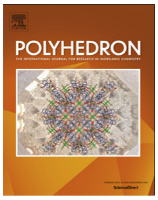
Polyhedron 81 (2014) 555–563

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



Synthesis and magneto-structural characterization of copper(II) nitrobenzoate complexes containing nicotinamide or methylnicotinamide ligands

Zuzana Vasková [a], Nives Kitanovski [b], Zvonko Jagličić [c,d], Peter Strauch [e], Zdeňka Růžičková [f], Dušan Valigura [g], Marian Koman [g], Bojan Kozlevčar [b], Jan Moncol [g,*]

[a] Institute of Inorganic Chemistry, Slovak Academy of Sciences, SK-84536 Bratislava, Slovakia
[b] Faculty of Chemistry and Chemical Technology, University of Ljubljana, 1000 Ljubljana, Slovenia
[c] Institute of Mathematics, Physics and Mechanics, 1000 Ljubljana, Slovenia
[d] Faculty of Civil and Geodetic Engineering, University of Ljubljana, 1000 Ljubljana, Slovenia
[e] Institute of Chemistry, University of Potsdam, 14476 Golm, Germany
[f] Department of General and Inorganic Chemistry, Faculty of Chemical Technology, University of Pardubice, CZ-532 10 Pardubice, Czech Republic
[g] Department of Inorganic Chemistry, Faculty of Chemical and Food Technology, Slovak Technical University, SK-81237 Bratislava, Slovakia

ARTICLE INFO

Article history:
Received 9 November 2013
Accepted 8 July 2014
Available online 17 July 2014

Keywords:
Copper(II)
Nicotinamide
N-methylnicotinamide
Crystal structure
Magnetic properties

ABSTRACT

Three new copper(II) 4-nitrobenzoato coordination compounds (4-NO_2bz^- = 4-nitrobenzoate anions) with N-methylnicotinamide (mna) $[Cu(4\text{-}NO_2bz)_2(mna)_2(H_2O)]$ (**1**), $[Cu(4\text{-}NO_2bz)_2(\mu\text{-}mna)(H_2O)]_2$ (**2**) and $[Cu(\mu\text{-}4\text{-}NO_2bz)_2(mna)]_2$ (**3**) were synthesized and characterized. Due to a comparison, additional two related compounds $[Cu(3,5\text{-}(NO_2)_2bz)_2(nia)_2(H_2O)]$ (**4**) (nia = nicotinamide, 3,5-$(NO_2)_2bz^-$ = 3,5-dinitrobenzoate anions) and $[Cu(\mu\text{-}2\text{-}NO_2bz)_2(mna)]_2$ (**5**) (2-NO_2bz^- = 2-nitrobenzoate anions) were isolated. The mononuclear compounds with mna **1** and nia **4** show CuO_2N_2O chromophores with the water molecule placed at the apex of the square pyramid. The square-pyramidal coordination sphere CuO_3NO in **2** differs to CuO_2N_2O in **1** and **4**. Differently, the water molecule is in **2** at the basal-plane, while two mna molecules serve also as bridges via *N*-py and *O*-amido enabling a dinuclear molecular structure **1**, **2** and **4** are paramagnetic though a dinuclear structure is seen in **2**, while a clear-cut strong antiferromagnetic (AFM) coupling ($2J$ -300 cm^{-1}) is found for the compounds **3** and **5**.

1. Introduction

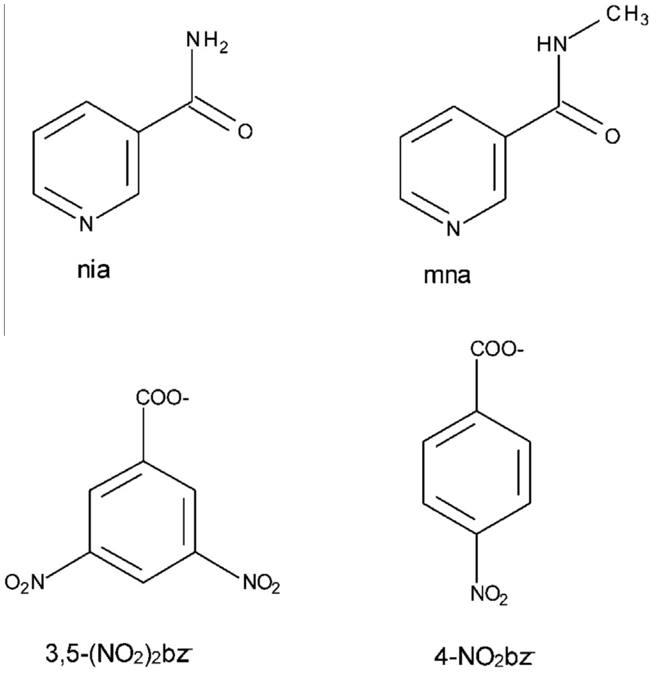
There has been significant interest in the field of structural and supramolecular chemistry of mixed coordination complexes owing to their potential applications in magnetic devices, non-linear optics, supramolecular catalysis, dynamic porous and zeolite-like materials [1]. Nicotinamide is one of the most popular pyridine-like N-donor ligands for construction due to these purposes [2]. Because, the nicotinamide is also a component of several enzymes e.g. vital coenzyme NAD (nicotinamide adenine dinucleotide) [3], it is often used for a synthesis of metal complexes as models for the bioinorganic species and for the metallodrugs development [4]. The hydrogen-bonding coordination supramolecular systems based on nicotinamide have been prepared and intensely studied using different transition metals [5]. The nicotinamide as a ligand in metal complexes can link to the other molecules through hydrogen bonds of their carboxamide groups [6,7]. The copper(II) carboxylate complexes with nicotinamide have been also tested for antibacterial, antifungal activities [8,9], and in the medicine [10]. On the other hand, only a few metal complexes with *N*-methylnicotinamide (Scheme 1) have been studied as an object for supramolecular coordination chemistry [11,12], though it differs to nicotinamide only by one methyl group replacing the hydrogen atom.

In this paper, we describe a preparation, spectral and magnetic properties, structural characterization, and supramolecular organization of five new coordination compounds with nicotinamide (nia) and N-methylnicotinamide (mna) (Scheme 1). Among them, three 4-nitrobenzoato/mna species precipitate from very similar reaction mixtures, but giving structurally different, though all square-pyramidal coordination sets CuO_2N_2O, CuO_3NO, CuO_4N. The synthetic mechanism and stability of these compounds is clearly related to the amido group and water molecules hydrogen bonds.

---

* Corresponding author. Tel.: +421 2593 25 186; fax: +421 2524 93 198.
E-mail address: jan.moncol@stuba.sk (J. Moncol).

http://dx.doi.org/10.1016/j.poly.2014.07.017
0277-5387/



Scheme 1. The related pyridine-based nicotinamide (nia), N-methylnicotinamide (mna) and two nitro-benzoato ligands (Accelrys Draw 4.1 [13] has been used for drawing).

2. Experimental

All chemicals were of analytical grade (Aldrich, Sigma) and used without further purification. Carbon, hydrogen and nitrogen analyses were carried out using a CHNSO FlashEA™ 1112 Automatic Elemental Analyzer. The electronic spectra (190–1100 nm) were measured in nujol suspensions with a SPECORD 200 (Carl Zeiss Jena) spectrophotometer at room temperature. IR spectra (4000–100 cm^{-1}) were recorded on a Nicolet 5700 FTIR spectrophotometer using an ATR attachment at room temperature. EPR spectra were recorded at room temperature with a Bruker ER 200E-SRC and Bruker ESP 300 spectrometers operating at X-band equipped with a Bruker ER 035 NMR gaussmeter and Hewlett Packard 5350B microwave frequency counter. Magnetic susceptibility was investigated with Quantum Design MPMS-XL-5 SQUID susceptometer. Magnetic susceptibility was investigated between 2 and 300 K in a constant magnetic field of H = 1000 Oe. The data were corrected for the sample holder contribution and a temperature independent magnetic susceptibility of inner shell electrons (Larmor diamagnetism) as obtained from Pascall's tables [14]. The powder samples were measured with PANalytical EMPYREAN diffractometer using β-filtered Cu Kα radiation.

2.1. Preparation of complexes

2.1.1. [Cu(4-NO$_2$bz)$_2$(mna)$_2$(H$_2$O)], **1**

The compound **1** was prepared by the reaction of an aqueous solution (50 mL) of copper(II) acetate monohydrate (1.0 mmol, 0.200 g) with N-methylnicotinamide (mna, 2.0 mmol, 0.272 g) followed by an addition of the 4-nitrobenzoic acid (2.0 mmol, 0.334 g) and one pellet of potassium hydroxide. The reaction mixture was stirred until the blue product precipitated (1 h). It was filtered off, washed with a small portion of water and dried at the ambient temperature. The mother liquor obtained from filtration was left for crystallization at ambient temperature on air. The single crystals suitable for X-ray structure determination were separated after several days. Yield: 0.20 g (57%). *Anal.* Calc. for $C_{28}H_{26}O_{11}N_6Cu$ (M_r = 686.09): C, 49.02; H, 3.82; N, 12.25. Found: C, 49.52; H, 3.60; N, 12.53%. IR (cm^{-1}): ν(C=O) 1670, $\nu_{as}(COO^-)$ 1572, $\nu_s(COO^-)$ 1385, UV-Vis (cm^{-1}): 15300. EPR: $g = 2.10$.

2.1.2. [Cu(4-NO$_2$bz)$_2$(μ-mna)(H$_2$O)]$_2$, **2**

The synthesis procedure for the compound **2** is similar as for the complex **1**, but with less N-methylnicotinamide (mna; 1.0 mmol, 0.136 g). After a few hours of stirring to dissolve the solid starting compounds, the resulting turquoise solution was left at ambient temperature. The turquoise coloured crystals suitable also for X-ray structure determination were separated after several weeks.

Table 1
Crystallographic data for **1**–**2** and **4**–**5**.

	1	**1**	**2**	**2**	**4**	**5**
Chemical formula	$C_{28}H_{26}CuN_6O_{11}$	$C_{28}H_{26}CuN_6O_{11}$	$C_{42}H_{36}Cu_2N_8O_{20}$	$C_{42}H_{36}Cu_2N_8O_{20}$	$C_{26}H_{20}CuN_8O_{15}$	$C_{42}H_{32}Cu_2N_8O_{18}$
M_r	686.09	686.09	1099.87	1099.87	748.05	1063.84
Cell setting	monoclinic	monoclinic	triclinic	triclinic	monoclinic	monoclinic
Space group	$C2/c$	$C2/c$	$P\bar{1}$	$P\bar{1}$	$P2/n$	$P2_1/c$
T (K)	293(2)	150(2)	293(2)	150(2)	293(2)	150(2)
a (Å)	25.096(6)	25.050(5)	8.7061(3)	8.674(2)	10.278(1)	10.539(2)
b (Å)	5.607(1)	5.572(1)	10.9217(7)	10.886(2)	5.863(1)	23.154(5)
c (Å)	23.691(8)	23.588(5)	13.3053(7)	13.276(3)	24.829(3)	8.9450(18)
α (°)	90	90	113.382(6)	113.27(3)	90	90
β (°)	114.41(2)	114.14(3)	104.247(4)	104.56(3)	98.48(1)	94.93(3)
γ (°)	90	90	91.402(4)	91.23(3)	90	90
V (Å^3)	3035.5(14)	3004.5(13)	1114.87(10)	1104.2(4)	1479.8(3)	2174.7(8)
Z	4	4	1	1	2	2
Radiation type	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ (mm^{-1})	0.790	0.798	1.047	1.057	0.829	1.067
Crystal size (mm)	0.36 × 0.26 × 0.14	0.30 × 0.25 × 0.21	0.50 × 0.32 × 0.10	0.35 × 0.30 × 0.30	0.45 × 0.25 × 0.15	0.33 × 0.22 × 0.20
Diffractometer	Bruker Kappa APEXII CCD	Bruker-Nonius KappaCCD	Xcalibur S CCD	Bruker-Nonius KappaCCD	Siemens P4	Bruker-Nonius KappaCCD
Abs. correction	SADABS	SADABS	CrysAlisPro	SADABS	XEMP	SADABS
T_{min}, T_{max}	0.824, 0.910	0.796, 0.853	0.623, 0.903	0.709, 0.742	0.707, 0.886	0.709, 0.822
S	1.062	1.063	1.079	1.074	1.036	1.049
$R_1[F^2 > 2\sigma(F^2)]$, $wR_2(F^2)$	0.0278, 0.0787	0.0321, 0.0739	0.0356, 0.0837	0.0461, 0.1035	0.0490, 0.1032	0.0395, 0.0820
Data/restrains/ parameters	3046/16/214	3004/16/213	4520/0/326	4493/0/326	3015/0/227	4350/0/317
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.298, −0.216	0.289, −0.250	0.281, −0.368	0.313, −0.342	0.381, −0.297	0.310, −0.335
CCDC	860144	860145	924383	860146	860143	924384