

Scientific paper

Preparation, Characterization and Crystal Structure of $[\text{Cu}_2(\text{O}_2\text{CH})_4(\text{nicotinamide})_2]$

Marta Kasunič,* Ksenija Gačnik, Primož Šegedin
and Amalija Golobič

Faculty of Chemistry and Chemical Technology, University of Ljubljana, Aškerčeva 5,
1000 Ljubljana, Slovenia

* Corresponding author: E-mail: marta.kasunic@fkt.uni-lj.si

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Abstract

The novel copper(II) coordination compound, $[\text{Cu}_2(\text{O}_2\text{CH})_4(\text{nia})_2]$ (nia = nicotinamide), was isolated from the reaction mixture containing $\text{Cu}_2(\text{OH})_2\text{CO}_3$, nicotinamide, methanoic acid and ethanol. The new complex was characterized by X-ray single crystal diffraction and other standard physico-chemical methods. The structure contains binuclear centrosymmetric molecules in which two central atoms are bridged by four methanoate bridges forming a *paddle-wheel* structure type. The fifth coordination site completing the distorted square pyramid around copper is occupied by aromatic nitrogen of nicotinamide. The molecules pack together *via* hydrogen bonds resulting in a formation of extended supramolecular sheets. The results of other physical measurements are also in a complete agreement with the obtained structure.

Keywords: X-ray structure analysis; copper(II) carboxylates; methanoate; nicotinamide; *paddle-wheel* structure type.

1. Introduction

The chemistry of copper(II) carboxylates with different N-ligands has been extensively studied due to the promising practical applications of such compounds, e. g. for potential medicinal use¹ or in the field of wood protection.² Of special interest are binuclear copper(II) compounds with four *syn-syn* bridging carboxylato ligands being known for their fungicidal activity which should arise from the unique coordination sphere around central copper(II) ions. Such a *paddle-wheel* structure type was first described in 1953 for the case of cupric acetate dihydrate.³ Till now a lot of time and effort was dedicated to the studies of related acetate complexes (180 structures of the *paddle-wheel* type listed in CCDC⁴). When considering related methanoate complexes, CCDC⁴ lists only 15 structures, eight of these with an additional N-ligand occupying the apical site above the basal plane formed by four oxygens from carboxylate ligands (refcodes CAXBUS,⁵ CAXCAG,⁵ CAXCEK,⁵ CEGHIG,⁶ CEGHOM,⁶ SIZSAV,⁷ SIZSEZ,⁷ SIZSID⁷).^{5–7}

The presence of the N-ligands should enhance the chances of potential medicinal applications, especially if

the N-ligand is a medicinal substance itself as in our case nicotinamide. This is the reason why the chemistry of copper carboxylates with nicotinamide is also quite studied. Until now, the structures of five binuclear copper(II) coordination compounds of the *paddle-wheel* type with nicotinamide ligands have been reported, *i.e.* with acetate,⁸ propionate,⁹ pentanoate,¹⁰ heptanoate and nonanoate¹¹ ligands. In spite of the fact that nicotinamide possesses three potential donor atoms from which a significant number of possibilities to coordinate itself in different manners should arise, in all five compounds nicotinamide is coordinated *via* aromatic nitrogen atom which occupies the apical site of a distorted square pyramid around the central atom.

Among the compounds of copper(II) with methanoate and nicotinamide ligands only two monomeric compounds (refcodes ANCTCU¹², FANKEK¹³) have been structurally characterized.^{12,13} In this paper, we report on the preparation and the crystal structure of binuclear copper coordination compound with aforementioned ligands which also completes the series of the above mentioned dimeric *paddle-wheel* type structures of Cu(II) carboxylates with nicotinamide.

2. Experimental

2. 1. Materials and Synthesis

All reagents and chemicals were purchased from commercial sources and used without further purification – with exception of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ which was re-crystallized before use.

[Cu₂(O₂CH)₄(nia)₂]. The reaction mixture containing ethanol (40 mL, 96%), methanoic acid (2 mL, 53 mmol), $\text{Cu}_2(\text{OH})_2\text{CO}_3$ (0.33 g, 1.5 mmol) and nicotinamide (0.48 g, 4 mmol) was refluxed at 60 °C for 1 h. Hot reaction solution of intense green colour was poured through the filter paper and the filtrate was left to stand in the refrigerator at approximately 8 °C. After 72 h a mixture of blue needles and green platelets was obtained; only the latter were of appropriate quality for the X-ray single crystal analysis. Every synthesis resulted in a formation of both crystal types of which the green ones were separated for the subsequent analyses. Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{Cu}_2\text{N}_4\text{O}_{10}$: C, 34.85; H, 2.92; N, 10.16; Cu, 23.05. Found: C, 34.76; H, 2.96; N, 9.97; Cu, 23.03. Magnetic susceptibility (RT): μ_{eff} , 1.07 BM. IR: $\nu_{\text{asym}}(\text{CO}_2)$, 1626 cm^{-1} , $\nu_{\text{sym}}(\text{CO}_2)$, 1425 cm^{-1} . UV-VIS (nujol): λ_{max} 270, 370 (sh), 710 nm.

2. 2. Physical Measurements

CHN elemental analyses were performed with a Perkin-Elmer 2400 CHN Elemental Analyzer. The amount of copper was determined electrogravimetrically with Pt electrodes.

The infrared spectra were measured on solid samples using a Perkin-Elmer Spectrum 100 series FT-IR spectrometer equipped with ATR.

Electronic spectra were recorded as Nujol mulls on Perkin Elmer UV/VIS/NIR Spectrometer Lambda 19 between 200 and 860 nm.

Magnetic susceptibility of the substance was determined at room temperature by the Evans method using powdered samples and a Sherwood Scientific MSB-1 balance with $\text{HgCo}(\text{NCS})_4$ as a calibrant. Diamagnetic corrections were estimated from Pascal's constants and the effective magnetic moments were calculated using the equation: $\mu_{\text{eff}} = 2.828(\chi_M T)^{1/2}$.

Thermogravimetric analyses were performed on Mettler Thermoanalyzer TA 2000 C. The measurements were carried out in nitrogen flow with flux 100 mL/min and heating rate of 2 K/min up to 250 °C.

For X-ray structure determination, the crystals used were mounted on the tip of glass fibers. Data were collected on a Nonius Kappa CCD diffractometer using graphite monochromated Mo $K\alpha$ radiation at 293(1) K. Data reduction and integration were performed with the software package DENZO-SMN.¹⁴ The coordinates of all of the non-hydrogen atoms were found *via* direct methods using

the SIR97¹⁵ structure solution program. A full-matrix least-squares refinement on F magnitudes with anisotropic displacement factors for all non-hydrogen atoms using Xtal3.6¹⁶ was employed. The positions of hydrogen atoms were obtained from the difference Fourier map and were refined with isotropic displacement parameters. Details on crystal data, data collection and refinement are given in Table 1. Figures depicting the structure were prepared by

Table 1 Crystal data, data collection and structure refinement for the title compound.

<i>Crystal data</i>	
Formula	$\text{C}_{16}\text{H}_{16}\text{Cu}_2\text{N}_4\text{O}_{10}$
M_r	551.43
Cell setting, space group	Triclinic, $P-1$
Temperature (K)	293(1)
a (Å)	6.4461(2)
a (Å)	6.4904(2)
c (Å)	12.5106(4)
α (°)	79.8044(10)
β (°)	85.6199(10)
γ (°)	77.2575(10)
V (Å ³)	502.08(3)
Z	1
D_x (Mg m ⁻³)	1.824
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	2.182
Crystal form, colour	plate, green
Crystal size (mm)	0.20 × 0.12 × 0.04
<i>Data collection</i>	
Diffractometer	Nonius Kappa CCD
Data collection method	φ and ω scan
Absorption correction	multi-scan
No. of measured, independent and observed reflections	8688, 2139, 1969
Criterion for observed reflections	$F^2 > 2.0 \sigma(F^2)$
R_{int}	0.031
θ range (°)	3.24–27.00
h range	–8 → 7
k range	–8 → 8
l range	–15 → 15
<i>Refinement</i>	
Refinement on	F
R (on F_{obs}), wR (on F_{obs}), S	0.030, 0.024, 0.997
No. of contributing reflections	2063
No. of parameters	177
H-atom treatment	obtained from difference Fourier map; refined with isotropic displacement parameters
$(\Delta/\sigma)_{\text{max}}$, $(\Delta/\sigma)_{\text{ave}}$	< 0.001, < 0.001
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (eÅ ⁻³)	0.535, –1.178

$$R = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}, wR = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}, S = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{(N_R - N_P)} \right]^{1/2}$$

ORTEP-3¹⁷ and MERCURY.¹⁸ CCDC-746228 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3. Results and Discussion

The centrosymmetric binuclear molecular title coordination compound is formed by two copper(II) ions bridged by four *syn-syn* methanoic anions forming the *paddle-wheel* structure type. Each copper is coordinated by four methanoic oxygens which form a basal plane of the square pyramid and by aromatic nitrogen atom from nicotinamide ligand lying on the apex of aforementioned (distorted) square pyramid. Bond lengths Cu–O range from 1.961(1)–1.989(1) Å. However, the Cu–N bond is substantially longer (2.179(1) Å) and can be explained as a consequence of Jahn-Teller effect. The copper atom lies 0.2161(10) Å away from the basal plane. The separation between copper atoms from the same molecule is 2.667(1) Å which is longer than the interatomic distance in elemental copper (2.553(4) Å).¹⁹ The second copper atom could be considered as completing the octahedral coordination of the first one. The drawing of the molecule is presented in Figure 1. The details on some relevant bond distances and angles are given in Table 2.

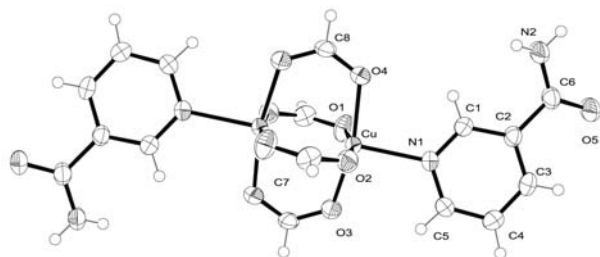


Figure 1 The ORTEP drawing of the molecule of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

The packing of the molecules in title compound, which is shown in Figure 2, is stabilized by intermolecular hydrogen bonds whose geometrical details are given in Table 2. The packing motif consists of hydrogen bonded molecules which pack together via N–H[⋯]O intermolecular hydrogen bonds proceeding from the amide nitrogen (N2) of nicotinamide ligand towards the methanoate (O1) and amide (O5) oxygens of two adjacent molecules. Both hydrogen bonds of moderate strength lead to the formation of extended sheets parallel to *ac* plane, i.e. twodimensional supramolecular architecture.

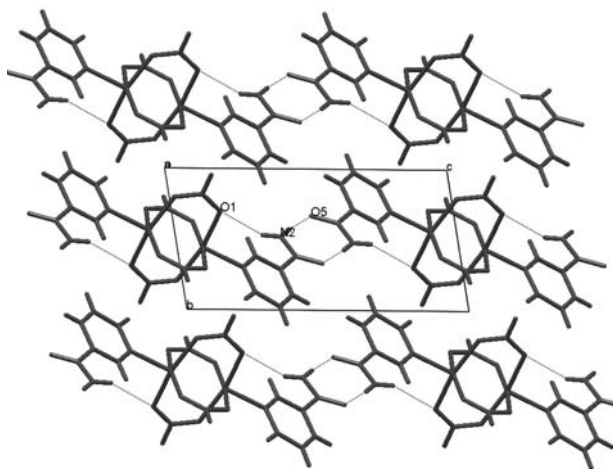


Figure 2 The packing of the title compound, viewed along the *a* axis. Hydrogen bonds are presented by dotted lines.

Since the title compound completes a series of analogous coordination compounds of which those with acetate,⁸ propionate,⁹ pentanoate,¹⁰ heptanoate and nonanoate¹¹ ligands in addition to ligated nicotinamide have been structurally characterized some similarities would be expected. The resemblance of the title compound with its analogues can be confirmed with similar bond distances and angles. Like the title compound, first three possess *P*-1 space group symmetry and the last two crystallize in *C2/c* space group of higher symmetry. In all, an inversion centre is placed in between the copper atoms and only a half of the molecule belongs to the asymmetric unit. Some differences among related structures also exist. Firstly, the orientation of amide and pyridine nitrogen atoms with regard to the bond C(amide)–C(aromatic) in the title compound is *cis*, resembling the orientation in pure nicotinamide.²⁰ In all other compounds, the represented nitrogens are *trans* oriented (see Figure 3). Secondly, a comparison of hydrogen bonding for all six compounds reveals that the same type of hydrogen bonding as present in the title compound is characteristic for acetate, propionate and pentanoate complexes.^{8–10} Compounds with heptanoate and nonanoate ligands¹¹ which crystallize in *C2/c* space group symmetry show another hydrogen bonds network:

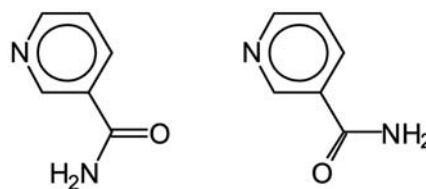


Figure 3 The orientation of nitrogen atoms with regard to C(amide)–C(aromatic) bond as in the title compound and pure nicotinamide (left) and in the other related complexes (right, see text).

both possess the hydrogen bonding similar to that in pure nicotinamide²⁰ leading to the formation of N – H⁺⋯O hydrogen bond chains. Due to longer C-atom carboxylate chains the packing of molecules in both monoclinic compounds changes: the formation of nicotinamide dimers is prevented and additionally, weaker hydrogen bonds are formed.

Table 2 Some relevant distances, angles and hydrogen bonds geometry for the title compound.

Distance [Å]		Angle [°]	
Cu - O1	1.9852(11)	O1 - Cu - O2	167.50(5)
Cu - O2	1.9888(10)	O1 - Cu - O3	87.74(5)
Cu - O3	1.9646(14)	O1 - Cu - O4	88.76(5)
Cu - O4	1.9612(13)	O2 - Cu - O3	90.05(5)
Cu - N1	2.1790(13)	O2 - Cu - O4	90.71(5)
Cu - Cu ⁱ	2.6673(2)	O3 - Cu - O4	167.16(5)
		N1 - Cu - O1	100.85(5)
		N1 - Cu - O2	91.63(4)
		N1 - Cu - O3	96.80(5)
		N1 - Cu - O4	95.98(5)
Hydrogen bonds			
A-H ⁺ ⋯B	Distance A-B [Å]	Angle A-H ⁺ ⋯B	
N2-H2a ⁱⁱ ⋯O5 ⁱⁱ	2.930(2)	173.8(18)	
N2-H2b ⁱⁱⁱ ⋯O1 ⁱⁱⁱ	3.054(3)	142.5(19)	

Symmetry codes: (i) $-x, -y + 1, -z + 2$; (ii) $-x + 2, -y + 1, -z + 1$; (iii) $x + 1, y, z$.

Besides the above described differences in molecular packing there are also significant differences in magnetic properties of the title compound and other analogues. Namely, magnetic susceptibility of the title compound amounts to 1.07 BM, a value typical for dimeric copper methanoates. Such a value is substantially lower than values of copper dimers with other carboxylate ligands. The studies that may explain this difference are still underway.^{21,22}

As magnetic properties, the results of UV-VIS and infrared measurements are also characteristic for dimeric copper methanoates. A shoulder at 370 nm confirms the existence of binuclear moiety, and the difference between symmetric and asymmetric vibrations in infrared spectrum (101 cm^{-1}) proves the bidentate bridging mode of methanoate ligands.

Thermal decomposition of the title compound proceeds in two stages which can be seen in Figure 4. In the first step till 145 °C, 33.4% of initial mass is lost corresponding to the decomposition of coordinated methanoates. In the second step until 220 °C the mass loss amounts to another 40.8% which should be contributed to thermal decomposition of nicotinamide ligands. The obtained residue comprises copper(I) oxide and the total mass loss of 74.2% is in accordance with the theoretical when expecting the aforementioned product.

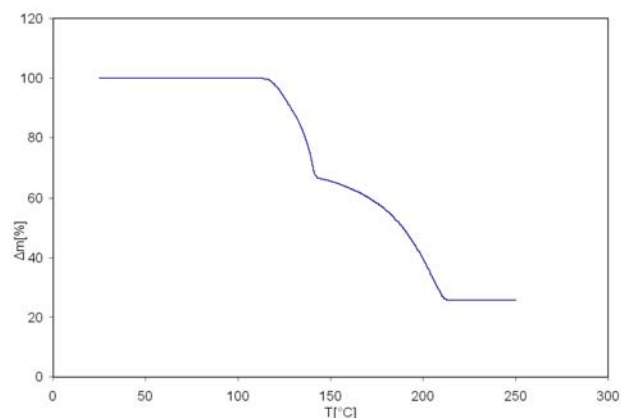


Figure 4 Thermogravimetry results of compound 1.

4. Acknowledgement

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Povzetek

Koordinacijsko spojino bakra(II), $[\text{Cu}_2(\text{O}_2\text{CH})_4(\text{nia})_2]$ (nia = nikotinamid), smo izolirali iz reakcijske zmesi, ki je vsebovala $\text{Cu}_2(\text{OH})_2\text{CO}_3$, nikotinamid, metanojsko kislino in etanol. Kristalno strukturo smo določili z rentgensko strukturno analizo monokristala ter spojino okarakterizirali še z ostalimi klasičnimi fizikalno-kemijskimi metodami. Strukturo sestavljajo dvojedrne centrosimetrične molekule, v katerih sta kovinska atoma povezana s štirimi metanoatnimi mostovi, pri čemer se tvori t. i. strukturni tip lopatastega kolesa. Peto koordinacijsko mesto, tj. vrh popačene kvadratne piramide, zaseda aromatski dušikov atom nikotinamidnega liganda. Molekule se povezujejo z vodikovimi vezmi, kar se odrazi v nastanku supramolekularnih plasti. Rezultati drugih fizikalnih meritev se ujemajo z opisano strukturo.