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# Synthesis and Characterization of bis(Nicotinamide) *m*-Hydroxybenzoate Complexes of Co(II), Ni(II), Cu(II), and Zn(II)<sup>1</sup>

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Abstract—Mixed-ligand *m*-hydroxybenzoate complexes of Co(II), Ni(II), Cu(II), and Zn(II) with nicotinamide were synthesized and characterized by elemental analysis, FT-IR spectrometry, solid state UV-vis spectrometry, and magnetic susceptibility measurements. The thermal behavior of the complexes was studied by simultaneous TG–DTA methods in static air atmosphere. The infrared spectral characteristics of the complexes are discussed and the mass spectra data are recorded. The complexes contain two water molecules, two *m*-hydroxybenzoato (*m*-hba), and two nicotinamide (na) ligands per formula unit. In these complexes, the *m*-hydroxybenzoate and nicotinamide behave as a monodentate ligand through acidic oxygen and nitrogen of the pyridine ring. The decomposition pathways and the stability of the complexes are interpreted in terms of the structural data. The final decomposition products were found to be the respective metal oxides.

DOI: 10.1134/S0036023607090124

Nicotinamide is known as a component of the vitamin B complex as well as a component of the coenzyme, nicotinamide adenine dinucleotide (NAD). 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]. These are highly important for transfer of hydrogen in cell breathing. The presence of a pyridine ring in numerous naturally abundant compounds, adducts of nicotinamide, is also of scientific interest. Therefore, the structure of nicotinamide has been the subject of many studies [4–7]. Also, nicotinamide itself plays an important role in the metabolism of living cells and some of its metal complexes are biologically active as antibacterial or insulin-mimetic agents [8].

Phenolic antioxidants such as hydroxybenzoates are an important class of natural antioxidants [9]. *m*-Hydroxybenzoic acid is widely used as an antimicrobial agent in foods, drugs, cosmetics, and toiletries [10]. Metal complexes of biologically important ligands are sometimes more effective than the free ligands [11]. Structural reports of metal ( $Zn^{2+}$ ) nicotinamide complexes exist in [12].

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

### **EXPERIMENTAL**

### Materials and Instrumentation



All chemicals used were analytical reagent products.  $CoSO_4 \cdot 6H_2O$ ,  $NiSO_4 \cdot 6H_2O$ ,  $CuSO_4 \cdot 5H_2O$ , ZnSO<sub>4</sub> · 7H<sub>2</sub>O, *m*-hydroxybenzoic acid, and nicotinamide were obtained from Merck (Darmstadt, Germany). Elemental analyses (C, H, N) were carried out by standard methods (Tubitak Marmara Research Center). Magnetic susceptibility measurements at room temperature were performed using a Sherwood Scientific MXI model Gouy magnetic balance. IR spectra were recorded in the 4000–400 cm<sup>-1</sup> region with a Perkin Elmer 1000 FT-IR spectrophotometer using KBr pellets. Thermal analysis curves (TG-DTA) were recorded simultaneously in a static air atmosphere with a Schimadzu DTG 60 thermal analyzer. The samples weighed approximately 10 mg and highly sintered  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> was used as a reference material. The heating rate was 10°C min<sup>-1</sup> and the DTG sensitivity was 0.05 mg s<sup>-1</sup>. We used for electronic spectra a Schimadzu 3600/UV-VIS-NIR Spectrophotometer. Mass

<sup>&</sup>lt;sup>1</sup> The text was submitted by the author in English.

Analytical data of the metal complexes

Complex	M/g mol <sup>-1</sup>	Yield (%)	Found (calcd.), %			Color	$d = a^{0}(C)$	
			С	Н	Ν	Color	u.p. ( C)	$\mu_{\rm eff}, \mu_{\rm B}.$
$[\mathrm{Co}(m-\mathrm{hba})_2(\mathrm{na})_2(\mathrm{H}_2\mathrm{O})_2]$	613.45	67	50.80	4.22	9.14	pink	127	4.11
$C_{26}H_{26}N_4O_{10}Co$			(50.89)	(4.24)	(9.14)			
$[Ni(m-hba)_2(na)_2(H_2O)_2]$	613.21	72	51.20	3.83	9.20	green	171	2.69
C <sub>26</sub> H <sub>26</sub> N <sub>4</sub> O <sub>10</sub> Ni			(50.92)	(4.20)	(9.14)			
$[Cu(m-hba)_2(na)_2(H_2O)]$	618.05	73	51.01	4.00	9.30	blue	102	1.51
$C_{26}H_{26}N_4O_{10}Cu$			(50.53)	(3.20)	(9.10)			
$[Zn(m-hba)_2(na)_2(H_2O)_2]$	619.89	80	49.95	4.47	9.03	colorless	101	diamagnetic
$C_{26}H_{26}O_{10}Zn$			(50.30)	(4.20)	(9.04)			

<sup>a</sup> Decomposition point.

spectrum data was recorded on an Agilent Technologies 5973 spectrophotometer using the DIP-MS method.

 $M(m-hba)_2(H_2O)_n + 2na \longrightarrow M(m-hba)_2(na)_2(H_2O)_n$ 

### *Preparation of m-hydroxybenzoate complexes*

At the first step, *m*-hydroxybenzoic acid sodium salt was prepared according to the following equation: 2m-hba +  $2NaHCO_3 \rightarrow 2Na(m$ -hba) +  $2CO_2 + 2H_2O_2$ .

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

$$2Na(m-hba) + MSO_4 \cdot nH_2O$$
  

$$\longrightarrow M(m-hba)_2 \cdot nH_2O + Na_2SO_4$$
  

$$[M = Co(II), Ni(II), Cu(II), Zn(II)].$$

The M(*m*-hba)<sub>2</sub>  $\cdot$  *n*H<sub>2</sub>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 vacuum.

### Synthesis of Mixed-Ligand Complexes

A solution of na (2 mmol) in distilled water (30 mL) was added dropwise with stirring to a solution of  $M(m-hba)_2(H_2O)_n$  (1 mmol) in hot distilled water (50 mL). The solutions were heated to 50°C in a temperature-controlled bath and stirred for 4 h and then cooled to room temperature and allowed 10-12 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:

[M = Co(II), Ni(II), Cu(II), Zn(II)].

## **RESULTS 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 *m*-hydroxybenzoato and nicotinamide ligands per mole formula units. All of the complexes contain two mole aqua ligands, and these are directly coordinated to the metal ion. The presence of aqua ligands was confirmed by the FT-IR spectra and mass loss and endothermic peaks in the TG-DTA curves. In the complexes with the aqua ligands, the octahedral coordination of the metal ion formed by two carboxylic oxygen atoms from two *m*-hyroxybenzoates and two nitrogen atoms from two nicotinamides. The elemental analysis data in the Table confirm the proposed formula of the complexes. Due to the low solubility, the electronic spectrum of the complexes was taken in the solid state. The electronic spectrum of the Co(II), Ni(II), and Cu(II) complexes shows absorption bands at 595, 620, and 670 nm, respectively [13, 14]. These peaks belong to the d-d transitions in metals, which may be assigned to  ${}^{4}A_{2g}(F) - {}^{4}T_{1g}(F)$  for Co(II),  ${}^{3}T_{1g}(F) - {}^{3}A_{2g}(F)$ for Ni(II), and  ${}^{2}T_{2g} \leftarrow {}^{2}E_{g}$  for Cu(II) transitions. UV-visible peaks corresponding to the  $\pi \longrightarrow \pi^*$  transitions in the ligands were observed at 270 and 320 nm. The peaks belonging to the  $\pi \longrightarrow \pi^*$  transitions are shifted to a longer wavelength as a consequence of



**Fig. 1.** FT-IR spectra of the complexes. (a) Cu(II), (b) Ni(II), (c) Co(II), and (d) Zn(II).

coordination when binding with metal, confirming the formation of *m*-hba–na metal complexes. According to magnetic susceptibility results, the metal complexes are high-spin type and paramagnetic, except for the Zn(II) complexes. As expected, the Zn(II) complexes are diamagnetic. All of the complexes may be thought to have octahedral coordination around the metal ions.

### FT-IR Spectra

The FT-IR spectra of the complexes are given in Fig. 1. The absorption bands in the range of 3350–2900 cm<sup>-1</sup> in the complexes correspond to the asymmetric and symmetric stretching vibration of water molecules. The peaks for the N-H stretches of primary amides are strong in the range of 3370-3170 cm<sup>-1</sup>. We observed two bands in the range of 3476–3186 cm<sup>-1</sup> in all of the complexes and assigned them to asymmetric and symmetric stretching vibrations of NH<sub>2</sub>. Also, a N-H bending peak of the complexes is shown approximately in the range of 1599 cm<sup>-1</sup>. The na complexes give rise to strong bands responsible for 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<sup>-1</sup> are assigned to this mode. This band remained almost in the same range amide group of the free na ligand, so the na ligand did not coordinate to the amide group. The pyridine ring



Fig. 2. TG–DTA curve of the  $[Co(m-hba)_2(na)_2(H_2O)_2]$ .

vibrations of free nicotinamide at 1580 cm<sup>-1</sup> shift to lower frequencies in the spectrum of the metal complexes. These shifts are shown in the range of 1443 cm<sup>-1</sup>; this may indicate that the pyridine ring is coordinated. The main difference in the spectrum of *m*-hydroxybenzoic acid is that the C=O stretching vibration of the carboxyl group at 1718 cm<sup>-1</sup> is shifted to a lower frequency in all the metal complexes. The absorption bands of carboxylate in the metal complexes occur in the range of 1543 cm<sup>-1</sup>. This shows that the coordination takes place through the carboxyl group [15]. The –OH bending peak for the *m*-hydroxybenzoic acid remained almost in the same position at around 1259 cm<sup>-1</sup> in all metal complexes. The low intensity bands in the region of 600–400 cm<sup>-1</sup> are attributed to M–N and M–O vibrations [16, 17].

### Thermal Data

 $[Co(m-hba)_2(na)_2(H_2O)_2]$ . The coordination waters of the Co(II) complex are dehydrated in the two-step temperature ranges of 116-145°C and 148-179°C (Fig. 2). The endothermic DTA peaks at 142°C and 162°C correspond to the liberation of two water molecules that are coordinated to the metal ion. In the next stage, two mole nicotinamide ligands decompose in the temperature range of 190–305°C (exp. 38.97%; cal. 39.8%). The related endothermic DTA peak is at 285°C. This type of behavior of neutral ligands has been reported earlier [16–18]. Consequently, the decomposition of the *m*-hydroxybenzoato ligands starts with the release of CO<sub>2</sub> molecules. The descending continuous TG curve is obtained in the temperature range of 306–575°C (DTA peaks at 345, 484, 518, and 556°C) and these are relevant to the decomposition of mhydroxybenzoato ligands. The final decomposition product is CoO (exp. 12.92%; calc. 12.31%).

 $[Ni(m-hba)_2(na)_2(H_2O)_2]$ . The thermal dehydration of the Ni(II) complex occurred in two steps by giving endothermic DTA peaks at 170°C and 188°C corresponding to the liberation of two water molecules that are coordinated to the metal ion (Fig. 3). The tempera-



Fig. 3. TG–DTA curve of the  $[Ni(m-hba)_2(na)_2(H_2O)_2]$ .

ture ranges of these steps are  $155-174^{\circ}$ C and  $175-204^{\circ}$ C. In the second stage, two mole nicotinamide ligands decompose and are removed in the temperature range of  $215-307^{\circ}$ C by giving an endothermic DTA peak at  $284^{\circ}$ C (exp. 40.72%; cal. 39.80%). Finally, the decomposition of the *m*-hydroxybenzoato ligands starts and the loss of the weight-continuous complex is obtained in the temperature ranges of  $208-452^{\circ}$ C (DTA peaks at 313, 391, 402, and  $425^{\circ}$ C). The final decomposition product, namely NiO, was identified (exp. 11.71%; calc. 12.23%) by IR spectroscopy with the corresponding spectra obtained under the same conditions as the pure oxides.

 $[Cu(m-hba)_2(na)_2(H_2O)_2]$ . The TG–DTA curves for the Cu(II) complex are given in Fig. 4. The first stage of the thermal decomposition of Cu(II) nicotinamide *m*-hydroxybenzoate starts at the 110–196°C temperature range with the release of the two aqua ligands (exp. 6.76%; calc. 5.99%). The decomposition occurs in one step, giving an endothermic DTA peak at 191°C. The anhydrous complex,  $[Cu(m-hba)_2(na)_2]$ , is not stable in air and begins to decompose with the removal of the water molecules. At the 205 and 272°C DTA peaks, na and *m*-hba ligands decompose in the temperature range of 197-880°C. Similar behavior was observed in the nicotinamide-acetylsalicylato and nicotinamide-phydroxybenzoato mixed-ligand complexes of Cu(II) [18, 19]. At the result of the removal of ligands, CuO is produced (exp. 12.63%; calc. 12.87%).

 $[Zn(m-hba)_2(na)_2(H_2O)_2]$ . Decomposition of the Zn(II) complex is similar to that of the Cu(II) complex. Firstly, two mol water are removed from the complex structure in one step (92–126°C). Water decomposition is given at the DTA peak at 117°C. This behavior was also observed in our earlier studies with Zn(II) complexes [18–20]. The following stage is related to decomposition of the diethylnicotinamide and *p*-hydroxybenzoate ligands (127–585°C) and the decomposition DTA peaks are 277, 320, 560°C.



Fig. 4. TG–DTA curve of the  $[Cu(m-hba)_2(na)_2(H_2O)_2]$ .

According to the mass loss, the final product is ZnO (exp. 85.97, calcd. 86.87%) at 576°C (Fig. 5).

All of the complexes contain two moles of coordination water. In these complexes, the first stage from approximately 92 to 196°C corresponds to dehydration. The experimental values for the mass loss of the dehydration stage are consistent with the calculated values. Regardless of the coordination, the decomposition of the complexes starts with a dehydration process. The results indicate that the metal-water bond strength is almost the same for all of the water molecules. The complexes of Co(II) and Ni(II) lose water molecules in two steps, whereas those of Cu(II) and Zn(II) lose water in one step. This behavior was also observed in previous studies and this may be attributed to the electron density of the Cu(II) and Zn(II) ions [21]. By the loss of two coordinated the originally octahedral complexes convert into a new arrangement. After the dehydration process, the decomposition stages of the anhydrous complexes are related to the release of nicotinamide and the partial decomposition of *m*-hydroxybenzoate involving the release of CO<sub>2</sub>. Previous studies show



Fig. 5. TG–DTA curve of the  $[Zn(m-hba)_2(na)_2(H_2O)_2]$ .



Fig. 6. Suggested structure of the complexes.

that the benzoate-metal complexes decompose by releasing CO<sub>2</sub> [21–26]. In complexes, all ligands are coordinated to the metal ion as monodendate ligands. The IR spectra of the intermediate products show similar results. The final decomposition products were found to be the respective metal oxides in the 450–600°C temperature intervals. The thermal stabilities of the complexes increase in the following order:

### Zn(II) < Cu(II) < Co(II) Ni(II) - m-hba-na.

The suggested structure of the complexes is given in Fig. 6.

### Mass Spectra

To conclude, the thermal decomposition pathway of the  $[Ni(m-hba)_2(na)_2(H_2O)_2]$  complex mass spectrum was recorded (Fig. 7) using the method of direct insertion probe pyrolysis mass spectrometry. The molecular ion peak is not detected in the mass spectrum recorded. The obtained mass spectrum is relatively complex and exhibits a large number of peaks that extend to the m/zvalue above 612. These peaks belong to the decomposition products of the complex and ligands. A schematic representation including the main fragmentation process for the  $[Ni(m-hba)_2(na)_2(H_2O)_2]$  complex and ligands is given in Scheme 2.



Fig. 7. Mass Spectrum of [Ni(*m*-hba)<sub>2</sub>(na)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>] complex.



Scheme 2. Mass spectral fragmentation pattern of the  $[Ni(m-hba)_2(na)_2(H_2O)_2]$ .

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