

UDC 548.736:546.561

*O.V. Pavlyuk, Yu.I. Slyvka, N.T. Pokhodylo, M.G. Mys'kiv***SYNTHESIS, CRYSTAL STRUCTURE AND HIRSHFELD SURFACE ANALYSIS OF COPPER(I) NITRATE  $\pi$ -COMPLEX BASED ON 1-(2,6-DIMETHYLPHENYL)-5-ALLYLSULFANYL-1H-TETRAZOLE****Ivan Franko National University of Lviv, Lviv, Ukraine**

By means of the alternating current electrochemical technique and starting from copper wire electrodes in propanol solution of corresponding ligand and copper(II) nitrate, novel copper(I)  $\pi$ -complex  $[\text{Cu}_2(\text{C}_{12}\text{H}_{14}\text{SN}_4)_2(\text{NO}_3)_2]$  (1) has been obtained and X-ray structurally investigated: sp. gr.  $P\bar{1}$ ,  $a=7.352(3)$  Å,  $b=8.269(3)$  Å,  $c=12.723(4)$  Å,  $\alpha=82.08(3)^\circ$ ,  $\beta=82.74(3)^\circ$ ,  $\gamma=88.37(3)^\circ$ ,  $V=759.9(5)$  Å<sup>3</sup>,  $Z=2$ ,  $d_{\text{calc}}=1.625$  g cm<sup>-3</sup>,  $\mu(\text{CuK}\alpha)=3.502$  mm<sup>-1</sup>,  $\theta_{\text{max}}=67.96^\circ$ , 4119 measured reflections, 1248 used reflections, 201 refined parameters,  $R(F^2)=0.0915$ ,  $S=0.95$ . The trigonal-pyramidal copper(I) coordination environment consists of nitrogen atom and allylic group of ligand, and of two oxygen atoms from crystallographically distinct nitrate anions. Due to a bridging function of oxygen atoms of nitrate anions, two metal-containing polyhedra are connected into  $\{\text{Cu}_2\text{L}_2(\text{NO}_3)_2\}$  topological units which are additionally stabilized by noncovalent interaction  $\text{Cu}\cdots\text{O}(2)$ . Comparatively weak hydrogen bonds  $\text{C}-\text{H}\cdots\text{O}$  exist in the crystal structure of  $[\text{Cu}_2(\text{C}_{12}\text{H}_{14}\text{SN}_4)_2(\text{NO}_3)_2]$  (1).

**Keywords:** copper(I),  $\pi$ -complex, crystal structure, electrochemical synthesis, tetrazole.**DOI:** 10.32434/0321-4095-2021-138-5-84-89**Introduction**

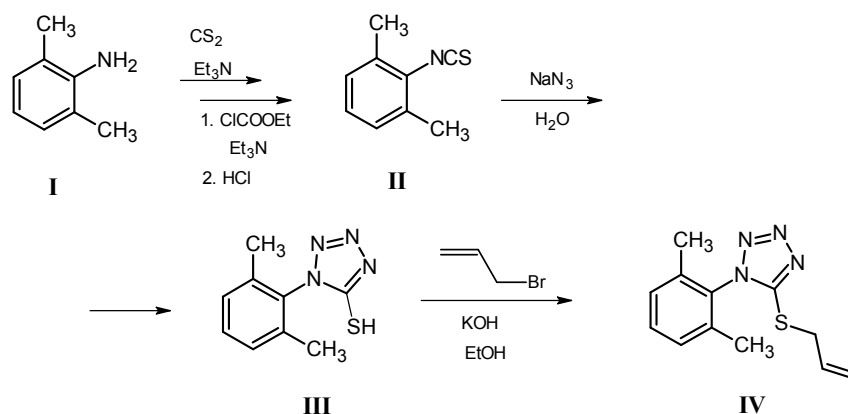
Tetrazoles are well known heterocyclic compounds that have intensively investigated for their employment in pharmacy (due to anti-tuberculosis, antibacterial, anticonvulsant, anticancer activities, etc.), the agrarian sector (plant growth regulators and pesticides) and as useful ligands in the design of new coordination compounds [1–4]. Incorporation of the olefin C=C bond into a skeleton of the tetrazole ring substituents in a specific manner changes their coordination ability and plays a key role in the selective coordination of transition metal ions due to metal–olefin  $\pi$ -bonding [5]. The connection of heterocyclic cores to allylic radical in  $\text{Cu}^+$  coordination environment was found to be a useful determinant in the formation of  $\pi$ -coordination compounds with unknown (or less-stable) in a free state Cu(I) salts [6]. Moreover, recently an appearance of high second and third-order NLO properties was observed for copper(I)  $\pi$ -complexes with 1-allyloxybenzotriazole, 3-allyl-2-(allylimino)-1.3-thiazolidin-4-one ligands and with some thioallyl derivatives of tetrazoles [7–9]. Therefore, an investigation of the coordination behavior of new

allyl derivatives of azoles with Cu(I) attracts special attention. Allylic derivatives of tetrazoles were also found as very useful ligands for a design of new copper(I)  $\pi$ -coordination compounds with the structures which are strongly dependent on the inorganic anion nature. Taking into account that the metal–olefine  $\pi$ -coordination in the presence of tetrazole nucleus is studied poorly enough, this article is focused on the synthesis and characterization of novel  $[\text{Cu}_2(2,6\text{-Dmpht})_2(\text{NO}_3)_2]$  (1)  $\pi$ -complex with 1-(2,6-dimethylphenyl)-5-allylsulfanyl-1H-tetrazole (2,6-Dmpht).

**Experimental**

*Synthesis of 1-(2,6-dimethylphenyl)-5-allylsulfanyl-1H-tetrazole (2,6-Dmpht)*

2,6-Dmpht was prepared in several steps in accordance with the earlier reported method [8] (Scheme 1). Yield 97%. 2,6-Dmpht: <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>),  $\delta$ , 7.41 (t,  $J=7.5$  Hz, 1H,  $H_{\text{PH}}-4$ ), 7.27 (d,  $J=7.5$  Hz, 2H,  $H_{\text{PH}}-2,6$ ), 5.96 (td,  $J=16.8, 7.0$  Hz, 1H, =CH), 5.38 (d,  $J=16.8$  Hz, 1H,  $\text{CH}_2=$ ), 5.18 (d,  $J=10.0$  Hz, 1H,  $\text{CH}_2=$ ), 4.00 (d,  $J=7.0$  Hz, 2H,  $\text{CH}_2$ ), 1.94 (s, 6H,  $\text{CH}_3$ ).

Scheme 1. Synthesis of the ligand 2,6-*Dmpht*

### Synthesis of copper(I) $\pi$ -complex $[\text{Cu}_2(2,6\text{-Dmpht})_2(\text{NO}_3)_2] (1)$

Single crystals of complex 1 were obtained under the alternating current electrochemical technique conditions starting from propanol/water solution of the organic ligand and copper(II) nitrate. A mixture of 0.9 mmol (0.222 g) 2,6-*Dmpht* and 1.0 mmol (0.242 g)  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in 4.5 mL of 95% *n*-propanol was prepared. The solution was placed into a small 5 mL test-tube and then copper-wire electrodes in cork were inserted. By using of alternating current (frequency of 50 Hz) of 0.6 V for 4 days, colorless crystals of 1 appeared on copper electrodes. The yield was about 35%. Crystals melts with decomposition at the temperature of 117°C.

#### Single crystal X-ray diffraction study

Diffraction data for 1 crystal were collected using an Agilent Xcalibur four-circle diffractometer ( $\text{CuK}\alpha$  radiation,  $\lambda=1.54184 \text{ \AA}$ ) equipped with an Onyx CCD detector. The collected diffraction data were processed by the CrysAlis PRO software [10]. The structure was solved by SHELXS program and refined by least squares method on  $F^2$  by SHELXL program with the following graphical user interface of OLEX<sup>2</sup> [11,12]. Atomic displacements for non-hydrogen atoms were refined using an anisotropic model. Hydrogen atoms were placed into ideal positions and refined as riding atoms with relative isotropic displacement parameters. The crystallographic parameters and summary of data collection for 1 are presented in Table 1.

#### Results and discussion

The trigonal-pyramidal coordination environment of copper ( $\tau_4=0.79$ ,  $\Delta=0.01 \text{ \AA}$  [13]) in 1 consists of one nitrogen atom ( $\text{Cu-N}(4) 1.951(2) \text{ \AA}$ , Table 2), allylic group of ligand ( $\text{Cu-C} 2.012(9)\text{--}2.031(9) \text{ \AA}$ ) and two oxygen atoms from crystallographically distinct nitrate anions ( $\text{Cu-O} 1.993(7)\text{--}2.580(1) \text{ \AA}$ , solid angle 19.1 sr and 10.1 sr according Voronoy-Dirichlet polyhedron approach [14]).

Table 1  
Selected crystal data and structure refinement parameters of 1

CCDC number <sup>a</sup>	2091717
Empirical formula	$\text{C}_{12}\text{H}_{14}\text{CuN}_5\text{O}_3\text{S}$
Formula weight, $\text{g mol}^{-1}$	371.88
Temperature, K	105(2)
Wavelength, $\text{ \AA}$	1.54184
Crystal system, sp. gr.	triclinic, $P\bar{1}$
Unit cell dimensions a, $\text{ \AA}$	7.352(3)
b, $\text{ \AA}$	8.269(3)
c, $\text{ \AA}$	12.723(4)
$\alpha$ , $^\circ$	82.08(3)
$\beta$ , $^\circ$	82.74(3)
$\gamma$ , $^\circ$	88.37(3)
$V$ , $\text{ \AA}^3$	759.9(5)
Z	2
Absorption coeff., $\text{mm}^{-1}$	3.502
$F(000)$	380
Color, shape	colorless, prism
Theta range for data collection, $^\circ$	3.53–78.04
Limiting indices	$-7 \leq h \leq 8$ , $-9 \leq k \leq 9$ , $-13 \leq l \leq 15$
Refinement method	Full-matrix least-squares on $F^2$
Measured reflections	4119
Unique reflections	2495
Reflections with $I > 2\sigma(I)$	1248
Refined parameters	201
R values	$R_1=0.0915$ , $wR_2=0.2847$
Largest diff. peak and hole, $\text{e} \cdot \text{ \AA}^{-3}$	0.714 and $-1.393$
Calculated density, $\text{g cm}^{-3}$	1.625

Note: <sup>a</sup> CCDC 2091717 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via <https://www.ccdc.cam.ac.uk/structures/>.

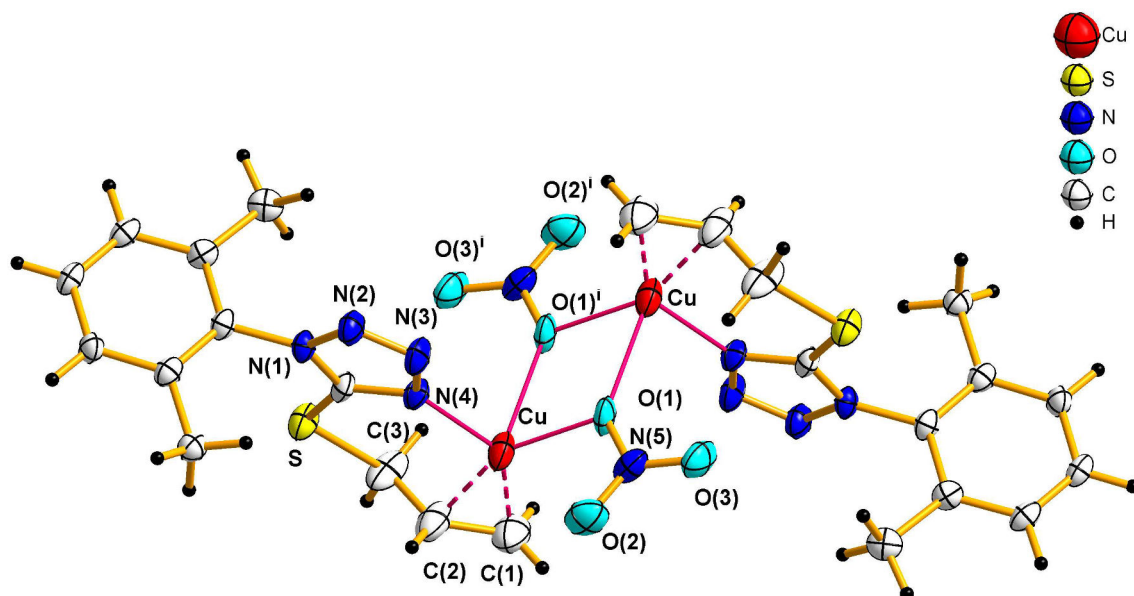


Fig. 1. Dimeric topological unit  $\{Cu_2(2,6\text{-}Dmpht)_2(NO_3)_2\}$  in structure 1. Symmetry code: (i)  $-x, 1-y, 2-z$

The molecule of 1-(2,6-dimethylphenyl)-5-allylsulfanyl-1*H*-tetrazole, which contains five potential coordination centers connected to Cu(I) atoms only through the C=C bond of the allyl group and one nitrogen of tetrazole ring (Fig. 1). The C(1)=C(2) bond of allylic group of the ligand is elongated up to 1.38(2) Å (1.34 Å in ethylene, respectively) due to the  $\pi$ -coordination by Cu(I) atom. For allythiol group, the anticlinal conformation relatively to the C(2)–C(3) bond in the 2,6-*Dmpht* is implemented, the corresponding torsion angle C(1)–C(2)–C(3)–S(1) is 153.1(12)<sup>o</sup>.

Table 2

Selected interatomic distances and valence angle for  $[Cu_2(2,6\text{-}Dmpht)_2(NO_3)_2]$  (1)

Bond	d, Å	Angle <sup>b</sup>	$\omega$ , <sup>o</sup>
Cu–N4	1.951(7)	N4–Cu– <i>m</i>	116.13(5)
Cu–O1	1.993(7)	O1–Cu– <i>m</i>	132.26(5)
Cu–O1 <sup>i a</sup>	2.580(7)	O1 <sup>i</sup> –Cu– <i>m</i>	104.45(5)
Cu–O2	2.650(7)	O2–Cu– <i>m</i>	109.48(5)
Cu–C1	2.033(9)	O1–Cu–N4	111.6(3)
Cu–C2	2.012(9)	O1–Cu–O1 <sup>i</sup>	71.6(5)
Cu– <i>m</i>	1.899(9)	C1–Cu–C2	40.1(6)
C1–C2	1.384(16)	C1–C2–C3	120.0(14)
N1–N2	1.360(10)	C5–S1–C3	103.0(5)
N2–N3	1.270(12)	N2–N1–C6	121.8(7)
N3–N4	1.365(12)	N3–N2–N1	106.4(8)
N1–C5	1.328(11)	N2–N3–N4	111.0(8)

Note: <sup>a</sup> Symmetry code: (i)  $-x, 1-y, 2-z$ ; <sup>b</sup> *m* – middle of C1=C2 bond.

Due to a bridging function of O(1) atoms, two metal-containing polyhedra are connected in  $\{Cu_2(2,6\text{-}Dmpht)(NO_3)_2\}$  topological units which additionally stabilized by relatively weak interaction Cu...O(2) (Cu–O(2) solid angle 8.94 sr [14]). The above building blocks are stacking into 3-*D* skeleton (Fig. 2) by means of relatively weak hydrogen bonds C–H...O (H...O 2.37–2.47 Å,  $\angle$ C–H...O 149–158<sup>o</sup>).

The Hirshfeld surface was built for  $[Cu_2(2,6\text{-}Dmpht)_2(NO_3)_2]$  to analyze the interactions between the units [15]. The most prominent interactions between 2,6-*Dmpht* H atoms and nitrate O can be seen in the Hirshfeld surface plots as the bright and pale-pink areas (Fig. 3,a). Fingerprint plots were produced to show the intermolecular surface bond lengths, with the regions highlighted for H...O interactions, the contribution to the surface area for corresponding contacts is 20.5%. The weakness of hydrogen contacts and high value of globularity of surface (0.697 r.u.) can explain a rather dense packing of dimeric units in the structure.

From our point of view, the features of the crystalline structure in  $[Cu_2(2,6\text{-}Dmpht)_2(NO_3)_2]$  described above are mainly due to the steric configuration and distribution of the electron density in the ligand cation. Confirmation of the correctness of this assumption is the formation of different topological units, depending on the number and location of substituents in the benzene core of the 1-(*R*-phenyl)-5-allylsulfanyl-1*H*-tetrazole (*R*=hydrogen, methyl, and dimethyl). Crystal structure of  $[Cu_2(Ph)_2(H_2O)_2](BF_4)_2$  (here *Ph* – 1-(*R*-phenyl)-5-allylsulfanyl-1*H*-tetrazole) [9]

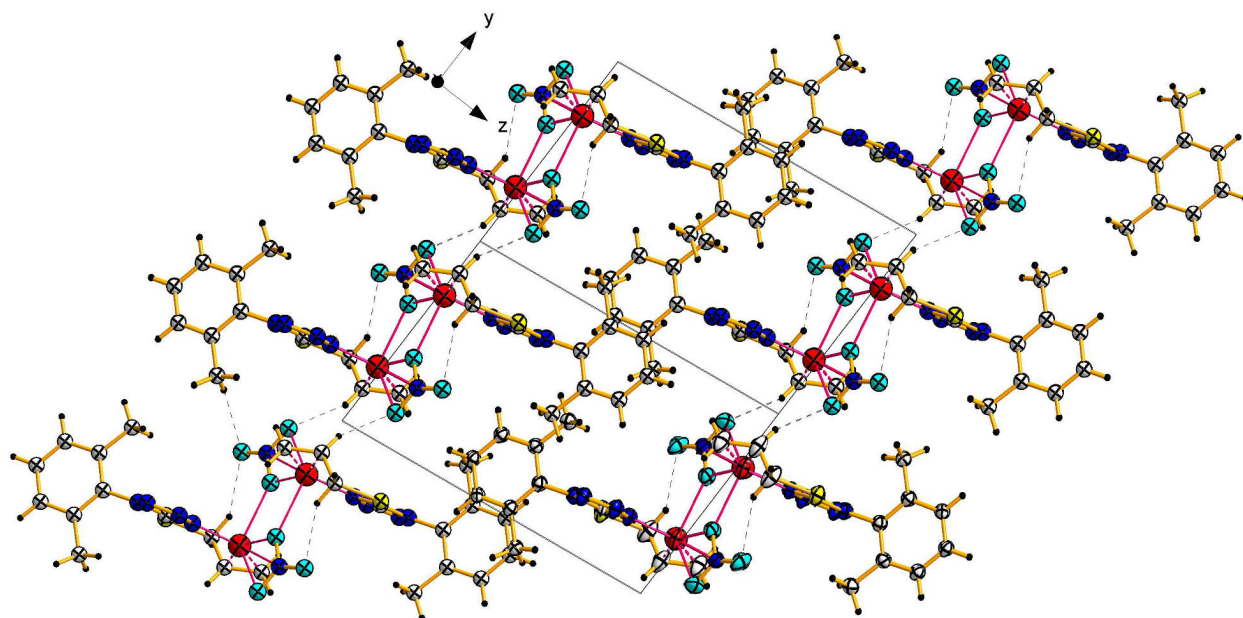


Fig. 2. Topological unit packing and hydrogen bonding in  $[\text{Cu}_2(2,6\text{-Dmpht})_2(\text{NO}_3)_2]$  structure

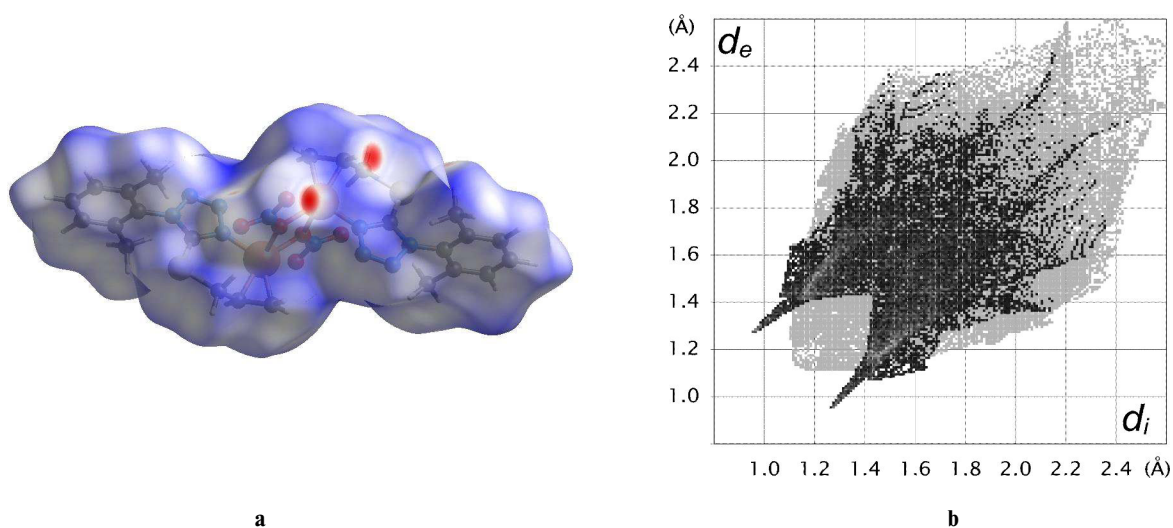


Fig. 3. Hirshfeld surface (a – color online) and fingerprints plot  $d_i$  vs.  $d_e$  (b – black H...O contacts, gray – other interactions) for  $[\text{Cu}_2(2,6\text{-Dmpht})_2(\text{NO}_3)_2]$  (1)

consists of  $\{[\text{Cu}_2(\text{Ph}t)_2(\text{H}_2\text{O})_2]\}$  dimeric topological units with  $[\text{CuON}_2(\text{C}=\text{C})]$  metal coordination environment, and the angle between the phenyl ring and the tetrazole cycle is  $38.8^\circ$ . In turn, in the crystal structure of  $[\text{Cu}_2(\text{Mpht})_2(\text{H}_2\text{O})_2](\text{BF}_4)_2$  (here *Mpht* – 1-(4-methylphenyl)-5-allylsulfanyl-1*H*-tetrazole) [8] the building blocks  $\{[\text{Cu}_2(\text{Mpht})_2(\text{H}_2\text{O})_2]\}$  exists with  $[\text{CuON}_2(\text{C}=\text{C})]$  metal coordination environment, and the angle between the phenyl ring and the tetrazole cycle is  $41.1^\circ$ . The presence of substituents at 3<sup>rd</sup> and 5<sup>th</sup> positions of the phenyl ring (located quite far from the tetrazole core) slightly changes the steric configuration of the ligand

moieties. In the crystal structure of  $[\text{Cu}(3,5\text{-Dmpht})\text{NH}_2\text{SO}_3]$  (here 3,5-*Dmpht* – 5-(allylthio)-1-(3,5-dimethylphenyl)-1*H*-tetrazole) [7], the polymeric units  $\{\text{Cu}(3,5\text{-Dmpht})\text{NH}_2\text{SO}_3\}_n$  appear with  $[\text{CuON}_2(\text{C}=\text{C})]$  coordination environment and corresponding angle between two rings is  $39.1^\circ$ . Contrary to the above, the steric hindrance between 2,6- substituted phenyl ring and tetrazole core in  $[\text{Cu}_2(2,6\text{-Dmpht})_2(\text{NO}_3)_2]$  dramatically change the steric configuration of ligand and the phenyl ring as well as the tetrazole cycle located practically perpendicular (the corresponding angle is  $86.5(9)^\circ$ ).

### Conclusions

Thus, novel copper(I)  $\pi$ -complex  $[\text{Cu}_2(\text{C}_{12}\text{H}_{14}\text{SN}_4)_2(\text{NO}_3)_2]$  has been synthesized by means of the alternating current electrochemical method and X-ray structurally investigated in this work.

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Received 14.06.2021

### СИНТЕЗ, КРИСТАЛІЧНА СТРУКТУРА І АНАЛІЗ ПОВЕРХНІ ХІРШФЕЛЬДА КУПРУМУ(І) НІТРАТНОГО $\pi$ -КОМПЛЕКСУ З 1-(2,6-ДИМЕТИЛФЕНІЛ)-5-АЛІЛСУЛЬФАНІЛ-1H-ТЕТРАЗОЛОМ

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Методом змінно-струмового електрохімічного синтезу, виходячи із пропанольного розчину відповідного органічного ліганду та купруму(II) нітрату, одержано та рентгеноструктурно досліджено новий  $\pi$ -комплекс купруму(I) із 1-(2,6-диметилфеніл)-5-алілсульфаніл-1H-тетразолом  $[\text{Cu}_2(\text{C}_{12}\text{H}_{14}\text{SN}_4)_2(\text{NO}_3)_2]$  (I): просторова група  $P\bar{1}$ ,  $a=7.352(3)$ ,  $b=8.269(3)$ ,  $c=12.723(4)$  Å,  $\alpha=82.08(3)$ ,  $\beta=82.74(3)$ ,  $\gamma=88.37(3)^\circ$ ,  $V=759.9(5)$  Å<sup>3</sup>,  $Z=2$ ,  $d_{\text{обч}}=1.625$  г/см<sup>3</sup>,  $\mu(\text{CuK}\alpha)=3.502$  мм<sup>-1</sup>,  $\theta_{\text{max}}=67.96^\circ$ , 4119 виміряних відбиттів, 1248 використаних відбиттів, 201 параметрів уточнення,  $R(F^2)=0.0915$ ,  $S=0.95$ . Деформоване тригонально-пірамідалне координаційне оточення атомів металу містить атом нітрогену та C=C зв'язок алільної групи ліганду разом з двома атомами кисню кристалграфічно незалежних нітрат-аніонів. Місточкова функція останніх приводить до утворення димерних топологічних одиниць  $\{\text{Cu}_2\text{L}_2(\text{NO}_3)_2\}$ , додатково стабілізованих слабкою взаємодією  $\text{Cu}\cdots\text{O}$ . Кристалічна ґратка сполуки  $[\text{Cu}_2\text{L}_2(\text{NO}_3)_2]$  додатково стабілізована слабкими водневими контактами C–H $\cdots$ O.

**Ключові слова:** купрум(I),  $\pi$ -комплекс, кристалічна структура, електрохімічний синтез, тетразол.

**SYNTHESIS, CRYSTAL STRUCTURE AND HIRSHFELD SURFACE ANALYSIS OF COPPER(I) NITRATE  $\pi$ -COMPLEX BASED ON 1-(2,6-DIMETHYLPHENYL)-5-ALLYLSULFANYL-1H-TETRAZOLE**

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By means of the alternating current electrochemical technique and starting from copper wire electrodes in propanol solution of corresponding ligand and copper(II) nitrate, novel copper(I)  $\pi$ -complex  $[\text{Cu}_2(\text{C}_{12}\text{H}_{14}\text{SN}_4)_2(\text{NO}_3)_2]$  (**1**) has been obtained and X-ray structurally investigated: sp. gr.  $P\bar{1}$ ,  $a=7.352(3)$  Å,  $b=8.269(3)$  Å,  $c=12.723(4)$  Å,  $\alpha=82.08(3)^\circ$ ,  $\beta=82.74(3)^\circ$ ,  $\gamma=88.37(3)^\circ$ ,  $V=759.9(5)$  Å<sup>3</sup>,  $Z=2$ ,  $d_{\text{calc}}=1.625$  g cm<sup>-3</sup>,  $\mu(\text{CuK}\alpha)=3.502$  mm<sup>-1</sup>,  $\theta_{\text{max}}=67.96^\circ$ , 4119 measured reflections, 1248 used reflections, 201 refined parameters,  $R(F^2)=0.0915$ ,  $S=0.95$ . The trigonal-pyramidal copper(I) coordination environment consists of nitrogen atom and allylic group of ligand, and of two oxygen atoms from crystallographically distinct nitrate anions. Due to a bridging function of oxygen atoms of nitrate anions, two metal-containing polyhedra are connected into  $\{\text{Cu}_2\text{L}_2(\text{NO}_3)_2\}$  topological units which are additionally stabilized by noncovalent interaction  $\text{Cu}\cdots\text{O}(2)$ . Comparatively weak hydrogen bonds  $\text{C}\cdots\text{H}\cdots\text{O}$  exist in the crystal structure of  $[\text{Cu}_2(\text{C}_{12}\text{H}_{14}\text{SN}_4)_2(\text{NO}_3)_2]$  (**1**).

**Keywords:** copper(I);  $\pi$ -complex; crystal structure; electrochemical synthesis; tetrazole.

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