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Copper(II) 2-Nitrobenzoatecomplexes with Nicotinamide, Preparation and Properties

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Abstract

Two new complexes $[Cu(2\text{-}NO_2bz)_2(nia)_2]$ (**1**), $[Cu_2(2\text{-}NO_2bz)_4(nia)_2]\cdot(AC)$ (**2**) were obtained in addition to known ones $[Cu_2(2\text{-}NO_2bz)_4(nia)_2]\cdot(ACN)$ (**3)** and $[Cu(2\text{-}NO_2bz)_2(nia)_2(H_2O)_2]$ (**4**) were obtained by the study of copper(II) acetate reactions with nicotinamide (nia) and 2-nitrobenzoic acid in different solvents and using different molar ratios of copper(II) : nia. All complexes under study were characterized by elemental analysis and by IR, or UV/VIS spectra and X-ray powder diffraction pattern were obtained to characterize samples and to compare obtained products with known ones.

Keywords: copper complexes, nicotinamide, 2-nitrobenzoate

Introduction

Nicotinamide (nia) is one of the esential compound for growth cells (Lin 2001) and its excess in human body causes increase of lipid peroxidation and its shortage decreasing level of atioxidants such as Vitamin E, or glutathione (Melo 2000). Moreover, nicotinamide is known for as substance helping against cell apoptosis caused by free radical presence (Lin 2001), it is frequently used in treatment of different skin diseases (Kang 2000, Hara 2002) or in prevention against some neurodegenerative diseases as Alzheimer one (Green 2008). Presence of copper in human body liquids and its functioning in different vital processes is connected with copper atom ability to form complexes with different ligands. Copper complex formation with different biologically active substances is an object of great interest. This could be well documented by great and still growing number of copper(II) complexes with nicotinamide in CCD (*Cambridge Crystallographic Database*) that also shows the nicotinamide ability to act as monodentate or bridging ligand. Moreover, more than two thirds of all over fifty structurally studied complexes contain some carboxylate anions as ligands. Carboxylate anions exhibit a versatile coordination behaviour towards metal cations due to their ability to act as monodentate, bidentate chelating, bidentate bridging or polydentate bridging ligands. Carboxylatocopper(II) complexes are well known for their great variability of coordination polyhedron they can possess for each of coordination numbers ranging mainly from four to six. In this paper we report preparation, spectral characteristics and analysis of four copper(II) complexes containing nia ligand $[Cu(2\text{-}NO_2bz)_2(nia)_2]$ (**1**), $[Cu_2(2\text{-}NO_2bz)_4(nia)_2]\cdot(AC)$ (**2**), $[Cu_2(2\text{-}NO_2bz)_4(nia)_2]\cdot(ACN)$ (**3**) and $[Cu(2\text{-}NO_2bz)_2(nia)_2(H_2O)_2]$ (**4**) that were obtained by the similar reactions in different solvents.

Experimental

Preparation

*$[Cu(2\text{-}NO_2Bz)_2(nia)_2]$ (**1**)* Copper(II) acetate (1 mmol, 200 mg) was solved in acetonitrile (30 mL) at temperature about 30 – 40°C and the nicotinamide (2 mmol) was added under stirring. After few minutes of reaction mixture stirring the stoichiometric amount of 2-nitrobenzoic acid (2 mmol) and mixture was stirred for several minutes. Then purple solid product was filtered off and dried under infra lamp.
Found: C: 48.7 %; H: 3.2 %; N: 12.2 %
Calc.: C: 48.8 %; H: 3.2 %; N: 13.1 %; Cu: 9.9 %

*$[Cu_2(2\text{-}NO_2bz)_4(nia)_2]\cdot(AC)$ (**2**)* Copper(II) acetate (1 mmol, 200 mg) was for each experiment solved in acetone (20 mL) and the nicotinamide (0.5, 1 or 2 mmol) was added under stirring to the each solution of copper(II) acetate to keep the stoichiometric ratio of copper(II) to ligand 1 : 0.5, 1 : 1, or 1 : 2. After few minutes of stirring of reaction mixture the stoichiometric amount of 2-nitrobenzoic acid (2 mmol) was added to each solution. Mixtures were stirred with a magnetic stirrer for several minutes. Then green solid product was filtered off, washed with small amount of solvent and dried in air at ambient temperature.
Found: C: 45.9 %; H: 3.2 %; N: 10.1 %
Calc.: C: 47.2 %; H: 3.1 %; N: 10.2 %; Cu: 11.6 %

*$[Cu_2(2\text{-}NO_2Bz)_4(nia)_2]\cdot(ACN)$ (**3**)* Copper(II) acetate (1 mmol, 200 mg) was solved in acetonitrile (30 mL) and the nicotinamide (0.5 mmol, 1 or 2 mmol) was added under stirring.

After few minutes of reaction mixture stirring the stoichiometric amount of 2-nitrobenzoic acid (2 mmol) was added and mixture was stirred for several minutes. Then green solid products were filtered off, washed with small amount of solvent and dried in air at ambient temperature.
Found: C: 46.2 %; H: 3.1 %; N: 10.9 %
Calc.: C: 46.8 %; H: 2.9 %; N: 11.7 %; Cu: 11.8 %

[Cu(2-NO_2Bz)$_2$(nia)$_2$(H_2O)$_2$] ***(4)*** Copper(II) acetate (1 mmol, 200 mg) was solved in ethanol (20 mL) or water (10 mL). Nicotinamide (0.5 mmol, 1 or 2 mmol) was added under stirring. After few minutes of reaction mixture stirring the stoichiometric amount of 2-nitrobenzoic acid (2 mmol) was added and mixture was stirred for several minutes. Blue microcrystal powder was excluded from reaction mixture. Product was filtered off, washed with small amount of solvent and dried in air at ambient temperature.
Found: C: 46.3 %; H: 3.7 %; N: 12.9 %
Calc.: C: 46.2 %; H: 3.6 %; N: 12.4 %; Cu: 9.4 %

Apparatus and equipment

Carbon, hydrogen and nitrogen analyses were carried out on a CHNSO FlashEA^{TM} 1112 Automatic Elemental Analyzer.
Electronic spectra (190 – 1100 nm) of the complexes were measured in Nujol suspension with a SPECORD 200 (Carl Zeiss Jena) spectrophotometer.
Infrared spectra (4000 – 400 cm^{-1}) were measured with a Nicolet 5700 FT-IR spectrometer fy Nicolet using ATR techniques at room temperature.
To obtain X-ray powder patterns of the samples were measured with Bragg-Brentano diffractometer Philips PW 1730/1050, using ß-filtered Co*K*α radiation, 40kV/35mA in the range of 3° – 51° 2Θ, step 0.02°.

Results and Discussion

Properties of complexes

The light purple complex [Cu(2-NO_2bz)$_2$(nia)$_2$] (**1**) composition was determined by elemental analysis and IR spectra of obtained samples have proved absence of water molecules in its content. The higher $\Delta\nu(COO^-)$ difference allows to suggest asymetric bonding mode of

2-nitrobenzoate carboxylato group to the copper(II) central atom. The light purple colour is consistent with our experience concerning the colour changes due to less number of oxygen atoms strongly bonded to copper atom and partly confirms suggested asymetric carboxylate bonding mode. Moreover, the CCD (*Cambridge Crystallographic Database*) data show molecular complexes of both $[Cu(RCOO)_2(nia)_2]$, and $[Cu(RCOO)_2(nia)_2(H_2O)_2]$ composition have been structurally studied and the stoichiometry $[Cu(RCOO)_2(nia)_2]$ prevails (ten known structures e.g. Fig. 1) over the $[Cu(RCOO)_2(nia)_2(H_2O)_2]$ (six known examples, Fig. 2).

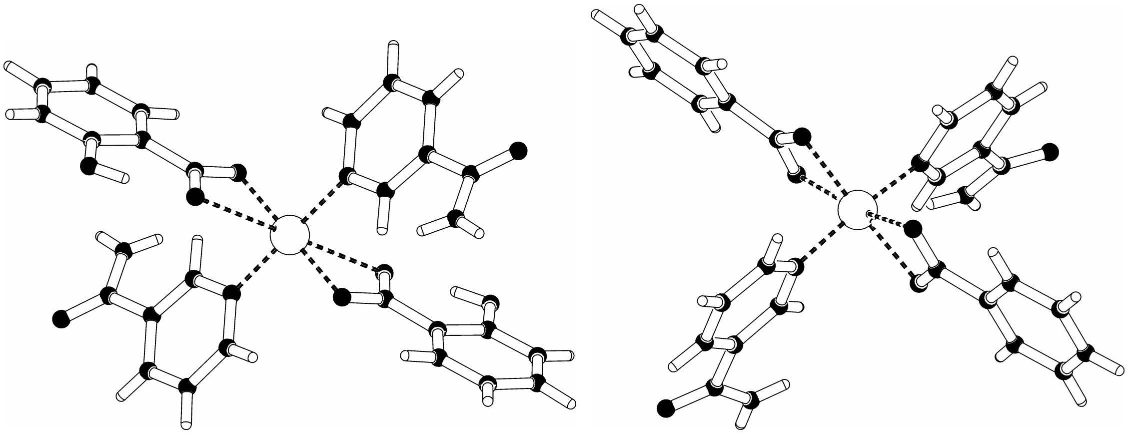

Fig. 1. The molecular structure of the $[Cu(RCOO)_2(nia)_2]$; left RCOO = salicylate (Leban 1997), right RCOO = benzoate (Leban 1996).

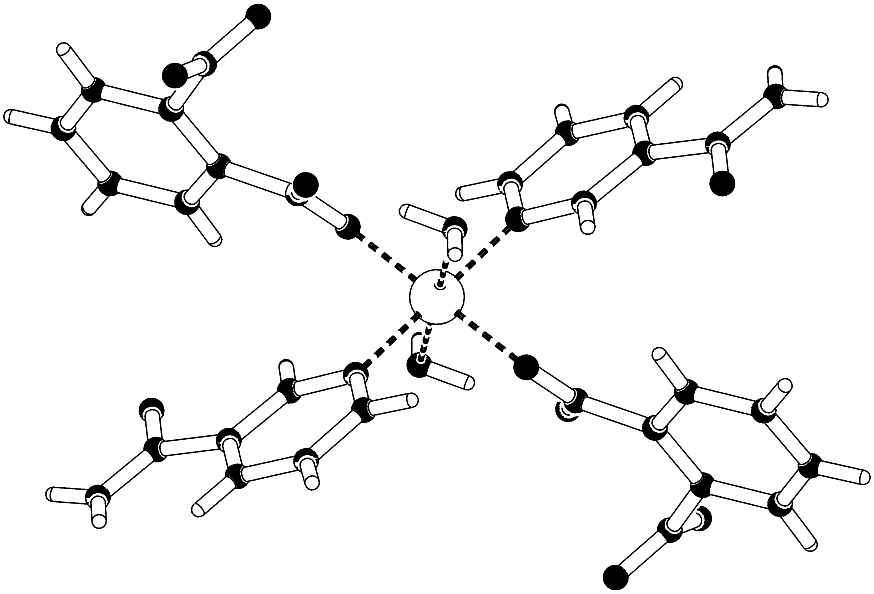

Fig. 2. The molecular structure of the $[Cu(RCOO)_2(nia)_2(H_2O)_2]$ RCOO = 2-nitrobenzoate (Stachova 2007)

It is interesting that six of ten structurally studied complexes are exhibiting some shade of purple or violet colour. Moreover detailed view of known structures has shown that there is a great variation of the longer Cu–O$_{carbox}$ distances within the range 2.209–3.141 Å and all mentioned examples of some sort violet colour are showing this distance around the centre of this range.

Table 1. Infrared spectra data (cm^{-1}).

Compound	$\nu_{as}(COO^-)$	$\nu_s(COO^-)$	$\Delta\nu(COO^-)$	ν(N–H)	ν(O–H)
$[Cu(2\text{-}NO_2bz)_2(nia)_2]$ (**1**)	1593	1377	216	3416, 3199	-
$[Cu_2(2\text{-}NO_2bz)_4(nia)_2]\cdot(AC)$ (**2**)	1575	1392	183	3433, 3186	-
$[Cu_2(2\text{-}NO_2bz)_4(nia)_2]\cdot(ACN)$ (**3**)	1575	1391	184	3436, 3162	-
$[Cu(2\text{-}NO_2bz)_2(nia)_2(H_2O)_2]$ (**4**)	1590	1372	218	3387, 3198	3543

Table 2. Electron spectra data (nm).

Compound	$\lambda(d \rightarrow d)$
$[Cu(2\text{-}NO_2bz)_2(nia)_2]$ (**1**)	560, 666
$[Cu_2(2\text{-}NO_2bz)_4(nia)_2]\cdot(AC)$ (**2**)	747
$[Cu_2(2\text{-}NO_2bz)_4(nia)_2]\cdot(ACN)$ (**3**)	750
$[Cu(2\text{-}NO_2bz)_2(nia)_2(H_2O)_2]$ (**4**)	636

The another new product $[Cu_2(2\text{-}NO_2bz)_4(nia)_2]\cdot(AC)$ (**2**) obtained from different reaction mixtures in acetone as solvent has its stoichiometry confirmed by elemental analysis. The IR spectra similarity of complex (**2**) in comparison to complex $[Cu_2(2\text{-}NO_2bz)_4(nia)_2]\cdot(ACN)$ (**3**) in all parts of spectra except the incorporated solvent molecules bands (1707, 1361, 1206 and 531 cm^{-1} attributed to acetone molecule in (**2**) or 2324, 1375, 1029 and 934 cm^{-1} for acetonitrile in (**3**). The known structure of (**3**) is shown in Fig. 3.

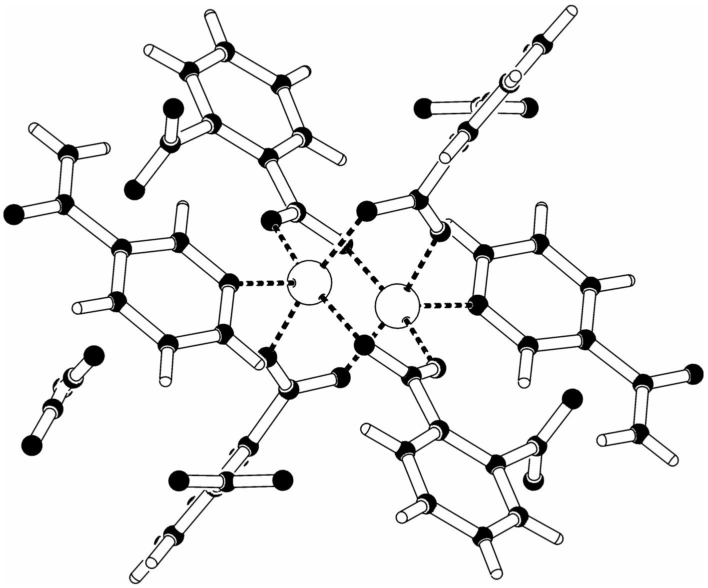

Fig. 3. The molecular structure of the [Cu_2(2-NO_2bz)$_4$(nia)$_2$]·(ACN) (**3**) (Moncol 2010).

The comparison of diffraction pattern of both (**2**) and (**3**) (Fig. 4) shows that complexes are probably isostructural.

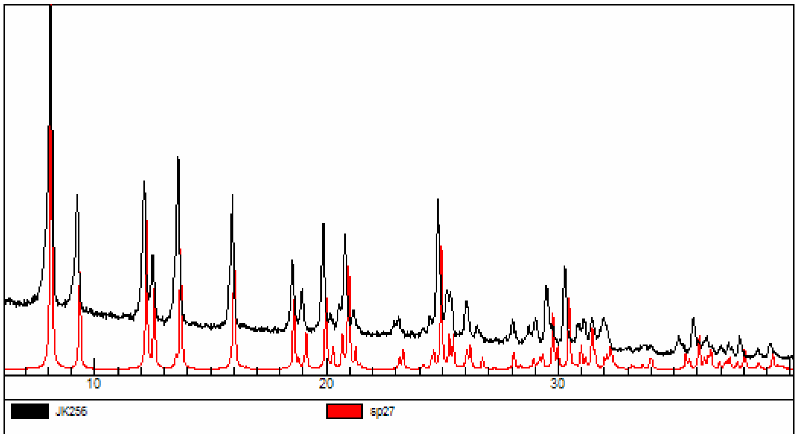

Fig. 4. The diffraction pattern comparison for complexes (**2**) (upper line) and (**3**) (lower line).

It worthy to stress that structure of complex [Cu_2(2-NO_2bz)$_4$(nia)$_2$]·(ACN) (**3**) contains the acetonitrile molecules inserted into cavities of the complex in two different positions and this was the base for calculations using the PLATON (Spek 2003) program that allowed us to visualize the size and shape of cavities (Fig. 5).

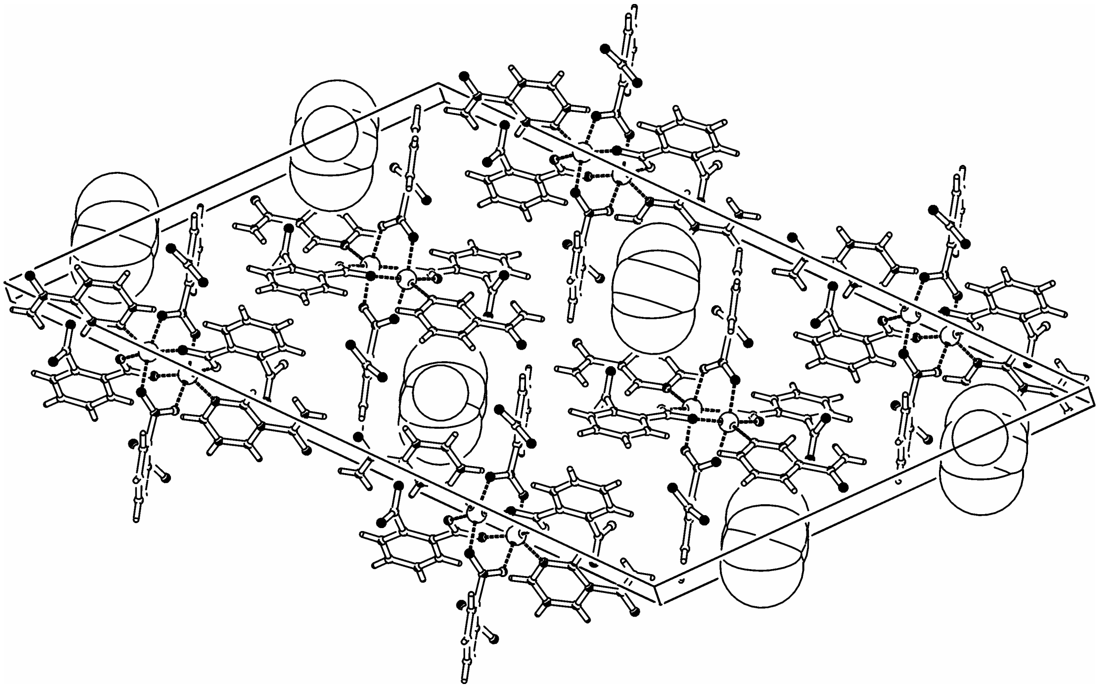

Fig. 5. The cavities inside the crystal structure of $[Cu_2(2\text{-}NO_2bz)_4(nia)_2]\cdot(ACN)$ (**3**) (Moncol 2010)

Preparation course

There are some interesting features concerning the way of (**1**) – (**4**) complexes preparation. All preparations cover the same sequence of reactions – the first step is copper(II)-nicotinamide complexes formation and the second one is the formation of the final 2-nitrobenzoatoanion containing product. The last one seems to be the most dependent on the type of used solvent. The most common solvent used in preparations – water – gives in some experiments (some specific conditions, e.g. the initial concentration of copper salt, temperature and the speed of dissolving of 2-nitrobenzoic acid) light purple product, that was more or less quickly transformed into more dark blue already known and published (Stachová 2007) product (**4**). The attempts to obtain light purple complex by changing the reaction conditions usually failed because of proceeding transformation already formed purple product into blue product (**4**). The ethanolic medium behaves similarly and only product (**4**) was obtainable. The formation of blue final product (**4**) in both used solvent does not depend on the copper(II) : nicotinamide reactants stoichiometry and it could be stressed that 1 : 2, 1 : 1 and 2 : 1 stoichiometry was applied in all systems under study.

The best results, from the point of view purple product preparation and isolation, were obtained from acetonitrile as solvent used and with copper(II) : nicotinamide 1 : 2 stoichiometry but very gentle preheating of reaction mixture (up to 30–35 ^{o}C) prior to the addition of 2-nitrobezoic acid was needed and the purple product was formed quickly and after few minutes of stirring the reaction was completed. Drying of the product after its filtering off was another problem of the procedure because presence of mother liquid, or presence of the solvent used for product washing caused slow and incomplete transformation of purple product into complex (**4**). The best way of keeping the purple product (**1**) unchanged was to remove the rest of mother/washing liquid from solid product as soon as possible by its gentle heating as it is shown in preparation of complex $[Cu(2\text{-}NO_2bz)_2(nia)_2]$ (**1**).

The reaction procedure in acetonitrile without preheating gives the green product (**3**). The same green product (**3**) was obtained from acetonitrile solutions simply by decreasing nicotinamide content in reaction mixture and analysis together with spectral properties and X-ray powder patterns proved that these obtained green products were identical with complex $[Cu_2(2\text{-}NO_2bz)_4(nia)_2]\cdot(ACN)$ published (Moncol 2010).

Changing the solvent used to acetone, known for its preference to formation of “acetate” type of dimmers, led in all synthesis (independently from the copper(II) : nicotinamide molar ratio) to formation of green product $[Cu_2(2\text{-}NO_2bz)_4(nia)_2]\cdot(AC)$ (**2**). Spectral properties and powder X-ray diffraction pattern have proved structural similarities of (**2**) to the above mentioned complex (**3**) obtained from acetonitrile solutions.

A suspicion that water content in solvents used for synthesis and air humidity during the drying of some solid samples are the main reason for the complex (**1**) formation was partially proved by experiments in which a small amounts of water (< 10%) were added to the reaction mixtures containing already formed green products (**2**) or (**3**). In all cases the primarily formed green complexes have been smoothly changed to the final blue product of composition $[Cu(2\text{-}NO_2bz)_2(nia)_2(H_2O)_2]$ (**1**).

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