

Synthesis and crystal structure of a new heteroligand copper(I) π -complex $[\text{Cu}_8(\text{C}_9\text{H}_9\text{N}_3)_4\text{Cl}_6(\text{ClO}_4)_2(\text{EtOH})_2]$ based on 1-allyl-1H-benzotriazole

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By means of the alternating current electrochemical technique a new heteroligand π -complex $[\text{Cu}_8(1\text{-Abtr})_4\text{Cl}_6(\text{ClO}_4)_2(\text{EtOH})_2]$ (**1**) (1-Abtr = 1-allyl-1H-benzotriazole) has been obtained and characterized by X-ray single-crystal diffraction. Crystals of **1** are monoclinic, space group $P2_1/n$, $a = 7.936(3)$, $b = 24.781(6)$, $c = 13.908(4)$ Å, $\beta = 99.42(3)^\circ$, $V = 2698.3(15)$ Å³ at 200 K, $Z = 2$. A large centrosymmetric fragment contains four crystallographically independent copper(I) atoms, two of which (Cu1 and Cu2) are π -connected with allylic groups of two 1-Abtr molecules and adopt similar trigonal pyramidal surrounding, including two bridging halogen atoms. The two other independent σ -coordinated Cu3 and Cu4 atoms connect two triazole rings of two 1-Abtr molecules, forming six-membered $\{\text{Cu}_2\text{N}_4\}$ cycles. Within the centrosymmetric fragment the neighboring benzotriazole rings are rotated relative to each other by $178.5(8)^\circ$, being involved in π - π -stacking.

1,2,3-Triazole / Copper(I) / π -Complex / Crystal structure

1. Introduction

1,2,3-Triazole derivatives possess a huge range of biological activities and their transition metal complexes are intensively explored for their application in light-emitting devices, solar energy conversion, as well as in catalysis [1-4]. Allyl groups, attached to a skeleton of 1,2,3-triazoles, serve as the actual key to the selected coordination of the transition metal ions due to metal-olefin π -bonding [5,6]. The specific contribution of allyl-triazoles to the unusual Cu(I) coordination abilities made it possible to isolate and structurally study the first CuHSO_4 and $\text{Cu}(p\text{-CH}_3\text{C}_6\text{H}_4\text{SO}_3)$ π -complexes and allowed observing the direct $\text{Cu(I)} \cdots \text{F}(\text{SiF}_6^{2-})$ interaction for the first time [7,8]. The coordination abilities of 1-allylbenzotriazole (1-Abtr) towards copper(I) halides have been studied in the case of three crystalline $[\text{Cu}_2(1\text{-Abtr})_2\text{Cl}_2]$, $[\text{Cu}_2(1\text{-Abtr})_2\text{Cl}_{1.7}\text{Br}_{0.3}]$, and $[\text{Cu}_2\text{Cl}_2(1\text{-Abtr})(\text{Py})]_2$ π -compounds, (in which the 1-Abtr molecule acts as N,(C=C)-bridging ligand) and one $[\text{Cu}(1\text{-Abtr})\text{Br}]$ σ -complex [9-12]. In the present work, we focused on the synthesis and structural characterization of a novel π -coordination compound,

$[\text{Cu}_8(1\text{-Abtr})_4\text{Cl}_6(\text{ClO}_4)_2(\text{EtOH})_2]$ (**1**), emphasizing the impact of various ligands on the formation of π, σ -complexes with 1-Abtr.

2. Experimental section

2.1 Synthesis of N-allylbenzotriazole

Allylbenzotriazole (Abtr, $\text{C}_9\text{H}_9\text{N}_3$) was prepared from commercially available benzotriazole, freshly distilled allyl chloride, and NaHCO_3 in ethanol, in accordance with the procedure described in [13]. The ¹H NMR spectrum of the ligand agreed well with earlier described ones, showing the presence of both 1- (1-Abtr) and 2-isomers (2-Abtr) of N-allylbenzotriazole in an approximately equimolar ratio.

2.2 Preparation of $[\text{Cu}_8(1\text{-Abtr})_4\text{Cl}_6(\text{ClO}_4)_2(\text{EtOH})_2]$ (**1**)

Crystals of the complex **1** were obtained under conditions of the alternating-current electrochemical

synthesis [14] starting from a mixture of N-allylbenzotriazoles (2.0 mmol), $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.6 mmol) and NaCl (1.5 mmol) in 4.5 mL of ethanol, acidified by two drops of a 60% aqueous solution of HClO_4 . The prepared mixture was placed 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 0.7 V for 3 days, good-quality colorless crystals of **1** appeared on the copper electrodes in a very small amount.

2.3 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 program package [15]. The structure was solved by SHELXS and refined by the least-squares method on F^2 by SHELXL software with the graphical user interface OLEX² [16,17]. The carbon atoms were refined isotropically. The atomic displacements of the other 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, details of the data collection and refinement, are summarized in Table 1. Fractional atomic coordinates and displacement parameters for **1** are listed in Table 2.

3. Results and discussion

The π -complex **1** crystallizes in the centrosymmetric space group $P2_1/n$. In the structure a large centrosymmetric $[\text{Cu}_8(1\text{-Abtr})_4\text{Cl}_6(\text{ClO}_4)_2(\text{EtOH})_2]$ fragment contains four crystallographically independent copper(I) atoms (two of which, Cu1 and Cu2, are π -connected with allylic groups of two 1-Abtr molecules (Fig. 1)), as well as four different ligand types: 1-Abtr, Cl^- , ClO_4^- , and EtOH. Cu1 and Cu2 adopt similar trigonal pyramidal surrounding, which in its basal plane includes two bridging halogen atoms and a double C=C bond of the allyl substituent. The apical position of the Cu2 polyhedron is occupied by an O1 atom of the ClO_4^- anion, while the corresponding position in the case of Cu1 is occupied by an O5 atom of the EtOH. The four-coordinate geometry index (τ_4) [18] for Cu1 is 0.77, and for Cu2 $\tau_4 = 0.72$. It should be noted that the trigonal-pyramidal environment of the Cu2 atom is more pronounced than that of the neighboring Cu1, due to the significant remoteness of the O1 atom of the anion from the metal center (2.659(9) Å), compared with the O5 atom of ethanol (Table 3). The Cu1 and Cu2 atoms are displaced from the base of the trigonal pyramid by 0.42 and 0.18 Å, respectively. For comparison, in the crystal structures of two previously studied π -complexes of CuClO_4 with N-allylbenzotriazole ($[\text{Cu}(1\text{-Abtr})\text{ClO}_4]$ and $[\text{Cu}(1\text{-Abtr})(2\text{-Abtr})\text{ClO}_4]$), the apical position of the copper trigonal pyramid is also occupied by an anion O atom but only a 2-Abtr ligand is π -attached to the copper(I) [6].

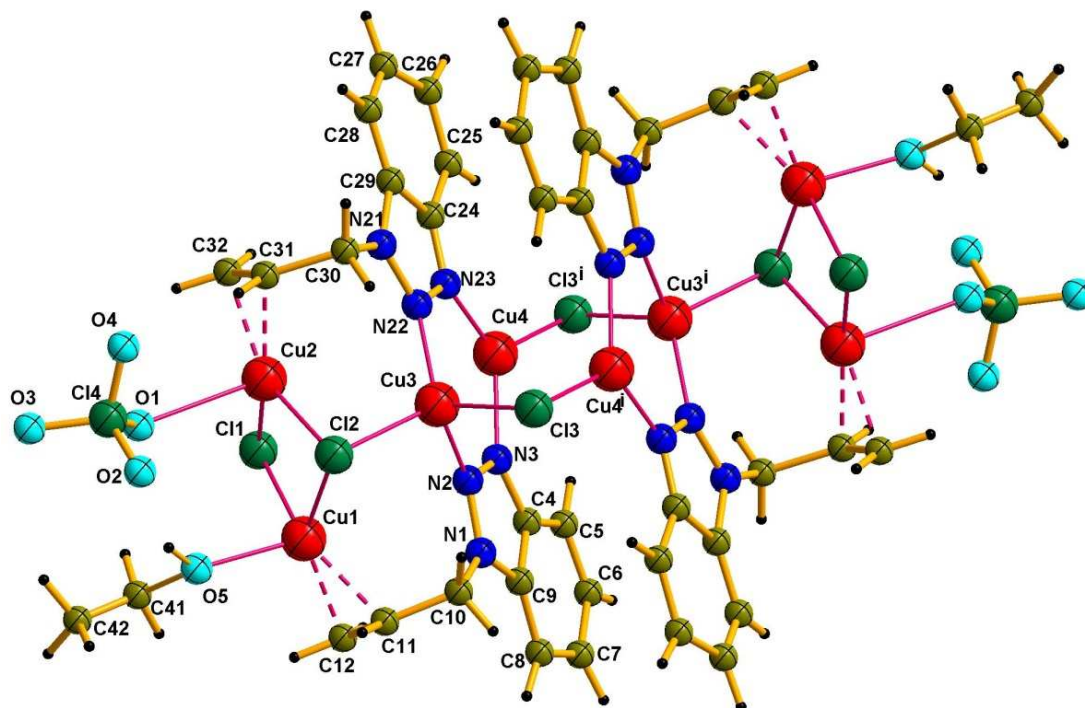


Fig. 1 Centrosymmetric $[\text{Cu}_8(1\text{-Abtr})_4\text{Cl}_6(\text{ClO}_4)_2(\text{EtOH})_2]$ fragment in **1**. Symmetry code: (i) $-x, -y, 1-z$.

Table 1. Selected crystallographic data and structure refinement parameters of **1**.

CCDC number ^a	2005345		
Empirical formula	C ₄₀ H ₄₈ Cl ₈ Cu ₈ N ₁₂ O ₁₀	Color, shape	colorless, block
Formula weight, g/mol	1648.82	Theta range for data collection, °	1.6 – 17.5
Temperature, K	200	Limiting indices	$-6 \leq h \leq 6, -20 \leq k \leq 20,$ $-11 \leq l \leq 10$
Wavelength, Å	0.71069	Refinement method	Full-matrix least-squares on F^2
Crystal system, space group	monoclinic, $P2_1/n$	Measured reflections	4559
Unit-cell dimensions a , Å	7.936(3)	Unique reflections	1717
b , Å	24.781(6)	Reflections with $I > 2\sigma(I)$	1075
c , Å	13.908(4)	Free parameters	204
β , °	99.42(3)	Goodness-of-fit on F^2	1.076
V , Å ³	2698.3(15)	R values	$R_1 = 0.0924, wR_2 = 0.2219$
Z	2	Largest diff. peak and hole, e/Å ³	0.815 and -0.654
Absorption coeff., mm ⁻¹	3.551	Calculated density, g/cm ³	2.029
$F(000)$	1640		

^a CCDC 2005345 contains the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge filling the corresponding form on <https://www.ccdc.cam.ac.uk/structures/?> page of CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

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

Atom	x	y	z	U_{iso}^*/U_{eq}^a
Cu1	0.1804(5)	0.05262(16)	0.1371(2)	0.0450(13)
Cu2	0.0308(5)	0.14914(16)	0.2196(2)	0.0453(13)
Cu3	-0.0688(4)	0.04161(15)	0.3159(2)	0.0408(13)
Cu4	-0.2079(5)	-0.03811(17)	0.4666(2)	0.0516(14)
Cl1	0.3047(10)	0.1217(3)	0.2399(5)	0.051(3)
Cl2	-0.1038(9)	0.0728(3)	0.1501(4)	0.036(2)
Cl3	-0.3008(9)	-0.0161(3)	0.3135(5)	0.045(2)
Cl4	-0.1224(11)	0.2128(4)	-0.0302(5)	0.042(2)
O1	0.019(2)	0.1951(8)	0.0458(12)	0.056(3)
O2	-0.197(2)	0.1695(9)	-0.0889(12)	0.056(3)
O3	-0.067(2)	0.2512(9)	-0.0931(13)	0.056(3)
O4	-0.247(2)	0.2377(9)	0.0167(12)	0.056(3)
O5	0.184(2)	0.0962(8)	0.0015(12)	0.049(6)
N1	0.178(3)	-0.0498(9)	0.2889(14)	0.028(3)
N2	0.144(3)	-0.0088(9)	0.3437(14)	0.028(3)
N3	0.238(3)	-0.0134(9)	0.4286(14)	0.028(3)
N21	-0.146(3)	0.1472(9)	0.4122(14)	0.028(3)
N22	-0.052(3)	0.0999(9)	0.4148(14)	0.028(3)
N23	0.044(2)	0.0968(8)	0.5014(14)	0.028(3)
C10	0.090(3)	-0.0579(12)	0.1893(19)	0.043(9)*
C4	0.340(3)	-0.0597(10)	0.4310(15)	0.011(7)*
C25	0.071(3)	0.1533(11)	0.6511(16)	0.023(7)*
C26	0.014(3)	0.1995(12)	0.6867(18)	0.039(8)*
C27	-0.106(3)	0.2333(11)	0.6287(18)	0.037(8)*
C28	-0.168(4)	0.2191(12)	0.5404(19)	0.043(9)*
C29	-0.119(3)	0.1740(11)	0.4965(17)	0.024(7)*
C31	-0.169(4)	0.1966(12)	0.2608(19)	0.051(9)*
C30	-0.262(4)	0.1627(11)	0.3257(18)	0.039(8)*
C11	0.173(3)	-0.0321(11)	0.1159(17)	0.029(8)*
C9	0.301(3)	-0.0827(12)	0.3427(18)	0.035(8)*
C8	0.392(3)	-0.1270(10)	0.3178(15)	0.020(7)*
C7	0.504(3)	-0.1487(12)	0.3911(18)	0.039(8)*
C6	0.539(3)	-0.1234(12)	0.4846(17)	0.034(8)*
C5	0.460(3)	-0.0768(10)	0.5064(16)	0.021(7)*

Table 2 (*continued*)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}^a$
C24	0.011(3)	0.1414(11)	0.5564(17)	0.025(8)*
C32	-0.015(3)	0.2202(12)	0.2856(17)	0.038(8)*
C12	0.337(4)	-0.0133(12)	0.1259(18)	0.042(9)*
C42	0.356(6)	0.1410(18)	-0.104(3)	0.122(16)*
C41	0.369(5)	0.1183(16)	-0.012(3)	0.095(13)*
H25	0.154150	0.131861	0.685570	0.030*
H26	0.054850	0.205509	0.752980	0.056*
H27	-0.134689	0.266560	0.654030	0.054*
H28	-0.257980	0.242459	0.503469	0.048*
H31	-0.220671	0.201221	0.194110	0.052*
H11	0.097130	-0.025572	0.056429	0.047*
H8	0.388121	-0.141809	0.252920	0.027*
H7	0.548720	-0.183331	0.382689	0.048*
H6	0.627331	-0.138729	0.531040	0.031*
H5A	0.481880	-0.060760	0.567801	0.037*
H32A	0.046229	0.216920	0.350961	0.068*
H32B	0.036849	0.240390	0.239529	0.068*
H12A	0.413180	-0.019521	0.183830	0.051*
H12B	0.373301	0.002910	0.071030	0.051*
H10A	0.086109	-0.096060	0.177200	0.042*
H10B	-0.021360	-0.044800	0.188110	0.042*
H30A	-0.308310	0.132100	0.291560	0.049*
H30B	-0.352270	0.184381	0.343600	0.049*
H41A	0.404809	0.145000	0.037310	0.107*
H41B	0.446369	0.088921	-0.002501	0.107*
H42A	0.312449	0.175600	-0.103200	0.117*
H42B	0.462820	0.139569	-0.123131	0.117*
H42C	0.276679	0.118450	-0.147360	0.117*
H5	0.095321	0.120501	-0.032830	0.057*

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

The allylic C11=C12 bond in **1** is slightly elongated to 1.37(3) Å (due to a back-donation from an occupied 3*d* metal orbital to a low-lying empty π^* orbital of the olefin) with respect to the values for free ethylene: 1.338(1) Å (gas phase [19]), 1.3142(3) Å (at 85 K [20]).

Two other crystallographically independent central atoms, Cu3 and Cu4, act as a bridge, connecting two triazole rings of two π -bonded 1-*Abtr* molecules and forming six-membered {Cu₂N₄} cycles [21-23]. The coordination environment of these copper(I) atoms is different: Cu3 atom has a distorted tetrahedral surrounding ($\tau_4 = 0.93$), composed of two 1,2,3-triazole N atoms and two μ_2 -Cl atoms, while the trigonal surrounding of Cu4 includes two nitrogen atoms and one Cl atom. Thus, in **1** the π -coordinated Cu1 and Cu2 atoms form two inorganic subunits – rhombic {Cu₂Cl₂} fragments, which are attached to the rest of the inorganic fragment through Cu3–Cl2 (2.404(7) Å) bonds. Similar {Cu₂Cl₂} rhombs were also found in previously studied π -complexes of CuCl with 1-*Abtr* [9,10], but in those structures the rhombs

are interconnected by bridging organic molecules into 2D-coordination polymers.

Within the [Cu₈(1-*Abtr*)₄Cl₆(ClO₄)₂(EtOH)₂] fragment the centers of the {Cu₂N₄} cycles are distant from each other by 3.43(3) Å, while neighboring benzotriazole rings are rotated relative to each other by 178.5(8)° and involved in π - π -stacking (3.36–3.38 Å). The crystal packing of **1** is shown in Fig. 2.

4. Conclusion

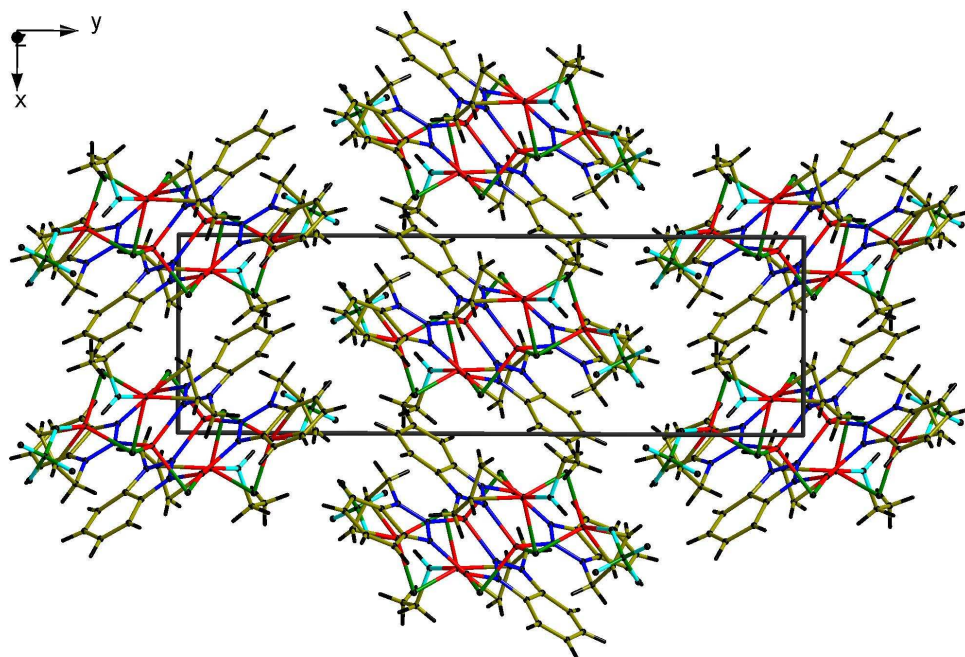
The halide anions play a decisive role in the formation of the structures of complexes with 1-allylbenzotriazole (1-*Abtr*), since these anions possess a high affinity to Cu⁺ ions and tend to combine metal centers into binuclear fragments or polynuclear oligomers. This is why, in all copper(I) chloride π -complexes with 1-*Abtr*, metal centers π -connected to the olefin bond are joined into rhombic {Cu₂Cl₂} fragments, which, in turn, strongly interfere

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

Bond	Value	Angle	Value
Cu1—Cl1	2.342(8)	Cl1—Cu1— <i>m</i> 1	130.8(7)
Cu1—Cl2	2.346(8)	Cl2—Cu1— <i>m</i> 1	121.2(7)
Cu1—O5	2.177(17)	O5—Cu1— <i>m</i> 1	108.8(8)
Cu1— <i>m</i> 1 ^[a]	1.98(3)	Cl1—Cu1—O5	95.9(5)
Cu2—Cl1	2.251(8)	Cl2—Cu1—O5	96.3(5)
Cu2—Cl2	2.306(8)	Cl1—Cu1—Cl2	96.4(3)
Cu2—O1	2.659(9)	Cl1—Cu2— <i>m</i> 2	134.7(8)
Cu2— <i>m</i> 2 ^[a]	1.98(3)	Cl2—Cu2— <i>m</i> 2	123.0(8)
Cu3—Cl2	2.404(7)	O1—Cu2— <i>m</i> 2	94.5(9)
Cu3—Cl3	2.327(8)	Cl1—Cu2—O1	97.6(8)
Cu3—N2	2.08(2)	Cl2—Cu2—O1	91.5(8)
Cu3—N22	1.99(2)	Cl1—Cu2—Cl2	100.2(3)
Cu4—Cl3 ^[b]	2.205(7)	Cl2—Cu3—Cl3	102.5(3)
Cu4—N3	1.98(2)	N22—Cu3—Cl2	114.5(6)
Cu4—N23	1.95(2)	N3—Cu4—Cl3 ^[b]	119.3(7)
C11=C12	1.37(3)	C10—C11—Cl2	127(1)
C31=C32	1.34(3)	C30—C31—C32	127(1)

^a *m*1 and *m*2 are the middle points of the C11=C12 and C31=C32 bonds, respectively;

^b symmetry code: (*i*) $-x, -y, 1-z$.

**Fig. 2** Crystal packing of **1** along the [001] direction.

with the chelate function of the organic ligand. In the presence of only Cl^- anions (or mixed Cl^-/Br^-), bridging 1-*Abtr* molecules bind $\{\text{Cu}_2\text{Cl}_2\}$ rhombs into 2D-coordination polymers [9,10]. Additional participation of pyridine in the Cu(I) coordination strongly prevents polymer formation and two $\{\text{Cu}_2\text{Cl}_2\}$ rhombs connect through bridging triazole cores into isolated $[\text{Cu}_2\text{Cl}_2(1\text{-}Abtr)(Py)]_2$ dimers [11] with a $\{\text{Cu}_4\text{Cl}_4\}$ inorganic subunit. The addition of a copper(I) ionic salt (CuClO_4) in the presence of Cl^- does not destroy the

$\{\text{Cu}_2\text{Cl}_2\}$ rhombs, but causes the organization of a more complicated inorganic $\{\text{Cu}_8\text{Cl}_6(\text{ClO}_4)_2\}$ fragment in **1**.

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