

Diverse coordination of CuX (X = Cl, Br) towards N-allylbenzotriazole

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The crystalline Cu(I) complex [Cu(1-*Abtr*)Br] (1-*Abtr* = 1-allylbenzotriazole) was obtained by means of the alternating-current electrochemical technique and was characterized by X-ray single crystal diffraction. The crystal structure is monoclinic, space group $P2_1/c$, $Z = 4$, $a = 4.110(2)$, $b = 13.858(4)$, $c = 17.272(5)$ Å, $\beta = 90.14(3)^\circ$, $V = 983.7(6)$ Å³, at 200 K. The Cu(I) atoms possess a distorted tetrahedral coordination environment involving two N atoms from two adjacent triazole molecules and two bridging Br atoms, while the allylic C=C bond of 1-*Abtr* does not participate in the metal coordination. On the contrary, reaction of CuCl and Cu(Cl,Br) with *N*-allylbenzotriazole under similar conditions results in π,σ -complexes, revealing the (C=C),N-bidentate bridging role of 1-*Abtr*.

Triazole / Copper(I) / Complex / Crystal structure

1. Introduction

1,2,3-Triazoles have a broad range of potential applications in pharmaceutical chemistry, materials science and chemical biology [1]. They have also found use as suitable “building blocks” in crystal engineering of organometallic compounds [2]. The existence of an olefin C=C bond (which according to the HSAB theory acts as a “soft base”), attached to the skeleton of the 1,2,3-triazole, may serve as the actual key for the selected coordination of the transition metal ions, due to metal-olefin π -bonding.

Recently, a specific contribution of allyl derivatives of heterocyclic compounds, to compounds with extremely rare inorganic fragments, was found [3,4]. For example, a significant influence of 1-allylbenzotriazole (1-*Abtr*) on the unusual Cu(I) coordination abilities was found in the [Cu₂(1-*Abtr*)₂(H₂O)₂SiF₆]·2H₂O π -complex, in which rare Cu¹...F(SiF₆²⁻) interactions were observed [5]. Isomer-selective complexation of copper(I) ionic salts (CuBF₄, CuClO₄, and CuHSO₄) towards 1-allylbenzotriazole and 2-allylbenzotriazole (2-*Abtr*) has also been studied previously [6]. The structure of [Cu(2-*Abtr*)(HSO₄)] was found to be the first known example of a CuHSO₄ π -complex.

The π -coordination abilities of 1-allylbenzotriazole towards copper(I) halides have been studied only in the case of the two crystalline π -compounds [Cu₂(1-*Abtr*)₂Cl₂] and [Cu₂(1-*Abtr*)₂Cl_{1.7}Br_{0.3}] [7,8], in which the 1-*Abtr* molecule acts as N,(C=C)-bidentate bridging ligand, while entirely cuprous bromide π -complexes with olefine derivatives of 1,2,3-triazole have only been studied for 1-allyloxybenzotriazole and 1,3-diallylbenzotriazolium bromide [4,9,10]. In order to study the role of bromine anions on isomer-selective complexation of Cu⁺ towards 1-*Abtr* and 2-*Abtr*, we undertook the synthesis and structural characterization of the new complex [Cu(1-*Abtr*)Br] (1), presented below.

2. Experimental section

N-allylbenzotriazole was prepared from commercially available benzotriazole, freshly distilled allyl chloride, and NaHCO₃ in ethanol, in accordance with the procedure described in [6]. The ¹H NMR spectrum of the ligand agreed well with earlier reports, and showed the presence of the 1- (1-*Abtr*) and 2-isomers (2-*Abtr*) of *N*-allylbenzotriazole in an approximately equimolar ratio.

2.1 Preparation of [Cu(1-*Abtr*)Br] (1)

Crystals of the complex **1** were obtained by alternating-current electrochemical synthesis [11], starting from a water-ethanol solution of the 1-*Abtr* and 2-*Abtr* mixture (the acidity was adjusted to pH 4 using HBr) and copper(II) bromide. The prepared solution was transferred into a small 5 mL test-tube and then copper-wire electrodes in cork were inserted. After application of an alternating-current tension (frequency 50 Hz) of 0.45 V for 5 days, good-quality colorless crystals of **1** appeared on the copper electrodes.

2.2 X-ray crystal structure determination

Diffraction data for a crystal of **1** were collected on a Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector and graphite-monochromatized Mo $K\alpha$ radiation. The collected data were processed with the Rigaku CrystalClear software suite [12]. The structure was solved by direct methods using SHELXS-97 and refined by the least-squares method on F^2 by SHELXL-2014 with graphical user interfaces of OLEX² [13,14]. The atomic displacements of the non-hydrogen atoms were refined using an anisotropic model. The hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. The crystallographic parameters, data collection and refinement are summarized in Table 1. Fractional atomic coordinates and atomic displacement parameters are listed in Table 2.

3. Results and discussion

The reaction of CuBr (appearing *in situ* under *ac* electrochemical conditions) with the 1-allyl (1-*Abtr*) and 2-allylbenzotriazole (2-*Abtr*) mixture in the water-ethanol solution leads to isomer-selective

complexation of Cu⁺ with 1-*Abtr* only, resulting in the [Cu(1-*Abtr*)Br] (**1**) σ -complex. According to the four-coordinate geometry index (proposed by Addison *et al.* [15]), the copper(I) atom in **1** adopts a distorted tetrahedral surrounding ($\tau_4 = 0.92$), formed by one N3 atom of an 1-*Abtr* molecule, one N2 atom of a neighboring organic moiety, and two bridging Br atoms (Fig. 1, Table 3). Thus, 1-*Abtr* acts as a N,N-bridging ligand, connecting two Cu(I) atoms into a centrosymmetric {[Cu(1-*Abtr*)]₂}²⁺ dimer (having a six-membered {Cu₂N₄} ring). The dimers, in turn, are interconnected *via* bridging bromide anions into {Cu(1-*Abtr*)Br}_n infinite chains (Fig. 2). The allyl group of 1-*Abtr* does not participate in the metal coordination, but is only involved in weak C-H...Br interactions. The dihedral angle between the triazole ring and the C10-C11 bond of the allyl group is 85.6(6)°. The allyl group in **1** is characterized by anticlinal conformation (121.0(14)°) with respect to the C10-C11 bond.

Taking into account that, according to the HSAB theory [16], the olefin C=C bond acts as a “soft base”, the appearance of Cu–(C=C) interaction is caused by Cu⁺ ion “soft acidity”. But, due to the higher polarizability of the Br[−] ion (in comparison with Cl[−]) and the increase of bond covalency within the row CuCl < CuBr < CuI, metal-olefin π -complexation is less obvious for CuBr (even less for CuI). In contrast to **1**, in the earlier studied compounds [Cu₂(1-*Abtr*)₂Cl₂] (**2**) and [Cu₂(1-*Abtr*)₂Cl_{1.7}Br_{0.3}] (**3**) [7,8], the 1-*Abtr* molecule acts as a N,(C=C)-bidentate bridging ligand, being attached to the metal center by the allylic C=C bond and the most nucleophilic triazole atom, while bridging halogen atoms bind the organometallic chains into a 2D-coordination polymer (Fig. 3a). In the presence of pseudo-halide NO₃[−] anions, the same N,(C=C)-bidentate role of 1-*Abtr* ensures the connection of {[Cu(1-*Abtr*)]⁺}_n into double polymeric chains [17].

Table 1 Crystal data and structure refinement for **1**.

Empirical formula	C ₉ H ₉ BrCuN ₃	Color, shape	colorless, needle
Formula weight	302.64 g·mol ^{−1}	Theta range for data collection	2.18–29.07°
Temperature, K	200(2)	Limiting indices	−5 ≤ <i>h</i> ≤ 3, −16 ≤ <i>k</i> ≤ 17, −23 ≤ <i>l</i> ≤ 17
Wavelength	0.71069 Å	Refinement method	full-matrix least-squares on F^2
Crystal system; space group	monoclinic; $P2_1/c$	Measured reflections	4318
Unit cell dimensions:		Unique reflections	2094
<i>a</i> , Å	4.110(2)	R_{int} value	0.054
<i>b</i> , Å	13.858(4)	Used in refinement	2094
<i>c</i> , Å	17.272(5)	Free parameters	128
β , °	90.14(3)	Goodness-of-fit on F^2	1.10
<i>V</i> , Å ³	983.7(6)	R values	$R1 = 0.088$, $wR2 = 0.270$
Formula units per cell, <i>Z</i>	4	Largest diff. peak and hole	2.14 and −1.32 e·Å ^{−3}
Absorption coeff., mm ^{−1}	6.241		
Calculated density, g·cm ^{−3}	2.043		
$F(000)$	592		

Table 2 Fractional atomic coordinates and (equivalent) isotropic displacement parameters (in Å²) for **1**.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}/U_{iso}^a
Br	−0.1325(4)	0.88773(8)	0.34486(7)	0.0375(4)
Cu	0.3519(5)	0.94001(10)	0.41692(9)	0.0402(5)
N1	0.551(3)	0.8511(7)	0.6395(5)	0.034(2)
N2	0.549(2)	0.9138(7)	0.5801(5)	0.029(2)
N3	0.377(3)	0.8766(7)	0.5235(5)	0.032(2)
C4	0.268(3)	0.7879(10)	0.5468(7)	0.038(3)
C5	0.370(3)	0.7711(8)	0.6203(6)	0.034(2)
C6	0.294(4)	0.6853(9)	0.6610(7)	0.045(3)
C7	0.107(4)	0.6206(9)	0.6226(9)	0.046(3)
C8	0.002(4)	0.6378(11)	0.5463(9)	0.052(4)
C9	0.053(3)	0.7220(9)	0.5051(6)	0.039(3)
C10	0.733(3)	0.8703(10)	0.7112(7)	0.037(3)
C11	0.509(4)	0.9143(12)	0.7737(7)	0.046(3)
C12	0.464(4)	0.8744(10)	0.8394(7)	0.042(3)
H6	0.3691	0.6739	0.7122	0.054
H7	0.0455	0.5624	0.6477	0.056
H8	−0.1136	0.5874	0.5210	0.063
H9	−0.0395	0.7352	0.4558	0.047
H10A	0.9135	0.9155	0.7002	0.045
H10B	0.8278	0.8093	0.7308	0.045
H11	0.3998	0.9732	0.7627	0.056
H12A	0.5709	0.8155	0.8515	0.051
H12B	0.3244	0.9037	0.8763	0.051

^a For non-hydrogen atoms U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor, for hydrogen atoms U_{iso} .

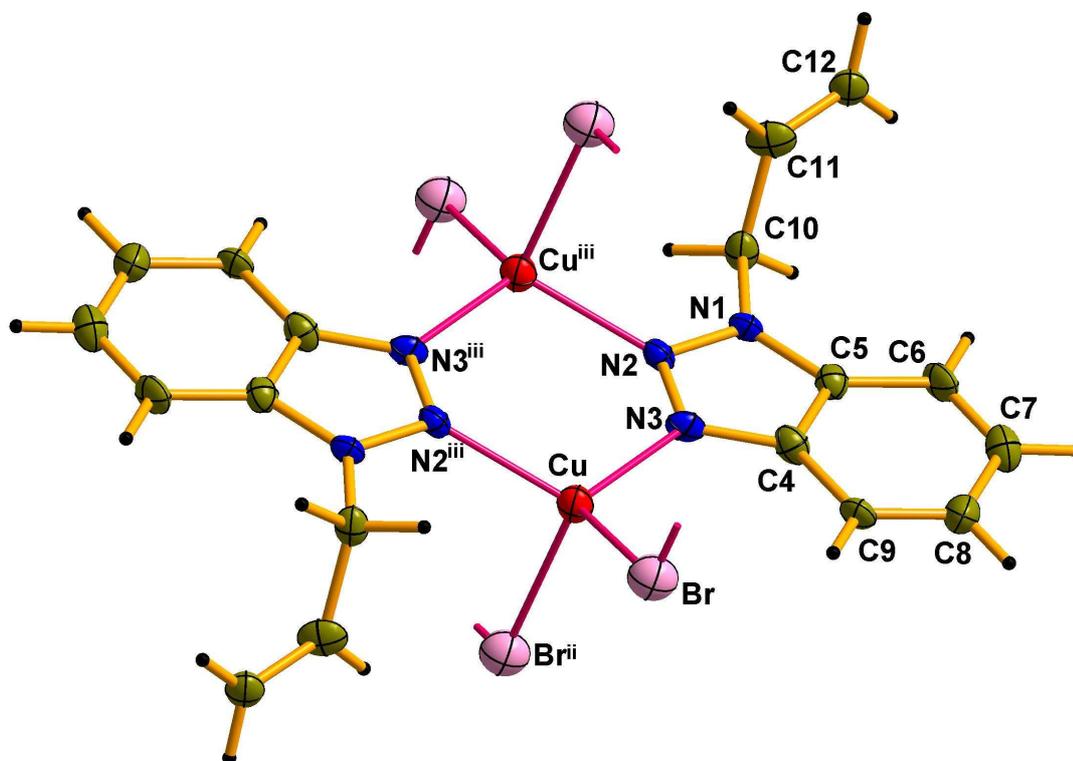
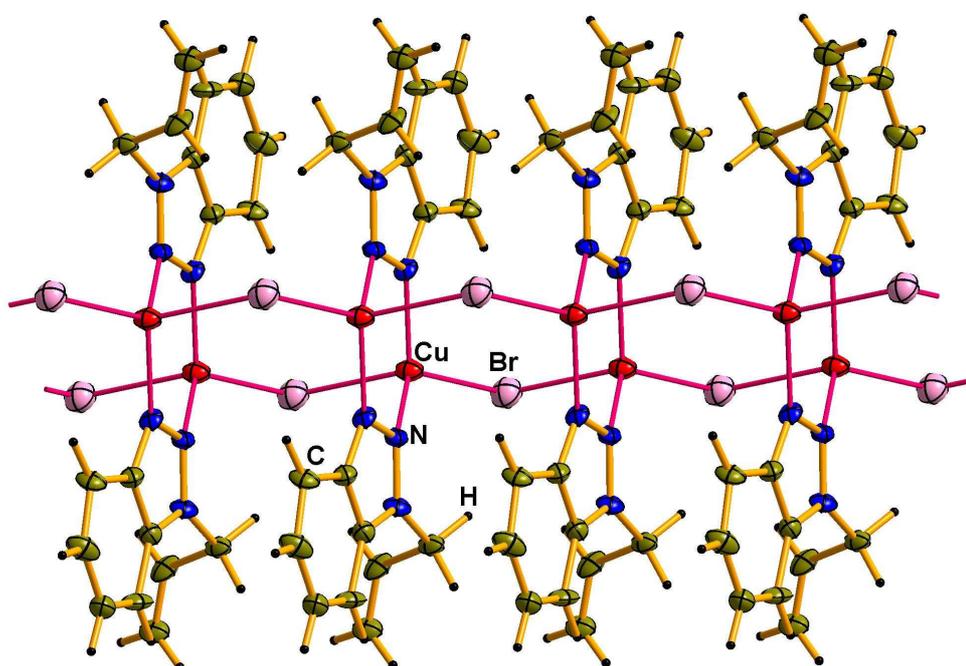
**Fig. 1** Part of the $\{Cu(1-Abtr)Br\}_n$ infinite chain in **1**. Symmetry codes: (ii) $x+1, y, z$; (iii) $1-x, 2-y, 1-z$.

Table 3 Selected bond lengths (in Å) and angles (in °) in the structure of **1**.

Bond ^a	Value	Angle ^a	Value
Br–Cu	2.455(2)	Cu–Br–Cu ⁱ	109.91(7)
Br–Cu ⁱ	2.565(3)	Br–Cu–Br ⁱⁱ	109.91(7)
Cu–Br ⁱⁱ	2.565(3)	N3–Cu–Br ⁱⁱ	106.0(3)
Cu–N3	2.042(9)	N3–Cu–Br	111.7(3)
Cu–N2 ⁱⁱⁱ	2.066(10)	N3–Cu–N2 ⁱⁱⁱ	112.9(4)
N3–N2	1.311(14)	N2 ⁱⁱⁱ –Cu–Br	117.5(3)
N3–C4	1.369(16)	N2 ⁱⁱⁱ –Cu–Br ⁱⁱ	97.3(3)
N2–Cu ⁱⁱⁱ	2.066(10)	N2–N3–Cu	121.9(8)
N2–N1	1.345(13)	N2–N3–C4	108.1(9)
C5–N1	1.375(15)	C12–C11–C10	122.5(14)

^a symmetry codes: (i) $-1+x, y, z$; (ii) $x+1, y, z$; (iii) $1-x, 2-y, 1-z$

**Fig. 2** Coordination polymer in **1**.

The reaction of a mixture of isomeric 1-*Abtr* and 2-*Abtr* with CuBF₄, CuClO₄, and CuHSO₄, in an alcohol solution (acidified by the corresponding acid to pH ~4) under *ac*-electrochemical conditions, results in the π -complexes [Cu(2-*Abtr*)(H₂O)]BF₄ (**4**), [Cu(2-*Abtr*)(ClO₄)] (**5**), and [Cu(2-*Abtr*)(HSO₄)] (**6**), with selective participation of 2-*Abtr* in the metal coordination (Fig. 3b) [6]. Due to the ionic character of the copper salts in **4** and **5**, the organic ligand is simultaneously coordinated to Cu(I) in chelate and bridge fashions by means of all the three available active centers (N1 and N3 triazole atoms and the allylic C=C bond), forming infinite chains. Therefore, it can be assumed that the isomer-selective

complexation of Cu(I) towards 1-*Abtr* and 2-*Abtr* is greatly related to the polarizability of the inorganic anion, while both isomers tend to produce polymeric structures.

4. Supplementary material

CCDC number 1483152 contains the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on applications to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code +(1223)336-033; e-mail for inquiry: fileserv@ccdc.cam.ac.uk).

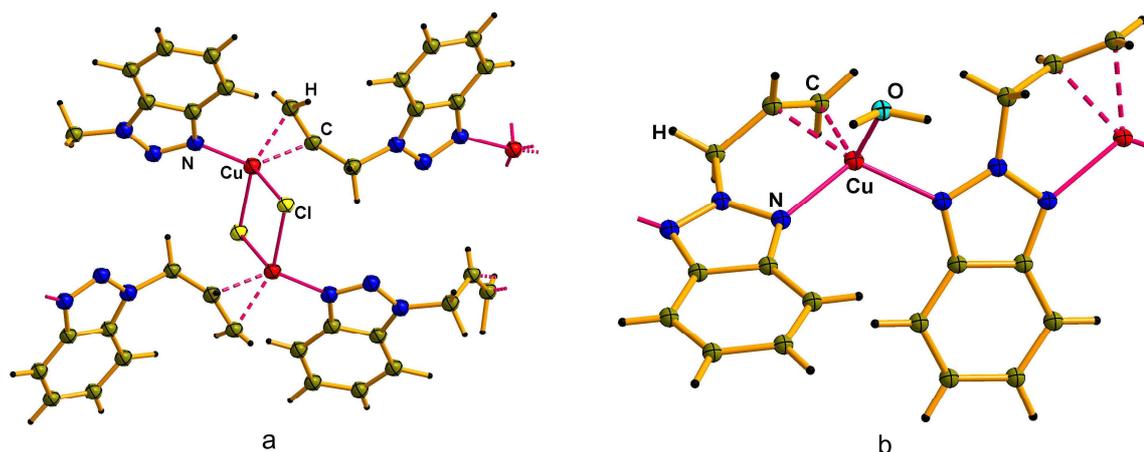


Fig. 3 Fragment of the $[\text{Cu}_2(1\text{-Abtr})_2\text{Cl}_2]$ π -complex (a) and part of the cationic chain in $[\text{Cu}(2\text{-Abtr})(\text{H}_2\text{O})]\text{BF}_4$ compound (b).

Table 4 Geometry of weak hydrogen bonds in the structure of **1**.

Atoms involved D–H···A	Symmetry	Distances, Å			Angle, deg
		D···H	H···A	D···A	D–H···A
C10–H10A···Br1	1–x, 2–y, 1–z	0.99	2.98	3.859(13)	149
C9–H9···Br1		0.95	2.88	3.676(12)	142
C11–H11···Br1	–x, 2–y, 1–z	0.95	2.89	3.754(15)	152

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