová [b], Katarína Györyová [a]

[a] *Department of Inorganic Chemistry, Institute of Chemical Sciences, University of P.J.Š afárik, Moyzesova 11, 041 54 Koš ice, Slovak Republic*
[b] *Department of Inorganic Chemistry, Faculty of Science Charles University, Hlavova 2030, Prague, Czech Republic*

Received 26 June 2003; received in revised form 28 January 2004; accepted 16 March 2004

Abstract

Three zinc(II) pyridinecarboxylate complexes, namely $[Zn(nicot)_2(H_2O)_4]$, $[Zn(picol)_2(H_2O)_2]\cdot 2H_2O$ and $[Zn(dipicolH)_2]\cdot 3H_2O$, where nicot = nicotinate, picol = picolinate and dipicolH = hydrogenpicolinate were prepared and characterised by the methods of the thermal analysis (TG/DTG, DTA), infrared spectroscopy and elemental analysis. The structure of the complex $[Zn(nicot)_2(H_2O)_4]$ was studied by the single crystal XRD. The correlation of the thermal and spectral properties of the complexes with their structures is discussed in the study. The correlation of the spectral data with the structures leads to ambiguous results while the accord and coherence was found between thermal properties and structures of the complexes for both steps of the thermal decomposition (dehydratation and pyrolysis of organic ligand).

Keywords: Zinc complexes; Thermal decomposition; Structures; Nicotinic acid; Picolinic acid; Dipicolinic acid

---

1. Introduction

Pyridinecarboxylic acids (nicotinic, picolinic or dipicolinic acid; see Scheme 1), are beneficial compounds for human organism and they are involved in several essential biochemical processes. Nicotinic acid (pyridine 3-carboxylic acid) is converted to nicotinamide adenine nucleotide (NAD) which serves as intermediate in two-electron transfer in organism [1]. Effect of insulin in the body is optimised by glucose tolerance factor (GTF), formulated by two nicotinic acid ligands coordinated to chromium(III) ion [2]. Moreover to these, nicotinic acid is used in clinical applications as a lipid-altering agent preventing atherosclerosis and significantly reducing cardiovascular risks [3,4]. Nicotinic acid is also applied in the skin following topical applications as vasodilator of the peripheral blood capillaries [5] or in the treatment of ailment pellagra [6,7]. In this line, zinc picolinate (zinc(II) pyridine 2-carboxylate) has healing effect against Herpes Simplex virus [8] and recent investigations of the dipicolinic acid show, that this acid prevents the oxidation of low density lipoprotein, the substance, which oxidation is involved in the pathogenesis of arteriosclerosis [9].

The pyridinecarboxylic acids can interact with a number of metal ions when they are present in the body. One of the ways to understand chemistry and properties of these acids is to study the structures and physicochemical properties of their metal complexes. In this frame we have described in our previous works physico-chemical properties, crystal structures and biological activity zinc(II) complexes of aliphatic carboxylic acids [10]. As a part of our ongoing research in this area this paper deals with the Zn(II) complexes containing aromatic carboxylic ligands nicotinate (further denoted as nicot), picolinate (further denoted as picol) and hydrogendipicolinate (further denoted as dipicolH).

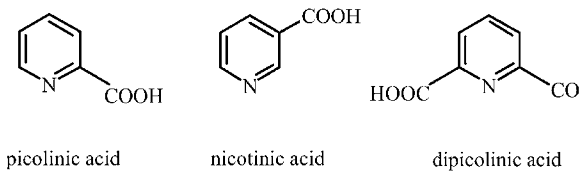
2. Experimental

Nicotinic, picolinic, dipicolinic acid were obtained from Aldrich and used without further purification. Zinc(II) acetate dihydrate, which was used as reactant in the synthesis,

---

[*] Corresponding author.
E-mail address: vargovaz@kosice.upjs.sk (Z. Vargová).

0040-6031/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2004.03.016



Scheme 1.

was prepared from zinc(II) hydroxide and acetic acid produced in Lachema.

2.1. Synthesis

2.1.1. [Zn(nicot)$_2$(H$_2$O)$_4$] (*I*)

Nicotinic acid (0.64 g; 5.2 mmol) was dissolved in 70 cm^3 of hot water (80 °C) and then cooled to room temperature. This solution was then added to the solution of zinc acetate (0.45 g; 2.6 mmol). The mixture was stirred for a few minutes, filtered and stored at room temperature. White crystals of (**I**) were formed after 2 days. The crystals were filtered off and air dried. Anal. Calc. for $C_{12}H_{18}N_2O_8Zn$: C, 37.82; H, 4.23; N, 7.34; Zn, 17.15%. Found: C, 38.50; H, 3.89; N, 6.91; Zn, 17.37%.

2.1.2. [Zn(picol)$_2$(H$_2$O)$_2$]·2H$_2$O (*II*)

The aqueous solution (50 ml) of picolinic acid (0.64 g; 5.2 mmol) was added to the solution of zinc acetate (0.45 g; 2.6 mmol). The mixture was stirred for a few minutes, then filtered and filtrate as a clear solution was stored at the room temperature. White crystals of (**II**) appeared after 4 days. The crystals were filtered off and air dried. Anal. Calc. for $C_{12}H_{18}N_2O_8Zn$: C, 37.57; H, 4.73; N, 7.30; Zn, 17.04%. Found: C, 37.78; H, 4.21; N, 7.09; Zn 17.27%.

2.1.3. [Zn(dipicolH)$_2$]·3H$_2$O (*III*)

Dipicolinic acid (0.73 g; 4.4 mmol) was dissolved in 100 cm^3 of hot water (90 °C). After cooling this solution was added to the water solution of $Zn(CH_3COO)_2$ (0.38 g; 2.2 mmol). The mixture was stirred for a few minutes, filtered and the filtrate was stored at the room temperature. After 2 days white crystals of (**III**) crystallised. The crystals were filtered off and air dried. Anal. Calc. for $C_{14}H_{16}N_2O_{11}Zn$: C, 37.07; H, 3.55; N, 6.18; Zn, 14.41%. Found: C, 36.74; H, 2.77; N, 5.90; Zn, 15.32%.

2.2. Instrumentation

Elemental analyses (C, H, N) were carried out on a Perkin-Elmer 2400 automatic analyser. Zinc content was determined complexometrically. IR spectra of the complexes were recorded on a Perkin-Elmer 781 spectrophotometer in the region 4000–600 cm^{-1} as KBr discs. The thermal analyses (TG/DTG and DTA) were carried out using a Derivatograph OD 102 in ceramic crucibles, static air atmosphere, heating rate 10 K min^{-1} and sample mass 50 mg.

2.3. Crystal structure solution and refinement of the complex (*I*)

Diffraction experiments were performed with a Nonius KappaCCD diffractometer (Mo Kα radiation, λ = 0.7107 Å) equipped with a graphite monochromator. Data were corrected for Lorentz and polarisation factors, the absorption correction was carried on based on symmetry related measurement [11]. The details of the data collection and refinement are summarised in Table 1. The zinc atom

Table 1
Crystal data and structure refinement

Empirical formula	$C_{12}H_{16}N_2O_8Zn$
Formula weight	381.64
Crystal parameters	
Crystal shape	Plate
Crystal colour	Colourless
Crystal size (mm)	0.35 × 0.3 × 0.2
Crystal system	Monoclinic
Space group	*C*2/*m* (no. 12)
Unit-cell dimensions	
a (Å)	14.1670(5)
b (Å)	6.8240(2)
c (Å)	8.4630(3)
β (°)	117.995(2)
V_c (A^{-3})	722.43(4)
Molecules per cell, Z	2
D_x (g cm^{-3})	1.754
Measurement of intensity data	
Instrument	Nonius KappaCCD
Temperature (K)	150
Radiation X (Å)	0.71070
Monochromator	Graphite
Scan mode	ö and ù scans
θ range (°)	2.73–27.47
Reflections measured	5210
Independent reflections; R_{int}	893; 0.0315
Reflections observed	884 ($I \geq 2a(I)$)
Linear absorption coefficient, μ (mm^{-1})	1.754
Absorption correction	Multiscans
T_{min}; T_{max}	0.732; 0.879
F(0 0 0)	392
Reflections for cell measurement	3201
Indices	
h	−17 to 18
k	−8 to 8
l	−9 to 10
Refinement	
Refinement-method	Full-matrix least-squares on F^2
Parameters	77
Goodness-of-fit on F^2	1.154
R_1	0.0187 (observed); 0.0188 (all)
wR_2	0.0501 (observed); 0.0502 (all)
Max./min. height in final difference synthesis (e Å^{-3})	0.377/−0.348

Table 2
Bond distances (Å) and angles (°) in the complex $[Zn(nicot)_2(H_2O)_4]$

Bond distances	
Zn–O1	2.1186(9)
Zn–N1	2.147(2)
O2–C6	1.260(2)
O3–C6	1.256(2)
N1–C1	1.340(2)
N1–C5	1.350(2)
C1–C2	1.390(2)
C2–C3	1.392(2)
C2–C6	1.506(2)
C3–C4	1.389(3)
C4–C5	1.384(3)
Bond angles	
O1–Zn–O1[a]	90.88(6)
O1–Zn–O1[b]	89.12(6)
O1–Zn–O1[c]	180.00
O1–Zn–N1[b]	88.74(4)
O1–Zn–N1	91.26(4)
N1–Zn–N1[c]	180.0
C1–N1–C5	117.6(2)
N1–C1–C2	123.4(2)
C1–C2–C3	118.6(2)
C1–C2–C6	119.2(2)
C3–C2–C6	122.3(2)
C4–C3–C2	118.5(2)
C3–C4–C5	119.3(2)
N1–C5–C4	122.7(2)
O2–C6–O3	125.2(2)
O2–C6–C2	116.5(2)
O3–C6–C2	118.4(2)

[a] $x, -y, z$.
[b] $-x, y, -z$.
[c] $-x, -y, -z$.

was located from Patterson synthesis using SHELXS97 program [12]. Fourier maps, calculated using SHELXL97 [13], enabled the location of all non-hydrogen atoms. Full-matrix least-squares refinements on F^2 were carried out with anisotropic thermal parameters. After checking their presence in difference map, the hydrogen atoms bonded to carbon atoms were introduced to their calculated positions and kept riding on parent atom with isotropic thermal parameters $U_{iso} = 1.2U_{eq}$ of the parent atom [13]. The hydrogen atoms of water molecules were obtained from difference Fourier synthesis and refined freely. The final reliability values are summarised in Table 1 while selected bond distances and angles are listed in Table 2. The figures were made using DIAMOND software [14]. The rest of the crystallographic data has been submitted as supplementary material to the Cambridge Crystallographic Data Centre, as the supplementary material No. CCDC 225794. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. Synthesis

In the present study the compounds $[Zn(nicot)_2(H_2O)_4]$, $[Zn(picol)_2(H_2O)_2]\cdot 2H_2O$ and $[Zn(dipicolH)_2]\cdot 3H_2O$ were prepared by reaction of water solution of zinc(II) acetate with respective pyridinecarboxylic acid. The zinc(II) acetate was used in order to investigate possibility of the preparation of mixed-ligand zinc(II) complexes, containing both acetate as well as pyridinecarboxylate ligands. We did not observe the formation of mixed-ligand complexes from water solution at pH ∼6. However, the formation of such complex, $Zn(nicot)(ac)_2$, was observed from ethanolic solution [15].

The prepared complexes are insoluble in water at room temperature and they crystallise after overreaching of their solubility product. The formation of the complexes with the same composition as described in our work was also observed from aqueous solution using not zinc(II) acetate but sulfate, nitrate, formate orbutyrate [16–20].

3.2. Description of the structure of the complex $[Zn(nicot)_2(H_2O)_4]$

A view of the structure of the complex $[Zn(nicot)_2(H_2O)_4]$ is shown in Fig. 1, selected bond distances and angles are in Table 2. The complex crystallises in the monoclinic space group *C*2/*m* with two formula units in the unit cell. Zinc atom, which is octahedrally coordinated, lies in the special position on crystallographic inversion centre. Nicotinate anions occupy special positions on mirror plane. Four oxygen atoms of the water molecules form equatorial plane of the octahedron around zinc (distance Zn–O = 2.1186(9) Å, 4×), while two nitrogen atoms of nicotinate anions are in

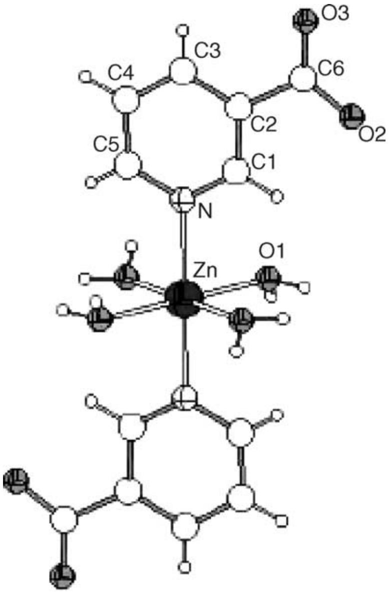


Fig. 1. The structure of the complex $[Zn(nicot)_2(H_2O)_4]$.

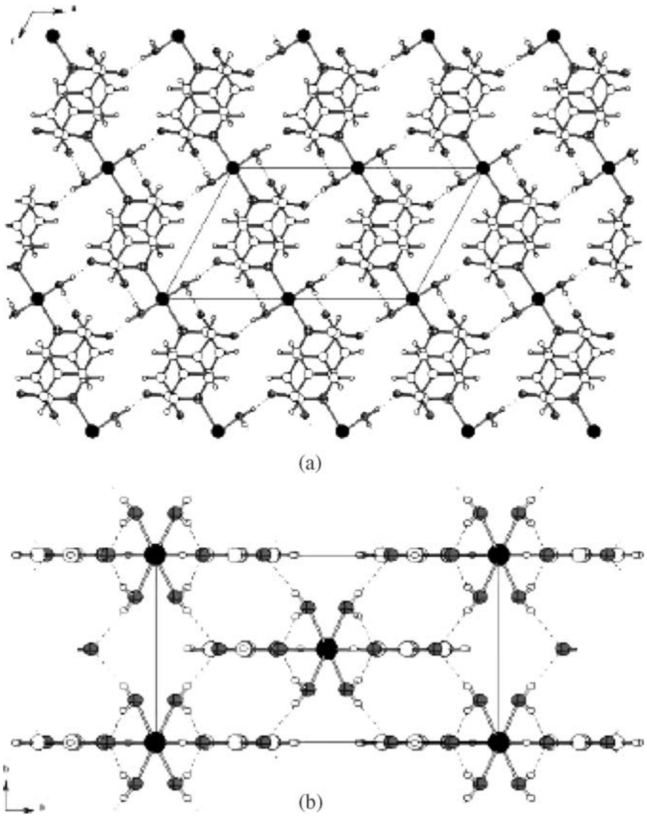


Fig. 2. Hydrogen bonding geometry in the complex $[Zn(nicot)_2(H_2O)_4]$. Hydrogen bonds are displayed as dashed lines. (a) View along *b* axis; (b) view along *c* axis. The possible formation of π–π stacking interactions can be observed in both views.

the apical positions of this slightly tetragonally deformed octahedron (Zn–N bond lengths are 2.147(2) Å, 2×). The angles in the octahedron are near to ideal 90° values (see Table 2). Due to regular delocalisation of electron density in the carboxylate anion the C6–O2 and C6–O3 bond lengths are the same within an experimental uncertainties (1.260(2) and 1.256(2) Å, respectively).

Molecules of the complex $[Zn(nicot)_2(H_2O)_4]$ are held together by intermolecular hydrogen bonds, formed by oxygen atoms of the carboxylate groups and hydrogen atoms of water molecules (see Fig. 2). Considering these hydrogen bonds the structure can be viewed as infinite three-dimensional framework. The details of hydrogen bonding geometry are in Table 3. Moreover, the distances between pyridine rings, situated in neighbouring mirror planes of are 3.412 Å, which may indicate weak spatial π–π stacking interactions in the *b* direction (Fig. 2).

Table 3
Intermolecular hydrogen bonds in the complex (**I**)

D–H	D–H (Å)	H···A (Å)	DHA (°)	D···A (Å)	A
O1–H6	0.81(2)	1.92(2)	160(2)	2.693(2)	O2 [*x*, *y*, −1+z]
O1–H7	0.78(2)	1.93(2)	177(2)	2.708(1)	O3 [1/2 − *x*, 1/2 − *y*, 1 − *z*]

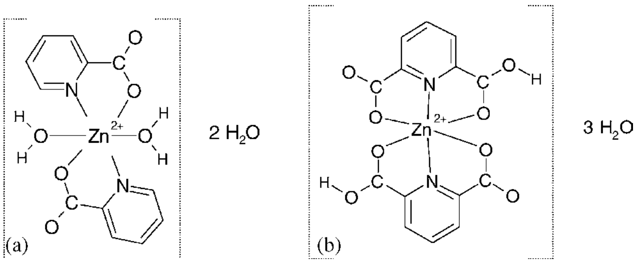


Fig. 3. The molecular diagram of the complex (a) $[Zn(picol)_2(H_2O)_2]\cdot 2H_2O$ and (b) $[Zn(dipicolH)_2]\cdot 3H_2O$.

The same structural type was found, e.g. for cobalt nicotinate, $[Co(nicot)_2(H_2O)_4]$ [21] prepared by hydrothermal synthesis. On contrary hydrothermal conditions used in the synthesis of zinc(II) complex lead to the anhydrous complex $[Zn(nicot)_2]_n$. In this complex the oxygen atoms of carboxylate groups are also involved in the coordination to zinc which led to the formation of 2D polymeric sheets [22].

3.3. *Description of the structures of $[Zn(picol)_2(H_2O)_2]\cdot 2H_2O$ (**II**) and $[Zn(dipicolH)_2]\cdot 3H_2O$ (**III**)*

Only a brief description of the structures of these complexes [23,24] as a reference point for the discussion of the thermal decompositions and spectral data is given below. The molecular diagrams of the complexes are shown in Fig. 3. In zinc(II) picolinate terahydrate the picolinate anion coordinates as chelate through nitrogen atom of pyridine ring as well as one of the carboxylate oxygen of the carboxylate group (see Fig. 3a) [23]. The second carboxylate oxygen remains uncoordinated. The octahedral geometry of zinc(II) atom is completed by two water molecules. The additional two water molecules are uncoordinated and involved in hydrogen bonding geometry.

In the complex $[Zn(dipicolH)_2]\cdot 3H_2O$ one of the carboxylic groups of dipicolinic acid is deprotonated ($–COO^-$), whereas the second one remains acidic (–COOH). The dipicolinate anionsin this complex are tridentate, coordinated through nitrogen atom of pyridine ring and oxygen atoms of both carboxylate and carboxylic group (see Fig. 3b) [24]. The water molecules are uncoordinated and involved in hydrogen bonds.

3.4. *IR spectra and structure correlation*

The IR spectra confirmed the presence of water as well as organic moieties in the complexes. The most important spectral bands are listed in Table 4.

For the correlation of the infrared spectra with the structures of metal carboxylates the difference between the asymmetric and symmetric carboxylate stretches ($\Delta = \nu_{as}(COO^-) - \nu_s(COO^-)$) is often used. This value is approximately $170\,cm^{-1}$ for ionic carboxylate group, i.e. group which does not interact strongly with the metal ion

Table 4
Characteristic absorption bands in the IR spectra of the prepared complexes

Assignment	Compound		
	[Zn(nicot)$_2$(H$_2$O)$_4$]	[Zn(picol)$_2$(H$_2$O)$_2$]·2H$_2$O	[Zn(dipicolH)$_2$]·3H$_2$O
ν(O–H)$_{water}$	3300s, broad	3400s, broad	3400s, broad
ν(C=O)	–	–	1695m
δ(H$_2$O)	1630s	1650s	1630s
ν_{as}(COO–)	1580s	1580s	1590s
ν(C=C), ν(C=N)	1600s, 1520m	1600s, 1490m	–
ν_s(COO$^-$)	1400s	1445m	1450m
δ(C–H)$_{pyrid}$	1380s	1380s, 1300m	1390s
ν(C–O)	–	–	1280s
	1200w	1245w	–
	1160w, 1060s	1060m, 1020m	1070m, 1030w
y(C–H)$_{pyrid}$	850m	855w	750s
	780m, 650m	765s, 690s	710m, 650m

w—weak, m—medium, s—strong.

[25]. In monodentate coordination the redistribution of electron density takes place, which shifts the asymmetric carboxylate stretch ν_{as}(COO$^-$) to higher wavenumbers in comparison to ionic group. Consequently the Δ value for monodentate carboxylate coordination is higher. On contrary, bidentate coordination shifts the position of the asymmetric carboxylate stretch to lower wavenumbers in comparison to ionic group and thus lowers the value of Δ. According the Δ values, the following order was proposed for carboxylate complexes of divalent metal cations [26,27]:

$$\Delta\,(\text{monodentate}) > \Delta\,(\text{ionic}) > \Delta\,(\text{bridging bidentate}) > \Delta\,(\text{chelating bidentate}).$$

The application of this theory to the spectra of the studied zinc(II) pyridinecarboxylates leads to the following results. For the complex [Zn(nicot)$_2$(H$_2$O)$_4$] the asymmetric and symmetric stretches ν_{as}(COO$^-$) and ν_s(COO$^-$ were observed at 1580 and 1400 cm^{-1}, respectively and therefore $\Delta = 180\,\text{cm}^{-1}$. This value is only a slightly higher as expected by described theory and as observed for ionic carboxylate group in acetates (170 cm^{-1} [25]). The higher value can be due to presence of strong hydrogen bonds, formed by both carboxylate oxygens as well as electron effect of pyridine ring to the carboxylate group. However, in the case of the complexes [Zn(picol)$_2$(H$_2$O)$_2$]·2H$_2$O and [Zn(dipicolH)$_2$]·3H$_2$O this theory does not match with the experimental results. The presence of carboxylate group in the complex [Zn(picol)$_2$(H$_2$O)$_2$]·2H$_2$O was reflected by bands at the values 1580 and 1445 cm^{-1} and consequently the observed Δ value for the complexes (**II**) (135 cm^{-1}) suggests bidentate coordination in contrast to the real structure of the complex. In the infrared spectrum of the complex [Zn(dipicolH)$_2$]·3H$_2$O both carboxylic and carboxylate groups were observed. The presence of carboxylate COO$^-$ anion is reflected by IR spectra in absorption bands of the asymmetric and symmetric stretches (ν_{as}(COO$^-$) and ν_s(COO$^-$)) at 1590 and 1450 cm^{-1}, respectively. The absorption band at 1695 cm^{-1} is due to carbonyl ν(C=O) vibration of –COOH group. The ν(C–O) vibration of this group is at 1280 cm^{-1}. The similar spectral results were obtained for the compounds [Mg(dipicol)(H$_2$O)], [Mg(dipicol)(H$_2$O)$_3$], [Mg(dipicol)(H$_2$O)$_4$] and [Cu(dipicol)(H$_2$O)$_5$] [28]. The observed A value for the complexes (**III**) is 140 cm^{-1} and again suggests bidentate coordination of carboxylate group in contrast to the real structure. Recently, Eq. (1) was proposed for calculation of Δ values from structural data [27]. The equation was derived from molecular orbital calculation and can be expressed as:

$$\Delta = 1818.1\delta_r + 16.47\,(\theta_{oco} - 120) + 66.8 \qquad (1)$$

where δ_r is difference between the two CO bond lengths (Å) and θ_{oco} is the OCO angle (°) [27].

The Δ value calculated by Eq. (1) from the structural data of the complex (**I**) is 158 cm^{-1}, the values for complexes (**II**) and (**III**) calculated using structural data from refs. [23,24], are 283 and 253 cm^{-1}, respectively. Comparison of the calculated results with observed values shows small difference for the zinc(II) nicotinate, but the differences for picolinate and dipicolinate complex are very remarkable. We suppose, that this may be due to chelate coordination of the carboxylate ligands through nitrogen atoms of pyridine ring and one of the carboxylate oxygens. For such types of coordination probably modification of Eq. (1) will be required. The differences between observed A values and calculated by Eq. (1) were also reported for zinc(II) acetate dihydrate [29].

3.5. *Thermal analysis*

3.5.1. *Phenomenological aspect*

*3.5.1.1. [Zn(nicot)$_2$(H$_2$O)$_4$] (**I**).* Thermal decomposition of the complex [Zn(nicot)$_2$(H$_2$O)$_4$] is shown in Fig. 4. The compound is thermally stable up to 80 °C. Above this temperature four molecules of water are evolved in one step in the range 80–125 °C (exp. weight loss 20.0%; calcd.

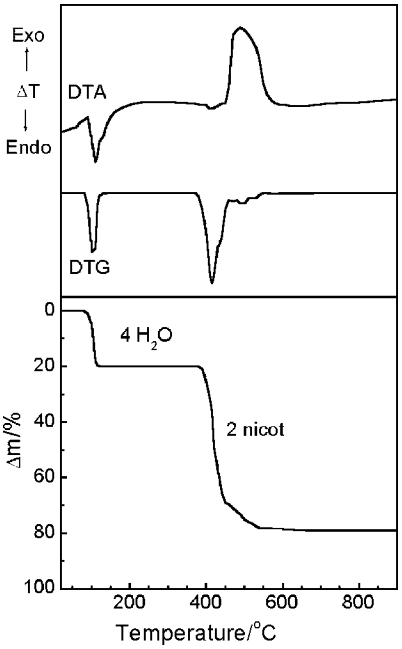


Fig. 4. Thermoanalytical curves of [Zn(nicot)$_2$(H$_2$O)$_4$].

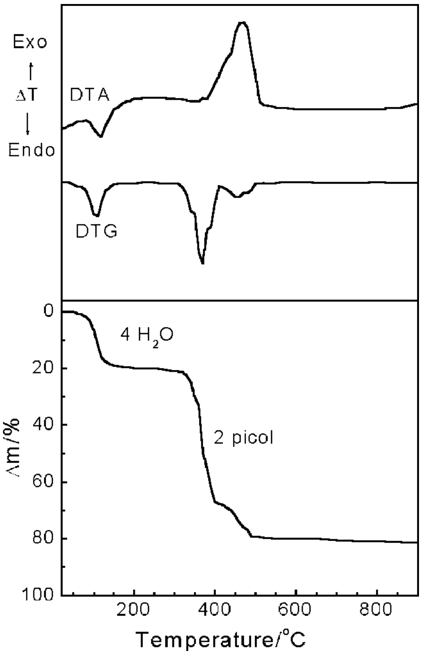


Fig. 5. Thermoanalytical curves of [Zn(picol)$_2$(H$_2$O)$_2$]·2H$_2$O.

18.8%). The release of crystalline water was accompanied by endothermic effect on the DTA curve observed at 110 °C. The dehydrated product Zn(nicot)$_2$ is thermally stable up to 390 °C. Thermal stability of this dehydrated product is lower than stability of anhydrous zinc(II) nicotinate (433 °C) prepared by hydrothermal synthesis [22]. However, this difference can be due to experimental conditions of thermogravimetric analysis. As there is no information concerning gas atmosphere in ref. [22] (inert or air) the further discussion would not be appropriate. For comparison, the temperature of the decomposition of the analogous cobalt complex in air is only slightly higher (415 °C) [21] than the onset of the decomposition of the studied zinc(II) nicotinate. In addition it should be pointed out that the thermal analysis of the complex [Zn(nicot)$_2$(H$_2$O)$_4$] was already described [30]. Anyway, in the study two different temperatures are reported for the decomposition of the complex in the text and the table (140 and 210 °C, respectively). In our opinion these values are not exact and correspond to the decomposition of the not chemically pure zinc(II) nicotinate, but mixture of the nicotinic acid and zinc nicotinate. On the basis of our results the correct onset of the thermal decomposition of the zinc(II) nicotinate is 390 °C.

In the temperature range 390–540 °C pyrolysis of two molecules of organic ligand took place (exp. weight loss 60.0%; calcd. 64.2%). The decomposition in the range 390–440 °C the decomposition is very intense while in the range 440–540 °C the mass loss is slowing down (see Fig. 4). The decomposition of the organic moiety was reflected by an intense exothermic effect on DTA curve with maximum at 490 °C, which reflects the oxidation of organic part of the complex in air. The final product of the decomposition, ZnO, was determined by X-ray powder diffraction. Scheme of the thermal decomposition of zinc(II) nicotinate can be represented as:

$$(\mathbf{I})\quad [\mathrm{Zn(nicot)_2(H_2O)_4}] \xrightarrow{80\text{–}125\,^\circ\mathrm{C}} [\mathrm{Zn(nicot)_2}] + 4\mathrm{H_2O} \xrightarrow{390\text{–}540\,^\circ\mathrm{C}} 2\mathrm{nicot} + \mathrm{ZnO}$$

3.5.1.2. [Zn(picol)$_2$(H$_2$O)$_2$]·2H$_2$O. TG, DTG and DTA curves for the complex [Zn(picol)$_2$(H$_2$O)$_2$]·2H$_2$O are shown in Fig. 5. The crystals are stable in air up to 70 °C. Four molecules of water are released in the temperature range 70–130 °C (exp. weight loss 19.0%; calcd. 18.8%) accompanied on the DTA curve by endothermic effect at 110°.

Further step of the thermal decomposition, which takes place in the temperature range of 300–500 °C, is characterised by release of two picolinate molecules. The mass loss in the range 300–380 °C is very intense, whereas in the range 380–500 °C the mass change is slowing down (see Fig. 6). Pyrolysis of two organic moieties is again accompanied by exothermic process (maximum on the DTA curve 465 °C) corresponding oxidation of the ligands in air. The final product of decomposition was ZnO and its presence in the solid residue was confirmed by X-ray powder diffraction. Scheme of the thermal decomposition of zinc(II) picolinate can be represented as:

$$(\mathbf{II})\quad [\mathrm{Zn(picol)_2(H_2O)_2}]\cdot 2\mathrm{H_2O} \xrightarrow{70\text{–}130\,^\circ\mathrm{C}} [\mathrm{Zn(picol)_2}] + 4\mathrm{H_2O} \xrightarrow{300\text{–}500\,^\circ\mathrm{C}} 2\mathrm{picol} + \mathrm{ZnO}$$

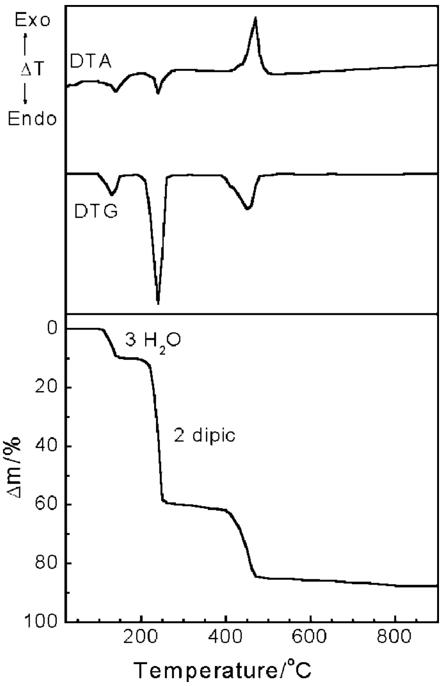


Fig. 6. Thermoanalytical curves of $[Zn(dipicolH)_2]\cdot 3H_2O$.

3.5.1.3. $[Zn(dipicolH)_2]\cdot 3H_2O$. The thermoanalytical curves of the complex $[Zn(dipicolH)_2]\cdot 3H_2O$ during heating in air are in Fig. 6. The thermal stability of this compound, as determined from TG curve, is up to 110 °C. The three molecules of water are evolved in the temperature range 110–150 °C during the endothermic process with minimum at 140 °C.

The thermal decomposition continues through two steps, the first one in the temperature range of 200–265 °C and the second one in the range 385–485 °C. We suppose that the fracture of C–C bond in each of the dipicolinic ligands took place to form two free radicals $^\bullet C_5H_3NCOOH$ which were liberated and probably further reacted to form 3,5′-dipyridyl-2′,6-dicarboxylic acid $HCOONH_3C_3$–C_5H_3NCOOH (calcd. mass loss 55%, observed 54%). Such formation of radicals was observed also by Sun et al. in zinc phthalate [31]. The rest of the dipicolinic moiety probably formed oxalate anion, which decomposed in the final step forming carbon dioxide, carbon monoxide (exp. weight loss 18.0%; calcd. 15.9%) and zinc oxide (exp. weight loss 16.0%; calcd. 18.0%). The presence of zinc(II) oxide in final solid residue was detected by powder XRD.

Two effects were observed on the DTA curve corresponding to the decomposition of zinc(II) dipicolinate. An endothermic effect at 240 °C (see Fig. 6) corresponds to the described fracture of C–C and Zn–O bonds in the complex and release of two $^\bullet C_5H_3NCOOH$ fragments. The second exothermic effect at 470 °C corresponds the oxidation of formed zinc(II) oxalate in air. Similar two-step process of the thermal decomposition was reported for copper and magnesium complexes of dipicolinic acid [28]. Scheme of the thermal decompositions can be represented as:

$$\textbf{(III)}\quad [Zn(dipicH)_2]\cdot 3H_2O$$

$$\xrightarrow{110\text{–}150\,^\circ C} [Zn(dipicH)_2] + 3H_2O$$

$$\xrightarrow{200\text{–}265\,^\circ C} ZnC_2O_4 + 2C_5H_3NCOOH$$

$$\xrightarrow{385\text{–}485\,^\circ C} CO_2 + CO + ZnO$$

3.5.2. Thermal stability and structure correlation

The careful study of the onset of the dehydration of the complexes as well as thermal stability of the dehydrated products showed that for both steps of the thermal decomposition the correlation with the structures can be found. The onset of the dehydration of the studied complexes increases as follows:

$$\underset{70\,^\circ C}{[Zn(picol)_2(H_2O)_2]\cdot 2H_2O} < \underset{80\,^\circ C}{[Zn(nicot)_2(H_2O)_4]} < \underset{110\,^\circ C}{[Zn(dipicolH)_2]\cdot 3H_2O}$$

This order well correlates with the structures of the compounds. In the structure of the complex $[Zn(picol)_2(H_2O)_2]\cdot 2H_2O$ two water molecules are not coordinated to zinc(II) atom (see Fig. 3a). These water molecules are hydrogen bonded to other water molecules and oxygen atom of neighbouring carboxylate group. For thermal stability of this complex is crucial, that all uncoordinated water molecules in the crystal are situated in the planes parallel with the (*ab*) plane (see Fig. 7a). We suppose that these planes probably serve as structural channels for dehydration of the complexes and therefore the complex (II) dehydrates easily after heating to 70 °C.

In the complex $[Zn(nicot)_2(H_2O)_4]$ all water molecules are coordinated to zinc and situated between mirror planes occupied by nicotinate anions (see Fig. 2). The water molecules are accumulated again in “planes” and due to this structural characteristic the complex also dehydrates easily, supposedly in the directions parallel to the (*ac*) plane. The onset of the dehydration of the complex $[Zn(nicot)_2(H_2O)_4]$ (80 °C) is a little higher in comparison to zinc(II) picolinate what may be a result of different ways of the bonding of the water in both complexes (coordinated or uncoordinated to metal).

The complex $[Zn(dipicolH)_2]\cdot 3H_2O$ contains similarly to zinc(II) picolinate the water molecules not coordinated to the zinc. However, in contrast to zinc(II) picolinate these molecules are not accumulated in the “planes” but are interlaced by the hydrogenpicolinate molecules (see Fig. 7b). Consequently, there are no structural channels for the dehydration present in the structure. This fact together with the extended hydrogen bonding geometry of the water molecules determines the highest onset of the dehydration for this complex. Similar trends of dehydration were also observed for copper dipicolinates [32].

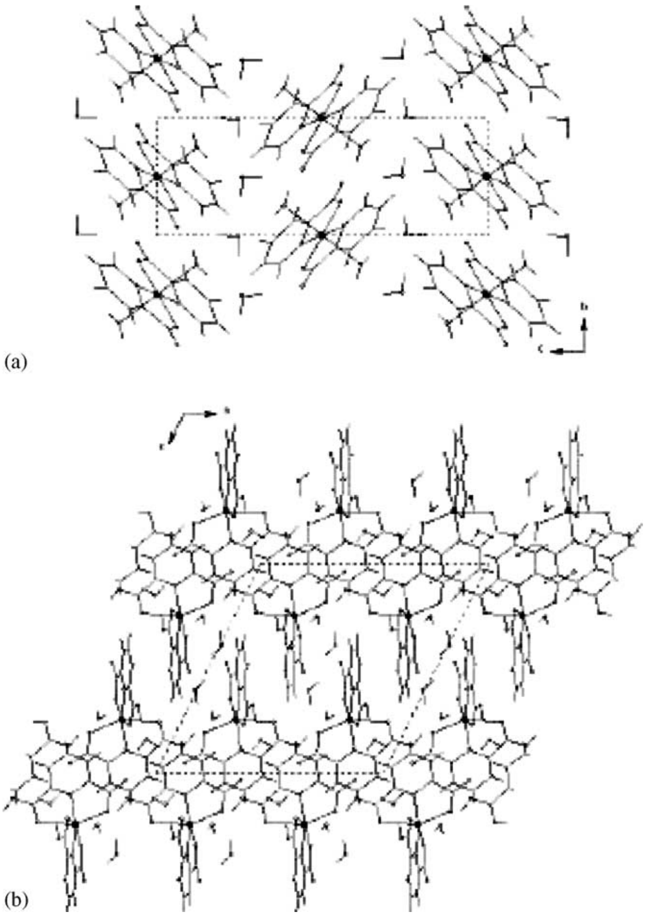


Fig. 7. Packing of the water molecules in the complex (a) [Zn(picol)$_2$(H$_2$O)$_2$]·2H$_2$O and (b) [Zn(dipicolH)$_2$]·3H$_2$O drawn on the basis of reference data [23,24].

The dehydrated complexes posses different thermal stability, the zinc(II) nicotinate being the most stable. We suppose that the non-coordinated carboxylate oxygens, which were involved in hydrogen bonds with water molecules in the native zinc(II) nicotinate tetrahydrate (see Fig. 2), take part in formation of new bonds after dehydration. The high thermal stability of the complex suggests, that these atoms can coordinate zinc(II) ions, forming polymeric structure similar to those described for anhydrous zinc(II) nicotinate prepared by hydrothermal synthesis [22]. On contrary, in the zinc(II) picolinate, probably molecular structure of the complex, characterised coordination of two picolinates as chelates through nitrogen atom of pyridine ring and one carboxylate oxygen, remains intact after dehydration. Consequently, the thermal stability of this molecular structure is lower, in comparison to supposed polymeric structure of the zinc(II) nicotinate. Finally, the lowest thermal stability was observed for the zinc(II) hydrogendipicolinate, due to splitting of the C–C bonds in the hydrogenpicolinate anion and probably formation of dipyridine derivative and oxalate as described in the text.

Acknowledgements

This work was supported by Slovak Ministry of Education grant No. 1/9247/02. This financial support is gratefully acknowledged.

References

[1] J.L. York, in: T.M. Delvin (Ed.), Textbook of Biochemistry with Clinical Correlations, Wiley, New York, 1992, p. 135.
[2] W. Kaim, B. Schwederski, Bioinorganic Chemistry: Inorganic Elements in the Chemistry of Life, Wiley, Chichester, England, 1994, p. 238.
[3] R.S. Rosenson, Atherosclerosis 171 (2003) 87–96.
[4] A.N. Klimov, V.O. Konstantinov, B.M. Lipovetsky, Cardiovasc. Drug Ther. 9 (1995) 779.
[5] B. Müller, M. Kasper, Ch. Surber, G. Imanidis, Eur. J. Pharm. Sci. 20 (2003) 181.
[6] T.A. Ban, Prog. Neuro-Psychoph. 25 (2001) 709.
[7] P. Llancapi, E. Wagemann, M. Namoncura, Rev. Med. Chile 126 (1998) 435.
[8] T.L. Varadinova, P.R. Bontehev, C.K. Nachev, S.A. Shiskov, J. Chemother. 5 (1993) 3.
[9] K. Murakami, Y. Tanemura, M. Yoshino, J. Nutr. Biochem. 14 (2003) 99.
[10] (a) K. Györyová, V. Balek, V. Zeleòák, Thermochim. Acta 234 (1994) 221;
(b) V. Zeleòák, K. Györyová, J. Simon, J. Therm. Anal. 46 (1996) 573;
(c) V. Zeleòák, K. Györyová, I. Císaøová, J. Loub, Acta Cryst. C52 (1996) 1917;
(d) J. Skoršepa, K. Györyová, M. Melník, K. Smolander, M. Ahlgren, Acta Cryst. C51 (1995) 1069;
(e) K. Györyová, J. Kováøová, M. Melník, E. Andogova, J. Therm. Anal. Calorim. 56 (1999) 503;
(f) V. Zeleòák, K. Györyová, D. Mlynarèík, Metal Based Drugs 8 (2002) 269;
(g) K. Györyová, E. Szunyogova, J. Kováøová, D. Hudecova, D. Mudroòva, E. Juhaszová, J. Therm. Anal. Calorim. 72 (2003) 587.
[11] A.L. Speck, PLATON, J. Appl. Cryst. 36 (2003) 7.
[12] G.M. Sheldrick, SHELXS-97, Program for the solution of crystal structures, University of Göttingen, Göttingen, Germany, 1997.
[13] G.M. Sheldrick, SHELXL-97, Program for the refinement of crystal structures, University of Göttingen, Göttingen, Germany, 1997.
[14] K. Brandenburg, DIAMOND 2. 1d, Crystal Impact GbR, Bonn 2000.
[15] I.S. Ahuja, R. Sing, R. Sriramulu, J. Mol. Struct. 53 (1979) 301.
[16] P. Lumme, G. Lundgren, W. Mark, Acta Chem. Scand. 23 (1969) 3011.
[17] I.S. Ahuja, R. Sriramulu, R. Singh, Indian J. Chem. 19A (1980) 909.
[18] W.E. Broderick, M.R. Pressprich, U. Geiser, R.D. Willett, J.I. Legg, Inorg. Chem. 25 (1986) 3372.
[19] K. Györyová, J. Skoršepa, K. Smolander, M. Melník, Proc. Conf. Coord. Chem. 15 (1995) 173.
[20] K. Hakansson, M. Lindahl, G. Svensson, J. Albertsson, Acta Chim. Scand. 5 (1993) 449.
[21] H.B. Jia, J.H. Yu, J.Q. Xu, L. Ye, H. Ding, W.J. Jing, T.G. Wang, J.N. Xu, Z.C. Li, J. Mol. Struct. 641 (2002) 23.
[22] J.Y. Lu, E.E. Kohler, Inorg. Chem. Commun. 5 (2002) 600.
[23] A.N. Yunuskhodzhaev, U.A. Mukarramova, Z. Karimov, Kristallogr. Rep. 43 (1998) 42.
[24] N. Okabe, N. Oya, Acta Crystallogr. C56 (2000) 305.
[25] G.B. Deacon, R.J. Phillip, Coord. Chem. Rev. 33 (1980) 227.

[26] D. Martini, M. Pellei, C. Pettinari, B.W. Skelton, A.H. White, Inorg. Chim. Acta 333 (2002) 72.
[27] M. Nara, H. Torii, M. Tasumi, J. Phys. Chem. 100 (1996) 19812.
[28] S.C. Mojumdar, M. Melnik, E. Jona, J. Anal. Appl. Pyrol. 48 (1999) 111.
[29] T. Ishioka, Y. Shibata, M. Takahaski, I. Kanesaka, Y. Kitagawa, K.T. Nakamura, Spectrochim. Acta A54 (1998) 1827.
[30] J.R. Allan, W.C. Gedde, C.S. Hindle, A.E. Or, Thermochim. Acta 153 (1989) 249.
[31] J. Sun, L. Yuan, K. Zhang, D. Wang, Thermochim. Acta 343 (2000) 105.
[32] E.E. Sileo, G. Rigotti, B.E. Rivero, M.A. Blesa, J. Phys. Chem. Solids 58 (1997) 1127.