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 (3d-metal complexation, the 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 CuHSO$_3$ π-complex and the direct Cu(I)–F(SiF$_3$)$_2$ 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-(allylmino)-1,3-thiazolidin-4-one, 1-allyloxobenzotriazole and 5-(allylthio)-1-(3,5-dimethyl-phenyl)-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–olefin 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 complexes 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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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 \([\text{Cu}((2-\text{F}-\text{Ph})\text{TSA})(\text{NH}_2\text{SO}_3)]\) (I), \([\text{Cu}((2-\text{F}-\text{Ph})\text{TSA})\text{Cl}_2]\) (II) and \([\text{Cu}_2((2-\text{EtO}-\text{Ph})\text{TSA})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2]\) (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 \([\text{Cu}((2-\text{F}-\text{Ph})\text{TSA})(\text{NH}_2\text{SO}_3)]\) (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(\text{NH}_2\text{SO}_3)\text{Cl} (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 \([\text{Cu}((2-\text{F}-\text{Ph})\text{TSA})\text{Cl}_2]\) (II) π-complex**

To 2.5 mL of alcohol solution (1.3 mL of ethanol and 1.2 mL of n-propanol) of CuCl\text{2H}_2\text{O} (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 \([\text{Cu}_2((2-\text{EtO}-\text{Ph})\text{TSA})_2(\text{H}_2\text{O})_2](\text{NO}_3)_2]\) (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(NO\text{3})\text{2H}_2\text{O} (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\text{α} radiation (\(\lambda=0.71073\) Å). Diffraction data for II were collected on an Agilent Xcalibur four-circle diffractometer with MoK\text{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 F\text{2} by ShelXL program with the following graphical user interface of OLEX\text{2} [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

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Copper(I) π-complexes with allyl substituted 1-aryl-1H-tetrazole-5-thiols: synthesis and their structural features

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**Scheme. Synthesis of the tetrazole ligands**

I a, b

NCS

R

CS\text{2}

1. O\text{CODEt}

Et\text{N}

2. HCl

I - IVa ((2-F-Ph)TSA) : R = F

I - IVb ((2-EtO-Ph)TSA) : R = OEt

N

N

S

R

KOH

EtOH

IV a, b

I a, b

II a, b

N

N

S

R

Br

KOH

EtOH

N

N

S

R

Br
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}(NH₃SO₄)] (I) crystallizes in the orthorhombic acentric space group P2₁2₁2₁, with one copper(I) ion, one NH₃SO₄⁻ 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}(NH₃SO₄)] (IV) π-complex with 3,5-dimethylphenyl substituent [11], Cu⁺ ion in structure I possesses trigonal pyramidal environment (τ₄=0.77, τ₄ 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 NH₃SO₄⁻ 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 NH₃SO₄⁻ 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

| Note – ± 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). |

| Characteristics | I | II | III |
|-----------------|---|----|-----|
| CCDC number     | 1886871 | 1886872 | 1886873 |
| Empirical formula | C₁₀H₁₂CuFN₂O₃S₂ | C₂₀H₁₂ClCu₂F₃N₂S₂S₂ | C₂₄H₂₂Cu₂N₁₀O₁₀S₂ |
| 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, P2₁2₁2₁ | triclinic, P-1 | triclinic, P-1 |
| (Flack par. x = 0.04(2)) |  |

**Table 1**

Selected crystal data and structure refinement parameters of I–III

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Copper(I) $\pi$-complexes with allyl substituted 1-aryl-1H-tetrazole-5-thiols: synthesis and their structural features

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

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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 \( \varphi = 12.3(3) \)° also confirms this conclusion.

### Table 2

| Bond | d, Å | Angle |
|------|------|-------|
| Cu–N4 | 1.956(5) | C1–Cu–C2 39.4(3) |
| Cu–N5 | 1.997(6) | m–Cu–O2′ 94.2(3) |
| Cu–O2′, m | 2.482(6) | m–Cu–N4 116.2(3) |
| Cu–m | 1.914(6) | m–Cu–N5 135.1(3) |
| C1–C2 | 1.369(10) | N5–Cu–O2′ 95.2(3) |

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

The structure of \([\text{Cu}_4\{(2-F-Ph)\text{TSA}\}_2\text{Cl}_4]\) (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 \( \pi, \sigma \)-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 (\( \tau = 0.79 \)) includes N4 atom, allylic C=C bond of (2-F-Ph)TSA ligand and two bridging Cl atoms. The coordinated to the metal Cl=C2 bond is also elongated to 1.381(8) Å (\( \Delta = 0.417(5) \) Å, \( \varphi = 18.2(2) \)°).

Closed to trigonal-pyramidal coordination environment of Cu2 (\( \tau = 0.70 \)) includes one N atom of tetrazole ring and tree bridging Cl atoms. Atom Cl1 is removed from the metal center by 2.805(2) Å. Despite the last Cu2–Cl1 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 Cu4Cl4.

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

### Table 3

| Atoms involved | Symmetry | Distances, Å | Angle, deg |
|----------------|----------|-------------|------------|
| D–H···A        |          | D···H       | H···A      | D···A       | D–H···A     |
| 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        |
| 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

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Table 4

Selected bond distances and angles in structure II

| Bond           | d, Å  | Angle | ω, deg |
|----------------|-------|-------|--------|
| Cu1–N4         | 2.032(2) | 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          | 1.951(5) | m–Cu1–Cl2 | 106.3(2) |
| Cu2–N3         | 1.975(4) | Cu1–C1–Cu2 | 92.48(6) |
| Cu2–Cl1        | 2.465(2) | N3–Cu2–Cl1 | 98.5(1) |
| Cu2–Cl1*       | 2.805(2) | N3–Cu2–Cl1* | 99.0(1) |
| Cu2–Cl2        | 2.215(2) | N3–Cu2–Cl2 | 150.0(1) |
| Cl1–C2         | 1.381(8) | Cl1–C2–C3 | 121.1(6) |

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

Table 5

Selected bond distances and angles in structure II

| Bond           | d, Å  | Angle | ω, deg |
|----------------|-------|-------|--------|
| Cu–N3*         | 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 | 128.89(7) |
| Cu–m*          | 1.962(2) | m–Cu1–O2 | 98.29(7) |
| Cl1–C2         | 1.368(2) | Cl1–C2–C3 | 123.2(2) |

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

The first f1 type is formed only in the case of Cu(NH4SO3) 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 NH3SO3– anions, coordination of CH3OH molecule to copper(I) leads to the monomer [Cu(L)(NH4SO3)(CH3OH)] fragment formation.

The second f2 type is the most common among the π-complexes of 1-aryl substituted TSA ligands with copper(I) salts. In this case (Ar)TSA ligands reveal halate-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 [Cu(L)2]2+. Copper atom of which in its trigonal pyramidal apical position selectively coordinates water molecule or O atom of the anion. In the structure of [Cu(L)2Cl]n the centrosymmetric dimers [Cu(L)2] and polymeric inorganic chains [CuCl4] are combined through bridging Cl atoms into 2D-layer. The f4 type is represented by the only [Cu(L)2(2-F-Ph)TSA]Cl4 (II) structure with «stepped cubane» tetramer Cu4Cl4.

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### Table 6
Table: Geometry of Coordination Nodes in Copper(I) π-Complexes with S-allyl Substituted 1-aryl-tetrazole-5-thioles ((Pht)TSA)

| Type of Coordination Node Formed by the Tetrazole Ligand L | Ligand, L | Complex Composition |
|-----------------------------------------------------------|-----------|---------------------|
| f1 (3-CH$_3$5-CH$_3$-Ph)TSA                               | (3-CH$_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)] |
|                                                           | (Ph)TSA | [Cu$_2$(L)$(H_2$O)$_2$](BF$_4$)$_2$ |
|                                                           | (4-CH$_3$-Ph)TSA | [Cu$_2$(L)$(H_2$O)$_2$](BF$_4$)$_2$ |
|                                                           | (4-CI-Ph)TSA | [Cu$_2$(L)$_2$Cl$_2$]$_n$ |
|                                                           | (4-CI-Ph)TSA | [Cu$_2$(L)$(H_2$O)$_2$](NO$_3$)$_2$ |
|                                                           | (3-CI,4-CH$_3$-Ph)TSA | [Cu$_2$(L)$_2$(ClO$_4$)$_2$] |
|                                                           | (2-EtO-Ph)TSA | [Cu$_2$(L)$(H_2$O)$_2$](NO$_3$)$_2$ |
|                                                           | (2-CF$_3$-Ph)TSA | [Cu$_2$(L)$_2$(CF$_3$SO)$_2$] |
| f2 (2-F-Ph)TSA                                             | (2-F-Ph)TSA | [Cu(L)$_2$](BF$_4$)$_2$ |
|                                                           | (2-CF$_3$-Ph)TSA | [Cu(L)$_2$](BF$_4$)$_2$ |
| f3 (2-F-Ph)TSA                                             | (2-F-Ph)TSA | [Cu$_4${(2-F-Ph)TSA$_2$}]$_2$Cl$_4$ |

Note – 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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COPPER(I) \* COMPLEXES WITH ALLYL SUBSTITUTED 1-ARYL-1H-TETRAZOLE-5-TIOLS: SYNTHESIS AND THEIR STRUCTURAL FEATURES

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Three new copper(I) \( \pi \)-complexes with 1-(2-fluorophenyl)-((2-F-Ph)TSA) and 1-(2-ethoxyphenyl)-((2-EtO-Ph)TSA) 5-allylsulfonyl-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$_2$SO$_4$)}(I), [Cu$2$((2-F-Ph)TSA)$_2$Cl$_2$]Cl$_2$](II) and [Cu$_3$((2-EtO-Ph)TSA)$(_2$H$_2$O)$_2$$(NO_3)$]$_2$] (III) were obtained under conditions of the alternating-current electrochemical synthesis starting from the alcohol solution of the appropriate organic ligand and copper(II) salt. [Cu{((2-F-Ph)TSA)(NH$_2$SO$_4$)}] crystallizes in acentric space group P2$_1$/2, (a=7.545(3) Å, b=12.890(4) Å, c=14.249(4) Å, \( V = 1385.8(8) \) Å$^3$), Z=4 and characterizes by a formation of polymeric chains with bridging sulfamate anions. \( \pi \)-Complexes [Cu$_2$((2-F-Ph)TSA)$_2$]Cl$_2$ (II) and [Cu$_3$((2-EtO-Ph)TSA)$(_2$H$_2$O)$_2$$(NO_3)$] (III) crystallize in the centrosymmetric space group P-1 (II: a=7.837(3) Å, b=8.695(3) Å, c=11.429(4) Å, a=109.61(3)$^\circ$, b=93.82(3)$^\circ$, c=105.08(3)$^\circ$, \( V = 698.1(5) \) Å$^3$, Z=1; III: a=8.094(3) Å, b=10.243(4) Å, c=11.221(4) Å, a=113.44(3)$^\circ$, b=97.11(3)$^\circ$, c=106.79(3)$^\circ$, \( V = 786.6(5) \) Å$^3$, 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$_2$O)$_2$$(NO_3)$] dimers in which (2-EtO-Ph)TSA acts as a tridentate chelate-bridging \( \pi \)-ligand. Molecule (2-F-Ph)TSA in II causes a formation of «stepped cubane» tetramer Cu$_4$Cl$_4$L$_4$ (L$^2$=1,3,4-thiadiazole) dimer. A brief review of all known Cu(I) \( \pi \)-complexes with allyl substituted 1-aryl-1H-tetrazole-5-thiols is given.

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

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