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*Yu.I. Slyvka, N.T. Pokhodylo, M.G. Mys'kiv***COPPER(I) π -COMPLEXES WITH ALLYL SUBSTITUTED 1-ARYL-1H-TETRAZOLE-5-THIOLS: SYNTHESIS AND THEIR STRUCTURAL FEATURES****Ivan Franko National University of Lviv, Lviv, Ukraine**

Three new copper(I) π,σ -complexes with 1-(2-fluorophenyl)-((2-F-Ph)TSA) and 1-(2-ethoxyphenyl)-((2-EtO-Ph)TSA) 5-allylsulfanyl-1H-tetrazoles were synthesized in a single crystal form and structurally characterized by X-ray diffraction method. Crystals of complexes [Cu{(2-F-Ph)TSA}(NH₂SO₃)] (I), [Cu₄{(2-F-Ph)TSA}₂Cl₄] (II) and [Cu₂{(2-EtO-Ph)TSA}₂(H₂O)₂](NO₃)₂ (III) were obtained under conditions of the alternating-current electrochemical synthesis starting from the alcohol solution of the appropriate organic ligand and copper(II) salt. [Cu{(2-F-Ph)TSA}(NH₂SO₃)] (I) crystallizes in acentric space group P2₁2₁2₁ (a=7.545(3) Å, b=12.890(4) Å, c=14.249(4) Å, V=1385.8(8) Å³, Z=4) and characterizes by a formation of polymeric chains with bridging sulfamate anions. π -Complexes [Cu₄{(2-F-Ph)TSA}₂Cl₄] (II) and [Cu₂{(2-EtO-Ph)TSA}₂(H₂O)₂](NO₃)₂ (III) crystallize in the centrosymmetric space group P-1 (II: a=7.837(3) Å, b=8.695(3) Å, c=11.429(4) Å, α =109.61(3)^o, β =93.82(3)^o, γ =105.08(3)^o, V=698.1(5) Å³, Z=1; III: a=8.094(3) Å, b=10.243(4) Å, c=11.221(4) Å, α =113.44(3)^o, β =97.11(3)^o, γ =106.79(3)^o, V=786.4(5) Å³, Z=1) but they show a significant difference in the fragment organization. Compound III is built of centrosymmetric [Cu₂{(2-EtO-Ph)TSA}₂(H₂O)₂]²⁺ dimers in which (2-EtO-Ph)TSA acts as a tridentate chelate-bridging π,σ -ligand. Molecule (2-F-Ph)TSA in II causes a formation of «stepped cubane» tetramer Cu₄Cl₄. A brief review of all known Cu(I) π -compounds with allyl substituted 1-aryl-1H-tetrazole-5-thiols is given.

Keywords: tetrazole; copper(I); π -complex; crystal structure; *ac*-electrochemical technique.**DOI:** 10.32434/0321-4095-2019-123-2-30-38**Introduction**

Tetrazoles are well known class of heterocyclic compounds that have found applications in the agricultural sector (plant growth regulators and pesticides), pharmaceutical chemistry (showing antibacterial, anti-tuberculosis, anticancer, anticonvulsant activity, etc.) and also have used as corrosion inhibitors, luminophores and effective precursors for transition metal complex preparation [1–5]. Many tetrazole derivatives serve as suitable ligands for a design and self-organization of molecules through the selective attachment to the metal ions by one, two, three or four nitrogen atoms of tetrazole ring and other donor atoms of substituents. An appearance of the olefin C=C bond in a skeleton of the above substituents may serve as actual key for the selected coordination of transition metal ions due to metal–olefin π -bonding [6]. As it was shown recently, allyl derivatives of heterocyclic compounds, which unite conformation-flexible allyl group and

rigid heterocyclic cores, are suitable for the preparation of π -compounds with unknown (or less-stable) in a free state copper(I) salts. For instance, the first examples of CuHSO₄ π -complex and the direct Cu(I)⋯F(SiF₆²⁻) interaction have been observed in copper π -compounds with 1-allyl-benzotriazole and with allyl-substituted 1,3,4-thiadiazoles [7,8]. Moreover, recently an appearance of high second and third order NLO susceptibilities was observed for copper(I) π -complexes with 3-allyl-2-(allylimino)-1,3-thiazolidin-4-one, 1-allyloxy-benzotriazole and 5-(allylthio)-1-(3,5-dimethylphenyl)-1H-tetrazole ligands [9–12]. Despite the huge advances in tetrazole chemistry and the fact that tetrazole molecules are well established ligands for 3d-metal complexation, the metal–olefine π -coordination in the presence of tetrazole nucleus is studied enough poorly and basically represented (in Cambridge Crystallographic Database [13]) by a number of Mo, Fe, Rh, Ir and Ru cyclopentadienyl

π -compounds. In order to examine coordinating behavior of S-allyl derivatives of different 1-(aryl)-1H-tetrazoles-5-thioles regarding to copper(I), this article describes synthesis and structural characterization of three novel π -complexes [Cu{(2-F-Ph)TSA}(NH₂SO₃)] (I), [Cu₄{(2-F-Ph)TSA}₂Cl₄] (II) and [Cu₂{(2-EtO-Ph)TSA}₂(H₂O)₂](NO₃)₂ (III) (where (2-F-Ph)TSA and (2-EtO-Ph)TSA are 1-(2-fluoro-phenyl)- and 1-(2-ethoxyphenyl)-5-allylsulfanyl-1H-tetrazoles, respectively), and gives a brief review of previously known π -compounds of the discussed type.

Experimental

Synthesis of the organic ligands

Ligands (2-F-Ph)TSA (1-(2-fluorophenyl)-5-allylsulfanyl-1H-tetrazole) and (2-EtO-Ph)TSA (1-(2-ethoxyphenyl)-5-allylsulfanyl-1H-tetrazole) were obtained in several steps in accordance with the method described in our unpublished work as shown in Scheme.

Synthesis of copper(I) π -complexes

Crystals of complexes I–III were obtained under conditions of the alternating-current electrochemical synthesis starting from the alcohol solution of the appropriate organic ligand and copper(II) salt.

Preparation of [Cu{(2-F-Ph)TSA}(NH₂SO₃)] (I) π -complex

To 5.0 mL of a saturated water-alcohol (1.0 mL of water and 4.0 mL of methanol) solution of Cu(NH₂SO₃)₂ 0.201 g (0.85 mmol) of (2-F-Ph)TSA was added. The mixture was carefully stirred. The resulting mixture was placed into a small 5.6 mL test-tube and then copper-wire electrodes in cork were inserted. By the application of alternating-current tension (frequency 50 Hz) of 0.6 V for 4 days, good quality colorless crystals of I appeared on copper electrodes, from which they were detached

by mechanical removal. The yield was about 45%.

Preparation of [Cu₄{(2-F-Ph)TSA}₂Cl₄] (II) π -complex

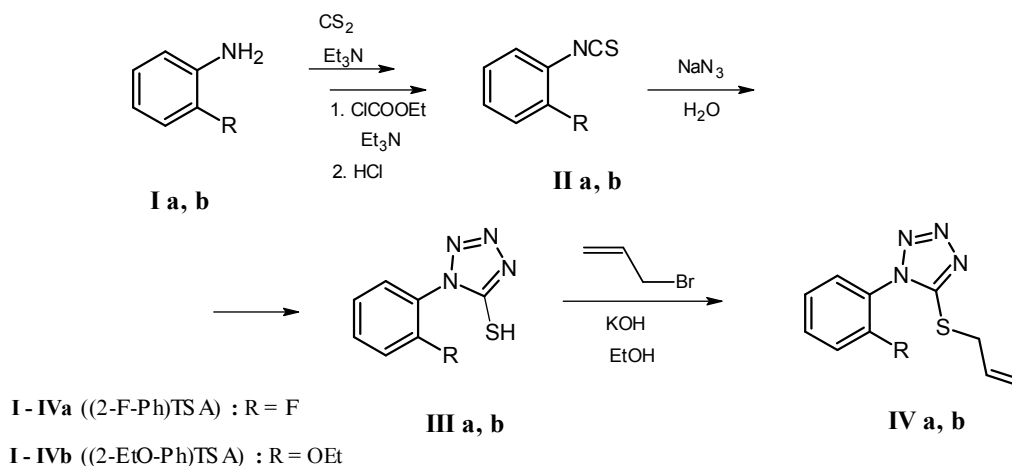
To 2.5 mL of alcohol solution (1.3 mL of ethanol and 1.2 mL of n-propanol) of CuCl₂·2H₂O (1.12 mmol, 0.191 g) 2.5 mL of n-propanol solution of (2-F-Ph)TSA (0.85 mmol, 0.201 g) was added. By the application of alternating-current tension (frequency 50 Hz) of 0.6 V for 3 days good quality colorless crystals of II appeared on copper electrodes, from which they were detached by mechanical removal. The yield was about 3%.

Preparation of [Cu₂{(2-EtO-Ph)TSA}₂(H₂O)₂](NO₃)₂ (III) π -complex

To 2.5 mL of ethanol solution of (2-EtO-Ph)TSA (0.80 mmol, 0.210 g) 2.5 mL of ethanol solution of Cu(NO₃)₂·3H₂O (0.90 mmol, 0.217 g) was added. The obtained mixture was carefully stirred and the resulting solution was subjected to alternating-current tension (frequency 50 Hz) of 0.6 V for 2 days. Good quality colorless crystals of III appeared on copper electrodes, from which they were detached by mechanical removal. The yield was about 30%.

Single crystal X-ray diffraction studies

Diffraction data for I and III crystals were collected on a Kuma KM-4-CCD diffractometer with MoK α radiation ($\lambda=0.71073$ Å). Diffraction data for II were collected on an Agilent Xcalibur four-circle diffractometer with MoK α radiation ($\lambda=0.71073$ Å) and a Ruby CCD detector. The collected diffraction data were processed with the CrysAlis PRO program. The structures were solved by ShelXT program and refined by least squares method on F² by ShelXL program with the following graphical user interface of OLEX² [14]. Atomic displacements for non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms (except N-bonded H atoms in I) were placed in ideal positions and refined as



Scheme. Synthesis of the tetrazole ligands

Table 1

Selected crystal data and structure refinement parameters of I–III

Characteristics	I	II	III
CCDC number ^a	1886871	1886872	1886873
Empirical formula	C ₁₀ H ₁₁ CuFN ₅ O ₃ S ₂	C ₂₀ H ₁₈ Cl ₄ Cu ₄ F ₂ N ₈ S ₂	C ₂₄ H ₃₂ Cu ₂ N ₁₀ O ₁₀ S ₂
Formula weight, g mol ⁻¹	395.90	868.50	811.79
Temperature, K	100(2)	120(2)	100(2)
Wavelength, Å	0.71073	0.71073	0.71073
Crystal system, space group	orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁ (Flack par. <i>x</i> = 0.04(2))	triclinic, <i>P</i> -1	triclinic, <i>P</i> -1
Unit cell dimensions:			
<i>a</i> , Å	7.545(3)	7.837(3)	8.094(3)
<i>b</i> , Å	12.890(4)	8.695(3)	10.243(4)
<i>c</i> , Å	14.249(4)	11.429(4)	11.221(4)
α , °	90	109.61(3)	113.44(3)
β , °	90	93.82(3)	97.11(3)
γ , °	90	105.08(3)	106.79(3)
<i>V</i> , Å ³	1385.8(8)	698.1(5)	786.4(5)
<i>Z</i>	4	1	1
Calculated density, g cm ⁻³	1.898	2.066	1.714
Absorption coeff., mm ⁻¹	1.909	3.580	1.557
<i>F</i> (000)	800	428	416
Crystal size, mm	0.05×0.06×0.17	0.08×0.10×0.18	0.17×0.23×0.35
Color	Colorless	Colorless	Colorless
Theta range for data collection, deg	2.1–28.8	3.1–36.8	2.1–28.9
Measured reflections	5363	7224	24066
Used in refinement	3065	4437	3905
Free parameters	207	181	219
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.0519, 0.1099, 1.073	0.0644, 0.1709, 1.055	0.0243, 0.0574, 1.048

Note – ^a CCDC 1886871, 1886872 and 1886873 contain 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).

riding atoms with relative isotropic displacement parameters. The crystallographic parameters and summaries of data collection for I–III are presented in Table 1.

Results and discussion

π -Complex [Cu{(2-F-Ph)TSA}(NH₂SO₃)] (I) crystallizes in the orthorhombic acentric space group *P*2₁2₁2₁, with one copper(I) ion, one NH₂SO₃⁻ ion and one {(2-F-Ph)TSA} molecule in the asymmetric unit. The crystal structure of I demonstrates the second example so far of any metal sulfamate coordination compound with tetrazole ligands (Fig. 1). Similarly to earlier studied [Cu{(3-Me, 5-Me-Ph)TSA}(NH₂SO₃)] (IV) π -complex with 3,5-dimethylphenyl substituent [11], Cu⁺ ion in structure I possesses trigonal pyramidal environment ($\tau_4=0.77$, τ_4 is the four-coordinated geometry index) arranged by N4 atom of the tetrazole core, a C=C bond from S-allyl group of the same ligand molecule and O

and N atoms of NH₂SO₃⁻ anions (Fig. 1, a, Table 2). The anion is coordinated to the two neighboring metal centers in the bridged mode, occupying a basal plane (through N) and an apical (through O) position of the two copper(I) trigonal pyramids. Thus, anionic NH₂SO₃⁻ linkers connect Cu{(2-F-Ph)TSA}⁺ fragments into infinite chain along [100] direction (Fig. 1, b). Two hydrogen atoms of the anion also participate in N–H...O hydrogen bonding with neighbouring anions and it provides a stabilization of this organometallic chain (Table 3).

Allylic C1=C2 bond is slightly elongated to 1.369(10) Å (due to back-donation from an occupied 3d metal orbital to a low-lying empty π^* orbital of the olefin) in contrast to the values for free ethylene: 1.338(1) Å (gas phase), 1.3142(3) Å (at 85 K). An efficiency of Cu(I)–(C=C) interaction in I is also confirmed by rather short Cu–m (where m is a middle point of C=C bond) distance of 1.914(6) Å

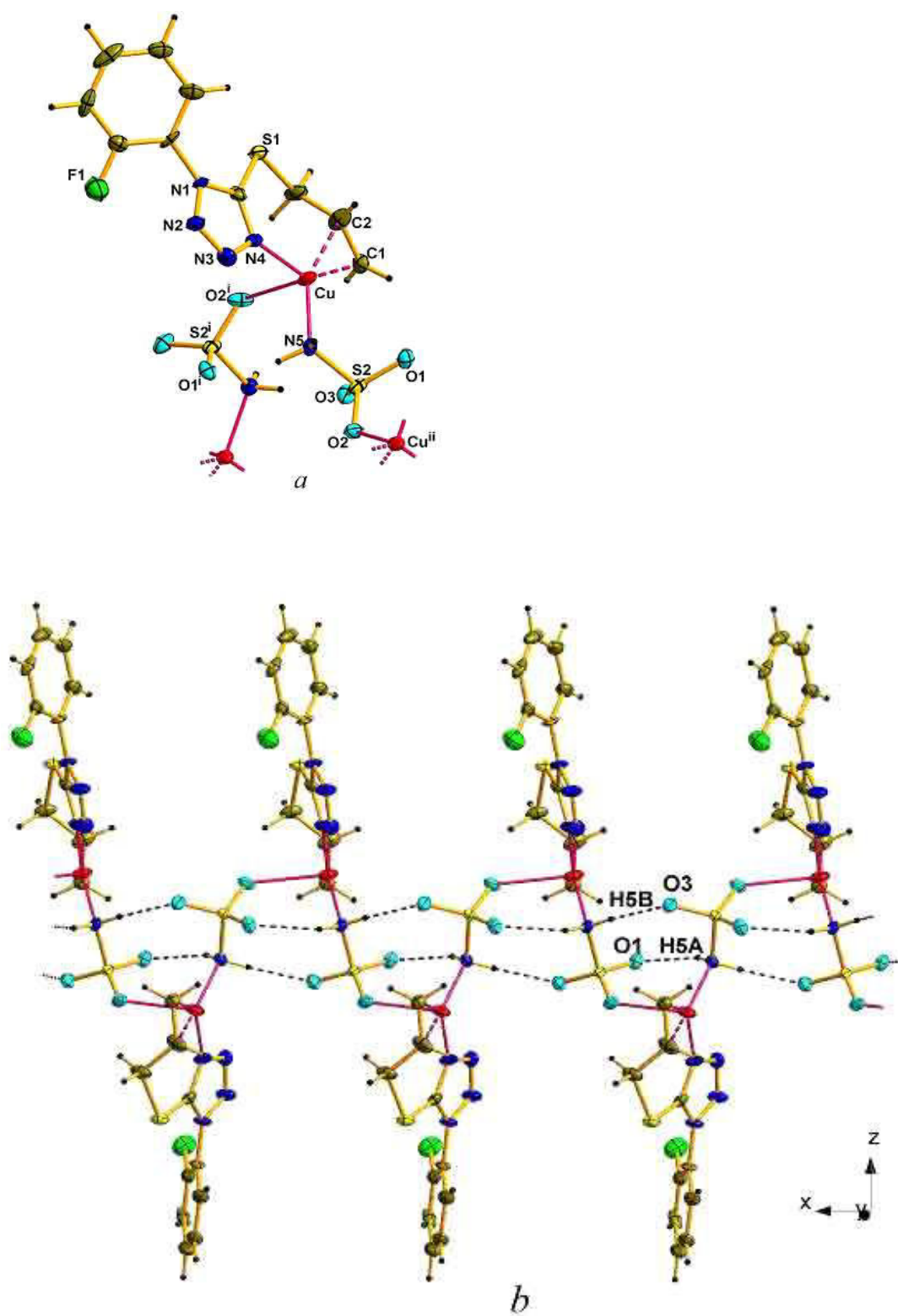


Fig. 1. Coordination environment of Cu(I) (a) and the infinite chain fragment along with the depicted hydrogen bonds (b) of crystal structure I. Symmetry codes: (i) $0.5+x, 0.5-y, -z$; (ii) $-0.5+x, 0.5-y, -z$

and large C–Cu–C angle. The fact that atom Cu(I) deviates from a base of the trigonal pyramid all-in-all by $\Delta=0.105(5)$ Å (angle value between C=C bond and polyhedron base plane makes $\varphi=12.3(3)^\circ$ also confirms this conclusion.

Table 2
Selected bond distances and angles in structure I

Bond	d, Å	Angle	ω , deg
Cu–N4	1.956(5)	C1–Cu–C2	39.4(3)
Cu–N5	1.997(6)	m–Cu–O2 ⁱ	94.2(3)
Cu–O2 ^{i a}	2.482(6)	m–Cu–N4	116.2(3)
Cu–m ^b	1.914(6)	m–Cu–N5	135.1(3)
C1–C2	1.369(10)	N5–Cu–O2 ⁱ	95.2(3)

Note – ^a Symmetry code: (i) 0.5+x, 0.5–y, –z. ^b m is a midpoint of C1–C2 double bond.

The structure of $[\text{Cu}_4\{(2\text{-F-Ph})\text{TSA}\}_2\text{Cl}_4]$ (II) is organized in a quite another mode. Complex II crystallizes in the centrosymmetric space group P-1, with four Cu(I) atoms and two (2-F-Ph)TSA molecules in the asymmetric unit. Molecule (2-F-Ph)TSA plays a role of chelate-bridging π,σ -ligand and is bound to two crystallographically different copper(I)

atoms (Cu1 and Cu2) through two N atoms of tetrazole core and a C=C bond of S-allyl group (Fig. 2, Table 4). Coordination environment of Cu1 ($\tau_4=0.79$) includes N4 atom, allylic C=C bond of (2-F-Ph)TSA ligand and two bridging Cl atoms. The coordinated to the metal C1=C2 bond is also elongated to 1.381(8) Å ($\Delta=0.417(5)$ Å, $\varphi=18.2(2)^\circ$). Closed to trigonal-pyramidal coordination environment of Cu2 ($\tau_4=0.70$) includes one N atom of tetrazole ring and three bridging Cl atoms. Atom Cl1ⁱ is removed from the metal center by 2.805(2) Å. Despite the last Cu2–Cl1ⁱ distance is markedly longer than the other analogue distances in the structure, this value still significantly shorter than the sum of Van der Waals radii of copper and chlorine. Thus, (2-F-Ph)TSA molecule causes a formation of «stepped cubane» tetramer Cu_4Cl_4 .

Crystal structure of the $[\text{Cu}_2\{(2\text{-EtO-Ph})\text{TSA}\}_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ (III) complex is built of centrosymmetric $[\text{Cu}_2\{(2\text{-EtO-Ph})\text{TSA}\}_2(\text{H}_2\text{O})_2]^{2+}$ dimers in which (2-EtO-Ph)TSA acts as a tridentate chelate-bridging π,σ -ligand being attached to the metal by means of two nucleophilic N3 and N4 atoms of the tetrazole

Table 3

Geometry of selected hydrogen bonds in I and III crystal structures

Atoms involved D–H...A	Symmetry	Distances, Å			Angle, deg
		D...H	H...A	D...A	D–H...A
I					
N5–H5A...O1	0.5+x, 0.5–y, –z	0.90(1)	2.19(4)	2.985(8)	148(6)
N5–H5B...O3	–0.5+x, 0.5–y, –z	0.89(1)	2.05(2)	2.939(8)	173(8)
C3–H3A...O2	0.5+x, 0.5–y, –z	0.99	2.37	3.195(9)	141
III					
O2–H2A...O3	–x, 1–y, 1–z	0.88	2.55	3.323(3)	147
O2–H2A...O4	–x, 1–y, 1–z	0.88	2.03	2.809(2)	148
O2–H2B...O3		0.88	1.91	2.741(2)	159

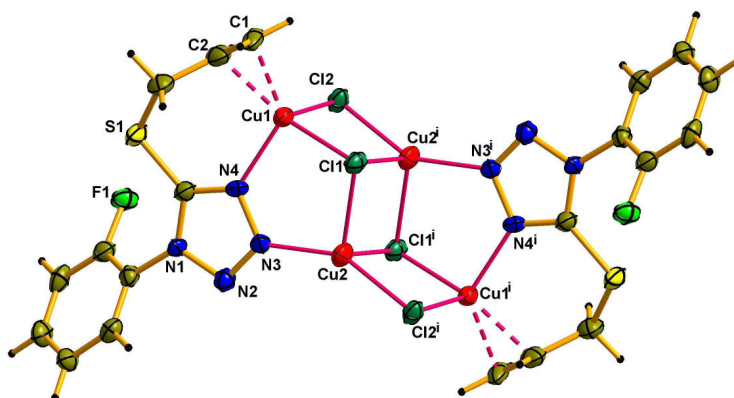


Fig. 2. Molecular fragment of crystal structure II. Symmetry code: (i) 2–x, 1–y, 1–z

Table 4
Selected bond distances and angles in structure II

Bond	d, Å	Angle	ω , deg
Cu1–N4	2.032(4)	C1–Cu1–C2	39.0(2)
Cu1–Cl1	2.284(2)	m–Cu1–N4	113.7(2)
Cu1–Cl2	2.464(2)	m–Cu1–Cl1	134.8(2)
Cu1–m ^a	1.951(5)	m–Cu1–Cl2	106.3(2)
Cu2–N3	1.975(4)	Cu1–Cl1–Cu2	92.48(6)
Cu2–Cl1	2.465(2)	N3–Cu2–Cl1	98.5(1)
Cu2–Cl1 ¹ ^b	2.805(2)	N3–Cu2–Cl1 ¹	99.0(1)
Cu2–Cl2 ¹	2.215(2)	N3–Cu2–Cl2 ¹	150.0(1)
C1–C2	1.381(8)	C1–C2–C3	121.1(6)

Note – ^a m is a mid-point of C1–C2 double bond. ^b Symmetry code: (i) 2–x, 1–y, 1–z.

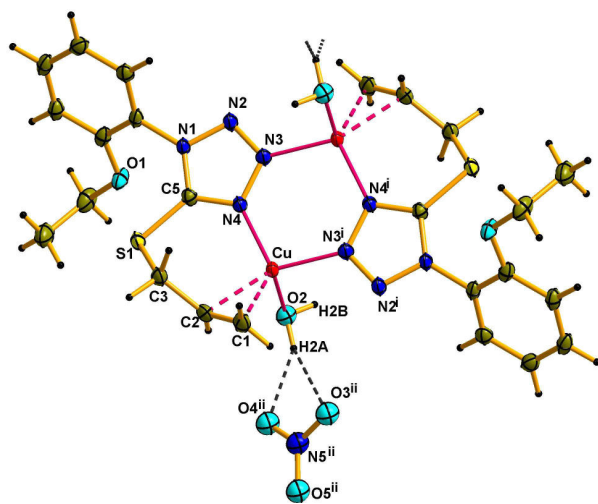


Fig. 3. Fragment of crystal structure III with depicted O–H...O hydrogen bonds. Symmetry codes: (i) 1–x, 1–y, 1–z; (ii) –x, 1–y, 1–z

core and the C=C bond from S-allyl group (Fig. 3, Table 5). Mentioned three active sites form the basal surrounding of the distorted Cu(I) trigonal pyramidal arrangement ($\tau_4=0.82$), the fourth apical position is occupied by H₂O molecule. Thus, cationic [Cu₂{(2-EtO-Ph)TSA}₂(H₂O)₂]²⁺ fragment contains two six-membered CuC₄SN (considering the C=C bond as one coordinating site) and one six-membered Cu₂N₄ rings. Coordinated water molecules play a role of the bridges, connecting neighboring [Cu₂{(2-EtO-Ph)TSA}₂(H₂O)₂]²⁺ cations and NO₃[–] anions, by means of O–H...O hydrogen bonds, into H-bonded infinite chain (Table 3).

Taking into account the discussed structures I–III and earlier studied Cu(I) π -complexes with 1-aryl substituted TSA ligands, four types (f1–f4) of coordination nodes can be distinguished (Table 6).

The first f1 type is formed only in the case of Cu(NH₂SO₃) salts. The reason is that the nitrogen atom of the anion –NH₂ group possesses high nucleophilic activity and effectively competes with N3 donor atom of the tetrazole ring in the metal coordination. So, in the case of f1 type copper(I) surrounding includes allylic C=C bond, one the most nucleophilic tetrazole N atom, one N atom from the sulfamate anion and O atom from the neighbouring bridging anion or the methanol molecule. In contrast to the polymeric structures with bridging NH₂SO₃[–] anions, coordination of CH₃OH molecule to copper(I) leads to the monomer [Cu(L)(NH₂SO₃)(CH₃OH)] fragment formation.

Table 5
Selected bond distances and angles in structure II

Bond	d, Å	Angle	ω , deg
Cu–N3 ¹ ^a	1.995(1)	C1–Cu1–C2	38.45(7)
Cu–N4	2.013(2)	m–Cu1–N4	115.32(7)
Cu–O2	2.188(1)	m–Cu1–N3 ¹	128.89(7)
Cu–m ^b	1.962(2)	m–Cu1–O2	98.29(7)
C1–C2	1.368(2)	C1–C2–C3	123.2(2)

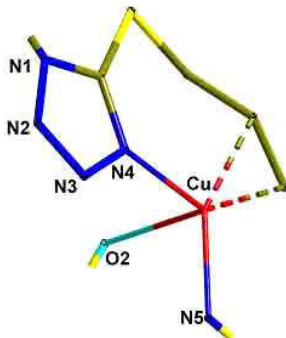
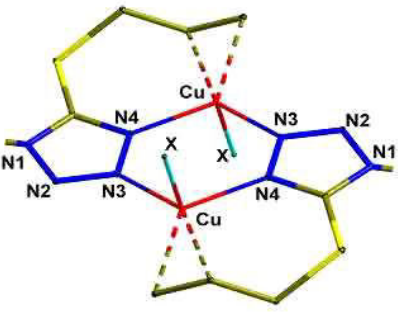
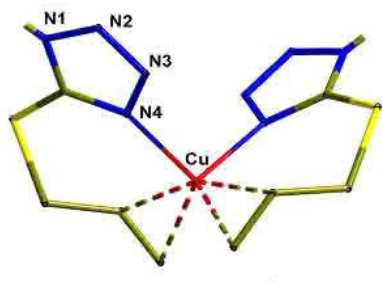
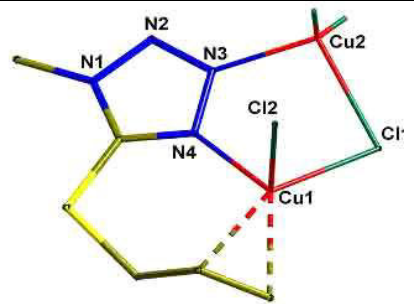
Note – ^a Symmetry code: (i) 1–x, 1–y, 1–z. ^b m is a mid-point of C1–C2 double bond.

The coordination of the only most nucleophilic tetrazole N atom (namely N4) to copper(I) was also found in the case of f3 type. In this case, there are two reasons for such an organization. The first one is related to the presence of acceptor (F[–] or CF₃[–]) substituent at the phenyl ring of (Ph)TSA, which reflected in the decrease in tetrazole ring nucleophilic activity. The second reason is related to a significant «hardness» in HSAB terms of fluorine atoms of BF₄[–] anion, which don't contribute to the bond formation with such «soft acid» as copper(I).

The f2 type is the most common among the π -complexes of 1-aryl substituted TSA ligands with ionic copper(I) salts. In this case (Ar)TSA ligands reveal helate-bridging functions and are coordinated to the metal centres by allylic C=C bond and by two N atoms of the tetrazole ring. As a result, two copper(I) and two organic ligands form a dimer [Cu₂(L)₂]²⁺, copper atom of which in its trigonal pyramid apical position selectively coordinates water molecule or O atom of the anion. In the structure of [Cu₃(L)₂Cl₃]_n the centrosymmetric dimers {Cu₂(L)₂} and polymeric inorganic chains {Cu₂Cl₃} are combined through bridging Cl atoms into 2D-layer. The f4 type is represented by the only [Cu₄{(2-F-Ph)TSA}₂Cl₄] (II) structure with «stepped cubane» tetramer Cu₄Cl₄.

Table 6

The geometry of coordination nodes in copper(I) π -complexes with S-allyl substituted 1-aryl-tetrazole-5-thioles ((Ph)TSA)

	Type of coordination node formed by the tetrazole ligand L	Ligand, L	Complex composition
f1		(3-CH ₃ ,5-CH ₃ -Ph)TSA	[Cu(L)(NH ₂ SO ₃) _n]
		(2-F-Ph)TSA	[Cu(L)(NH ₂ SO ₃) _n]
		(2-CF ₃ -Ph)TSA	[Cu(L)(NH ₂ SO ₃)(CH ₃ OH)]
f2		(Ph)TSA	[Cu ₂ (L) ₂ (H ₂ O) ₂](BF ₄) ₂
		(4-CH ₃ -Ph)TSA	[Cu ₂ (L) ₂ (H ₂ O) ₂](BF ₄) ₂
		(4-Cl-Ph)TSA	[Cu ₃ (L) ₂ Cl ₃] _n
		(4-Cl-Ph)TSA	[Cu ₂ (L) ₂ (H ₂ O) ₂](NO ₃) ₂
		(4-Cl-Ph)TSA	[Cu ₂ (L) ₂ (H ₂ O) ₂](BF ₄) ₂
		(3-Cl,4-CH ₃ -Ph)TSA	[Cu ₂ (L) ₂ (ClO ₄) ₂]
		(2-EtO-Ph)TSA	[Cu ₂ (L) ₂ (H ₂ O) ₂](NO ₃) ₂
f3		(2-F-Ph)TSA	[Cu(L) ₂](BF ₄) ^a
		(2-CF ₃ -Ph)TSA	[Cu(L) ₂](BF ₄)
f4		(2-F-Ph)TSA	[Cu ₄ {(2-F-Ph)TSA} ₂ Cl ₄]

Note – ^a CCDC 1887401 contains the supplementary crystallographic data for the structure, which was deposited as Private Communication in the Cambridge Crystallographic Data Centre.

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 π -КОМПЛЕКСИ КУПРУМУ(I) З АЛІЛЗАМІЩЕНИМИ 1-АРИЛ-1H-ТЕТРАЗОЛ-5-ТИОЛІВ: СИНТЕЗ І ЇХ СТРУКТУРНІ ОСОБЛИВОСТІ

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Синтезовано та рентгеноструктурно досліджено три нових π, σ -комплекси купруму(I) із 1-(2-флюорофеніл)-((2-F-Ph)TSA) та 1-(2-етоксифеніл)-((2-EtO-Ph)TSA) 5-алілсульфаніл-1H-тетразолами. Кристали комплексів $[\text{Cu}\{2\text{-F-Ph}\}\text{TSA}\{(\text{NH}_2\text{SO}_3)\}]$ (I), $[\text{Cu}_4\{2\text{-F-Ph}\}\text{TSA}_2\text{Cl}_4]$ (II) та $[\text{Cu}_2\{2\text{-EtO-Ph}\}\text{TSA}\{(\text{H}_2\text{O})_2\}\{(\text{NO}_3)_2\}]$ (III) були отримані методом змінного струмного електрохімічного синтезу, виходячи із спиртового розчину відповідного органічного ліганду та відповідної солі купруму(II). Сполука $[\text{Cu}\{2\text{-F-Ph}\}\text{TSA}\{(\text{NH}_2\text{SO}_3)\}]$ (I) кристалізується в ацентричній просторовій групі $P2_12_12_1$ ($a=7.545(3)$ Å, $b=12.890(4)$ Å, $c=14.249(4)$ Å, $V=1385.8(8)$ Å³, $Z=4$) та характеризується утворенням полімерних ланцюгів за участю місточкових сульфат-аніонів. π -Комплекси $[\text{Cu}_4\{2\text{-F-Ph}\}\text{TSA}_2\text{Cl}_4]$ (II) та $[\text{Cu}_2\{2\text{-EtO-Ph}\}\text{TSA}\{(\text{H}_2\text{O})_2\}\{(\text{NO}_3)_2\}]$ (III) кристалізуються в центросиметричній просторовій групі $P-1$ (II: $a=7.837(3)$ Å, $b=8.695(3)$ Å, $c=11.429(4)$ Å, $\alpha=109.61(3)^\circ$, $\beta=93.82(3)^\circ$, $\gamma=105.08(3)^\circ$, $V=698.1(5)$ Å³, $Z=1$; III: $a=8.094(3)$ Å, $b=10.243(4)$ Å, $c=11.221(4)$ Å, $\alpha=113.44(3)^\circ$, $\beta=97.11(3)^\circ$, $\gamma=106.79(3)^\circ$, $V=786.4(5)$ Å³, $Z=1$), однак вони суттєво відрізняються організацією структурних фрагментів. Сполука III побудована із центросиметричних димерів $[\text{Cu}_2\{2\text{-EtO-Ph}\}\text{TSA}\{(\text{H}_2\text{O})_2\}]^{2+}$, в яких молекула (2-EtO-Ph)TSA виконує роль триденатного місточково-хелатного π, σ -ліганду. Молекула (2-F-Ph)TSA в II зумовлює формування фрагментів Cu_4Cl_4 із топологією «східчастого кубану». Надано короткий огляд всіх відомих π -комплексів купруму(I) з алілзаміщеними 1-арил-1H-тетразол-5-тиоливі.

Ключові слова: тетразол, купрум(I), π -комплекс, синтез, кристалічна структура, електрохімічний синтез.

COPPER(I) π -COMPLEXES WITH ALLYL SUBSTITUTED 1-ARYL-1H-TETRAZOLE-5-THIOLS: SYNTHESIS AND THEIR STRUCTURAL FEATURES

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Three new copper(I) π, σ -complexes with 1-(2-fluorophenyl)-((2-F-Ph)TSA) and 1-(2-ethoxyphenyl)-((2-EtO-Ph)TSA) 5-allylsulfanyl-1H-tetrazoles were synthesized in a single crystal form and structurally characterized by X-ray diffraction method. Crystals of complexes $[Cu\{(2-F-Ph)TSA\}(NH_2SO_3)]$ (I), $[Cu_4\{(2-F-Ph)TSA\}_2Cl_4]$ (II) and $[Cu_2\{(2-EtO-Ph)TSA\}_2(H_2O)_2](NO_3)_2$ (III) were obtained under conditions of the alternating-current electrochemical synthesis starting from the alcohol solution of the appropriate organic ligand and copper(II) salt. $[Cu\{(2-F-Ph)TSA\}(NH_2SO_3)]$ (I) crystallizes in acentric space group $P2_12_12_1$ ($a=7.545(3)$ Å, $b=12.890(4)$ Å, $c=14.249(4)$ Å, $V=1385.8(8)$ Å³, $Z=4$) and characterizes by a formation of polymeric chains with bridging sulfamate anions. π -Complexes $[Cu_4\{(2-F-Ph)TSA\}_2Cl_4]$ (II) and $[Cu_2\{(2-EtO-Ph)TSA\}_2(H_2O)_2](NO_3)_2$ (III) crystallize in the centrosymmetric space group $P-1$ (II: $a=7.837(3)$ Å, $b=8.695(3)$ Å, $c=11.429(4)$ Å, $\alpha=109.61(3)^\circ$, $\beta=93.82(3)^\circ$, $\gamma=105.08(3)^\circ$, $V=698.1(5)$ Å³, $Z=1$; III: $a=8.094(3)$ Å, $b=10.243(4)$ Å, $c=11.221(4)$ Å, $\alpha=113.44(3)^\circ$, $\beta=97.11(3)^\circ$, $\gamma=106.79(3)^\circ$, $V=786.4(5)$ Å³, $Z=1$), but they show a significant difference in the fragment organization. Compound III is built of centrosymmetric $[Cu_2\{(2-EtO-Ph)TSA\}_2(H_2O)_2]^{2+}$ dimers in which (2-EtO-Ph)TSA acts as a tridentate chelate-bridging π, σ -ligand. Molecule (2-F-Ph)TSA in II causes a formation of «stepped cubane» tetramer Cu_4Cl_4 . A brief review of all known Cu(I) π -compounds with allyl substituted 1-aryl-1H-tetrazole-5-thiols is given.

Keywords: tetrazole; copper(I); π -complex; crystal structure; ac-electrochemical technique.

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