

A new hybrid inorganic-organic coordination copper(I) chloride π,σ -compound $[\text{Cu}_4(\text{C}_{18}\text{H}_{17}\text{N}_5\text{OS})_2\text{Cl}_4]\cdot 2\text{H}_2\text{O}\cdot 2\text{C}_3\text{H}_7\text{OH}$ based on N-phenyl-N'-{3-allylsulfanyl-4-amino-5-phenyl-4*H*-1,2,4-triazol-4-yl}urea: synthesis and structure characterization

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By means of alternating current electrochemical technique a new hybrid inorganic-organic π -complex $[\text{Cu}_4(\text{Atu})_2\text{Cl}_4]\cdot 2\text{H}_2\text{O}\cdot 2\text{C}_3\text{H}_7\text{OH}$ (**1**) (*Atu* = N-phenyl-N'-{3-allylsulfanyl-4-amino-5-phenyl-4*H*-1,2,4-triazol-4-yl}urea) has been synthesized and characterized by X-ray single-crystal diffraction. Crystals of **1** are monoclinic, space group $P2_1/c$, $a = 16.0745(10)$, $b = 18.0290(10)$, $c = 8.9794(6)$ Å, $\beta = 92.262(5)^\circ$, $V = 2600.3(3)$ Å³ at 150 K, $Z = 2$. In the structure of **1**, despite the presence of the urea fragment, *Atu* acts a chelating-bridging π,σ -ligand, connecting Cu(I) ions by means of allylic C=C bonds and triazole N donor atoms, into $\{\text{Cu}_2(\text{Atu})_2\}^{2+}$ dimers. The latter are connected by anionic $\{\text{Cu}_2\text{Cl}_4\}^{2-}$ subunits into infinite ladder-like chain. Not less interesting is the fact that molecules of *n*-propanol and water are included in the crystal structure, since both these molecules, through N—H \cdots O hydrogen bonding with the urea fragments of *Atu*, connect neighboring phenyl-urea substituents within the same infinite chain.

1,2,4-Triazole / Copper(I) / π -Complex / Crystal structure

1. Introduction

1,2,4-Triazole derivatives exhibit a large range of pharmacological properties such as antiviral, antifungal, and herbicidal. They are catalase inhibitors and there are numerous drugs based on them in clinical use for the treatment of various diseases [1–4]. Triazole-based molecules are highly suitable to prepare metal complexes, coordination polymers, and spin-crossover compounds [5–7]. Among these, allyl derivatives of 1,2,4-triazoles were found to be excellent precursors for the crystal engineering of organometallic materials, possessing nonlinear optical properties [8]. The presence of allyl groups, attached to the triazole skeleton, enables both bridging and chelating functions for ligands through the formation of strongly directed Cu(I)–(C=C) interactions [8–12]. Additional incorporation of other functional groups to such molecules should not only change their coordination capabilities, but also positively affect the functional properties of the obtained materials. We asked ourselves whether it would be possible to incorporate

urea or thiourea fragments into the ligand structure, while preserving the π -coordination of copper(I) in order to obtain new materials. In the present work we focused on the synthesis and structural characterization of a novel π,σ -coordination compound $[\text{Cu}_4(\text{Atu})_2\text{Cl}_4]\cdot 2\text{H}_2\text{O}\cdot 2\text{C}_3\text{H}_7\text{OH}$ (**1**) with N-phenyl-N'-{3-allylsulfanyl-4-amino-5-phenyl-4*H*-1,2,4-triazol-4-yl}urea (*Atu*).

2. Experimental section

2.1 N-phenyl-N'-{3-allylsulfanyl-4-amino-5-phenyl-4*H*-1,2,4-triazol-4-yl}urea (*Atu*)

4-Amino-5-phenyl-4*H*-1,2,4-triazole-3-thiol ($\text{C}_{18}\text{H}_{17}\text{N}_5\text{OS}$) was obtained from benzohydrazide in several steps (Scheme 1), following a method reported in the literature [13]. 3-Phenyl-5-allylsulfanyl-4*H*-1,2,4-triazol-4-amine was synthesized in one step by stirring 4-amino-5-phenyl-4*H*-1,2,4-triazole-3-thiol with 3-chloroprop-1-ene at 70°C in the presence of KOH in an ethanol solution for 8 h. The target *Atu* was synthesized by the reaction

of 3-phenyl-5-allylsulfanyl-4*H*-1,2,4-triazol-4-amine with phenyl isocyanate.

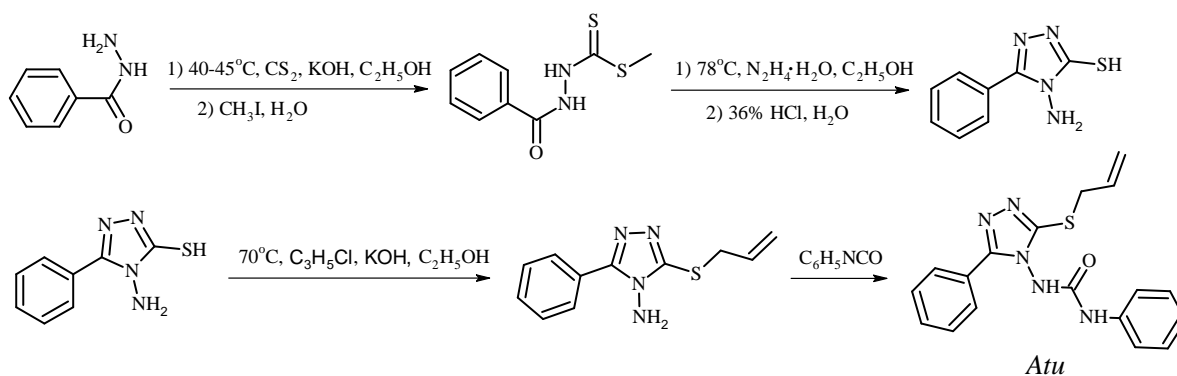
2.2 Preparation of $[\text{Cu}_4(\text{Atu})_2\text{Cl}_4]\cdot 2\text{H}_2\text{O}\cdot 2\text{C}_3\text{H}_7\text{OH}$ (**1**)

Crystals of the complex **1** were obtained under conditions of an alternating-current electrochemical synthesis [14] starting from the solution of *Atu* (0.351 g, 1.0 mmol) and $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.392 g, 2.3 mmol) in 5.0 mL of *n*-propanol. The prepared mixture was placed into a small (5.5 mL) test-tube and copper-wire electrodes were inserted into the cork. By the application of an alternating-current tension (frequency 50 Hz) of 0.7 V for 26 days good-quality brown crystals of **1** appeared on the copper electrodes in a very small amount. M.p. 119–121°C.

2.3 X-ray crystal structure determination

Diffraction data for **1** were collected on an Agilent Gemini A four-circle diffractometer with an Atlas

CCD detector, using $\text{Mo } K_\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The diffraction data were processed with the CrysAlis PRO program [15]. The structure was solved by ShelXT and refined by the least-squares method on F^2 by ShelXL software with the graphical user interface of OLEX² [16–18]. Atomic displacements for non-hydrogen atoms (with the exception of the disordered site Cu2) were refined using an anisotropic model. One of the copper atoms (Cu2) is disordered over two sites with an occupancy ratio of 0.795(6):0.205(6). The three carbon atoms of the *n*-propanol molecule are disordered over two sites with an occupancy ratio of 0.51(5):0.49(5). Water H atoms were derived from difference Fourier maps and refined with relative isotropic displacement parameters. The other hydrogen atoms were placed on geometrically calculated positions and refined as riding atoms with relative isotropic displacement parameters. The crystal parameters, data collection, and refinement details are summarized in Table 1.



Scheme 1 Synthesis of the ligand *Atu*.

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

CCDC number ^a	2163020	<i>F</i> (000)	1280
Empirical formula	$\text{C}_{42}\text{H}_{54}\text{Cl}_4\text{Cu}_4\text{N}_{10}\text{O}_6\text{S}_2$	Color, shape	brown, block
Formula weight, $\text{g}\cdot\text{mol}^{-1}$	1255.03	Theta range for data collection, °	2.5–28.8
Temperature, K	150	Limiting indices	$-21 \leq h \leq 19$, $-18 \leq k \leq 24$, $-10 \leq l \leq 10$
Wavelength, Å	0.71073	Refinement method	Full-matrix least-squares on F^2
Crystal system, space group	monoclinic, $P2_1/c$	Measured reflections	19062
Cell dimensions		Unique reflections	5422
<i>a</i> , Å	16.0745(10)	Reflections with $I > 2\sigma(I)$	3688
<i>b</i> , Å	18.0290(10)	Free parameters	318
<i>c</i> , Å	8.9794(6)	Goodness-of-fit on F^2	1.069
α , °	90.00	<i>R</i> values	$R_1 = 0.0879$, $wR_2 = 0.2360$
β , °	92.262(5)	$\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}}$, $\text{e}\cdot\text{\AA}^{-3}$	1.658/–1.290
γ , °	90.00	Calculated density, $\text{g}\cdot\text{cm}^{-3}$	1.603
<i>V</i> , Å ³	2600.3(3)		
<i>Z</i>	2		
Absorption coeff., mm^{-1}	1.954		

^a CCDC 2163020 contains supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge by filling the corresponding form on <https://www.ccdc.cam.ac.uk/structures/> page of CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

3. Results and discussion

The π -complex $[\text{Cu}_4^{\text{I}}(\text{Atu})_2\text{Cl}_4]\cdot 2\text{H}_2\text{O}\cdot 2\text{C}_3\text{H}_7\text{OH}$ (**1**) crystallizes in the centrosymmetric space group $P2_1/c$, with one *Atu* molecule and two copper(I) ions in the asymmetric unit. The structure of **1** may be considered as consisting of two subunits: the cationic organometallic part and an anionic inorganic fragment (Fig 1, Table 2). As in the copper(I) π -complexes with 3-allylsulfanyl-4-allyl-5-phenyl-4*H*-1,2,4-triazole and allyl derivatives of 1,3,4-thiadiazole studied earlier [8,11], the organometallic subunit in **1** is represented by a $\{\text{Cu}_2^{\text{I}}(\text{Atu})_2\}^{2+}$ dimer, which is formed due to the chelating-bridging coordination behavior of the organic ligand. Consequently, due to the formation of the stable dimeric moiety containing a six-membered ring $\{\text{Cu}_2\text{N}_4\}$ (containing two pairs of $[-\text{N}-\text{N}-]$ triazole fragments), the urea fragment

(-NHCONH-) of the ligand is not involved in the metal coordination. For comparison, 1,3-diallyl urea in the polymeric structure of copper(I) halide π,σ -coordination compounds fully proves its coordination ability being attached to the copper(I) ions through both allylic groups and the O atom of urea [19].

In the complex **1** the Cu1 atom adopts an approximately trigonal pyramidal coordination environment (the corresponding four-coordinate geometry index τ_4 [20] is 0.85). The basal plane of the copper coordination arrangement consists of the η^2 -allyl group and two triazole N atoms; the axial site is occupied by a μ_2 -Cl ion that is part of anionic inorganic fragments. The C=C bond of the η^2 -allyl group in **1** is elongated to 1.367(11) Å in comparison to the analogous bond (1.31-1.32 Å) in the uncoordinated allyl group [8,11].

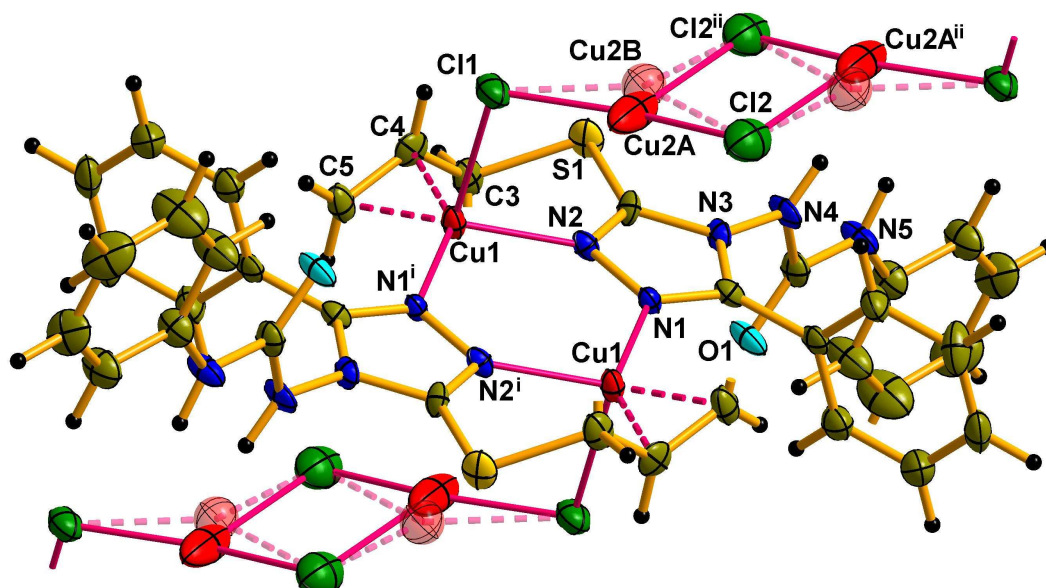


Fig. 1 Centrosymmetric fragment in the crystal structure of **1**. Displacement ellipsoids are drawn at the 50% probability level. One of the two disordered positions of the site Cu(2), *i.e.* with the lower site-occupancy factor, is shown in semi-transparent mode. Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x, -y+1, -z+2$.

Table 2 Selected bond lengths (in Å) and angles (in deg) in the structure of **1**.

Bond	Value	Angle	Value
Cu1—Cl1	2.544(2)	Cl1—Cu1— <i>m</i>	109.6(3)
Cu1—N2	2.022(6)	N2—Cu1— <i>m</i>	114.0(3)
Cu1—N1 ⁱ [a]	1.976(5)	N1 ⁱ —Cu1— <i>m</i>	126.8(3)
Cu1— <i>m</i> [b]	1.952(7)	Cl1—Cu1—N2	94.57(17)
C4—C5	1.367(11)	C3—C4—C5	121.9(7)
Cu2A—Cl1	2.130(3)	Cu1—Cl1—Cu2A	105.82(9)
Cu2A—Cl2	2.089(3)	Cl1—Cu2A—Cl2	160.4(2)
Cu2A—Cl2 ⁱⁱ [a]	3.031(3)	Cl1—Cu2A—Cl2 ⁱⁱ	104.9(2)
Cu2B—Cl1	2.217(7)	Cl1—Cu2B—Cl2	114.7(5)
Cu2B—Cl2	2.710(9)	Cl1—Cu2B—Cl2 ⁱⁱ	142.4(5)
Cu2B—Cl2 ⁱⁱ	2.144(8)	Cu2A—Cl2—Cu2A ⁱⁱ	86.1(2)

[a] symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x, -y+1, -z+2$; [b] *m* = mid-point of the C=C bond

The Cu2A atom of the anionic inorganic fragments in **1** tries to achieve a linear coordination environment (Cl1—Cu2A—Cl2, $160.4(2)^\circ$), but the coordination of one more Cl2ⁱⁱ at 3.031(3) Å (distance significantly shorter than the corresponding sum of Van der Waals radii [21]) changes the Cu2A environment to T-shaped. The Cu2B atom, with a site-occupancy factor of 0.205(6), has more clearly a trigonal coordination environment (Cl1—Cu2B—Cl2ⁱⁱ, $142.4(5)^\circ$). Thus, in the structure of **1**, the inorganic part is represented by an almost flat and centrosymmetric {Cu₂Cl₄} subunit. Being apically bonded to two copper(I) ions through bridging Cl1 ions, the {Cu₂(Atu)₂}²⁺ dimers are connected through {Cu₂Cl₄}²⁻ bridges into infinite ladder-like chains (Fig. 2). The distance between steps within the chain is 6.223(3) Å. It is interesting to note that the earlier studied heterometallic Cu^I/Ag^I complex with

3-allylsulfanyl-4-allyl-5-phenyl-4*H*-1,2,4-triazole is constructed in the same manner [8] as complex **1** considering the Cu2B part.

The N-phenyl-urea substituent of *Atu* in **1** is perpendicular to the plane of the triazole ring (the angle between the planes is $89.5(3)^\circ$) and its oxygen atom O1 is oriented toward the neighboring triazole ring. Thus, the O1 atom is involved in a weak intramolecular $n \rightarrow \pi^*$ _{Tr} interaction with an O1...N3 bond distance of 2.653(9) Å. The above O—N distance is shorter than the sum of the corresponding Van der Waals radii of O and N (3.07 Å by Bondi; 3.16 Å by Alvarez [21]). It is also interesting to note that molecules of *n*-propanol and water are included in the crystal structure of **1**. Both these molecules connect neighboring phenyl-urea substituents within the same infinite chain through N—H...O hydrogen bonding (Fig. 3, Table 3) with urea fragments of *Atu*.

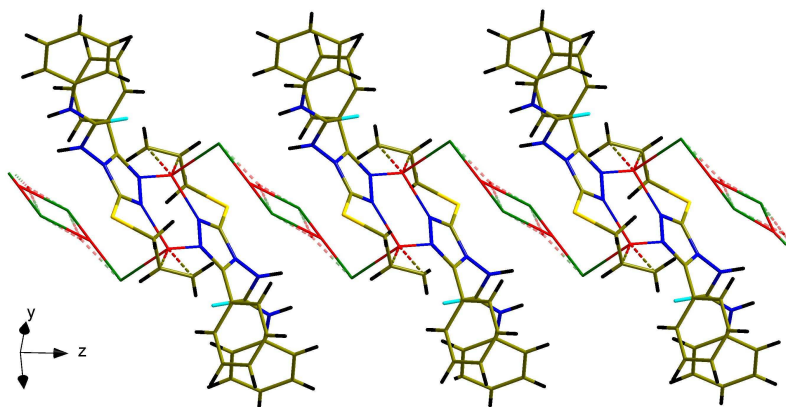


Fig. 2 Infinite ladder-like coordination polymer in **1**.

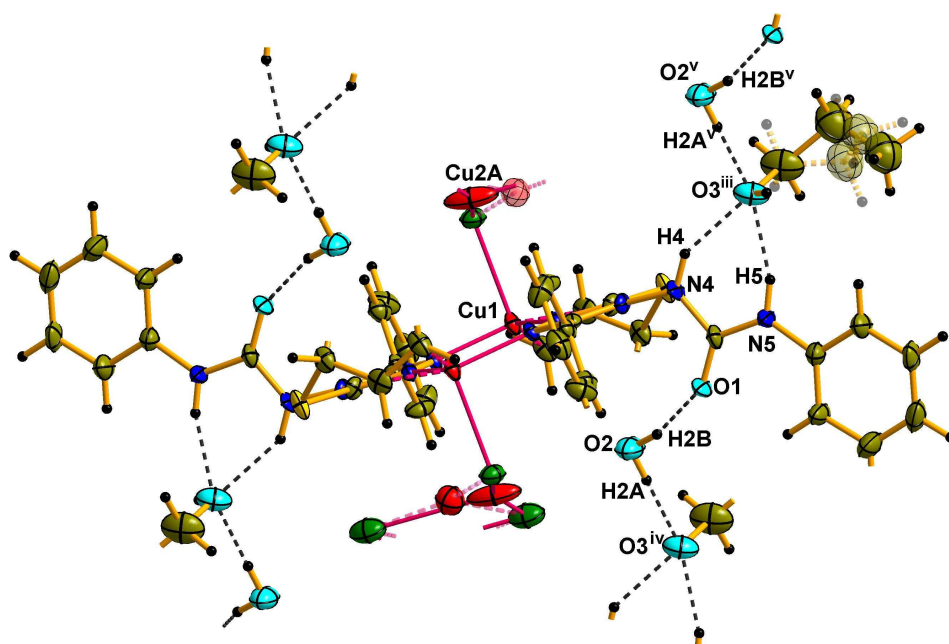


Fig. 3 Hydrogen bonds in the structure of **1**. The hydrogen bonds are shown as dashed lines. Symmetry codes: (iii) $x, -y+1.5, z+0.5$; (iv) $x, -y+1.5, z-0.5$; (v) $x, y, z+1$.

Table 3 Selected hydrogen bonds (\AA , deg) in **1**.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N4—H4 \cdots O3 ⁱⁱⁱ [a]	0.88	2.11	2.891(9)	147
N5—H5 \cdots O3 ⁱⁱⁱ	0.88	1.99	2.831(9)	160
O2—H2A \cdots O3 ^{iv}	0.873(6)	1.838(7)	2.712(9)	179.6(5)
O2—H2B \cdots O1	0.873(6)	1.962(5)	2.815(8)	165.3(4)

[a] symmetry codes: (iii) $x, -y+1.5, z+0.5$; (iv) $x, -y+1.5, z-0.5$

4. Conclusion

Despite the presence of a urea fragment in the *Atu* molecule, the coordination mode of *Atu* towards copper(I) halide was found to be more similar to the previously studied allyl derivatives of 1,2,4-triazole, than to allyl derivatives of urea. The reason is the formation of stable $\{\text{Cu}^I(\text{Atu})_2\}^{2+}$ dimers (“building blocks”), which are formed due to the chelating-bridging π,σ -coordination behavior of the organic ligand by means of allylic C=C bonds and triazole N donor atoms. It is most likely that the large size of the N-phenyl-urea substituent (oriented perpendicular to the plane of the triazole ring) contributes to the formation of almost flat and centrosymmetric anionic $\{\text{Cu}_2\text{Cl}_4\}^{2-}$ subunits, which, in turn, combine $\{\text{Cu}_2(\text{Atu})_2\}^{2+}$ dimers into infinite ladder-like chains.

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