Journal of Thermal Analysis and Calorimetry, Vol. 76 (2004) 837–851

bis(NICOTINAMIDE) AND *bis*(N,N-DIETHYL NICOTINAMIDE) *p*-HYDROXYBENZOATE COMPLEXES OF Ni(II), Cu(II) AND Zn(II)
Spectrothermal studies

H. Icbudak[1*], *Z. Heren*[1], *D. Ali Kose*[2] *and H. Necefoglu*[2]

[1]Department of Chemistry, Faculty of Arts and Sciences, Ondokuz Mayis University,
55139-Kurupelit-Samsun, Turkey
[2]Department of Chemistry, Faculty of Arts and Sciences, Kafkas University, Kars, Turkey

(Received November 4, 2003; in revised form January 20, 2004)

Abstract

The mixed-ligand *p*-hydroxybenzoate complexes of Ni(II), Cu(II) and Zn(II) with nicotinamide and N,N-diethylnicotinamide were synthesized and characterized by elemental analysis, magnetic susceptibility measurements and mass spectrometry. The thermal behavior of the complexes was studied by simultaneous TG, DTG and DTA methods in static air atmosphere. The infrared spectral characteristics of the complexes are also discussed. The complexes contain two water molecules, two *p*-hydroxybenzoato (*p*-hba) and two nicotinamide (na) (or diethylnicotinamide (dena)) ligands per formula unit. In these complexes, all ligands are coordinated to the metal ion as monodendate ligands. In Zn(II)-na and Cu(II)-dena complexes, the *p*-hydroxybenzoate behaves as bidentate chelating ligand through carboxylic oxygen atoms. The decomposition pathways and the stability of the complexes are interpreted in the terms of the structural data. The final decomposition products were found to be the respective metal oxides.

Keywords: diethylnicotinamide, metal complexes, nicotinamide, *p*-hydroxybenzoato, thermal decomposition

Introduction

It is documented that heterocyclic compounds play a significant role in many biological systems, especially N-donor ligand systems being a component of several vitamins and drugs such as nicotinamide [1–3]. Nicotinamide is known as a component of the vitamin B complex as well as a component of the coenzyme, nicotinamide adenine dinucleotide (NAD). These are more important for transfer of hydrogen in the cell breath. The presence of pyridine ring in numerous naturally abundant compounds, adducts of nicotinamide are also scientific interest. Therefore, the structure of nicotinamide has been the subject of many studies [4–7].

---

[*] Author for correspondence: E-mail: icbudak@omu.edu.tr

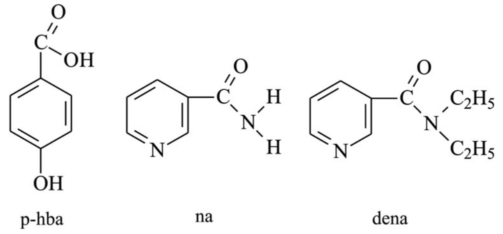
1388–6150/2004/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Phenolic antioxidants such as hydroxybenzoates are important classes of natural antioxidants [8]. *p*-hydroxybenzoic acid is widely used as antimicrobial agents in foods, drugs, cosmetics and toiletries [9]. Metal complexes of biologically important ligands are sometimes more effective than the free ligands [10]. Structural reports of metal (Zn^{2+}) nicotinamide complexes exist in [11].

In the present paper, we report the synthesis, spectroscopic and thermal properties of some new mixed-ligand complexes of Ni(II), Cu(II) and Zn(II) containing *p*-hydroxybenzoate-nicotinamide and -diethylnicotinamide. The structures of the ligands are shown in Scheme 1.

Experimental



Scheme 1

Materials and instrumentation

All chemicals used were analytical reagent products. $NiSO_4 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, *p*-hydroxybenzoic acid and nicotinamide were obtained from Merck (Darmstadt, Germany). Diethylnicotinamide was purchased from Darmitsa Chemicals Union (Kiev, Ukraine). Elemental analyses (C, H, N) were carried out by standard methods (Tubitak Marmara Research Center). Magnetic susceptibility measurements at room temperatures were performed using a Sherwood Scientific MXI model Gouy magnetic balance. IR spectra were recorded in 4000–400 cm^{-1} region with a Mattson 1000 FT-IR spectrometer using KBr pellets. Thermal analysis curves (TG-DTG and DTA) were recorded simultaneously in a static air atmosphere with a Rigaku TG8110 thermal analyzer. The samples weighed approximately 10 mg and highly sintered α-Al_2O_3 was used as a reference material. The heating rate was 10°C min^{-1} and the DTG sensitivity was 0.05 mg s^{-1}. The mass spectrum was recorded by Tubitak Marmara Research Center.

Preparation of p-hydroxybenzoate complexes

At the first step, *p*-hydroxybenzoic acid sodium salt was prepared according to the following equation:

$$2p\text{-hba}+2NaHCO_3 \rightarrow 2Na(p\text{-hba})+2CO_2+2H_2O$$

At the second step, metal *p*-hba salts were synthesized from Na(*p*-hba) salt by substitution reaction:

$$2\text{Na}(p\text{-hba})+\text{MSO}_4\cdot n\text{H}_2\text{O} \rightarrow \text{M}(p\text{-hba})_2\cdot n\text{H}_2\text{O}+\text{Na}_2\text{SO}_4 \ [M=\text{Ni(II), Cu(II), Zn(II)}]$$

The $\text{M}(p\text{-hba})_2\cdot n\text{H}_2\text{O}$ solution was allowed 5–7 days for crystallization at room temperature. The crystals formed were filtered and washed with cold distilled water and acetone and dried in vacuo.

Synthesis of mixed-ligand complexes

A solution of na and dena (2 mmol) in distilled water (30 mL) was added dropwise with stirring to a solution of $\text{M}(p\text{-hba})_2(\text{H}_2\text{O})_\text{n}$ (1 mmol) in hot distilled water (50 mL). The solutions were heated to 80°C in a temperature-controlled bath and stirred for 4 h and then cooled to room temperature and allowed 7–8 days for crystallization. The crystals formed were filtered and washed with cold water and acetone and dried in vacuo. The mixed-ligand complexes were prepared according to the following equations:

$$\text{M}(p\text{-hba})_2(\text{H}_2\text{O})_\text{n}+2\text{na} \rightarrow \text{M}(p\text{-hba})_2(\text{na})_2(\text{H}_2\text{O})_2 \ [M=\text{Ni(II), Cu(II)}]$$

$$\text{Zn}(p\text{-hba})_2(\text{H}_2\text{O})_\text{n}+2\text{na} \rightarrow \text{Zn}(p\text{-hba})_2(\text{na})_2+n\text{H}_2\text{O}$$

$$\text{M}(p\text{-hba})_2(\text{H}_2\text{O})_\text{n}+2\text{dena} \rightarrow \text{M}(p\text{-hba})_2(\text{dena})_2(\text{H}_2\text{O})_2\cdot \text{nH}_2\text{O} \ [M=\text{Ni(II), Zn(II)}]$$

$$[\text{Cu}(p\text{-hba})_2(\text{H}_2\text{O})_\text{n}]+2\text{dena} \rightarrow \text{Cu}(p\text{-hba})_2(\text{dena})_2+n\text{H}_2\text{O}$$

Result and discussion

Analytical results and compositions of the complexes are given in Table 1. The complexes were synthesized with high purity. The results of the elemental analysis indicated that the complexes contain two moles of *p*-hydroxybenzoato and nicotinamide ligands per mole formula units. The Ni(II)-na, Cu(II)-na and Ni(II)-dena and Zn(II)-dena complexes also include two moles of aqua ligands. Furthermore, the Ni(II)-dena and Zn(II)-dena complexes contain two moles of crystallization water per formula unit. The presence of aqua ligand was confirmed by the FT IR spectra and mass loss and endothermic peaks in the DTA curves. In the complexes with the aqua ligands, the octahedral coordination of the metal ion formed by two carboxylic oxygen atoms from two *p*-hyroxybenzoates and two nitrogen atoms from two nicotinamides (or diethylnicotinamides). In the Zn(II)-na and Cu(II)-dena complexes, the *p*-hydroxybenzoate behaves as bidentate chelating ligand through carboxylic oxygen atoms. The elemental analysis data in Table 1 confirm the proposed formulae of the complexes.

Due to the low solubility, it was not possible to record satisfactory UV-Vis spectra for the complexes. The metal complexes are of the high-spin type and paramagnetic, except for Zn(II) complexes. As expected, the Zn(II) complexes are diamagnetic. These values suggest octahedral coordination around the metal ions.

Table 1 Analytical data of the metal complexes

Complex	M/g mol^{-1}	Found (calcd.)/%			Color	D. p^{a}/°C	μ_{eff}/ B.M.
		C	H	N			
[Ni(p-hba)$_2$(na)$_2$(H$_2$O)$_2$] $C_{26}H_{26}N_4O_{10}Ni$	613.21	50.98 (50.91)	4.57 (4.24)	9.06 (9.14)	blue	110	3.13
[Cu(p-hba)$_2$(na)$_2$(H$_2$O)$_2$] $C_{26}H_{26}N_4O_{10}Cu$	617.7	50.46 (50.51)	4.07 (4.21)	8.39 (9.07)	dark-blue	58	1.66
[Zn(p-hba)$_2$(na)$_2$] $C_{26}H_{22}N_4O_8Zn$	583.6	53.25 (53.46)	3.92 (3.77)	9.35 (9.60)	colorless	191	diamagnetic
[Ni(p-hba)$_2$(dena)$_2$(H$_2$O)$_2$]·2H$_2$O $C_{34}H_{46}N_4O_{14}Ni$	761.19	53.47 (53.63)	6.60 (6.05)	7.20 (7.36)	light-blue	67	2.78
[Cu(p-hba)$_2$(dena)$_2$] $C_{34}H_{38}N_4O_{10}Cu$	694.02	58.98 (58.78)	5.90 (5.48)	7.90 (8.07)	dark-blue	175	1.46
[Zn(p-hba)$_2$(dena)$_2$(H$_2$O)$_2$]·2H$_2$O $C_{34}H_{46}N_4O_{14}Zn$	767.86	53.27 (53.13)	6.55 (5.99)	7.22 (7.29)	colorless	35	diamagnetic

[a] Decomposition point

IR spectra

The absorption bands in the range of 3472–3431 cm^{-1} in complexes correspond to the asymmetric and symmetric stretching vibration of water molecules. The wave number range for the N–H stretches of primary amides is 3370–3170 cm^{-1}. We observed two bands in the range of 3350–3245 cm^{-1} in the na complexes and assigned to asymmetric and symmetric stretching vibration of NH_2. The na complexes give rise to strong bands responsible from the C=O stretching. Conjugation between the carbonyl group and the amide nitrogen causes small frequency shifts. The strong bands observed at around 1680 cm^{-1} are assigned to this mode. Pyridine ring vibrations of free nicotinamide at 1592 cm^{-1} shifts to higher frequencies in the spectrum of the metal complexes. The shifts in the spectrum of the complexes may indicate that the pyridine ring is coordinated. The main difference in the spectrum of *p*-hydroxybenzoic acid is that the C–O stretching vibration of the carboxyl group at 1676 cm^{-1} is shifted to lower frequency in all the metal complexes. The bands due to the asymmetric and symmetric stretching of carboxylate in the metal complexes occur in the range of 1579–1533 and 1401–1385 cm^{-1}, respectively. This shows that the coordination takes place through the carboxyl group [12]. The $Zn(p\text{-hba})_2(na)_2$ and $Cu(p\text{-hba})_2(dena)_2$ complexes are bidendate and only one strong peak for each complex appears at 1384 and 1385 cm^{-1} with a small shoulder at 1579 and 1580 cm^{-1}, respectively [13]. The δ(OH) bending peak for the *p*-hydroxybenzoic acid remained almost in the same position at around 1250 cm^{-1} in all metal complexes. The low intensity bands in the region of 456–400 cm^{-1} are attributed to M–N and M–O vibration [14, 15].

Thermal data

$[Ni(p\text{-hba})_2(na)_2(H_2O)_2]$

The one-step dehydration of the Ni(II) complex occurs in the temperature range of 110–161°C (Fig. 1). The endothermic DTA peak at 143°C corresponds to the liberation of two water molecules that are coordinated to metal ion. In the second stage, two mole nicotinamide ligands decompose in the temperature range of 198–296°C (exp. 40.04%; calcd. 39.8%). This type of behavior of neutral ligands has been reported earlier [16–18]. Consequently, the decomposition of the *p*-hydroxybenzoato ligands starts with the release of two CO_2 molecules (exp. 7.40%; calcd. 7.18%). The IR spectra of the intermediate products show similar results. The descending continuous TG curve is obtained in the temperature range of 297–464°C (DTG peaks at 303, 339, 418°C) and these are relevant to the decomposition of *p*-hydroxybenzoato ligands. In the fifth stage, the residue decomposes vigorously followed by a strong exothermic DTA peak at 418°C implying the redox nature of this process. The final decomposition product, namely NiO was identified by IR spectroscopy with corresponding spectra obtained under the same conditions as the pure oxides.

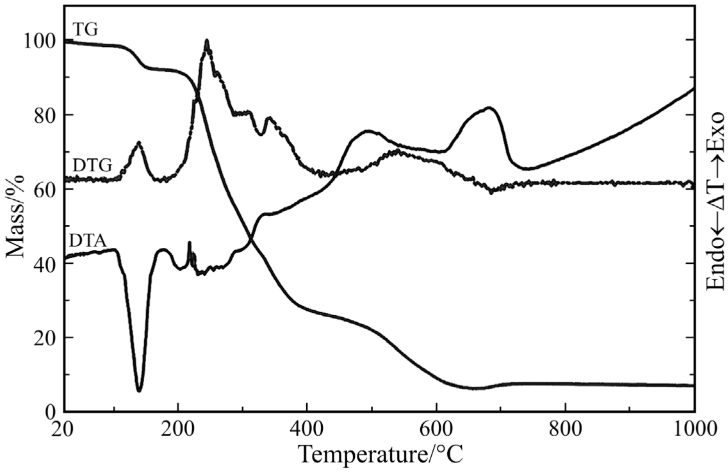


Fig. 1 The TG, DTG and DTA curves of $[Ni(p\text{-}hba)_2(na)_2(H_2O)_2]$

$[Cu(p\text{-}hba)_2(na)_2(H_2O)_2]$

The TG-DTG and DTA curves for the Cu(II) complex are given in Fig. 2. The first stage of the thermal decomposition of Cu(II) nicotinamide *p*-hydroxybenzoate starts at the 58–108°C temperature range with the release of the aqua ligands (exp. 6.16%; 5.82%). The anhydrous complex, $[Cu(p\text{-}hba)_2(na)_2]$ is stable in air up to 196°C and begins to decompose with melting at 205°C (DTA curve). Similar behavior was observed in the nicotinamide-acetylsalicylato mixed-ligand complex of Cu(II) [16]. In this consecutive stage (DTG peaks at 211, 227, 230 triplet), a number of undefined processes take place in this range eventually produce CuO.

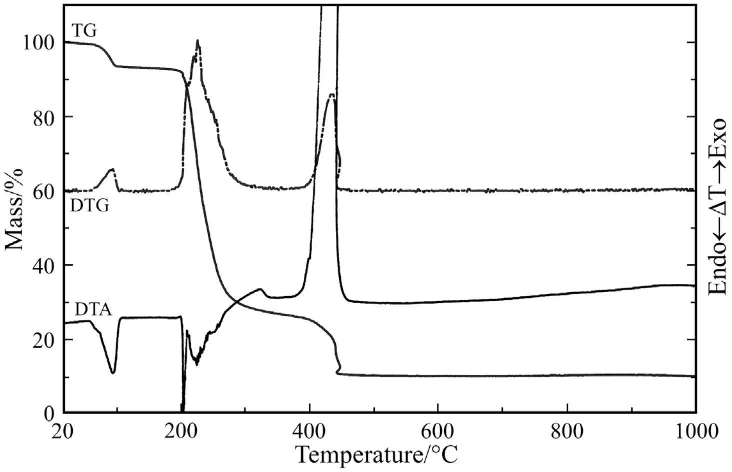


Fig. 2 The TG, DTG and DTA curves of $[Cu(p\text{-}hba)_2(na)_2(H_2O)_2]$

[Zn(p-hba)$_2$(na)$_2$]

Thermal analysis curves (TG-DTG and DTA) of the complex are shown Fig. 3. Obviously, due to the absence of the crystal water, Zn(II) complex is the most stable of all investigated nicotinamide-*p*-hydroxybenzoate complexes. The complex is thermally stable up to 191°C. The thermal decomposition of the complex begins with melting at 210°C (DTA peak) and reveals a 49.66% mass loss between 191–262°C. In this stage, decomposition of the nicotinamide ligands and *p*-hydroxybenzoato ligand with release of CO_2 proceeds. A good agreement between the experimental and calculated values was observed for the mass loss (exp. 49.66%; calcd. 49.35%). The IR spectrum of the intermediate product obtained in this step showed that the *p*-hydroxybenzoato ligand decomposes with release of CO_2. The strong exothermic peak at 490°C is associated with the burning of the organic residue. Final decomposition product is ZnO.

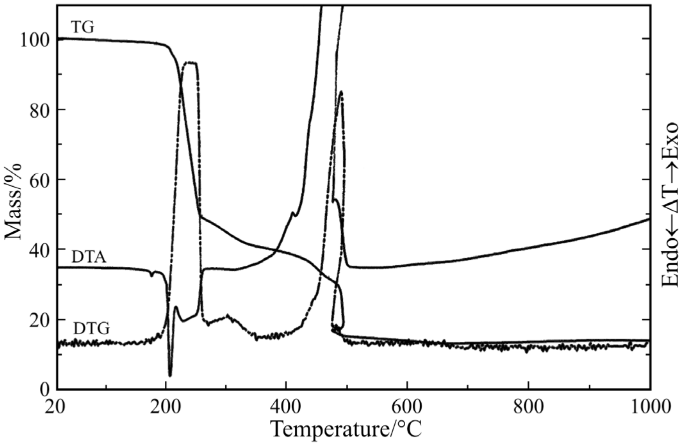


Fig. 3 The TG, DTG and DTA curves of [Zn(p-hba)$_2$(na)$_2$]

[Ni(p-hba)$_2$(dena)$_2$(H$_2$O)$_2$]·2H$_2$O

The complex contains both of the crystallization and coordination water, different from the Cu(II) nicotinamide *p*-hydroxybenzoate complex. The thermal dehydration of the complex occurred in one step by giving endothermic effect at 107°C (Fig. 4). According to the initial decomposition temperatures (Table 2), the thermal stability of the [Ni(p-hba)$_2$(dena)$_2$(H$_2$O)$_2$]·2H$_2$O is lower than that of the [Ni(p-hba)$_2$(na)$_2$(H$_2$O)$_2$]. Two moles of crystallization and two moles of coordination water are removed at this stage (exp. 9.75%; calcd. 9.46%). A color change from light-blue to green was noted by the removal of the water molecules. After dehydration the crystal structure of the complex is distorted, but on gradual heating the anhydrous complex shows a phase transition at 167°C (DTA peak) indicating rearrangement of species in the solid state. The anhydrous complex is stable to 220°C and decomposes in the 220–406°C temperature intervals. The

Table 2 Thermoanalytical results (TG, DTG and DTA) for the metal complexes

Complex	Temperature range/°C	DTG_{max}/ °C	Removed group	Mass loss/%		Total mass loss/%		Solid decomposition product	Colour
				Found	Calc.	Found	Calc.		
$[Ni(C_7H_5O_3)_2(C_6H_6N_2O)_2(H_2O)_2]$ (612.9)									
1	110–161	143(+)	$2H_2O$	5.21	5.87			$[Ni(C_7H_5O_3)_2(C_6H_6N_2O)_2]$	blue
2	198–296	237(–) 263(–)	$2(C_6H_6N_2O)$	40.04	39.81			$[Ni(C_7H_5O_3)_2]$	green
3	297–323	303	$2CO_2$	7.40	7.18				
4	324–370	339	–	10.07	–				
5	371–464	418(–)		24.18		86.90	87.81	NiO	green-black dark/blue
$[Cu(C_7H_5O_3)_2(C_6H_6N_2O)_2(H_2O)_2]$ (617.7)									
1	58–108	93.5(+)	$2H_2O$	6.16	5.82			$[Cu(C_7H_5O_3)_2(C_6H_6N_2O)_2]$	blue
2	196–246	211(+) 227(+) 230(+)	$2(C_6H_6N_2O)$ CO_2	45.71	46.62				green
3	247–320	–	–	18.70	–				
4	377–467	439(–)	–	15.79		86.36	87.12	CuO	black
$[Zn(C_7H_5O_3)_2(C_6H_6N_2O)_2]$ (583.6)									
1	191–262	235(+)	$2(C_6H_6N_2O)$ CO_2	49.66	49.35				colorless
2	263–357	304(+)	CO_2	8.12	7.54				colorless

Table 2 Continued

Complex	Temperature range/°C	DTG_{max}/ °C	Removed group	Mass loss/%		Total mass loss/%		Solid decomposition product	Colour
				Found	Calc.	Found	Calc.		
$[Ni(C_7H_5O_3)_2(C_9H_{14}N_2O)_2(H_2O)_2]\cdot 2H_2O$ (760.71)									
1	67–133	107(+)	$4H_2O$	9.75	9.46			$[Ni(C_7H_5O_3)_2(C_9H_{14}N_2O)_2(H_2O)_2]$	green
2	220–289	258(+)		33.41	–				
3	290–328	306(+)		13.82	–				
4	329–406	388(–)		33.95	90.93	90.18		NiO	green-black
$[Cu(C_7H_5O_3)_2(C_9H_{14}N_2O)_2]$ (693.54)									
1	175–359	214(+) 226(+) 247(+) 256(+) 266(+)	$2(C_9H_{14}N_2O)$ CO_2	66.52	64.02				dark-blue
2	359–531	443(–) 470(–)	22.40	22.40	–	88.92	88.53	CuO	black
$[Zn(C_7H_5O_3)_2(C_9H_{14}N_2O)_2(H_2O)_2]\cdot 2H_2O$ (767.38)									
1	35–84	54(+)	$2H_2O$	3.95	4.69				colorless
2	93–143	114(+)	$2H_2O$	4.84	4.69				colorless
3	143–278	233(+)	$2(C_9H_{14}N_2O)$ CO_2	54.49	52.13				colorless
4	279–371	341(+)		6.37	–				
5	372–438	412(–)		6.85	–				
6	439–505	495(–)		14.28	–	90.78	89.40	ZnO	colorless

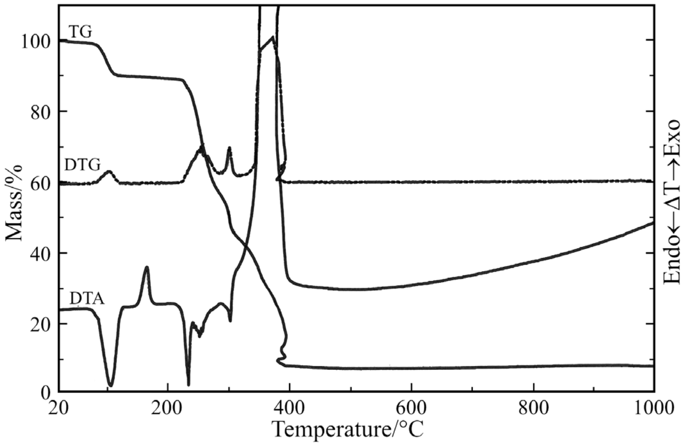


Fig. 4 The TG, DTG and DTA curves of $[Ni(p\text{-hba})_2(dena)_2(H_2O)_2]\cdot 2H_2O$

fourth mass loss process of the complex is vigorous and strongly exothermic (DTA peak at 388°C), and related to the burning of the organic residue. The final product obtained at 406°C is NiO (exp. 90.93%; calcd. 90.18%).

$[Cu(p\text{-hba})_2(dena)_2]$

The thermal analysis curves of this complex (Fig. 5) indicate that the complex is thermally stable to 175°C and begins to decompose with melting at 202°C (DTA curve). This decomposition stage with multi-step is indicative of a very complex process. The DTG curve of the complex displays five closely spaced peaks at 214, 226, 247, 256 and 266°C. These peaks can be attributed to the decomposition of the diethylnicotinamide and *p*-hydroxybenzoate ligands. The exothermic peaks at 443 and 470°C can be assigned to

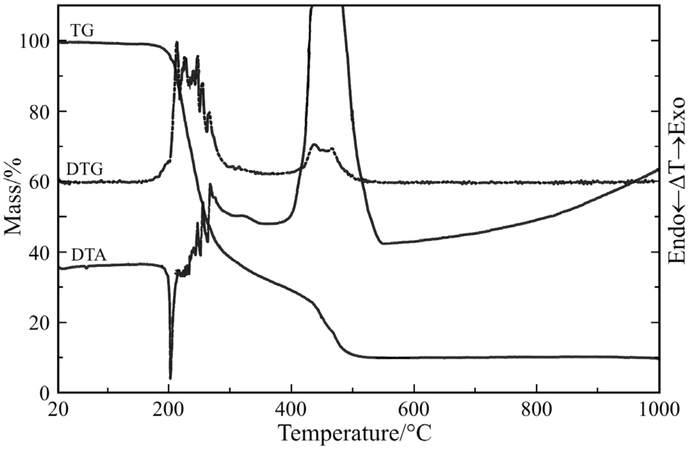


Fig. 5 The TG, DTG and DTA curves of $[Cu(p\text{-hba})_2(dena)_2]$

the burning of the organic residue formed in the previous stage. The final solid product of thermal decomposition was identified as CuO (exp. 88.92%; calcd. 88.53%).

$[Zn(p\text{-hba})_2(dena)_2(H_2O)_2]\cdot 2H_2O$

Zn(II) diethylnicotinamide *p*-hydroxybenzoate complex contains both of the crystallization and coordination waters similarly to $[Ni(p\text{-hba})_2(dena)_2(H_2O)_2]\cdot 2H_2O$. But the thermal dehydration of the Zn(II) complex occurred in two steps by giving endothermic effect at 54 and 114°C which is different from the other studied complexes. Two moles of crystallization water are released in the first step of the dehydration in the temperature range of 35–84°C. The dehydration temperature of $[Zn(p\text{-hba})_2(dena)_2(H_2O)_2]\cdot 2H_2O$ is lower than other all investigated complexes. In the second step of dehydration, the coordinated waters are removed in the temperature range of 93–143°C. This behavior was also observed in our early studies with Zn(II) complexes [16, 19]. The following stage is related to decomposition of the diethylnicotinamide and *p*-hydroxybenzoate ligands. According to the mass loss, the final product is ZnO (exp. 90.78, calcd. 89.40%) at 495°C (Fig. 6).

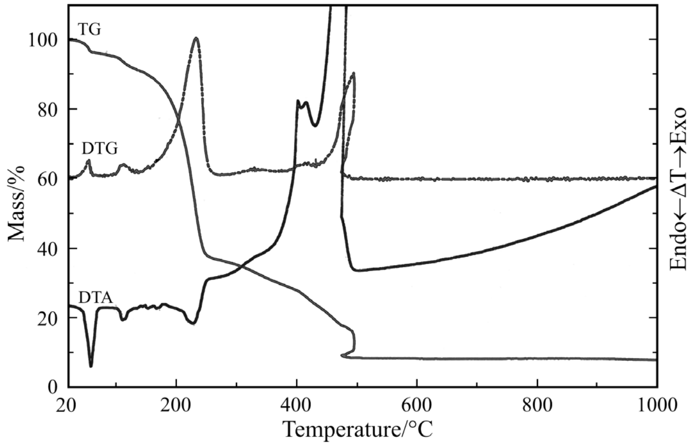


Fig. 6 The TG, DTG and DTA curves of $[Zn(p\text{-hba})_2(dena)_2(H_2O)_2]\cdot 2H_2O$

The complexes of Ni(II) and Cu(II) *p*-hydroxybenzoate-nicotinamide, Ni(II) and Zn(II) *p*-hydroxybenzoate-diethyl nicotinamide contain two and four moles of water, respectively. In these hydrated complexes, the first stage from approx. 35 to 161°C corresponds to dehydration. The experimental values for the mass loss of the dehydration stage are well consistent with the calculated values (Table 2). The water molecules present in the complexes of Ni(II) and Zn(II) *p*-hydroxybenzoate-diethyl nicotinamide can be divided into two groups. Two of them are directly coordinated to the metal ion as ligands while the rest is present as crystallization water. However, the results indicate that metal-water bond strength is almost the same for all of the water molecules. By the loss of two coordinated and two crystallization waters the originally octahedral complexes convert into new arrangement. This destabilizes the anhydrous complexes and a phase transition occurs at 167°C to rearrange the present species in the solid state. The phase transition was not observed in the other complex. Usually dehydration was followed by a color change. In the Zn(II) *p*-hydroxybenzoate-diethyl nicotinamide, the dehydration take places in two steps, different from the other complexes. After the dehydration process, decomposition stages of the anhydrous complexes are related to release nicotinamide (or decomposition of the diethyl nicotinamide) and the partial decomposition of *p*-hydroxybenzoate involving the release of CO_2. Previous studies show that the benzoate-metal complexes decompose by releasing of CO_2 [20–24]. The IR spectra of the intermediate products show similar results. The final decomposition products were found to be the respective metal oxides in the 400–530°C temperature intervals.

Mass spectra

To deduce the thermal decomposition pathway of the $[Ni(p\text{-hba})_2(na)_2(H_2O)_2]$ complex the positive-ion FAB mass spectrum was recorded (Fig. 7) to see if the thermal and ionization processes somehow resemble each other. The mass spectrum shows the fragmentation pattern and the most fragile points of the molecule. The obtained mass spectrum is relatively complex and exhibits a large number of peaks that extend to *m/z* value above 612. Beside the most abundant peaks, much fewer abundant peaks observed on the spectrum depend probably on the nature of ligands. In the mass spectrum recorded, the molecular ion is not detected. A schematic representation including the main fragmentation process for the $[Ni(p\text{-hba})_2(na)_2(H_2O)_2]$ complex is given in Scheme 2.

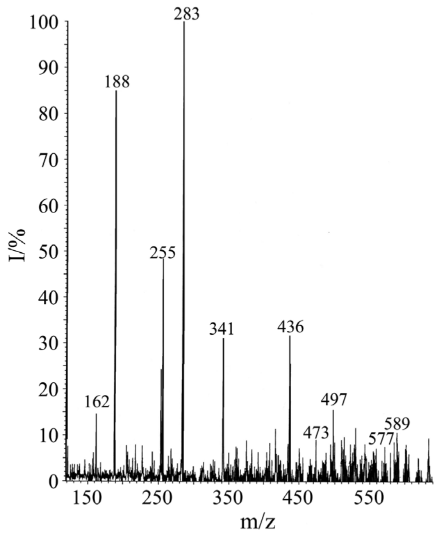
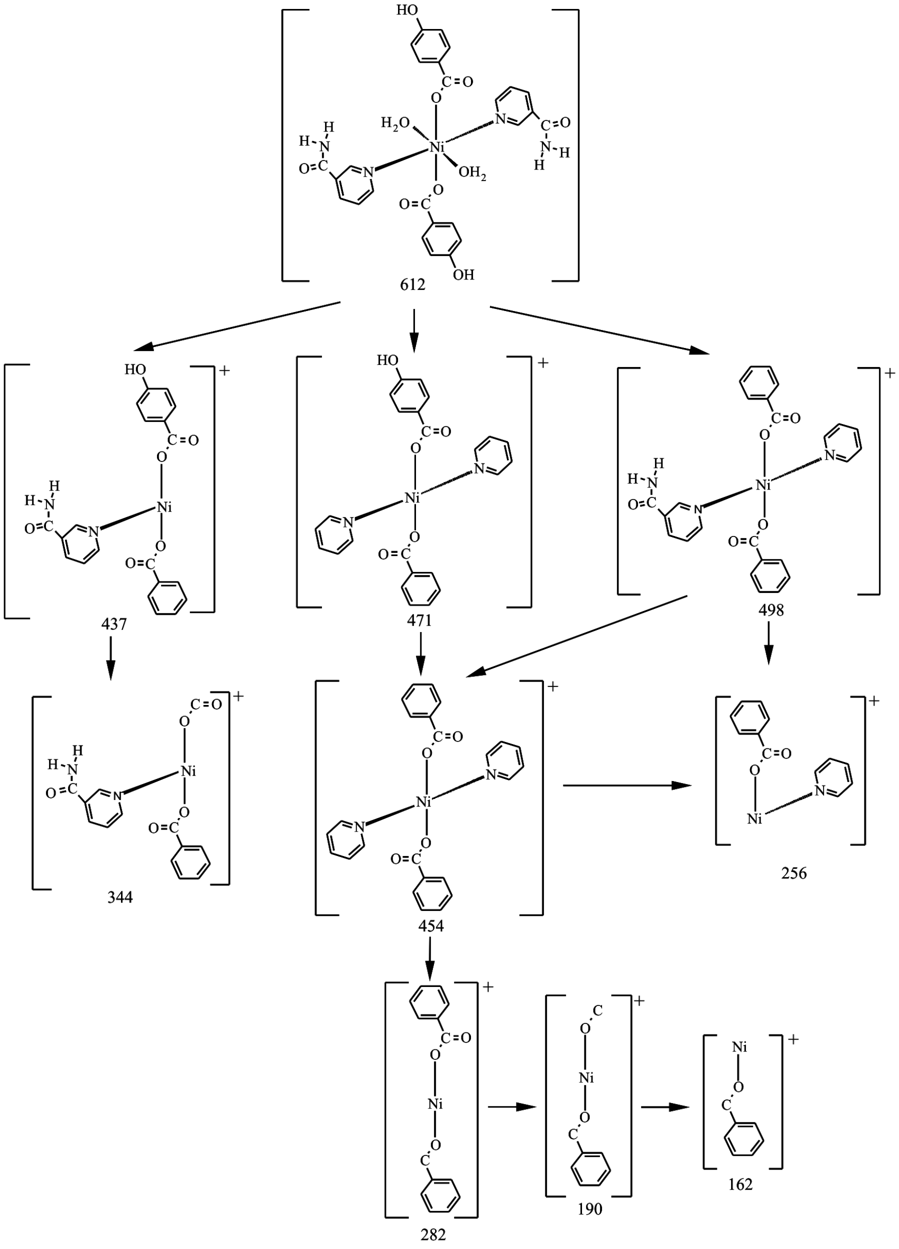
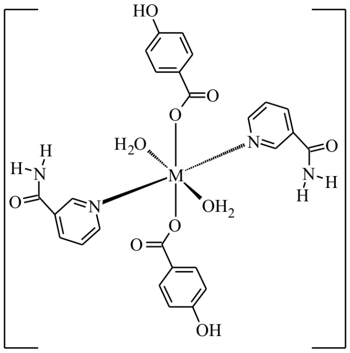


Fig. 7 The mass spectrum of $[Ni(p\text{-hba})_2(na)_2(H_2O)_2]$

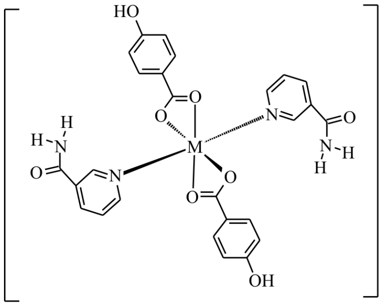


Scheme 2 Mass spectral fragmentation pattern of the [Ni(p-hba)$_2$(na)$_2$(H$_2$O)$_2$]

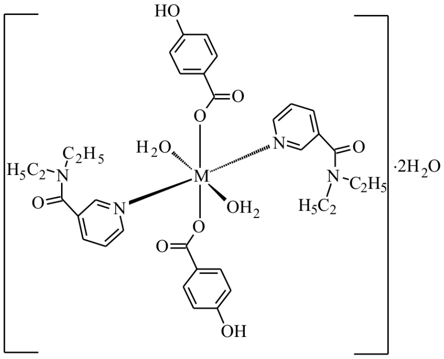
The structures of the synthesized complexes, which are presented in Fig. 8, are consistent with their chemical, thermal and spectroscopic properties.



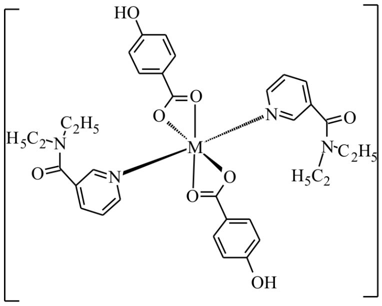
$[M(p\text{-hba})_2(na)_2(H_2O)_2]$
[M=Ni(II), Cu(II)]



$[Zn(p\text{-hba})_2(na)_2]$



$[M(p\text{-hba})_2(dena)_2(H_2O)_2]\cdot 2H_2O$
[M=Ni(II), Zn(II)]



$[Cu(p\text{-hba})_2(dena)_2]$

Fig. 8 Suggested structures of the complexes

* * *

Our thanks are due to the Researhc Fund of Ondokuz Mayis University and the Research Fund of Kafkas University for financial support.

References

1 U. Brühlmann and E. Hayon, J. Am. Chem. Soc., 96 (1974) 6169.
2 M. Kato and Y. Muto, Coord. Chem. Rev., 92 (1988) 45.
3 R. Nagar, J. Inorg. Biochem., 40 (1990) 349.
4 Y. Miwa, T. Mizuno, K. Tsuchiya, T. Taga and Y. Iwata, Acta Crystallogr., B55 (1999) 75.
5 B.Vogalsanger, R. D. Brown, P. D. Godfrey and A. P. Pierlot, J. Mol. Spectrosc., 145 (1991) 1.
6 P. Purcell, J. Phys. Chem., 68 (1964) 2666.
7 P. Purcell and A.J. Siger, J. Phys. Chem., 69 (1965) 4097.
8 C. A. Rice-Evans, N. J. Miller and G. Paganga, Free Radic. Biol. Med., 20 (1996) 933.

9 A. Hossaini, J. J. Larsen and J. C. Larsen, Food and Chemical Toxicology, 38 (2000) 19.

10 J. R. J. Sorensen, Metal Ions in Biological Systems, H. Sigel (Ed.),Vol. 14, Marcel Dekker, New York 1982, p. 77.

11 T. Hökelek and H. Necefoğlu, Anal. Sci., 17 (2001) 1241.

12 H. Icbudak, H. Olmez, O. Z. Yesilel, F. Arslan, P. Naumov, G. Jovanovski, A.R. Ibrahim, A. Usman, H. K. Fun, S. Chantrapromma and S.W. Ng, J. Mol. Struct., 657 (2003) 255.

13 K. Rissanen, J. Valkonen, P. Kokkonen and M. Leskela, Acta Chemica Scandinavica, A41 (1987) 299.

14 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley and Sons, New York, 1978, p. 197.

15 J. Zsakó, G. Pokol, Cs. Novák, Cs. Várhelyi, A. Dobó and G. Liptay, J. Therm. Anal. Cal., 64 (2001) 843.

16 H. Necefoğlu, H. Icbudak, D. A. Kose and A. Uyanik, Challenges for Coordination Chemistry in the New Century, (Monograph, edited by M. Melnik and A. Sirota), Vol. 5, Slovak Technical University Press, Bratislava 2001, p. 427.

17 P. Naumov, V. Jordonavska, O. Grupce, B. Boyanov and G. Jovanovski, J. Therm. Anal. Cal., 65 (2001) 59.

18 K. Györyova, E. Szunyogova, J. Kovarova, D. Hudecova, D. Mudronova and E. Juhaszova, J. Therm. Anal. Cal., 72 (2003) 587.

19 H. Icbudak, V. T. Yilmaz and H. Olmez, J. Thermal Anal., 53 (1998) 843.

20 P. Kokkonen, L. H. J. Lajunen, A. Jaakola and H. Ruotsalainen, Thermochim. Acta, 79 (1984) 289.

21 G. A. M. Hussein, H. M. Ismail and S. A. S. Mansour, J. Anal. Appl. Pyrolysis, 36 (1996) 17.

22 B. R. Srinivasan and S. C. Sawant, Thermochim. Acta, 402 (2003) 45.

23 W. Ferenc and B. Bocian, J. Therm. Anal. Cal., 74 (2003) 521.

24 M. Olczak-Kobza, R. Czylkowski and J. Karolak-Wojciechowska, J. Therm. Anal. Cal., 74 (2003) 895.