Journal of Thermal Analysis and Calorimetry, Vol. 93 (2008) 2, 509–514

SYNTHESIS AND CHARACTERIZATION OF *bis*(NICOTINAMIDE) *m*-HYDROXYBENZOATE COMPLEXES OF Co(II), Ni(II), Cu(II) AND Zn(II)

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The mixed-ligand *m*-hydroxybenzoate complexes of Co(II), Ni(II), Cu(II) and Zn(II) with nicotinamide were synthesized and characterized. The chemical, FT IR and UV-vis spectrophotometric, thermal and mass spectral analyses, magnetic susceptibility measurements revealed that the compounds contain two water molecules, two *m*-hydroxybenzoate (*m*-hba) and two nicotinamide (na) ligands per formula unit. *m*-Hydroxybenzoate and nicotinamide ligands bind to the metal atoms monodentately through their acidic oxygen and pyridinic nitrogen atoms, respectively. The thermal decomposition pathways and the stability of the complexes are interpreted in the terms of the structural data.

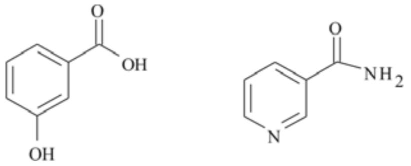
Keywords: *m-hydroxybenzoate, metal complexes, nicotinamide, thermal decomposition, transition metals*

Introduction

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]. The presence of pyridine ring in numerous naturally abundant compounds, are also of scientific interest. 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 [4]. Therefore, the structure of nicotinamide has been the subject of many studies [5–8].

On the other hand, phenolic antioxidants such as hydroxybenzoates are important classes of natural antioxidants [9]. *m*-Hydroxybenzoic acid is widely used as antimicrobial agents in foods, drugs, cosmetics and toiletries [10]. It is known that metal complexes of biologically important ligands are sometimes more effective than the free ligands [11]. Structural reports on metal (Zn^{2+}) nicotinamide complexes exist in [12].

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



Scheme 1

Experimental

Materials

All chemicals used were analytical reagent products. $CoSO_4·6H_2O$, $NiSO_4·6H_2O$, $CuSO_4·5H_2O$, $ZnSO_4·7H_2O$, *m*-hydroxybenzoic acid and nicotinamide were obtained from Merck.

Synthesis of mixed-ligand complexes

An aqueous solution of na (2 mmol, 30 mL) was added dropwise to a stirred solution of $M(m\text{-hba})_2(H_2O)_n$ (1 mmol) in hot distilled water (50 mL). The resulting solution was heated to 50°C in a temperature-controlled water 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:

$$M(m\text{-hba})_2(H_2O)_n+2na \rightarrow M(m\text{-hba})_2(na)_2(H_2O)_n \qquad (1)$$

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1388–6150/$20.00

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Preparation of m-hydroxybenzoate complexes

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

$$2m\text{-hba}+2\text{NaHCO}_3\rightarrow 2\text{Na}(m\text{-hba})+2\text{CO}_2+2\text{H}_2\text{O} \qquad (2)$$

In the second step, metal *m*-hba salt was synthesized from Na(*m*-hba) salt by the following substitution reaction:

$$2\text{Na}(m\text{-hba})+M\text{SO}_4\cdot n\text{H}_2\text{O}\rightarrow \text{M}(m\text{-hba})_2\cdot n\text{H}_2\text{O}+\text{Na}_2\text{SO}_4 \qquad (3)$$

where M=Co(II), Ni(II), Cu(II) and Zn(II).

The M(*m*-hba)$_2\cdot n$H$_2$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.

Instrumentation

Elemental analyses (C,H,N) were carried out by standard method (Tubitak Marmara Research Center). Magnetic susceptibility measurements were performed at room temperature using a Sherwood Scientific MXI model Gouy magnetic balance (England). 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 an inert gas (N_2) atmosphere with a Schimadzu DTG 60 thermal analyzer. The sample weighed approximately 10 mg and sintered α-Al$_2$O$_3$ was used as a reference material. The heating rate was 10°C min^{-1}. Electronic spectrum was recorded by a Schimadzu 3600/UV-VIS-NIR Spectrophotometer. Mass spectral data were recorded Agilent Technologies 5973 spectrophotometer using DIP-MS method.

Result and discussion

Effective magnetic moments, elemental analysis data and compositions of the complexes are given in Table 1. There is agreement with literature values for similar complexes [13, 14]. The complexes were synthesized with high purity. The results of the elemental analysis indicated that the complexes contain two moles of *m*-hydroxybenzoate and nicotinamide ligands per mole formula unit.

All of the complexes contain two moles of aqua ligand that are directly coordinated to metal ions. The octahedral coordination of the metal ions are completed by two carboxylic oxygen atoms from two *m*-hydroxybenzoates and two nitrogen atoms from two nicotinamides. Octahedral structure is confirmed by magnetic data. Due to the low solubility of the complexes, the electronic spectrum of the complexes were taken in the solid-state. The electronic spectra showed two absorption bands and *d–d* transition at 7000 cm^{-1} ($^4T_{1g}\rightarrow{}^4T_{2g}$) and 20000 cm^{-1} ($^4T_{1g}\rightarrow{}^4T_{1g}$)($^4P$) for Co(II) complex; three absorption bands and *d–d* transition at 7800 cm^{-1} ($^3A_{2g}\rightarrow{}^3T_{2g}$), 15600 cm^{-1} ($^3A_{2g}\rightarrow{}^3T_{1g}$)($^3F$) and 25500 cm^{-1} ($^3A_{2g}\rightarrow{}^3T_{1g}$)($^3P$) for Ni(II) complex respectively. In the Cu(II) complex multiple absorption band is observed at about 10700–17000 cm^{-1} but they are overlapped. Because, octahedral complexes of Cu(II) are observable distorted by Jahn–Teller effect and the structure of complex is to name pseudo-octahedral. It was to taken notice of top of the peak as absorption band and *d–d* transition at about 13000 cm^{-1} ($^2E_g\rightarrow{}^2T_{2g}$) for Cu(II) complex. UV-visible peaks corresponding to the the $\pi\rightarrow\pi^*$ transitions in the ligands were observed at 270 and 320 nm [15, 16]. The peaks belonging to $\pi\rightarrow\pi^*$ transitions are shifted to a higher wavelength as a consequence of coordination when binding with metal, confirming the formation of *m*-hba–na metal complexes. According to the magnetic susceptibility results, the Zn(II) complexes are diamagnetic as expected. All of the complexes may be thought octahedral coordination around the metal ions.

Table 1 Characteristic data of the metal complexes

Complex	MA/ g mol^{-1}	Yield/ %	d.p.^{a}/ °C	μ_{eff}/ B.M	C/%	H/%	N/%
					found (calculated)		
[Co(*m*-hba)$_2$(na)$_2$(H$_2$O)$_2$] $C_{26}H_{26}N_4O_{10}Co$	613.45	67	118	4.11	50.80 (50.89)	4.22 (4.24)	9.14 (9.14)
[Ni(*m*-hba)$_2$(na)$_2$(H$_2$O)$_2$] $C_{26}H_{26}N_4O_{10}Ni$	613.21	72	141	2.69	51.20 (50.92)	3.83 (4.20)	9.20 (9.14)
[Cu(*m*-hba)$_2$(na)$_2$(H$_2$O)] $C_{26}H_{26}N_4O_{10}Cu$	618.05	73	131	1.83	51.01 (50.53)	4.00 (3.20)	9.30 (9.10)
[Zn(*m*-hba)$_2$(na)$_2$(H$_2$O)$_2$] $C_{26}H_{26}N_4O_{10}Zn$	619.89	80	91	diamag.	49.95 (50.30)	4.47 (4.20)	9.03 (9.04)

[a] decomposition point

Table 2 Characteristic FTIR peaks of metal complexes

Gruplar	m-hba	Co(II)	Ni(II)	Cu(II)	Zn(II)
$\nu_{(\text{–OH})}$	2860–3100	–	–	–	–
$\nu_{(\text{–OH})_{H_2O}}$	–	3530–3100	3550–3060	3500–3050	3500–3000
$\nu_{(\text{NH})}$		3476	3477	3471	3474
$\nu_{(\text{C=O})_{\text{ester}}}$	1718	1676	1670	1685	1679
$\nu_{(\text{COO}^-)_{\text{as}}}$	1602	1545	1544	1552	1548
$\nu_{(\text{COO}^-)_{\text{s}}}$	1461	1393	1392	1390	1395
$\Delta\nu$	141	152	152	162	153
$\nu_{(\text{C–O–C})}$	1190	1135	1137	1198	1144
$\nu_{(\text{C–H})_{\text{CH}_3}}$	1374	1390	1391	1384	1399
$\nu_{(\text{C–N})_{\text{py}}}$	–	667	666	678	672
$\nu_{(\text{C–N})_{\text{amid}}}$	–	1253	1254	1229	1251
$\nu_{(\text{C=O})_{\text{amid}}}$	–	1632	1630	1685	1629
$\nu_{(\text{M–N})}$	–	563	564	599	564
$\nu_{(\text{M–O})}$	–	424	430	451	424

FTIR spectra

Characteristic FTIR peaks of the complexes are given in Table 2. The absorption bands in the range of 3350–2900 cm^{-1} correspond to the asymmetric and symmetric stretching vibrations of water molecules. The peaks for the N–H stretches of primary amides are strong in the range of 3370–3170 cm^{-1}. We observed two bands in the 3476–3186 cm^{-1} range for all complexes and assigned these peaks to asymmetric and symmetric stretching vibrations of NH_2. Also N–H bending vibrations appear approximately in 1599 cm^{-1}. 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. This band remained almost in the same range as the amide group of the free na ligand, indicating that the na ligand does not coordinate through amide group. Pyridine ring vibration of free nicotinamide at 1580 cm^{-1} shifts to 1443 cm^{-1} in the complexes indicating 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} shifts to lower frequency in all the metal complexes. The carboxylate peaks in the metal complexes appear in 1543 cm^{-1}. This shows that the coordination takes place through the carboxyl group [17]. The –OH bending peak for the *m*-hydroxybenzoic acid remained almost in the same position at around 1259 cm^{-1} in all metal complexes. The low intensity bands in the region of 600–400 cm^{-1} are attributed to M–N and M–O vibration [18, 19].

Thermal data

[Co(*m*-hba)$_2$(na)$_2$(H$_2$O)$_2$]

The coordinating water molecules of Co(II) complex are dehydrated in the two steps in the temperature ranges of 118–145 and 148–179°C (Fig. 1). The corresponding endothermic DTA peaks at 142 and 162°C confirm the release of the the water molecules. In the next stage, two moles of nicotinamide decompose in the temperature range of 190–305°C (exp. 38.97%; calc. 39.8%). Related endothermic DTA peak is at 285°C. This type of behavior of neutral ligands has been reported earlier [19, 20]. Consequently, the decomposition of the *m*-hydroxybenzoate ligands starts with the release of CO_2 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 *m*-hydroxybenzoato ligands. The final decomposition product is CoO (exp. 12.92%; calc. 12.31%).

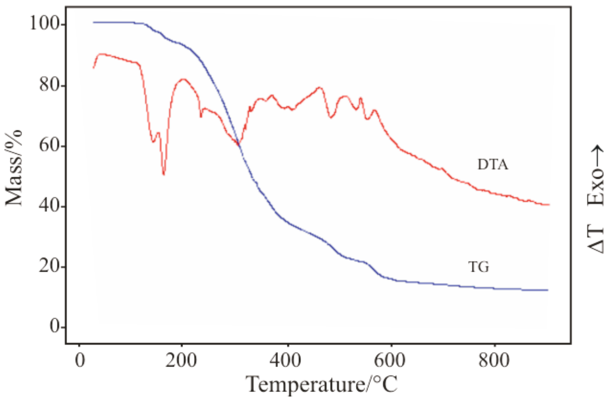


Fig. 1 TG-DTA curve of the [Co(*m*-hba)$_2$(na)$_2$(H$_2$O)$_2$]

[Ni(m-hba)$_2$(na)$_2$(H$_2$O)$_2$]

The thermal dehydration of the Ni(II) complex occurred in two-steps by giving two endothermic DTA peaks at 170 and 188°C corresponding to the liberation of two water molecules that are coordinated to metal ion (Fig. 2). In the second stage, two moles of nicotinamide ligands decompose and remove in the temperature range of 215–307°C by giving an endothermic DTA peak at 284°C (exp. 40.72%; calc. 39.80%). Finally, the decomposition of the *m*-hydroxybenzoate ligands starts and the mass loss continues in the temperature range of 208–452°C related (DTA peaks are at 313, 391, 402 and 425°C). The final decomposition product, namely NiO was identified (exp. 11.71%; calc. 12.23%) by comparing the IR spectrum with that of the pure oxide.

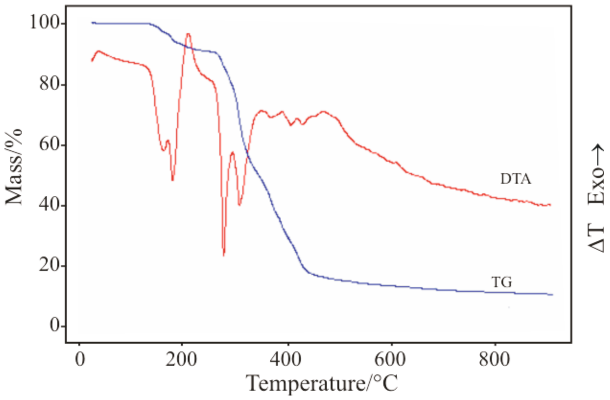


Fig. 2 TG-DTA curve of the [Ni(m-hba)$_2$(na)$_2$(H$_2$O)$_2$]

[Cu(m-hba)$_2$(na)$_2$(H$_2$O)$_2$]

TG-DTA curves for the Cu(II) complex are given in Fig. 3. The first stage of the thermal decomposition of Cu(II) nicotinamide *m*-hydroxybenzoate starts at 131°C with the release of two aqua ligands (exp. 6.76%; calc. 5.99%) at two steps. This corresponds to the endothermic DTA peaks at 191 and 205°C. The anhydrous complex, [Cu(m-hba)$_2$(na)$_2$] begins to decompose by eliminating na and *m*-hba ligands that is occurred in the temperature range of 217–880°C (DTA: 272°C). A similar behavior was observed in the nicotinamide–acetylsalicylato and nicotinamide–*p*-hydroxybenzoato mixed-ligand complexes of Cu(II) [20, 21]. Finally, the product was obtained in CuO form (exp. 12.63%; calc. 12.87%).

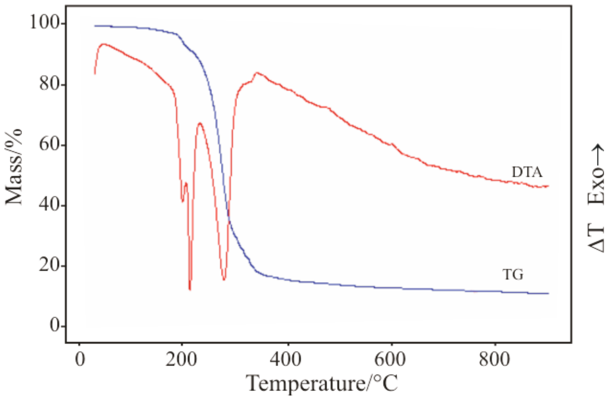


Fig. 3 TG-DTA curve of the [Cu(m-hba)$_2$(na)$_2$(H$_2$O)$_2$]

[Zn(m-hba)$_2$(na)$_2$(H$_2$O)$_2$]

Decomposition of the Zn(II) complex is different from others. Firstly, two mol of aqua ligands are removed from the complex structure in onestep (91–126°C) (DTA: 117°C). This behavior was also observed in our previous studies with Zn(II) complexes [21–23]. The following stage is related to the decomposition of the nicotinamide and *p*-hydroxybenzoate ligands (127–585°C) (the related DTA peaks are 277, 320, 560°C). According to the mass loss, the final product is ZnO (exp. 85.97, calc. 86.87%) at 576°C (Fig. 4) [24].

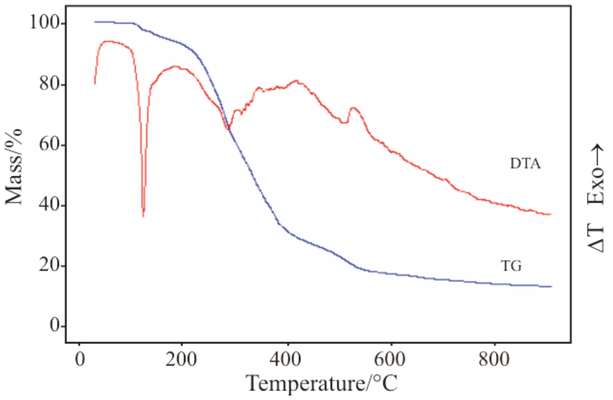


Fig. 4 TG-DTA curve of the [Zn(m-hba)$_2$(na)$_2$(H$_2$O)$_2$]

All of the complexes contain two moles of coordination water. In these complexes, the first stage from approximately 91 to 215°C corresponds to dehydration. The experimental values for the mass loss of the dehydration stage are well consistent with the calculated values. The results indicate that metal–water bond strength is almost the same for all of the water molecules. The complexes of Co(II), Ni(II) and Cu(II) lose water molecules in twosteps whereas those of Zn(II) lose water in onestep. This behaviour was also observed in previous studies and this may be attributed to the electrostatic density of Zn(II) ion [24]. After the dehydration process, decomposition stages of the anhydrous complexes are related to the release of nicotinamide and partial decomposition of *m*-hydroxybenzoate with the release of CO$_2$. Previous studies showed that the benzoate-metal complexes decompose by releasing of CO$_2$ [23–28]. In complexes, all ligands are coordinated to the metal ion as monodentate ligands. The IR spectra of the intermediate products showed similar results. The $(COO^-)_{sym.}$ peaks are located at 1545 cm^{-1} for Co(II), 1544 cm^{-1} for Ni(II), 1552 cm^{-1} for Cu(II) and 1548 cm^{-1} for Zn(II) complexes. $(COO^-)_{asym.}$ peaks are observed at 1393 cm^{-1} for Co(II), 1392 cm^{-1} for Ni(II), 1390 cm^{-1} for Cu(II) and 1395 cm^{-1} for Zn(II) complexes. The shift (Δ) between of the $\nu_{asym.}$ and $\nu_{sym.}$ bands of COO^- groups are for all of the complexes almost identical (162–152 cm^{-1}) and more than for the sodium salt *m*-hydroxybenzoic acid (141 cm^{-1}) [29] that monodentate carboxylate group exists [30, 31].

The coordination waters of Co(II) and Ni(II) complexes are removed two steps, but Zn(II) and Cu(II) complexes lose one step their coordination waters. According to the thermal stability of hydrated and non-hydrated complexes follow the order ;

Cu(II)<Zn(II)<Co(II)<Ni(II)–*m*-hba–na

This order is followed Pearson's arrangement of 2+ ions of metals.

The final decomposition products were found to be the respective metal oxides formed in the 450–600°C temperature intervals.

Mass spectra

To conclude the thermal decomposition pathway of the $[Ni(m\text{-hba})_2(na)_2(H_2O)_2]$ complex, mass spectrum was recorded (Fig. 5) using direct insertion probe pyrolysis mass spectrometry method. The molecular ion peak was not detected in the mass specrum recorded. The obtained pattern is relatively complex and exhibits a large number of peaks that extend to *m*/*z* value above 612 belonging to the decomposition products of the complex and ligands. A schematic representation including the main fragmentation process for the $[Ni(m\text{-hba})_2(na)_2(H_2O)_2]$ complex and ligands is given in Scheme 2.

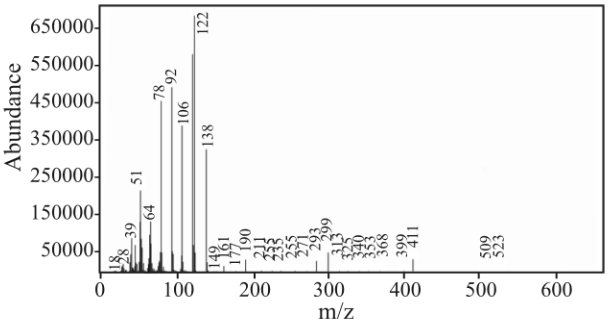


Fig. 5 Mass spectrum of $[Ni(m\text{-hba})_2(na)_2(H_2O)_2]$ complex

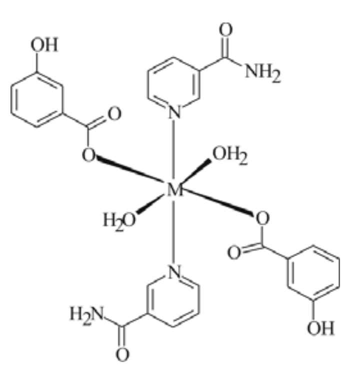
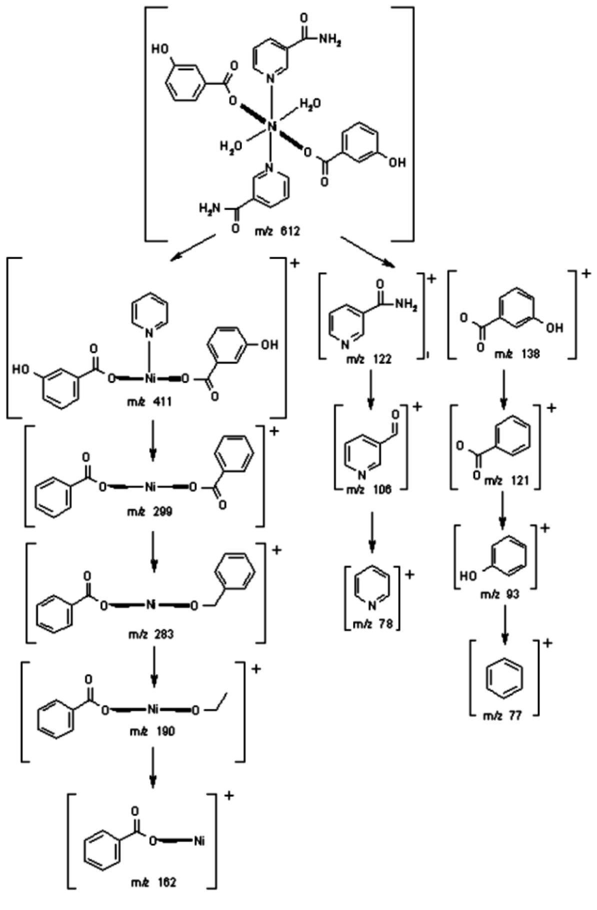


Fig. 6 Suggested structure of the complexes



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

Suggested structure of the complexes are given in Fig. 6.

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Received: September 17, 2007
Accepted: March 18, 2008

DOI: 10.1007/s10973-007-8712-5