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**π -COORDINATION COMPOUND OF COPPER(I) TETRAFLUOROBORATE
WITH N,N-DIMETHYL-4-[5-(ALLYLSULFANYL)-1H-TETRAZOL-1-
YL]ANILINE: SYNTHESIS AND STRUCTURE CHARACTERIZATION**

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A new ligand bearing a tetrazol heterocyclic core – N,N-dimethyl-4-[5-(allylsulfanyl)-1H-tetrazol-1-yl]aniline (*Dasta*) – was synthesized and used for preparation of copper(I) π -complex. Alternating current electrochemical method was used to obtain $[\text{Cu}(\text{Dasta})(\text{DastaH})][\text{BF}_4]_2 \cdot 3.5\text{H}_2\text{O}$ in form of single crystals suitable for X-ray study. This coordination compound crystallizes in monoclinic crystal system, space group *I2/a* ($a = 15.946(5) \text{ \AA}$, $b = 13.341(5) \text{ \AA}$, $c = 36.669(8) \text{ \AA}$, $\beta = 100.87(3)^\circ$, $V = 7661(4) \text{ \AA}^3$, $Z = 8$). The structure is formed by layers composed of $[\text{Cu}(\text{Dasta})(\text{DastaH})]^{2+}$ cations and a half of fluoroborate anions while the other half of the counterions connects the layers by means of intercalation. The resulting structure possesses pores which host disordered water molecules.

Keywords: copper(I), π -complex, tetrazole derivatives, crystal structure, porous structure.

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1. Introduction

π -Complexes of copper(I) and silver(I) attract attention regarding crystal engineering [1–3], catalysis [4] and as potential materials for non-linear optics applications [5, 6]. It has been shown that depending on the choice of ligand and counterions various types of structures are accessible which include ionic [7], polymer [8, 9] or molecular species [10].

A broad class of ligands for the formation of π -complexes includes heterocyclic compounds with unsaturated substituents, usually allyl [1]. The heterocyclic cores provide atoms capable of σ -coordination (N, S, O *etc*) and unsaturated fragments tend to be π -coordinated to the metal ion, therefore ligands of this type are bi- or polydentate and form either chelate cycles or coordination polymers. Many of those ligands also bear additional substituents that have an on effect the resulting crystal structure by means of non-covalent interactions [1].

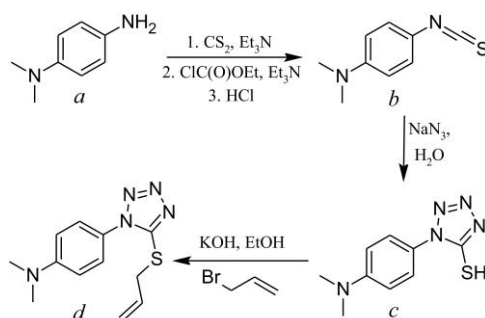
Compounds with this tetrazole moiety are extensively studied in the field of medicinal chemistry [11, 12]. Therefore, protocols for their preparation and functionalization are well-established and could be easily utilized for syntheses of “heterocycle-and-allyl” type ligands which have already been capable of forming copper π -complexes [5, 7].

In this work we prepared N,N-dimethyl-4-[5-(allylsulfanyl)-1H-tetrazol-1-yl] aniline (*Dasta*), crystallized its copper(I) π -complex $[\text{Cu}(\text{Dasta})(\text{DastaH})][\text{BF}_4]_2 \cdot 3.5\text{H}_2\text{O}$ (**1**) and studied it by means of single crystal X-ray diffraction.

2. Experimental section

2.1. Preparation of *Dasta*

Dasta was prepared in three synthetic steps according to the procedure reported previously [7] starting with *N,N*-dimethylbenzene-1,4-diamine (**a**) which was converted into respective isothiocyanate **b** via elimination of one sulfur atom from the thiocarbamate intermediate assisted by activation with ethylchloroformate (Scheme 1). Tetrazol derivative **c** was subsequently prepared through 1,3-dipolar cycloaddition reaction of **b** in water solution of sodium azide. Eventually, **c** was alkylated with allyl bromide in ethanol in presence of potassium hydroxide as a base yielding *Dasta* (**d**).



Scheme 1. Preparation of *Dasta* ligand

2.2. Preparation of $[\text{Cu}(\text{Dasta})(\text{DastaH})][\text{BF}_4]_2 \cdot 3.5\text{H}_2\text{O}$

Crystals of the coordination compound were obtained via alternating current electrochemical synthesis. Equivalent quantities of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and ligand were dissolved in ethanol. The solution was placed into a glass tube where it was sealed with a minimal volume of residual air using a rubber stopper equipped with two copper wire electrodes. Alternating voltage of 0.75 V with frequency of 50 Hz was applied to the electrodes for a day. Single crystals appropriate for X-ray diffraction measurements were collected from the electrodes.

2.3. Single crystal X-ray diffraction studies

Diffraction data for $[\text{Cu}(\text{Dasta})(\text{DastaH})][\text{BF}_4]_2 \cdot 3.5\text{H}_2\text{O}$ (**1**) crystal were collected on an Kuma KM-4-CCD diffractometer with MoK_α radiation ($\lambda = 0.71073 \text{ \AA}$). The collected diffraction data were processed with the CrysAlis PRO program [13]. The structure was solved by ShelXT program [14] and refined by least squares method on F^2 by ShelXL program [15] with the graphical user interface of OLEX² [16]. Atomic displacements for non-hydrogen atoms (except water O atoms) were refined using an anisotropic model. Position of N-bonded H atom was derived from difference Fourier maps. This H atom is statistically distributed over two sites (over two *Dasta* molecules) with an occupancy ratio of 0.699(18):0.301(18). The nearest to amino-group water O atoms are statistically disordered over three sites with an occupancy ratio of 0.699(18):0.42(3):0.301(18). Two fluorine atoms of the one anion are disordered over two sites with an occupancy ratio of 0.64(4):0.36(4). The contribution of the rest water molecules to the scattering factors was taken into account with PLATON/SQUEEZE [17]. The other hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

Table 1

Selected crystal data and structure-refinement parameters of $[\text{Cu}(\text{Dasta})(\text{DastaH})][\text{BF}_4]_2 \cdot 3.5\text{H}_2\text{O}$

CCDC number *	1962695
Empirical formula	$\text{C}_{24}\text{H}_{31}\text{CuN}_{10}\text{S}_2 \cdot 2(\text{BF}_4) \cdot 3.5\text{H}_2\text{O}$
Formula weight	823.92
Temperature, K	120
Crystal system, space group	Monoclinic, $I2/a$
a , Å	15.946(5)
b , Å	13.341(5)
c , Å	36.669(8)
β , °	100.87(3)
V , Å ³	7661(4)
Z	8
Calculated density, g/cm ³	1.429
Absorption coeff., mm ⁻¹	0.76
$F(000)$	3384
Crystal size, mm ³	$0.55 \times 0.32 \times 0.10$
Theta range for data collection, °	3.1–24.9
Measured reflections	33884
Used in refinement	6737
Refined parameters	461
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.097, 0.290, 1.02

* **CCDC 1962695** contains 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).

3. Results and discussion

π -Complex $[\text{Cu}(\text{Dasta})(\text{DastaH})][\text{BF}_4]_2 \cdot 3.5\text{H}_2\text{O}$ (**1**) crystallizes in a monoclinic crystal system, space group $I2/a$. Its structure contains one crystallographically independent Cu(I) ion and two organic moieties, which form a complex cation $[\text{Cu}(\text{Dasta})(\text{DastaH})]^{2+}$. One of the tetrazole ligand in each complex cation is statistically protonated and throughout the structure this proton is distributed between N15 and N25 atoms with an occupancy ratio of 0.301(18):0.699(18). It should be also noted that the disordering of fluoroborate anions with B1 atoms is largely associated with the disordering of N-bonded H atoms and hydrogen-bonded with it H_2O molecules. Tetrazole moieties act as chelate-bridging π, σ -ligand being attached to the metal center by η^2 -allyl group and by only one the most nucleophilic tetrazole N atom (Fig. 1, *a*). Copper(I) ion adopts distorted tetrahedral ($\tau_4=0.90$, τ_4 – four-coordinate geometry index) surrounding, including two heterocyclic N atoms and two allylic C=C bonds of the neighbouring ligands. Selected geometrical parameters of Cu1 atom are presented in Table 2.

Table 2

Bond lengths and angles in coordination sphere of Cu1 atom in $[\text{Cu}(\text{Dasta})(\text{DastaH})]^{2+}$ cation

Bond	d , Å	Angle	ω , deg.
Cu1—N14	2.054(6)	N24—Cu1—N14	105.7(2)
Cu1—N24	2.026(6)	N24—Cu1— m_1	106.1(2)
Cu1— m_1 ^a	2.068(7)	N24—Cu1— m_2	108.2(2)
Cu1— m_2	2.091(8)	N14—Cu1— m_1	107.6(2)
C13—C14	1.347(10)	N14—Cu1— m_2	103.6(2)
C23—C24	1.325(8)	m_1 —Cu1— m_2	124.3(4)

^a m_1 and m_2 – middle points of C13—C14 and C23—C24 double bonds.

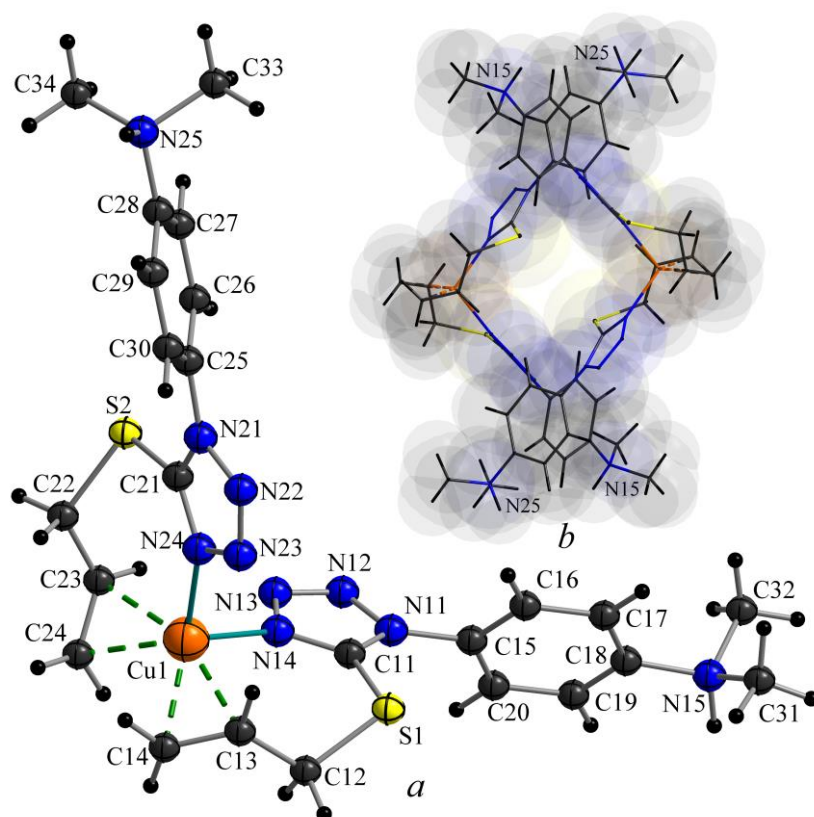


Fig. 1. (a) Structure of $[\text{Cu}(\text{Dasta})(\text{DastaH})]^{2+}$ cation. Proton is statistically distributed between N15 and N25 atoms. (b) The pair of $[\text{Cu}(\text{Dasta})(\text{DastaH})]^{2+}$ cations involved into a close contact

Cations $[\text{Cu}(\text{Dasta})(\text{DastaH})]^+$ approach each other to form pairs $\{[\text{Cu}(\text{Dasta})(\text{DastaH})]^+\}_2$ (Fig. 1, b) where the molecules contact close to the sum of Van der Waals radii. The N15 atom of one cation is situated closer to the N25 atom than to the N15 atom of the other cation resulting into a protonation pattern that avoids repulsion between adjacent moieties.

The structure of the coordination compound consists of layers formed by cation pairs arranged parallel to the xy -plane (Fig. 2, a). The structure of this two-dimensional sublattice contains voids where the fluoroborate anions with B1 atoms reside (Fig. 2, b) stabilizing the plane's integrity through electrostatic attraction.

The layers stack to form the bulk of the crystal adopting alternately two different spatial orientations (Fig. 3, a). Fluoroborate anions with B2 atoms intercalate between the layers (Fig. 3, b) contributing to the electrostatic bonding between them. Every $\{[\text{Cu}(\text{Dasta})(\text{DastaH})]^+\}_2$ pair possesses surrounding of 14 fluoroborate anions which provide electrostatic linkage between neighboring pairs of cations. Any given pair borders with four other $\{[\text{Cu}(\text{Dasta})(\text{DastaH})]^+\}_2$ pairs in its own layer, two in the layer above, and two in the layer below.

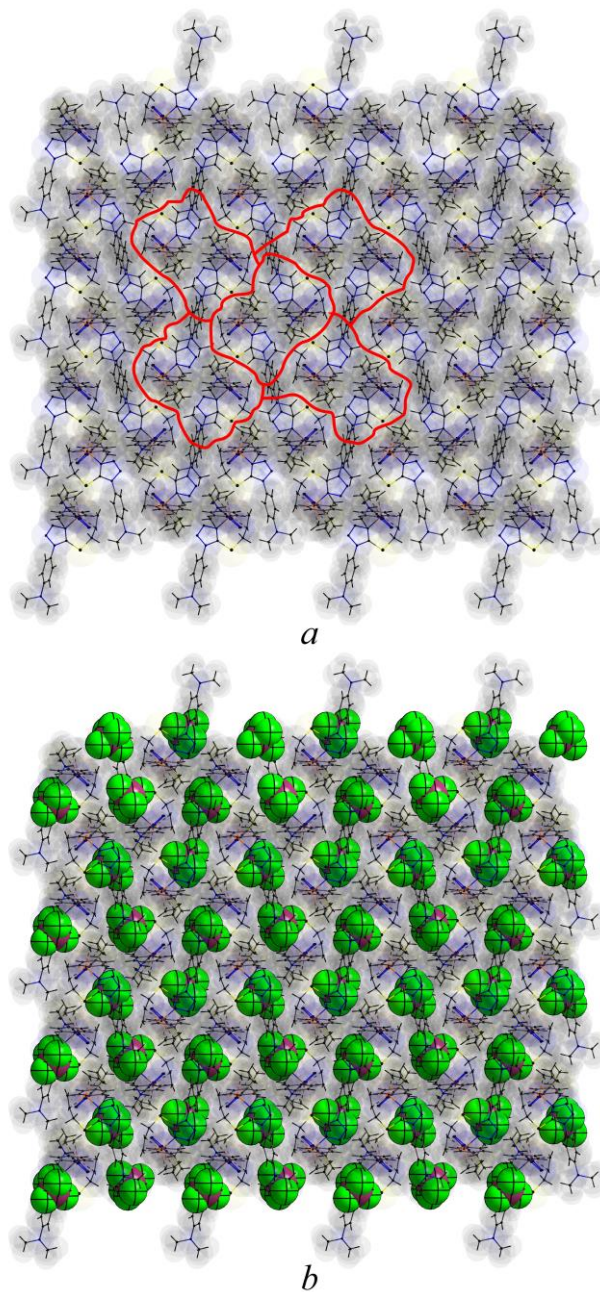


Fig. 2. (a) Fragment of the layer formed by cation pairs $\{[\text{Cu}(\text{Dasta})(\text{DastaH})]^+\}_2$ and fluoroborate counterions. Five adjacent pairs are circled for clarity.
(b) The same fragment with fluoroborate anions visible

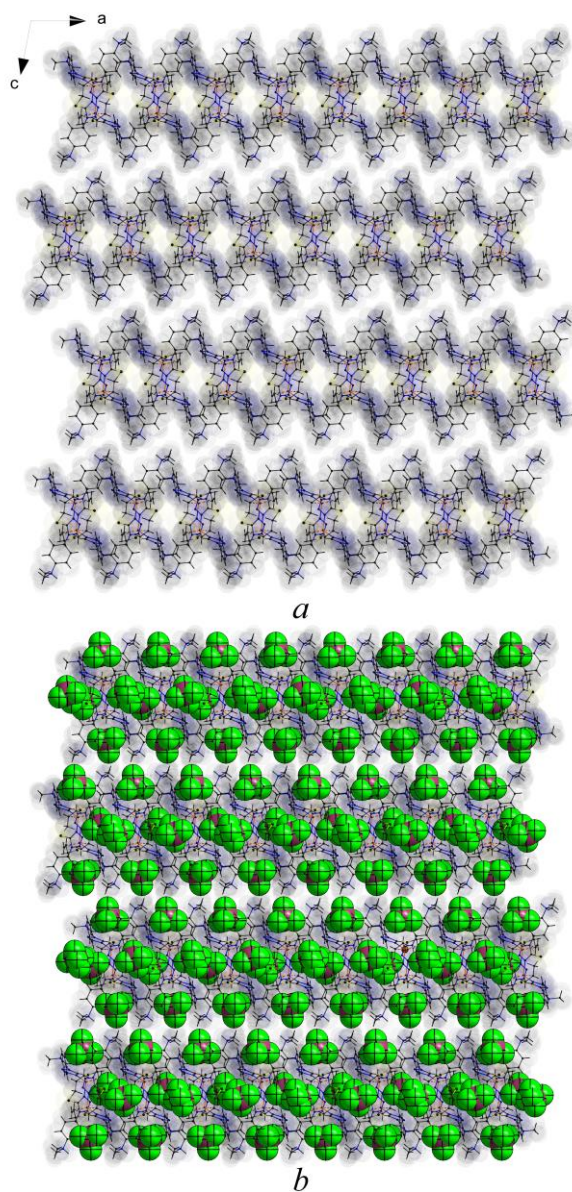


Fig. 3. (a) Packing of 2D-layers in structure of the compound.
(b) The same fragment with fluoroborate anions visible

The view along the *a* axis reveals channel-like pores in the structure where water molecules are situated (Fig. 4). Protonated N15 and N25 atoms of [Cu(*Dasta*)(*Dasta*H)]⁺ are involved into hydrogen bonding to them.

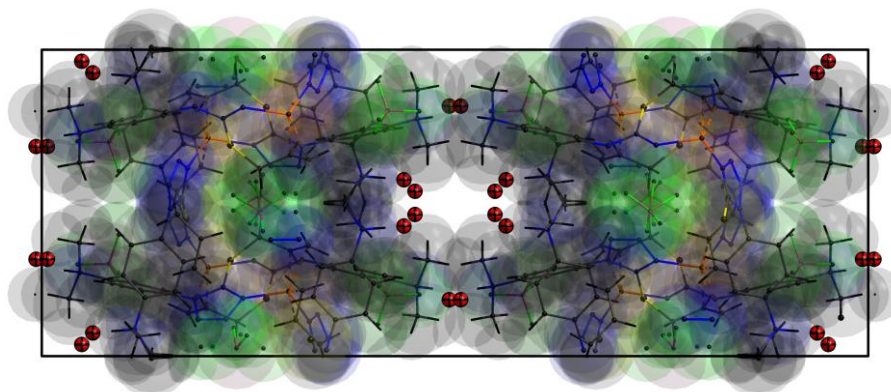


Fig. 4. Voids that stretch along the *a* axis. Positions of oxygen atoms of N–H···O-bonded intercalated water shown as red isotropic atoms

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**π -КООРДИНАЦІЙНА СПОЛУКА КУПРУМ(I) ТЕТРАФЛЮОРОБОРАТУ ІЗ
N,N-ДИМЕТИЛ-4-[5-(АЛІЛСУЛЬФАНІЛ)-1H-ТЕТРАЗОЛ-1-ІЛ]АНІЛІНОМ:
СИНТЕЗ ТА ХАРАКТЕРИСТИКА СТРУКТУРИ**

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Синтезовано новий ліганд із ядром тетразолу – N,N-диметил-4-[5-(алілсульфаніл)-1H-тетразол-1-іл]анілін (*Dasta*). Його використано для добування π -комплексу купруму(I). Змінно-струмний електрохімічний метод синтезу використали для отримання $[\text{Cu}(\text{Dasta})(\text{DastaH})][\text{BF}_4]_2 \cdot 3,5\text{H}_2\text{O}$ (**1**) у формі монокристалів, придатних для рентгеноструктурного дослідження методом монокристала. Одержана координаційна сполука кристалізується у моноклінній сингонії, просторова група $I2/a$ ($a = 15,946(5)$ Å, $b = 13,341(5)$ Å, $c = 36,669(8)$ Å, $\beta = 100,87(3)^\circ$, $V = 7661(4)$ Å³, $Z = 8$). Дифракційний масив для монокристала **1** отримано на дифрактометрі Kuma KM-4-CCD (випромінювання MoK_α , $\lambda = 0,71073$ Å). Структуру сполуки розв'язано за допомогою програми ShelXT та уточнено методом найменших квадратів по F^2 , використовуючи програму ShelXL та графічний інтерфейс OLEX². Параметри теплових зміщень для неводневих атомів (за винятком атомів O молекул води) уточнено в анізотропному наближенні. Позиції N-зв'язаного атома знайдено із різницевих синтезів Фурає. Структура комплексу містить один кристалографічно незалежний атом Cu(I) та дві незалежні органічні частинки, які формують комплексний катіон $[\text{Cu}(\text{Dasta})(\text{DastaH})]^{2+}$. Один із тетразольних лігандів кожного комплексного катіона статистично протонований і в межах структури цей протон статистично розподілений між атомами N15 і N25 зі співвідношенням КЗП 0.301(18):0.699(18). Протонована та непротонована тетразольні молекули слугують хелатно-містковими π, σ -лігандами, координуючись до металічного центру η^2 -алільною групою і лише одним найбільш нуклеофільним тетразольним атомом N. Отже, купрум(I) має деформовано-тетраедричне координаційне оточення ($\tau_4 = 0,90$, τ_4 – геометричний індекс), у яке входять два гетероциклічні атоми N та два алільні зв'язки C=C двох сусідніх лігандів. Структура побудована із шарів катіонів $[\text{Cu}(\text{Dasta})(\text{DastaH})]^{2+}$ і половини тетрафлюороборат-аніонів. Інша половина аніонів інтеркальована в структуру комплексу між шарами. Структура містить пори, у які включені молекули кристалізаційної води.

Ключові слова: купрум(I), π -комплекс, похідні тетразолу, кристалічна структура, порувата структура.

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