

Synthesis and Crystal Structure of Copper(I) Nitrate π -complex with 1-allylbenzotriazole of Equimolar Composition

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Abstract

The $\text{CuNO}_3 \cdot \text{C}_6\text{H}_4\text{N}_3(\text{C}_3\text{H}_5)$ compound (**I**) was obtained by alternating current electrochemical synthesis, starting from an ethanol solution containing $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and a mixture of 1- and 2-allylbenzotriazole titrated by HNO_3 to pH = 4. The C=C bond of one 1-allylbenzotriazole molecule, the nitrogen atom from another ligand moiety, and two oxygen atoms from two nitrate-anions form a trigonal-pyramidal environment of the metal atom. The bridging function of the ligand moiety results in infinite metal-organic chains, interconnected by weak CH...O hydrogen bonds, π - π and π - σ stacking and van der Waals interactions.

Keywords: Copper; π -interactions; nitrogen heterocycles

1. Introduction

Discussing the complexes of CuNO_3 one should note, that the copper(I) nitrate itself is unknown in a free state. Nevertheless, its derivatives could be stabilized by complexation, separated and studied. The first π -complex of the copper(I) nitrate has been synthesized and structurally investigated one and a half decade ago.¹ Using electrochemical alternating-current synthesis some other π -derivatives of this non-existent salt have been prepared.^{2–6} The NO_3^- anion demonstrates in these compounds various coordination abilities, acting usually bridging role. But sometimes the NO_3^- moiety is weakly coordinated to the central metal ion and as a counter-ion replaces, for example, the BF_4^- anion in the copper(I) π -complex with diallylamine.¹

Here we report the synthesis and structural characterisation of copper(I) nitrate π -complex with 1-allylbenzotriazole.

2. Results and Discussion

In the structure of complex **I** the 1-allylbenzotriazole molecule demonstrates a bridging function, being coordinated through the C=C-bond of the allyl group to one copper atom and through the nitrogen atom of triazole core to another symmetry related metal center (Fig. 1). The two remaining places in each metal coordination sphere are occupied by two bridging oxygen atoms from two NO_3^- anions symmetry related by a center of inversion (Table 2).

Due to a bridging function of organic ligand and due to centrosymmetric double Cu–O–Cu bridges polymer complex molecules of $[\text{Cu}(\text{C}_3\text{H}_5\text{–C}_6\text{H}_4\text{N}_3)(\text{NO}_3)_2]_n$ formula are formed (Fig. 2).

It is expediently to consider geometry of copper coordination sphere in context of effectiveness of metal-olefin interaction. The bonding in copper(I)–ethylene complexes can be described by the Dewar–Chatt–Dun-

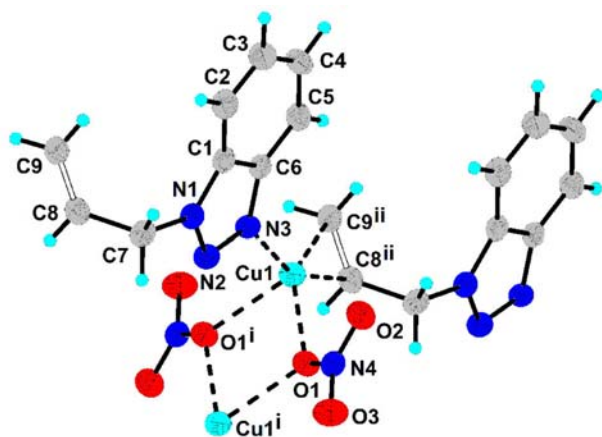


Figure 1. Metal coordination environment in crystal structure **I**. Symmetry codes: (i) $-x, -y, -z$; (ii) $x-1, y, z$;

canson model as a combination of two components: the $(\text{Cu(I)} \leftarrow \text{L})_{\sigma}$ donor-acceptor component arising from overlapping of the occupied olefinic π_p orbital and the unoccupied $4s^0$ orbital of the metal ion, and the $(\text{Cu(I)} \rightarrow \text{L})_{\pi}$ -dative component, formed upon electron-density drawing-off from the $3d^{10}$ copper(I) orbitals to the unoccupied anti-bonding orbitals of the $\text{C}=\text{C}$ -group.⁷ Both the σ -donor and π -back-bonding contributions of the $\text{Cu}^{\text{I}} - (\text{C}=\text{C})$ interaction result in an elongation of the coordinated double carbon-carbon bond. The $\text{C}-\text{Cu}-\text{C}$ angle value is a convenient measure of both lengthening of the coordinated $\text{C}=\text{C}$ -bond and shortening of $\text{Cu}-m$ (m is a middle of coordinated $\text{C}=\text{C}$ bond) distances. It is known that a strength of metal-olefin π -interaction causes trigonal-pyramidal deformation of an initial tetrahedral copper(I) environment with a relatively small deviation of the Cu(I) atom from a plane of equatorial ligands, lengthening of $\text{Cu(I)}-L_{\text{ax}}$ distance and an appropriate orientation of the $\text{C}=\text{C}$ -bond in an equatorial plane of the coordination polyhedron.⁸ In the structure discussed the Cu1 atom is in very slightly deformed trigonal-pyramidal environment. The oxygen atom at the apical position is noticeably moved

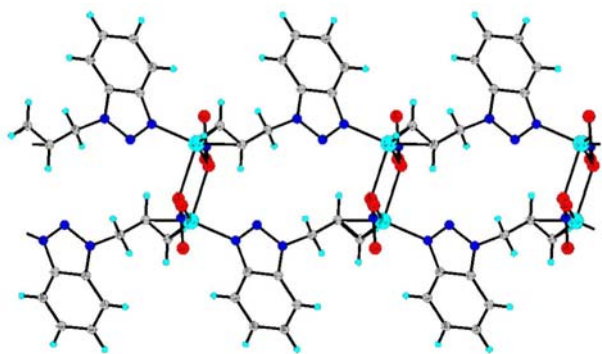


Figure 2. A view of crystal structure **I** along c axis.

($\text{Cu1}-\text{O2}_{\text{ax}}$ 2.319(4) Å against $\text{Cu1}-\text{O2}_{\text{eq}}$ 2.049(8) Å). The deviation of the central atom from the basal plane of coordination polyhedron is 0.19 Å and the $\text{C8}=\text{C9}$ bond lies practically in an equatorial plane. Such a geometry of the Cu1 coordination sphere is in a good agreement with a rather effective $\text{Cu1}-(\text{C8}=\text{C9})$ interaction which is confirmed by a $\text{C8}-\text{Cu1}-\text{C9}$ angle value of $39.1(2)^\circ$, lengthening of the coordinated $\text{C8}=\text{C9}$ bond to 1.356(6) Å against 1.34 Å in free olefins and a short $\text{Cu1}-m$ distance of 1.912(5) Å.⁹

An absence of the covalent bonding between mentioned 1-D chains, and the presence of two terminal (regarding to the metal coordination sphere) oxygen atoms in each anion have stimulated us to check carefully an existence of weak hydrogen bonds in structure **I**, even though the expected hydrogen-bonding groups are not present. The $\text{C}-\text{H}\cdots\text{O}$ contacts of 2.43–2.55 Å (Table 3), which, according to the criteria in,^{10,11} can be regarded as weak hydrogen bonds, were found. The crystal packing is also stabilized by $\pi\cdots\pi$ and $\pi\cdots\sigma$ stacking interactions between the aromatic rings of the neighbouring chains. The distance between centroids of two parallel aromatic rings related by a symmetry center is 3.684(3) Å (Fig. 3).

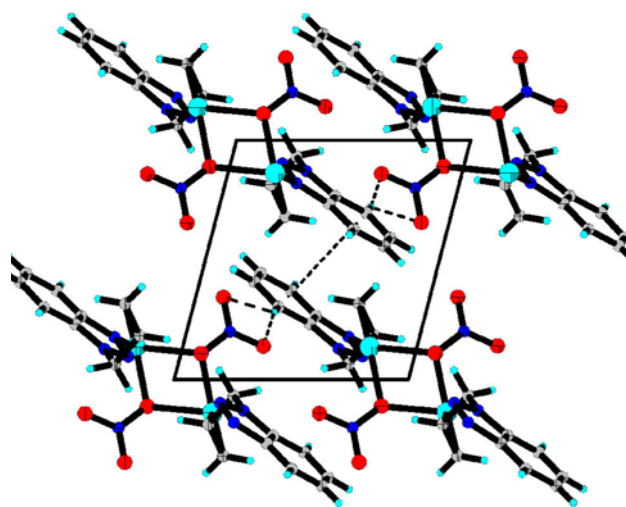


Figure 3. View of the crystal packing of **I** along a axis. Dotted lines represent $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds and the $\pi\cdots\pi$ stacking of aromatic rings.

3. Experimental Section

3.1 Synthesis of N-allylbenzotriazole

1-(/2)-Allylbenzotriazole (L) was obtained by refluxing on a glycerine bath and magnetic stirring the equimolar mixture of benzotriazole, fresh-distilled allyl chloride and NaHCO_3 in 95% ethanol during 10 days (with breaks for nights), total time was about 125 hrs. The weight of precipitated NaCl confirmed a practically quantitative transformation of benzotriazole into the desi-

red product. After a solvent distillation concentrated ethanolic solution of L was used for preparation of a target complex.

3. 2. Synthesis of $\text{Cu}(\text{NO}_3)_2 \cdot \text{C}_6\text{H}_4\text{N}_3(\text{C}_3\text{H}_5)$

Electrochemical synthesis is a powerful method for direct growing of high-quality single crystals of the copper(I) coordination compounds. Original direct-current technique¹² was modified, improved and converted to an alternating-current method.¹³ Usually electrical current is passed through the solution, containing copper(II) salt(s) and ligand(s), and a reaction $\text{Cu}^0 + \text{Cu}^{2+} \rightarrow 2\text{Cu}^+$ performs. Variation of voltage and current density, starting mixture composition and solvent allows growing high-quality single crystals. The important advantages of such technique are, at first, an absence of additional reducing agents, used frequently for copper(I) compounds synthesis. Respectively, any unneeded by-products (like oxidized reductants) appear. Additionally, such a method makes re-crystallization process unnecessary, which is sometimes complicated for rather unstable copper(I) π -complexes. Good quality crystals of $\text{CuNO}_3 \cdot \text{C}_6\text{H}_4\text{N}_3(\text{C}_3\text{H}_5)$ (I) have been obtained using the above alternating-current electrochemical technique. To 2 ml of ethanol solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1 mmol) 2 ml of ethanol solution containing a mixture of 1- and 2-allylbenzotriazole (1.2 mmol) was added. The prepared solution was placed into a small test-tube and copper-wire electrodes in cork were inserted. After 0.30 V alternating current (frequency 50 Hz) tension applying during 3 days colourless crystals of the compound I appeared on the copper electrodes. Crystals appear to be enough stable in dry atmosphere. The density was measured by flotation in a chloroform-bromoform mixture.

3. 3. Crystallography

Single-crystal data were collected on a Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector, using graphite monochromatized $\text{MoK}\alpha$ radiation. Data were treated using the Rigaku CrystalClear software suite package.¹⁴ The structure was solved by direct methods using the SIR-92¹⁵ program (teXan crystallographic software package of Molecular Structure Corporation¹⁶) and refined on F^2 with SHELXL-97¹⁷ software implemented in the program package WinGX.¹⁸ Because of twinning of used crystal with a strongly unequal domains volumes reflections from the second domain and overlapped reflections were excluded from the refinement resulting a decreasing of data completeness to 92.3% at 50° in 2θ . Hydrogen atoms were included on idealized positions and refined with geometrical restrictions. The figures were prepared using DIAMOND 3.1 software.¹⁹ Experimental details and crystallographic data are listed in Table 1.

Table 1. Details of experimental and crystallographic data for I

Compound	I
Empirical formula	$\text{C}_9\text{H}_9\text{CuN}_4\text{O}_3$
Shape and color	Colorless, chunk
Formula weight	284.74
Crystal size, mm	$0.12 \times 0.1 \times 0.08$
Temperature, K	200
Radiation	$\text{Mo K}\alpha$
Crystal system	triclinic
sp. gr.	$P\bar{1}$
Unit cell dimensions	
a , Å	8.0022(15)
b , Å	8.0076(16)
c , Å	8.7146(19)
α , deg	102.122(6)
β , deg	105.511(6)
γ , deg	96.888(7)
V , Å ³	516.8(2)
Z	2
D_c g/cm ³	1.83
D_m g/cm ³	1.8
μ , mm ⁻¹	2.115
$F(000)$	288
Scan range θ , °	2.51–29.05
Measured reflections, R_{int}	3325, 0.0247
Used ($I > 2\sigma(I)$)	2111
Parameters refined	154
$R(F)$	0.0475
$R(F)^2$	0.1181
Goodness-of-fit	1.152

CCDC 635809 (I) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 2. Selected bond distances (Å) in the structure I

Cu1–N3	1.991(3)	N3–N2	1.315(4)	C2–C3	1.374(6)
Cu1–C9 ⁱ	2.019(4)	N3–C1	1.382(5)	C3–C4	1.402(6)
Cu1–C8 ⁱ	2.037(4)	N2–N1	1.350(4)	C4–C5	1.363(7)
Cu1–O1	2.049(3)	N1–C6	1.356(5)	C5–C6	1.399(6)
Cu1–O1 ⁱⁱ	2.319(3)	N1–C7	1.468(5)	C7–C8	1.505(6)
Cu–m	1.912(5)	C1–C2	1.392(6)	C8–C9	1.356(6)
O1–N4	1.279(4)	C1–C6	1.399(5)	C2–C3	1.374(6)
O2–N4	1.233(4)	C2–C3	1.374(6)	C3–C4	1.402(6)
O3–N4	1.230(4)				

Symmetry codes: (i) $x-1, y, z$; (ii) $-x, -y, -z$. m is a mid-point of C8=C9 bond.

Table 3. Hydrogen-bonding geometry in I

D–H...A [Å]	D–H [Å]	H...A [Å]	D...A [Å]	D–H...A [°]
C2–H2–O2 ⁱ	0.93	2.43	3.334(6)	163.5
C2–H2–O3 ⁱ	0.93	2.55	3.310(6)	139.1

Symmetry codes: (i) $1-x, 1-y, -z$

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Povzetek

Spojina $\text{CuNO}_3 \cdot \text{C}_6\text{H}_4\text{N}_3(\text{C}_3\text{H}_5)$ je bila sintetizirana z elektrokemijskim postopkom iz etanolne raztopine $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, ki vsebuje mešanico 1- in 2-alilbenzotriazolov titrirano s HNO_3 do $\text{pH} = 4$. Vezi C=C prve molekule 1-alilbenzotriazola, atom dušika druge molekule liganda, ter dva atoma kisika iz dveh nitratnih anionov tvorijo okolico kovinskega atoma v obliki trigonalne piramide. Preko mostovnih ligandov nastajajo neskončne kovin-organske verige, povezane s šibkimi CH...O vodikovimi vezmi, van der Waalsovimi ter π - π in π - σ interakcijami med aromatskimi obroči.