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Synthesis and Characterization of Bis(N,N-diethylnicotinamide) *m*-Hydroxybenzoate Complexes of Co(II), Ni(H), Cu(II), and Zn(II)[1]

D. A. Köse[a], A. Kaya[b], and H. Necefoğlu[b]

[a] *Hacettepe University, Departmen of Chemistry, Beytepe Campus, Ankara, Turkey*
[b] *Kafkas University, Faculty of Art and Science, Department of Chemistry, Paşaçayiri, Kars, Turkey*
e-mail: dkose@hacettepe.edu.tr

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Abstract—Four novel mixed-ligand complexes of Co(II), Ni(II), Cu(II), and Zn(II) with *m*-hydroxybenzoate (m-Hba) and N,N-diethylnicotinamide (Dena) were synthesized and characterized on the basis of elemental analysis, FT-IR spectroscopic study, and solid state UV-Vis spectrophotometric and magnetic-susceptibility data. The thermal behavior of the complexes was studied by combined *TG–DTA* methods in static air atmosphere, and the mass spectra were recorded. The Co(II), Ni(II), and Zn(II) complexes, except for the Cu(II) complex, contain two molecules of coordinated water, two *m*-Hba, and two Dena ligands per formula unit. In these complexes, the *m*-Hba and Dena behave as monodentate ligands via acidic oxygen and nitrogen of the pyridine ring. In the Cu(II) complex, the *m*-Hba is coordinated as monoanionic bidentate ligand through acidic oxygen and carbonyl oxygen. Dena is bonded with Cu^{2+} as monodentate ligand by the nitrogen atom of the pyridine ring. The decomposition pathways and the stability of the complexes are interpreted in terms of the proposed structural data. The final decomposition products were found to be the respective metal oxides.

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INTRODUCTION

It is well 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 [1–4]. It is not surprising; therefore, many authors have investigated heterocyclic compounds and also examined them as ligands in coordination compounds of several central atoms. Metal complexes of biologically important ligands are sometimes more effective than the free ligands [5]. N,N-Diethylnicotinamide (**Dena**) is a derivative of nicotinamide (vitamin B) used as exhalation agent in respiratory systems in medicine [6]. The presence of the pyridine ring in numerous naturally abundant compounds, adducts of Dena are also of scientific interest. Therefore, the structure of Dena has been the subject of many studies [7–13]. Phenolic antioxidants such as hydroxybenzoates are important classes of natural antioxidants [14]. Benzoic acid and derivatives are widely used as antimicrobial agents in foods, and drugs [15]. Some carboxylate compounds (e.g., benzoates) are known to have antibacterial activity. Benzoic acid is used in combination with salicylic acid in dermatology as a fungicidal treatment for fungal skin diseases [16]. Structural reports of metal (Zn^{2+})complexes are available in [17].

In the several coordination compounds of Co, Cu, and Zn with aryl carboxylic acids, the bonding occurs by the acidic OH group of carboxylic acid as monodentate [18]. According to X-ray structures in literature, thephenolic OH group of aryl carboxylic acid does not participate in coordination and remains free [19–21]. In some metalcarboxylate complexes, coordination becomes as chelate by the carbonyl oxygen atom and acidic OH group of carboxylic acid [22]. The Dena ligand is coordinated by the nitrogen heteroatom of the pyridine ring. These type complexes resemble those described in literature [19]. The thermal decomposition curves of title compounds are compatible with published data [6, 23–25].

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 (***m*-Hba**)-diethylnicotinamide. The structures of the ligands are shown below:

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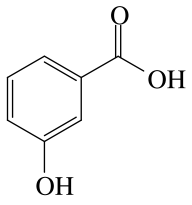
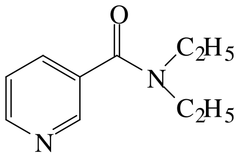
[1] The article was submitted by the authors in English.



(*m*-Bba)



(Dena)

EXPERIMENTAL

Materials and instruments. All used chemicals were analytical reagent products. $CoSO_4 \cdot 6H_2O$, $NiSO_4 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, $ZnSO_4 \cdot 7H_2O$, and *m*-hydroxybenzoic acid were obtained from Merck (Darnstadt, Germany). Diethylnicotinamide was purchased from Darnitsa Chemicals Union (Kiev, Ukraine). Elemental analyses (C, H, N) were performed by standard methods at the TUBITAK Laboratory (Scientific and Technical Research Council of Turkey). Magnetic susceptibility measurements at room temperature were determined on a Sherwood Scientific MXI model magnetic balance (Gouy method) using $Hg[Co(SCN)_4]$. IR spectra were recorded in the 4000–400 cm^{-1} 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 sample weight was approximately 10 mg, and highly sintered α-Al_2O_3 was used as a reference material. The heating rate was 10 K min^{-1}, and the *DTG* sensitivity was 0.05 mg s^{-1}. We used a Schimadzu UV3600/UV-VIS-NIR model spectrophotometer for solid-state UV-Vis range studies. Mass spectra data were recorded Agilent Technologies 5973 spectrophotometer using the DIP-MS method.

Synthesis of *p*-hydroxybenzoate complexes. In the first step, *m*-hydroxybenzoic acid sodium salt was prepared according to the following reaction:

$$2m\text{-Hba} + 2NaHCO_3 \longrightarrow 2Na(m\text{-Hba}) + 2CO_2 + 2H_2O.$$

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

$$2Na(m\text{-Hba}) + MSO_4 \cdot nH_2O \longrightarrow M(m\text{-Hba})_2 \cdot nH_2O + Na_2SO_4$$

$$(M = Co(II), Ni(II), Cu(II), \text{and } Zn(II)).$$

An $M(m\text{-Hba})_2 \cdot nH_2O$ solution was allowed to stand for 5–7 days for crystallization at room temperature. The crystals formed were filtered off, washed with cold distilled water and acetone, and dried in vacuo.

Synthesis of mixed-ligand complexes. A solution of Dena (2 mmol) in distilled water (30 ml) was added dropwise with stirring to a solution of $M(m\text{-Hba})_2(H_2O)_n$ (1 mmol) in hot distilled water (50 ml). The prepared solution was heated to 50°C in a temperature-controlled bath, stirred for 4 h, and then cooled to room temperature and allowed to stand for 10–12 days for crystallization. The crystals formed were filtered off, washed with cold water and acetone, and dried in vacuo. The mixed-ligand complexes were prepared according to the following reaction:

$$M(m\text{-Hba})_2(H_2O)_n + 2Dena \longrightarrow M(m\text{-Hba})_2(Dena)_2(H_2O)_n$$

$$(M = Co(II), Ni(II), Cu(II), \text{and } Zn(II)).$$

RESULTS AND DISCUSSION

Analytical results and compositions of the complexes are given in table. The complexes were synthesized with high purity. The results of elemental analysis indicated that the complexes contain two moles of *m*-Hba and Dena ligands per mole formula units. Except for the Cu(II) complex, other complexes also include two moles of aqua ligands. The Cu(II) complex has no water ligand. The presence or absence of aqua ligands was confirmed by the FT-IR spectra and mass loss and endothermic peaks in the *TG–DTA* curves. In the Co(II), Ni(II), and Zn(II) complexes with the aqua ligands, the octahedral coordination of the metal ion is formed by carboxylic acid oxygen atoms from two *m*-Hba and two nitrogen atoms from two Dena. However, in the anhydrous Cu(II) complex *m*-Hba behaves as monoanionic bidentate chelating ligand through carboxylic oxygen atoms. The elemental analysis data in table confirm the proposed formula of all investigated complexes.

Due to the low solubility, we studied a solid sample, recording satisfactory UV-Vis spectra for the complexes. The electronic spectra of the Co(II), Ni(H), and Cu(II) complexes show absorption bands at 550, 610, and 590 nm, respectively [26, 27]. These peaks belong to the *d–d* transitions in metals that can be assigned to ${}^4A_{2g}(F) \longleftarrow {}^4T_{1g}(F)$ for Co(II), ${}^3T_{1g}(F) \longleftarrow {}^3A_{2g}(F)$ for Ni(II), and ${}^2T_{2g} \longleftarrow {}^2E_g$ for Cu(II) transitions. The UV-Vis peaks corresponding to the $\pi \longrightarrow \pi^*$ transitions in the ligands were observed at 260 and 340 nm. The peaks belonging to the $\pi \longrightarrow \pi^*$ transitions are shifted to a longer wavelength as a consequence of coordination when binding with metal, confirming the formation of *m*-Hba–Dena metal complexes. The metal complexes are of the high-spin type and paramagnetic, except for the Zn(II) complexe, which is diamagnetic. The values of μ_{eff} suggest octahedral coordination around the metal ions.

In FT-IR spectra of the Co(II), Ni(II), and Zn(II) complexes, except of the Cu(II) complex, OH absorption bands of aqua ligands are present in a range of

Analytical data of the metal complexes

Complex	*M*	Yield, %	Contents (found/calcd), %			Color	D.p., °C*	$\mu_{eff.}$, μ_B
			C	H	N			
$[Co(m\text{-}Hba)_2(Dena)_2(H_2O)_2]$ $C_{34}H_{42}N_4O_{10}Co$	725.45	70	55.90/56.27	5.70/5.79	7.72/7.72	Pink	103	3.97
$[Ni(m\text{-}Hba)_2(Dena)_2(H_2O)_2]$ $C_{34}H_{42}N_4O_{10}Ni$	725.21	75	55.95/56.32	5.55/5.79	7.78/7.72	Light-green	119	2.70
$[Cu(m\text{-}Hba)_2(Dena)_2]$ $C_{34}H_{38}N_4O_8Cu$	730.05	80	59.00/58.90	6.01/5.50	8.07/8.07	Light-blue	102	1.49
$[Zn(m\text{-}Hba)_2(Dena)_2(H_2O)_2]$ $C_{34}H_{42}N_4O_{10}Zn$	731.89	82	55.74/55.78	6.17/5.80	7.69/7.67	Colorless	101	Dia

* Decomposition point.

3300–3000 cm^{-1} corresponding to asymmetric and symmetric stretching vibrations of water molecules. These results indicate no aqua ligand in the Cu(II) complex, while the other complexes have the water ligand. The complexes give rise to strong bands responsible for the C=O stretching. Conjugation between the carbonyl group and amide nitrogen causes small frequency shifts. The strong bands observed at ~1620 cm^{-1} are assigned to this mode. Pyridine ring vibrations of free dietylnicotinamide at 1580 cm^{-1} shifts to lower frequencies in the spectrum of the metal complexes. These shifts are shown in range of 1448–1443 cm^{-1}, approximately this can 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^{-1} is shifted to lower frequency in all the metal complexes. The absorption bands of carboxylate in the metal complexes are observed in a range of 1646–1617 cm^{-1}. This can be a consequence of coordination that takes place through the carboxyl group by deprotonation of the *m*-Hba molecule during coordination [23]. They $\nu_s(COO^-)$ bands are located at 1541 cm^{-1} for the Co(II) complex, 1514 cm^{-1} for the Cu(II) complex, and 1542 cm^{-1} for the Ni(II) and Zn(II) complexes. The $\nu_{as}(COO^-)$ peaks are observed at 1394 cm^{-1} for the Co(II), 1385 cm^{-1} for Cu(II), 1399 cm^{-1} for Ni(II), and 1402 cm^{-1} for Zn(II) complexes. The splitting of the ν_{as} and ν_s bands of the COO^- groups is almost identical for the Co(II), Ni(II), and Zn(II) complexes (144–147 cm^{-1}) and these bands are shifted slightly than that for the sodium salt (140 cm^{-1}) [28], because the monodentate carboxylate group exists [29, 30]. However, in the Cu(II) complex this splitting band of the COO^- group is almost identical (131 cm^{-1}) and is smaller than that in the sodium salt, this result proves that bonding of the carboxylate group is bidentate to the metal atom. The OH bending peak for the *m*-hydroxybenzoic acid remained almost in the same position at ~1259 cm^{-1} in all the metal complexes. The low-intensity bands in a region of 600–400 cm^{-1} are attributed to the M–N and M–O vibrations [6, 31–33].

The thermal data of the Co(II), Ni(II), and Zn(II) complexes are given in Fig. 1. Among all complexes investigated by us, $[Co(m\text{-}Hba)_2(Dena)_2(H_2O)_2]$ is more stable. Its thermal decompositions began at 85°C. The coordination waters of the Co(II) complex are dehydrated in the one-step temperature in a range of endothermic *DTA* peak at 103°C (found 5.01%; calcd 4.98%).The decomposition of the complex is associated with the complete pyrolysis of the organic part of the compound starts above this temperature. The thermoanalytical responses of the Co(II) complex are shown in Fig. 1a. The organic part of the complex decomposes with the release of CO_2 molecules. The descending continuous *TG* curve is obtained in a temperature range of 185–605°C (endothermic *DTA* peaks at 254, 455, 485, and 560°C). The final decomposition product is CoO (found 9.00%; calcd 10.31%).

The thermal dehydration of $[Ni(m\text{-}Hba)_2(Dena)_2(H_2O)_2]$ occured in one-step by giving an endothermic *DTA* peak at 119°C corresponding to the liberation of two water molecules that are coordinated to the metal ion (Fig. 1b) (found 5.05%; calcd 4.98%o). The temperature range of this step is 85–135°C. The anhydrous Ni(II) complex is stable in a range of 135–190°C. In the second stage, all of the organic ligands decompose and remove in a temperature range of 215–307°C by giving exothermic *DTA* peaks at 361 and 418°C. The final decomposition product, namely NiO, was identified (found 9.76%; calcd 10.32%) by IR spectroscopy with

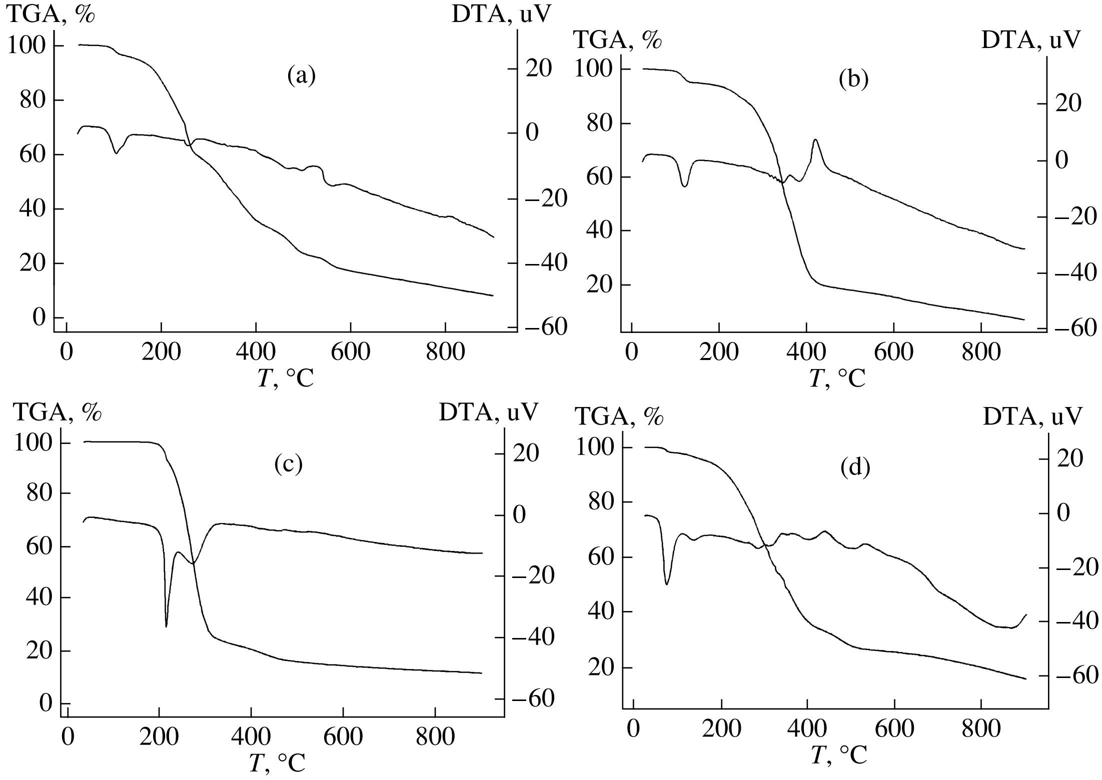


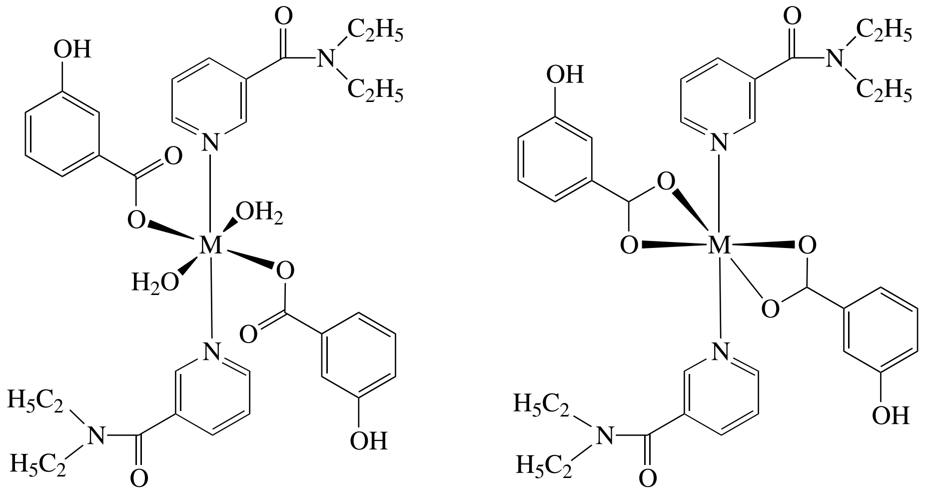
Fig. 1. *TG-DTA* curves of the complexes: (a) [Co(*m*-Hba)$_2$(Dena)$_2$(H$_2$O)$_2$]; (b) [Ni(*m*-Hba)$_2$(Dena)$_2$(H$_2$O)$_2$]; (c) [Cu(*m*-Hba)$_2$(Dena)$_2$], and (d) [Zn(*m*-Hba)$_2$(Dena)$_2$(H$_2$O)$_2$].

the corresponding spectra obtained under the same conditions as the pure oxides.

The *TG–DTA* curves for [Cu(*m*-Hba)$_2$(Dena)$_2$(H$_2$O)$_2$] are given in Fig. 1c. There is no aqua molecule in this complex and, hence, no aqua decomposition peak is shown. The anhydrous complex is stable untill to temperature of 185°C. After this temperature, the *m*-Hba and Dena ligands start to decompose all together. The decomposition occurs in a temperature range of 185–520°C in two steps by giving endothermic *DTA* peaks at 213 and 269°C. As a result of the removing organic ligands, CuO is produced (found 11.91%; calcd 10.97%).

The thermal decomposition of [Zn(*m*-Hba)$_2$(Dena)$_2$(H$_2$O)$_2$] is given in Fig. 1d. The first stage of its thermal decomposition starts at the 55–160°C temperature range with the release of two aqua ligands (found 4.97%; calcd 4.92%). The decomposition occurs in two steps by giving endothermic *DTA* peaks at 72 and 134°C. The anhydrous complex, [Zn(*m*-Hba)$_2$(Dena)$_2$], is not stable in air and begins to decompose with removing the water molecules. At 282, 400, and 502°C *DTA* peaks of the Dena and *m*-Hba ligands decompose in a temperature range of 161–555°C. The removing ligands produced ZnO (found 12.95%; calcd 11.15%). Similar decomposition behaviors are shown in literature [24, 25, 33].

Except for the Cu(II) complex, all the other complexes contain two coordinated water molecules. The aqua ligands of the complexes, the first stage from approximately 55 to 160°C corresponds to dehydration. The experimental values for the mass loss of the dehydration stage are well consistent with the calculated values. Regardless of coordination, the decomposition of the complexes starts with a dehydration process but the decomposition of the Cu(II) complex starts with to be smashed of organic ligands. The results indicate that the metal–water bond strength is almost the same for all the water molecules. The Co(II), Ni(II), and Zn(II) complexes lose water molecules in one-step. By the loss of two coordinated molecules the originally octahedral complexes convert into a new arrangement. After the dehydration process, decomposition stages of the anhydrous complexes are related to release nicotinamide, and the partial decomposition of *m*-hydroxybenzoate involving the release of CO$_2$ occurs. Previous studies show that the benzoate–metal complexes decompose by releasing CO$_2$ [34, 35]. In the Co(II), Ni(II), and Zn(II) complexes, all ligands are coordinated to the metal ion as monodendate (**a**) but, in the Cu(II) complex *m*-Hba ligands are coordinated as monoanionic bidentate (**b**). This type bonding is present in literature [36–38]. The IR spectra of the intermediate products show similar results. The final decomposition products were found to be the respective metal oxides in the 500–600°C temperature intervals. The suggested structures of the complexes are given below:



(a)
M = Co(II), Ni(II), and Zn(II)

(b)
M = Cu(II)

To conclude the thermal decomposition pathway of the $[Ni(m\text{-}Hba)_2(Dena)_2(H_2O)_2]$ complex, the mass spectrum was recorded (Fig. 2) using direct the insertion probe pyrolysis mass spectrometry method. 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*/*z* value above 722. These peaks belong to decomposition products of the complex and ligands.

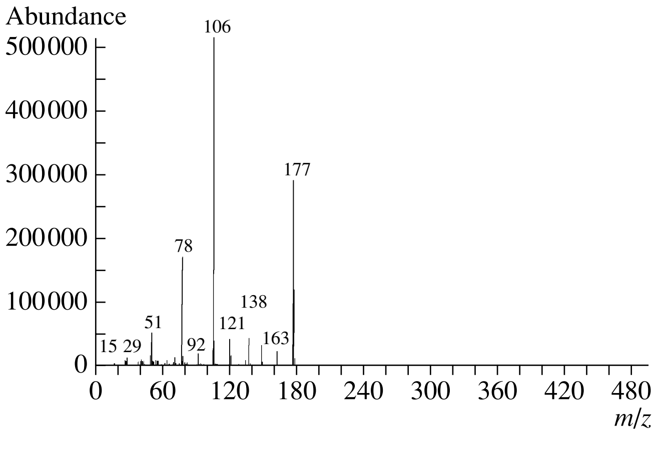


Fig. 2. Mass spectrum of $[Ni(m\text{-}Hba)_2(Dena)_2(H_2O)_2]$ complex.

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