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A new copper(I) chloride π,σ-complex based on 3,4-diphenyl-5-allylsulfanyl-4*H*-1,2,4-triazole: synthesis and structure characterization

Yurii SLYVKA[1]*

[1] *Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla i Mefodiya St. 6, 79005 Lviv, Ukraine*
* *Corresponding author. Tel.: +380-32-2600388; e-mail: yurii.slyvka@lnu.edu.ua*

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Using the alternating current electrochemical technique, the new π,σ-complex [Cu$_3$(*Dphatr*)$_2$Cl$_3$]·2H$_2$O (1) (*Dphatr* = 3,4-diphenyl-5-allylsulfanyl-4*H*-1,2,4-triazole) was synthesized and subsequently characterized by X-ray single-crystal diffraction. Crystals of 1 are monoclinic, space group *C*2, *a* = 24.683(6), *b* = 6.558(3), *c* = 12.153(4) Å, *β* = 103.59(3)°, *V* = 1912.1(12) Å^3 at 100 K, *Z* = 2. The structure contains two crystallographically independent Cu(I) atoms, one of which forms acentric organometallic {Cu$_2$(*Dphatr*)$_2$}$^{2+}$ dimers. The other one is bound to two Cl atoms of a triangular {CuCl$_3$} fragment that is disordered over two equivalent positions, forming half-occupied {Cu$_2$Cl$_6$} units.

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

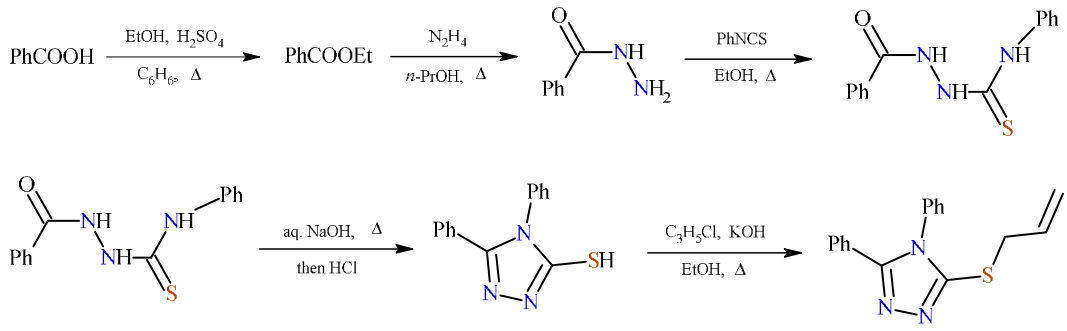
1. Introduction

1,2,4-Triazoles are part of a family of five-membered heterocycles that possess a huge range of applications in agriculture, pharmacy and material science [1-4]. Triazole-based molecules are very useful multitopic ligands in constructing metal complexes, coordination polymers and spin-crossover compounds [5-7]. The appearance of an olefin C=C bond in the ligand structure enables its specific coordination ability toward some 3*d*-metal ions and enhances the unusual complex architecture through the formation of both strongly directed *Me*–(C=C) interaction and metal bonds with triazole donor atoms [8-12]. In turn, the 1,2,4-triazole core defines some specific metal-ligand constructive modes, and additional incorporation of other functional groups to such a nuclear should not only change the coordination capabilities, but also positively affect the functional properties of the obtained materials. Recently, 3-allylsulfanyl-4-allyl-5-phenyl-4*H*-1,2,4-triazole (*Aat*) was found to be an excellent precursor for the crystal engineering of organometallic materials, possessing magnetic and nonlinear optical properties [8]. Despite the presence of a urea fragment in N-phenyl-N'-{3-allylsulfanyl-4-amino-5-phenyl-4*H*-1,2,4-triazol-4-yl}urea (*Patu*), this molecule revealed a more similar constructive mode regarding the formation of Cu(I) complexes, than to allyl derivative of urea [13,14]. In order to establish the coordination ability of 3,4-diphenyl-5-allylsulfanyl-4*H*-1,2,4-triazole (*Dphatr*) towards Cu(I), in the present work we focused on the synthesis and structural characterization of a new π,σ-complex, [Cu$_3$(*Dphatr*)$_2$Cl$_3$]·2H$_2$O (**1**).

2. Experimental Section

2.1 3,4-Diphenyl-5-allylsulfanyl-4*H*-1,2,4-triazole (*Dphatr*)

3,4-Diphenyl-5-allylsulfanyl-4*H*-1,2,4-triazole (*Dphatr*, C$_{17}$H$_{15}$N$_3$S) was obtained in several steps (Scheme 1), by a method similar to the method reported for 3-phenyl-4-allyl-5-allylsulfanyl-4*H*-1,2,4-triazole [8]. M.p. 112-113°C. Ligand (*Dphatr*): ^{1}H NMR (DMSO, 500 MHz) δ 7.53 (d, *J* = 2.6 Hz, 2H), 7.41-7.28 (m, 8H), 5.98-5.80 (m, 1H), 5.25 (d, *J* = 16.9 Hz, 1H), 5.10 (d, *J* = 9.8 Hz, 1H), 3.81 (d, *J* = 6.8 Hz, 2H). ^{13}C NMR (DMSO, 125 MHz) δ$_C$ 154.4, 151.2, 133.9, 133.2, 130.0, 129.9, 129.7, 128.5, 127.9, 127.7, 127.0, 34.9.



Scheme 1 Synthesis of the ligand *Dphatr*.

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

CCDC number [a]	2380741		
Empirical formula	$C_{34}H_{30}Cl_3Cu_3N_6S_2O_2$	$F(000)$	932
Formula weight, g/mol	919.76	Color, shape	yellow, block
Temperature, K	100	Theta range for data collection, °	1.7-30.7
Wavelength, Å	0.71073	Limiting indices	$-25 \le h \le 35$, $-8 \le k \le 9$, $-13 \le l \le 16$
Crystal system, sp. gr.	monoclinic, *C*2	Refinement method	full-matrix least-squares on F^2
Unit cell dimensions			
a, Å	24.683(6)	Measured reflections	5031
b, Å	6.558(3)	Unique reflections	4342
c, Å	12.153(4)	Reflections with $I > 2\sigma(I)$	1976
α, °	90.00	Free parameters	238
β, °	103.59(3)	Goodness-of-fit on F^2	1.021
γ, °	90.00	*R* values	$R_1 = 0.0994$, $wR_2 = 0.2496$
V, Å^3	1912.1(12)	$\Delta\rho_{max}/\Delta\rho_{min}$, e·Å^{-3}	1.355 and -0.869
Z	2		
Absorption coeff., mm^{-1}	2.012	Calculated density, g/cm^3	1.597

[a] CCDC 2380741 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.

2.2 Preparation of [Cu$_3$(*Dphatr*)$_2$Cl$_3$]·2H$_2$O (1)

Crystals of the complex **1** were obtained under the conditions of an alternating-current electrochemical synthesis [14], starting from a solution of *Dphatr* (1.50 mmol, 0.440 g) and $CuCl_2 \cdot 2H_2O$ (1.20 mmol, 0.205 g) in 5.0 mL of acetonitrile. The prepared mixture was placed into a small 5.5 mL test-tube and then copper-wire electrodes in cork were inserted. After the application of an alternating-current tension (frequency 50 Hz) of 0.75 V for 4 days good-quality yellow crystals of **1** appeared on the copper electrodes in a very small amount.

2.3 X-ray crystal structure determination

Diffraction data for compound **1** were collected on an Agilent Xcalibur four-circle diffractometer using Mo K_α radiation ($\lambda = 0.71073$ Å). The diffraction data collected for **1** 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 OLEX^2 [16-18]. Atomic displacements for non-hydrogen atoms (with the exception of the disordered water molecules) were refined using an anisotropic model. One of the copper atom (Cu2) and the corresponding chlorine atom (Cl2) are disordered over two sites with an occupancy ratio of 0.5 : 0.5. The water molecules are disordered over three positions with the occupancy ratio 0.25 : 0.30 : 0.45. The hydrogen atoms were placed on geometrically calculated positions and refined as riding atoms with relative isotropic displacement parameters. The crystallographic parameters, and details of the data collection and refinement are summarized in Table 1.

3. Results and discussion

The π,σ-complex $[Cu_3(Dphatr)_2Cl_3]\cdot 2H_2O$ (**1**) crystallizes in the acentric space group *C*2, with one *Dphatr* molecule and two copper(I) atoms in the asymmetric unit. The organometallic part in the crystal structure is represented by a $\{Cu_2(Dphatr)_2\}^{2+}$ dimer, which is formed thanks to the chelating-bridging coordination behavior of the *Dphatr* ligand (Figs. 1,2, Table 2). Cu1 adopts a close to trigonal pyramidal coordination environment (2N, (C=C) + Cl1), the basal plane of which consists of two N atoms of neighboring triazole molecules and one η^2-allyl group (the corresponding four-coordinate geometry index τ_4 [19] for Cu1 is 0.82). The axial position of the Cu1 polyhedron is occupied by a μ_2-Cl1 atom that is part of a triangular $\{CuCl_3\}$ inorganic fragment. The distance from the Cu2 atom to the plane of the chlorine atom triangle is 0.14 Å. Cu1—Cl1 bond length of 2.688(6) Å is comparable with the bond distance between π-bonded Cu(I) and apically located Cl atoms in the structures of related complexes with allyl derivatives of azoles. In contrast to all previously studied Cu(I) π-complexes with 3-allylsulfanyl-1,2,4-triazoles, which are constructed from centrosymmetric $\{Cu_2(L)_2\}^{2+}$ dimers [8,13], in complex **1** the dimer structure is influenced by the appearance of the 2-fold axis that is orthogonally crossing the hexagonal $\{Cu_2N_4\}$ plane of the dimer. This causes disordering of the Cu2 atom into two equivalent positions and appearance of a related $\{CuCl_3\}$ triangle sharing a common edge. Thus, two Cl1 atoms of the triangular Cu2 fragment bind two π-coordinated Cu1 atoms forming an island coordination fragment $\{Cu_3(Dphatr)_2Cl_3\}$ with a half-occupied Cu_2Cl_6 inorganic unit. The presence of such a fragment is unusual for copper(I) π-complexes with allylazoles and opens new routes for crystal engineering of novel functional materials.

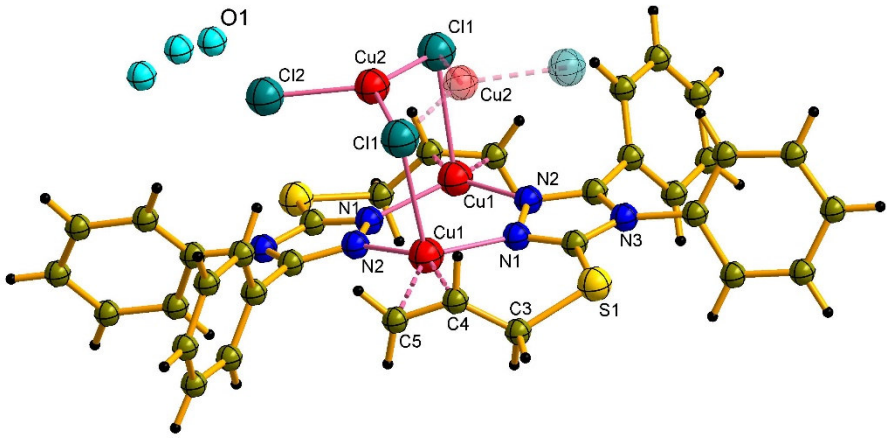


Fig. 1 Acentric fragment in the crystal structure of **1**.

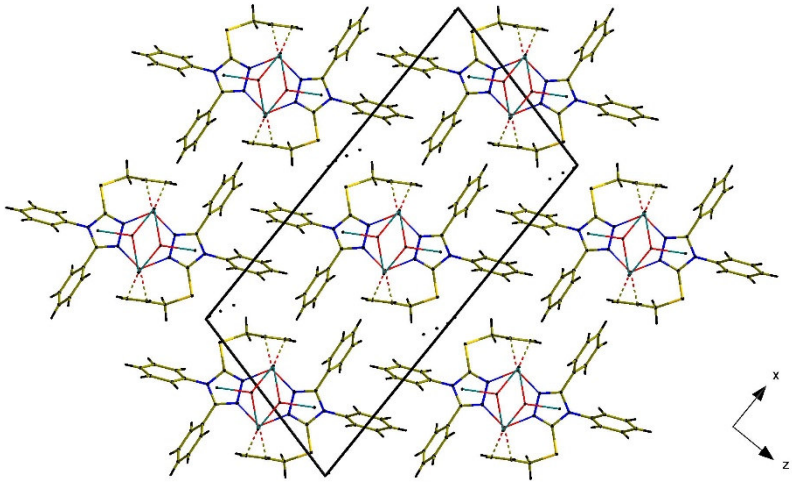


Fig. 2 Projection of the crystal structure of **1** onto the *xz* plane.

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

Bond	Value	Angle	Value
Cu1—Cl1	2.688(6)	Cl1—Cu1—*m*	95.4(10)
Cu1—N1	1.977(9)	N1—Cu1—*m*	115.3(4)
Cu1—N2^{i} [a]	1.977(10)	N2^{i}—Cu1—*m*	128.7(4)
Cu1—*m* [b]	1.943(11)	N1—Cu1—N2^{i}	111.7(4)
Cu2—Cl1	2.154(7)	Cl1—Cu2—Cl2	121.1(4)
Cu2—Cl1^{i}	2.310(9)	Cl1—Cu2—Cl1^{i}	129.6(3)
Cu2—Cl2	2.158(10)	Cu1—Cl1—Cu2	91.5(2)

[a] Symmetry codes: (*i*) –*x*+1, –*y*, –*z*+1; [b] *m* – mid-point of C4=C5 bond

4. Conclusion

To summarize, we have presented the synthesis and structure characterization of the novel π,σ-complex $[Cu_3(Dphatr)_2Cl_3]\cdot 2H_2O$ (**1**). Crystals of the compound were obtained by the alternating-current electrochemical method starting from an acetonitrile solution of *Dphatr* and copper(II) chloride using copper electrodes. The structure is constructed from acentric dimeric moieties $\{Cu_2(Dphatr)_2\}^{2+}$, which are formed by two η^2-π-coordinated copper(I) atoms and two pairs of N atoms of triazole cycles. The creation of triangular $\{CuCl_3\}$ fragments, which form half-occupied Cu_2Cl_6 units, and are bound to two π-coordinated copper(I) atoms of the same dimer, prevents the appearance of infinite chains, and gives new insight into the crystal engineering of copper(I) triazole complexes.

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