

Crystallosolvate Formation in Copper(II) 4-Nitrobenzoate Complex Systems

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Abstract

Three different products $[\text{Cu}_2(4\text{-NO}_2\text{bz})_4(\text{denia})]\cdot(\text{TOL})$ (**1**), $[\text{Cu}_2(4\text{-NO}_2\text{bz})_4(\text{EtOH})_2]$ (**2**), and $[\text{Cu}_2(4\text{-NO}_2\text{bz})_4(\text{H}_2\text{O})(\text{AC})]$ (**3**) were obtained by the reaction of copper(II) acetate, N,N-diethylnicotinamide and 4-nitrobenzoic acid in different solvents. Complexes under study were characterized by elemental analysis and by IR, EPR or UV/VIS spectra. X-ray powder diffraction pattern were obtained to characterize samples and to compare obtained products with known ones.

Keywords: copper complexes, diethylnicotinamide, 4-nitrobenzoate, crystallosolvate

Introduction

Formation of crystallosolvates have attracted chemist attention in different fields of chemistry due to the considerable changes in their properties caused by the presence of solvent, or some other “small” guest molecules in the host crystal structure. The “host-guest” interactions within the formed crystallosolvate could e.g. significantly improve thermal stability polymeric nano-crystals (Nakajima 2009), or it could be the part of procedure that may improve solvent accessibility to modified compound (Saito 2007). The crystal engineering using molecular (Golovanov 2008, Lebedeva 2007, Kristiansson 2001) or polymeric (Moulton 2001, Batten 1998) metal-organic complexes of different dimensionality has also covered the field of host-guest interaction because the coordination polymers exhibit fascinating structural diversities and interesting properties e.g. as microporous materials (Liu 2005, Rosi 2003, Evans 2002, Kristiansson 2001).

Carboxylate anions exhibit the versatile coordination behaviour towards metal cations due to their ability to act as monodentate, bidentate chelating, bidentate bridging or polydentate bridging ligands. Carboxylatecopper(II) complexes are well known for their great variability of coordination polyhedra they can possess for each of coordination numbers ranging mainly from four to six. These variability in coordination numbers and the shapes of coordination polyhedron have of course their consequence in properties of copper(II) coordination compounds including their biological activity that can and usually differ from the biological activity of free ligands.

N,N-Diethylnicotinamide (denia) is toxic agent, but coordinated to central atom it exhibit different biological activities (Arslantas 2007, Cullen 2006, Rasool 1991). It is well known, that the most of denia complexes of copper(II) contain monodentately bonded denia to copper atom mostly in monomeric complexes $[\text{Cu}(\text{RCOO})_2(\text{denia})_2(\text{H}_2\text{O})_2]$ (Kavalírová 2008, Moncol 2006, Moncol 2002, Melník 1998, Hökelek 1997, Melník 1996), or $[\text{Cu}(\text{RCOO})_2(\text{denia})_2]$ (Koman 1998, Hökelek 1996) and also in dimeric complexes $[\text{Cu}_2(\text{RCOO})_4(\text{denia})_2]$ (Moncol 2004, Kozlevcar 2000, Hökelek 1995). Only a few examples of denia bridging bonding are known and denia ligand is coordinated *via* nitrogen atom of pyridine ring to one of metal atom, and by carbonyl oxygen to the other one, e.g. $[\text{Cu}_2(\text{RCOO})_4(\mu\text{-denia})]_n$ (Kavalírová 2008, Moncol 2007).

In this paper we report preparation, spectral characteristics and analysis of possible structures of one new copper(II) complexes containing denia ligand $[\text{Cu}_2(4\text{-NO}_2\text{bz})_4(\text{denia})] \cdot (\text{TOL})$ (**1**) (where TOL = toluene), together with two other complexes $[\text{Cu}_2(4\text{-NO}_2\text{bz})_4(\text{EtOH})_2]$, (**2**) and $[\text{Cu}_2(4\text{-NO}_2\text{bz})_4(\text{H}_2\text{O})(\text{AC})]$ (**3**) (where AC = acetone) that were obtained from the similar reactions in different solvents.

Materials and Methods

Preparation

$[\text{Cu}_2(4\text{-NO}_2\text{bz})_4(\text{denia})] \cdot (\text{TOL})$ (**1**) Copper(II) acetate (1 mmol, 200 mg) was for each experiment solved in toluene (50 mL) and the N,N-diethylnicotinamide (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 4-nitrobenzoic acid (2 mmol) was added to each

solution. Mixtures were stirred with a magnetic stirrer under reflux for several hours. Then after slow cooling down to room temperature, dark green solid products were filtrated off, washed with small amount of solvent and dried in air at ambient temperature. Mother liquids were left for slow crystallization at room temperature.

Found: C: 50.2 %; H: 3.7 %; N: 8.1 %; Cu: 12.2 %

Calc.: C: 50.9 %; H: 3.6 %; N: 7.9 %; Cu: 12.0 %

$[Cu_2(4-NO_2Bz)_4(EtOH)_2]$ (**2**) The same procedure using ethanol instead of toluene gave in all three Cu : denia stoichiometric ratios the same products which did not contain the denia ligand.

Found: C: 43,1 %; H: 3,2 %; N: 6,4 %; Cu: 14,2 %

Calc.: C: 43,5 %; H: 3,2 %; N: 6,3 %; Cu: 14,4 %

$[Cu_2(4-NO_2Bz)_4(H_2O)(AC)]$ (**3**) Copper(II) acetate (1 mmol, 200 mg) was solved in acetone (50 mL) and the N,N-diethylnicotinamide (0.5 mmol) was added under stirring. After few minutes of reaction mixture stirring the stoichiometric amount of 4-nitrobenzoic acid (2 mmol) and mixture was heated and stirred for several hours.

Found: C: 41,9 %; H: 2,8 %; N: 6,7 %

Calc.: C: 42,9 %; H: 2,8 %; N: 6,5 %; Cu: 14,7 %

Apparatus and equipment

Carbon, hydrogen and nitrogen analyses were carried out on a CHNSO FlashEATM 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 by Nicolet using ATR techniques at room temperature.

EPR spectra were measured with spectrophotometer BRUKER ER 200E-SRC in X-band frequency (frequency 9GHz) at room temperature.

To obtain X-ray powder patterns of the samples were measured with Bragg-Brentano diffractometer Philips PW 1730/1050, using β -filtered $\text{CoK}\alpha$ radiation, 40kV/35mA in the range of $3^\circ - 51^\circ 2\Theta$, step 0.02° .

Results and Discussion

As it was mentioned above there were two main targets of our study. The first aim was to characterize properties of obtained compounds and the second one was to analyze the relation between composition of obtained products and the conditions of their preparation.

Properties of obtained products

The only product containing denia ligand was the $[\text{Cu}_2(4\text{-NO}_2\text{bz})_4(\text{denia})]\cdot(\text{TOL})$ (**1**) complex and it is of rather unusual stoichiometry – one denia ligand per two copper atoms – that implies denia bridging function similar to those in $[\text{Cu}_2(\text{RCOO})_4(\mu\text{-denia})]_n$ R = 2- NO_2bz , Cl_2ac (Kavalírová 2008, Moncol 2007). The dark green colour of complex is typical for dimeric one and presence of dimeric unit was confirmed by the EPR (Fig. 1). The data g_\perp and g_\parallel obtained by computer simulation of EPR spectrum are shown in Table 1.

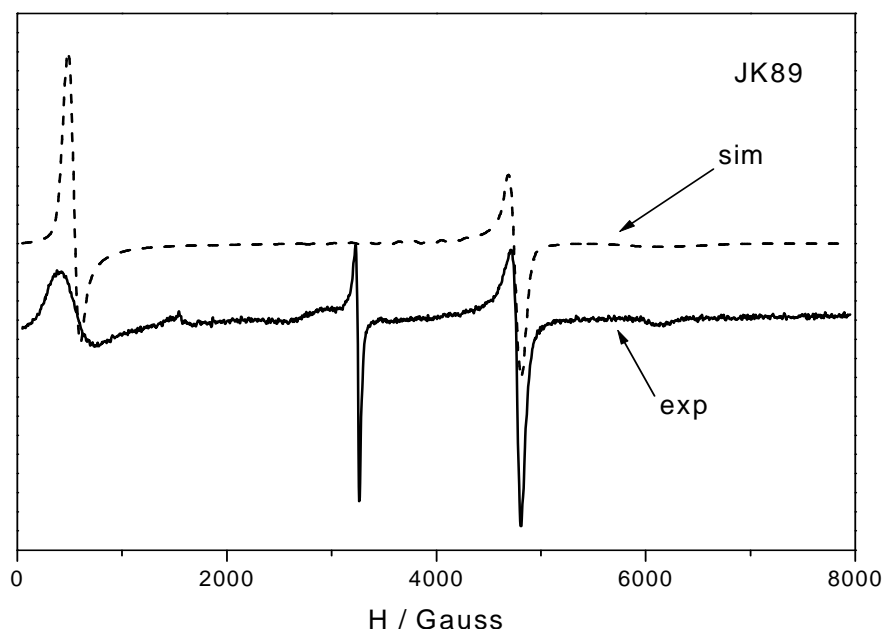


Fig.1. The EPR spectrum of $[\text{Cu}_2(4\text{-NO}_2\text{bz})_4(\text{denia})]\cdot(\text{TOL})$ (**1**)

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

Compound	g_{\parallel}	g_{\perp}
$\text{Cu}_2(4\text{-NO}_2\text{Bz})_4(\text{denia})(\text{TOL})$	2.330	2.034
$\text{Cu}_2(4\text{-NO}_2\text{Bz})_4(\text{EtOH})_2$	2.279	2.066
$\text{Cu}_2(4\text{-NO}_2\text{Bz})_4(\text{H}_2\text{O})(\text{AC})$	2.350	2.052

The presence 4-nitrobenzoate ligand and its bidentate bridging is confirmed by IR spectral data (Table 2) and other bands e.g. $\nu_{\text{as}}(\text{NO}_2)$, $\nu_{\text{s}}(\text{NO}_2)$ were found at 1519 and 1345 cm^{-1} , respectively were found at positions typical for 4-nitrobenzoate anion (Kavalířová 2007). The band at 1652 cm^{-1} confirms presence of denia ligand $\nu(\text{C}=\text{O})$ in complex (**1**). The presence of toluene was confirmed by all bands (at 3111, 1610, 1464, 722, 703 and 467 cm^{-1}) typical for this substance and can be taken as indirect proof that toluene molecules are present in structure as crystallosolvate.

Table 2. Infrared spectra data (cm^{-1})

Compound	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	$\Delta\nu(\text{COO}^-)$
$\text{Cu}_2(4\text{-NO}_2\text{Bz})_4(\text{denia})(\text{TOL})$	1592	1406	186
$\text{Cu}_2(4\text{-NO}_2\text{Bz})_4(\text{EtOH})_2$	1592	1408	184
$\text{Cu}_2(4\text{-NO}_2\text{Bz})_4(\text{H}_2\text{O})(\text{AC})$	1594	1409	185

The great effort to prepare crystals of (**1**) suitable for X-ray structure determination was not accomplished successfully thus only X-ray of powdered sample could be presented here. Using the X-ray powder diffraction method obtained diffractogram was compared to calculated one for $[\text{Cu}_2(2\text{-NO}_2\text{Bz})_4(\text{denia})_1]$ (Kavalířová 2008) the proof was found that the crystal structure of (**1**) completely differs from its 2-nitrobenzoate analog. The difference in diffractograms is greater than that one caused small change of basic structure parameters originated from the change of position of nitrosubstituent on nitrobenzoate anion from 2-position to 4-one.

The other two obtained complexes do not denia ligand and the obtained EPR or IR spectral data, similar colour and all appearance of products confirm that both complexes are dimeric ones. The complex (**2**) has shown all spectral properties (ES and IR) the same as it was published (Kristiansson 2001) and its powder diffraction pattern was nearly the same as that one calculated from data obtained from the crystallographic database. On the other hand

the obtained complex **(3)** differs by its composition from the complexes $[\text{Cu}_2(4\text{-NO}_2\text{Bz})_4(\text{H}_2\text{O})_2]$ and $[\text{Cu}_2(4\text{-NO}_2\text{Bz})_4(\text{H}_2\text{O})_2]\cdot(\text{AC})$ (Kristiansson 2001). The obtained IR spectra compared to published data cannot and do not give direct evidence of differences of all three substances, and similarly such evidence could not be found in EPR or UV-VIS spectra. The X-ray diffractogram of complex **(3)** gives clear evidence that our product could not be a simple mixture of both complexes studied by Kristiansson *et al* (Kristiansson 2001).

Complex formation in studied systems

There are interesting features concerning the preparation of complexes **1 – 3**. All three complexes have been obtained from the mixtures that contained some amount of the denia ligand and that were different in the type of solvent used. The most striking observation of all preparations done in toluene as solvent is the uniformity of the obtained product **(1)** despite the stoichiometric Cu : denia ratios, but this uniformity was only found in systems realized at elevated temperature. Synthesis in toluene done at room temperature have given some other products, e.g. the blue complex $[\text{Cu}(4\text{-NO}_2\text{bz})_2(\text{denia})_2(\text{H}_2\text{O})_2]$ of previously known structure (Hökelek 1997) was formed in reaction mixture containing Cu : denia = 1 : 2. The system with the Cu : denia = 1 : 1 ratio gave a new $\text{Cu}(4\text{-NO}_2\text{bz})_2(\text{denia})_1(\text{H}_2\text{O})_1$ complex (Kavalířová 2007) of unusual stoichiometry. This complex formation was later observed in some other solvents too and the X-ray structure determination confirmed (Vasková 2009) its polymeric structure $[\text{Cu}(4\text{-NO}_2\text{bz})_2(\text{denia})_1(\text{H}_2\text{O})_1]_n$. Thus it could be concluded that for toluene as solvent the complex $[\text{Cu}_2(4\text{-NO}_2\text{bz})_4(\text{denia})]\cdot(\text{TOL})$ **(1)** is the most stable product at elevated temperature and all products obtainable at room temperature are after heating up system transformed to complex **(1)**.

All synthesis done in ethanol at elevated temperature gave green $[\text{Cu}_2(4\text{-NO}_2\text{bz})_4(\text{EtOH})_2]$ **(2)** product despite the presence of different amounts of denia ligand. The room temperature syntheses gave in both systems of Cu : denia = 1 : 0.5 or 1 : 1 ratios the mixtures of green $[\text{Cu}_2(4\text{-NO}_2\text{bz})_4(\text{EtOH})_2]$ **(2)** crystals together with blue $[\text{Cu}(4\text{-NO}_2\text{bz})_2(\text{denia})_2(\text{H}_2\text{O})_2]$ crystals. Only the system with Cu : denia = 1 : 2 gave at room temperature blue complex of composition $[\text{Cu}(4\text{-NO}_2\text{bz})_2(\text{denia})_2(\text{H}_2\text{O})_2]$. Again it could be concluded that complex containing denia ligand $[\text{Cu}(4\text{-NO}_2\text{bz})_2(\text{denia})_2(\text{H}_2\text{O})_2]$ is stable in ethanolic solutions at room temperature and by heating up it is transformed into more stable $[\text{Cu}_2(4\text{-NO}_2\text{bz})_4(\text{EtOH})_2]$

complex. Contrary to the toluene as solvent, the complex $[\text{Cu}_2(4\text{-NO}_2\text{bz})_4(\text{EtOH})_2]$ also at room temperature in systems containing lesser amount of denia ligand.

Using the acetone as solvent the type of obtained product for all synthesis depended strongly only on the Cu : denia stoichiometric ratio and did not depend on the temperature used for synthesis. The systems with Cu : denia = 1 : 0.5 have given the $[\text{Cu}_2(4\text{-NO}_2\text{bz})_4(\text{H}_2\text{O})(\text{AC})]$ (**3**) that does not contain any denia ligand, while the systems with Cu : denia ratios 1 : 1, or 1 : 2 have given $\text{Cu}(4\text{-NO}_2\text{bz})_2(\text{denia})_1(\text{H}_2\text{O})_1$ complex in all cases.

It could be concluded that the system under study has proved that changing solvent used for synthesis different products could be obtained.

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