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The novel copper(I) π , σ -complexes with 1-(aryl)-5-(allylthio)-1*H*-tetrazoles: Synthesis, structure characterization, DFT-calculation and third-order nonlinear optics

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The present work is directed towards preparation, structure and optical property characterization of tetrazole-containing Cu(I) compounds. By means of the alternating-current electrochemical technique copper(I) π,σ -compounds with 1-(4-methylphenyl)- (*Matht*), 1-(3-chloro-4-methylphenyl)- (*Chmatht*) and 1-[2-(trifluoromethyl)phenyl]- (*Tfmatht*) 5-(allylthio)-1*H*-tetrazoles were obtained in a single crystal form and structurally characterized by X-ray diffraction and Raman spectroscopy. *Matht* and *Chmatht* ligands, being attached to the Cu(I) through S-allylic C=C-bond and two tetrazole N-atoms, form stable centrosymmetric dimers [Cu₂(*Matht*)₂(H₂O)₂](BF₄)₂ and [Cu₂(*Chmatht*)₂(ClO₄)₂]. The presence of an electron acceptor trifluoromethyl group promotes formation of the monomeric [Cu(*Tfmatht*)₂]BF₄ and [Cu(*Tfmatht*)(NH₂SO₃)(MeOH)] compounds. The compounds were investigated by means of Raman spectroscopy, third-order nonlinear optics and DFT calculations.

Keywords: Copper(I); Tetrazole; Crystal structure; DFT Calculation; Nonlinear optics

1. Introduction

The olefin copper(I) π -complexes are known to be an important class of coordination compounds possessing a versatile applicability in chemistry and biology as well as in other areas of science; they are useful as catalysts in organic syntheses, for their fluorescent activity, for their unique role in crystal structure engineering and many other useful properties [1-7]. Formation of the Cu(I)-(C=C) bond specifically reflects on the other interactions of copper(I) with σ -donor ligands

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and strongly depends on the anion type as well as on the heteroatomic organic molecule structure, its basicity, number of heteroatoms, *etc.* [2].

Copper ions may participate in a broad spectrum of intracellular processes under normal and pathologic conditions [8]. For instance, Cu(I) complexes were used for *in vitro* tests as potential anticancer drugs and have been found to be effective against A549 adenocarcinoma cells that are resistant to the widely used anticancer drug, cisplatin [9]. Moreover, cancer progression is accompanied by increased ceruloplasmin and copper levels in various tissues, and the elevated copper levels and increased oxidative stress in cancer cells provide for a prospect of selective cancer treatment [10, 11]. Taking into account that copper(I) complexes have also a couple of potential applications in advanced laser operated materials [12], the exploration of their nonlinear optical (NLO) features may be useful for the monitoring and clarification of the mentioned biochemical mechanisms.

As it was shown recently, allyl derivatives of heterocyclic compounds, which unite rigid heterocyclic cores and conformation-flexible allyl group, 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 -complexes and the direct Cu(I)...F(SiF₆²⁻) interaction have been observed in copper π -compounds with 1-allylbenzotriazole [13, 14] and with allyl-substituted 1,3,4-thiadiazoles [7, 15]. In this context, investigation of coordination behavior of allyl derivatives of some polyazoles with respect to Cu(I) in the presence of anionic Pearson's hard bases (BF₄⁻, ClO₄⁻, SO₄²⁻, *etc.*) [16] deserves special attention. Moreover, recently an appearance of high second and third order NLO susceptibilities was observed for copper(I) π -complexes with 1-allyloxybenzotriazole [4], 3-allyl-2-(allylimino)-1,3-thiazolidin-4-one and 5-(allylthio)-1-(3,5-dimethylphenyl)-1H-tetrazole ligands [17, 18].

Despite the fact that tetrazole molecules are well established ligands for 3*d*-metal complexation [19, 20], only some π -complexes of Cu(I) with allyl derivatives of tetrazole have been studied hitherto [2, 21, 22], which could be caused by complicated conditions of their preparation by classical methods. In order to examine coordinating behavior of S-allyl derivatives of different 1-(aryl)-1*H*-tetrazoles-5-thioles regarding Cu(I), this article describes synthesis and characterization of four novel [Cu₂(*Matht*)₂(H₂O)₂](BF₄)₂ (1), [Cu₂(*Chmatht*)₂(ClO₄)₂] (2), [Cu(*Tfmatht*)₂]BF₄ (3) and [Cu(*Tfmatht*)(NH₂SO₃)(MeOH)] (4)

 π -complexes with 1-(4-methylphenyl)- (*Matht*), 1-(3-chloro-4-methylphenyl)- (*Chmatht*) and 1-[2-(trifluoromethyl)phenyl]- (*Tfmatht*) 5-(allylthio)-1*H*-tetrazoles.

2. Experimental

2.1. Materials and instrumentation

Unless otherwise mentioned, all chemicals were obtained from Sigma Aldrich and used without purification. ¹H NMR spectra of *Matht*, *Chmatht* and *Tfmatht* were recorded on a Varian Mercury 400 instrument (400 MHz for ¹H) with tetramethylsilane (TMS) or a deuterated solvent as an internal reference. Single-crystal data were collected on a Rigaku AFC7 diffractometer equipped with a Mercury CCD area detector, graphite monochromated MoKa radiation. Raman spectra from crystals of **1-4** were recorded with a Horiba Jobin–Yvon LabRAM HR spectrometer with the use of the 632.81 nm excitation line of a He-Ne laser (17 mW). Carbon, hydrogen, nitrogen and sulfur contents for *Matht*, *Chmatht* and *Tfmatht* as well as for **1-4** were determined using a CHNS elemental analyzer vario EL cube (Elementar) operating in the CHNS mode (see Supplementary Materials).

2.2. Preparation of organic ligands

The target ligands **IV** (*Matht* (**a**), *Chmatht* (**b**) and *Tfmatht* (**c**)) were synthesized from 4-methyl (**I a**), 3-chloro-4-methyl- (**I b**) and 2-(trifluoromethyl)aniline (**I c**) by several procedures (scheme 1) [23-25]. The commercially available aniline **I** (0.01 mole) was dissolved in the minimum amount of benzene and treated with carbon disulphide (0.01 mole, 0.70 mL) and triethylamine (0.01 mole, 1.40 mL). The solution was cooled to 0 °C and left for 5 days. After complete precipitation of the triethylammonium dithiocarbamate salt, the solution was filtered. The solid was washed with anhydrous ether and air dried for about 10 min. The salt was then dissolved in about 7.5 mL of chloroform, treated with 1.4 mL of triethylamine and cooled to 0 °C. To the solution was added ethyl chloroformate (0.01 mole, 1.02 mL) dropwise over a 15 min period under intense stirring. The resulting solution was stirred at 0 °C for 10 min and allowed to warm to room temperature for 1 h. The chloroform solution was evaporated and the aryl isothiocyanate **II** was distilled *in vacuo*.

The obtained isothiocyanate **II** (0.005 mole) was mixed with water (10 ml) and NaN₃ (0.011 mole, 0.715 g) and refluxed with intense stirring until the suspension disappeared. The solution was cooled to room temperature and washed with TBME. Water was separated and acidified with 3M HCI (*Caution! The HN₃ elevation*). The sediment of 1*H*-tetrazole-5-thiol **III** was separated by the filtration and used for alkylation without further purification.

The 1*H*-tetrazole-5-thiol **III** (0.004 mole) was dissolved in solution of KOH (0.004 mole, 0.224 g) in ethanol (10 mL). To the solution allyl bromide (0.005 mole, 0.43 mL) was added and the mixture was heated at 50 °C for 1 h. Solvent removed *in vacuo* and to the residue was added water 5 mL and dichloromethane 10 mL. Dichloromethane was separated and removed to give target ligand **IV**.

1-(4-Methylphenyl)-5-[(prop-2-en-1-yl)sulfanyl]-1*H*-tetrazole, $C_{11}H_{12}N_4S$ (*Matht*), m.p. 34 °C; ¹H NMR (400 MHz, DMSO-d₆), δ , p.p.m. 7.46 (d, J = 8.2 Hz, 2H, H_{Ph} -3,5), 7.42 (d, J = 8.2 Hz, 2H, H_{Ph} -2,6), 5.97 (td, J = 16.8, 7.0 Hz, 1H, =CH), 5.36 (d, J = 17.0 Hz, 1H, CH₂=), 5.18 (d, J = 9.8 Hz, 1H, CH₂=), 3.99 (d, J = 7.0 Hz, 2H, CH₂), 2.46 (s, 3H, CH₃).

1-(3-Chloro-4-methylphenyl)-5-[(prop-2-en-1-yl)sulfanyl]-1*H*-tetrazole, $C_{11}H_{11}CIN_4S$ (*Chmatht*), m.p. 47 °C; ¹H NMR (400 MHz, DMSO-d₆), δ , p.p.m. 7.62 (s, 1H, H_{Ph}-2), 7.54 (d, J = 8.2 Hz, 1H, H_{Ph}-5), 7.45 (d, J = 8.2 Hz, 1H, H_{Ph}-6), 5.99 (td, J = 17.0, 7.0 Hz, 1H, =CH), 5.39 (d, J = 17.0 Hz, 1H, CH₂=), 5.20 (d, J = 9.9 Hz, 1H, CH₂=), 4.02 (d, J = 7.0 Hz, 2H, CH₂), 2.48 (s, 3H, CH₃).

 $5-[(Prop-2-en-1-yl)sulfanyl]-1-[2-(trifluoromethyl)phenyl]-1H-tetrazole, C_{11}H_9F_3N_4S$ (*Tfmatht*), m.p. 63 °C; ¹H NMR (400 MHz, DMSO-d₆), δ , p.p.m. 8.03 (d, *J* = 7.3 Hz, 1H, H_{Ph}-3), 7.98-7.88 (m, 2H, H_{Ph}-4,5), 7.71 (d, *J* = 7.3 Hz, 1H, H_{Ph}-6), 5.94 (td, *J* = 16.8, 7.2 Hz, 1H, =CH), 5.36 (d, *J* = 16.8 Hz, 1H, CH₂=), 5.18 (d, *J* = 9.9 Hz, 1H, CH₂=), 3.98 (d, *J* = 6.9 Hz, 2H, CH₂).



Scheme 1. Synthesis of the tetrazole ligands.

2.3. Synthesis of copper(I) π -complexes

Crystals of complexes were obtained under conditions of alternating-current electrochemical synthesis [26] starting from the alcohol solution of the appropriate organic ligand and copper(II) salt.

2.3.1. Preparation of $[Cu_2(Matht)_2(H_2O)_2](BF_4)_2$ (1). To 2.5 mL of *n*-propanol solution of $Cu(BF_4)_2 \cdot 6H_2O$ (1.000 mmol, 0.345 g) 2.0 mL of *n*-propanol solution of *Matht* (0.689 mmol, 0.160 g) was added. The prepared grass-green solution was placed into a small 5 mL test-tube and then copper-wire electrodes in cork were inserted. By the application of alternating-current tension (frequency 50 Hz) of 0.4 V for 3 days, good quality colorless crystals of 1 (bis(μ - η^2 -1-(4-methylphenyl)-5-[(prop-2-en-1-yl)sulfanyl]-1*H*-tetrazole)-diaqua-di-copper(I) bis(tetrafluoroborate)) appeared on copper electrodes. The formed crystals are easily detached from the electrode and accumulate at the bottom of the test-tube, from which they were isolated

2.3.2. Preparation of $[Cu_2(Chmatht)_2(ClO_4)_2]$ (2). To 2.0 mL of *n*-propanol solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.800 mmol, 0.296 g) 2.0 mL of *n*-propanol solution of *Chmatht* (0.791 mmol,

by the filtration. The yield was 0.028 g (10%). Decompose with partial melting at 283 °C.

0.211 g) was added. By the application of alternating-current tension (frequency 50 Hz) of 0.6 V for 7 days, the turquoise slightly turbid solution was discolored and good quality colorless crystals of **2** (bis(μ - η^2 -1-(3-chloro-4-methylphenyl)-5-[(prop-2-en-1-yl)sulfanyl]-1*H*-tetrazole)-bis((perchlorato-O))-di-copper(I)) appeared on copper electrodes. The formed crystals were isolated as in the previous example. The yield was 0.085 g (25%). Decompose with microexplosion at 230 °C.

2.3.3. Preparation of [Cu(Tfmatht)₂]**BF**₄ (3). To 2.5 mL of *n*-propanol solution of Cu(BF₄)₂·6H₂O (1.000 mmol, 0.345 g) 2.0 mL of *n*-propanol solution of *Tfmatht* (0.900 mmol, 0.258 g) was added. The resulting green solution was subjected to alternating-current tension (frequency 50 Hz) of 0.4 V for 4 days. Good quality colorless crystals of **3** (bis(μ - η^2 -5-[(prop-2-en-1-yl)sulfanyl]-1-[2-(trifluoromethyl)phenyl]-1*H*-tetrazole)-copper(**I**) tetrafluoroborate) appeared on copper electrodes. The formed crystals were isolated as in the previous examples. The yield was 0.114 g (35%). Decompose at 289 °C.

2.3.4. Preparation of [Cu(Tfmatht)(NH₂SO₃)(MeOH)] (4). To 3.0 mL of a saturated methanol solution of Cu(NH₂SO₃)₂ 1.5 mL of methanol solution of *Tfmatht* (0.700 mmol, 0.200 g) was added. The resulting yellow-green slightly turbid solution was subjected to alternating-current tension (frequency 50 Hz) of 0.6 V for 10 days. Good quality colorless crystals of **4** (methanol- $(\mu-\eta^2-5-[(\text{prop-2-en-1-yl})\text{sulfanyl}]-1-[2-(trifluoromethyl)\text{phenyl}]-1H-tetrazole)-(sulfamato-N)-copper(I)) appeared on copper electrodes, from which they were detached by mechanical removal. The yield was 0.084 g (25%). Melt with partial decomposition at 155 °C.$

2.4. Crystallographic studies

The crystallographic parameters and summaries of data collection for 1-4 are presented in table 1. The collected diffraction data were processed with the Rigaku CrystalClear software suite program package [27]. Structures 1-3 were solved by direct methods with the use of SIR-92 program (implemented in the program package WinGX [28, 29]) and structure 4 was solved by ShelXT program. All structures were refined by least squares method on F^2 by the ShelXL program with the following graphical user interface of OLEX² [30-32]. Full–matrix least–squares refinements based on F^2 were carried out for the positional and thermal parameters for

all non-hydrogen atoms. In **1**, three fluorine atoms of BF_4^- anion are disordered over two sites and refined anisotropically with occupancy of 0.5. In **3**, fluorine atoms of $-CF_3$ group are disordered over two sites with an occupancy ratio of 0.83(2):0.17(2). Positions of O-bonded H atoms in **1** were derived from the Fourier difference syntheses and refined isotropically with O–H fixed distance. Positions of the other H atoms in **1-4** were treated as riding atoms and refined with E–H fixed distances. The figures were prepared using DIAMOND 3.1 software [33]; the ellipsoids are drawn at 40% probability level.

2.5. Nonlinear optical measurements

Third harmonic generation (THG) studies were performed using Nd:YAG laser with pulse duration 10 ns and frequency reception 10 Hz. An interferometric filter at 355 nm was used for spectral separation of the third harmonic with respect to the fundamental beams. A rotating Glahn prism was used for tuning of the fundamental energy density and photomultiplier with relaxation about 1 ns is used for the THG detection.

2.6. Computational methods

All calculations were performed on the DFT/B3LYP/cc-PVDZ level [34, 35] using the GAMESS(US) program package [36]. A basis set with effective core potentials (ECPs) was applied for the copper atoms. The initial geometries, derived from the crystal structures, were assumed to have C_1 symmetry and were utilized for the geometry optimization. The equilibrium geometries obtained were used for the Forces Constants matrix calculation. Then polarizability tensor was calculated and the resulting Raman activities (S_i) were converted to Raman intensities (I_i) using the relationship from the intensity theory of Raman scattering [37, 38].

3. Results and discussion

3.1. Crystal structures

In crystal structure of $[Cu_2(Matht)_2(H_2O)_2](BF_4)_2$ (1) the organic molecule 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 core and the C=C bond from S-allyl group (see figure 1 and table 2). These three active sites form a basal surrounding of the Cu(I) in its trigonal pyramidal arrangement; the fourth apical position is occupied by H₂O molecule. As a result, copper(I) atoms links up the two

adjacent *Matht* molecules into centrosymmetric cationic $[Cu_2(Matht)_2(H_2O)_2]^{2+}$ dimer containing two six-membered CuC₄SN (considering the C=C bond as one coordinating site) and one six-membered Cu₂N₄ rings.

The analogous $[Cu_2(L)_2(H_2O)_2]^{2+}$ dimers have been found earlier in two π -complexes of CuBF₄ with 1-phenyl- and 1-(4-chlorophenyl)-5-(allylthio)-1*H*-tetrazoles [39]. Due to a significant hardness in HSAB terms of the fluorine atoms of BF₄⁻, they are substituted by OH₂ in the metal coordination environment, therefore outer-sphere BF₄⁻ anions are bound by the O-H…F(BF₄⁻) hydrogen bonds only (table S1, Supplementary Materials). All these facts are in a good agreement with the Pearson's HSAB principles [16], according to which the heterocyclic N atoms, possessing border line basicity as well as soft C=C base, are more favorable to coordination with soft Cu(I) ion than H₂O or even such hard bases as BF₄⁻ or SiF₆²⁻ anions.

Addition of *m*-Cl substituent at the 4-methylphenyl group does not prevent *Chmatht* molecule in structure of $[Cu_2(Chmatht)_2(ClO_4)_2]$ (2) from formation of centrosymmetric $[Cu_2(Chmatht)_2]^{2+}$ dimers. Copper(I) coordination environment is arranged in a similar way to 1 and includes in basal plane N atoms and C=C bond (see figure 2 and table 2). The apical position of the polyhedron is occupied by O atom of the ClO₄⁻ anion. It is worth noting that analogous stable "building blocks" $[Cu_2(L)_2]^{2+}$ were recently observed in structures of Cu(I) π -complexes with allyl-substituted 1,3,4-thiadizoles, 1,3,4-oxadiazoles and 1,2,4-triazoles [15, 40, 41].

In the case of *o*-substituted trifluoromethylphenyl derivative, *Tfinatht*, another mode of coordination was observed; both [Cu(*Tfmatht* $)_2]BF_4$ (**3**) and [Cu(*Tfmatht* $)(NH_2SO_3)(MeOH)]$ (**4**) appeared to be monomers (see figures 3 and 4). In the structure of **3**, Cu(I) atom lies on the two-fold axis and adopts disordered tetrahedral environment, comprised of two C=C bonds from allyl groups and two N4 atoms from *Tfmatht* molecules (see table 3). It is clear that the presence of CF₃ group in ortho-position of the phenyl ring significantly reduces nucleophilic activity of tetrazole N atoms. Most probably, not only electronic factors, but also significant steric hindrance prevents participation of N3 in the tetrazole in metal coordination. Also, such structural stress affects the geometry of the ligand: the dihedral angle between the planes of tetrazole and phenyl rings equals 78.0° in **3**, in comparison to 41.1° in **1** and 67.3° in **2**.

Simultaneous coordination of two N atoms and two C=C bonds to the same Cu(I) center occurs relatively rarely; hitherto, it has been found only in a few copper(I) π -complexes in the presence of BF₄⁻, ClO₄⁻ and PF₆⁻ anions only [42-45].

The N atom in the $NH_2SO_3^-$ anion successfully competes with the heterocyclic moiety, replacing tetrazole N atom in Cu(I) coordination environment. Due to a significant increase of d_{z2} -energy, this anion completely excludes another *Tfmatht* molecule from the metal coordination sphere in structure of [Cu(*Tfmatht* $)(NH_2SO_3)(MeOH)]$ (4). The Cu(I) atom environment in **4** is close to a trigonal pyramid. It is composed of two basal N atoms and allylic C=C bond, while the fourth apical position is occupied by O atom of CH₃OH molecule (see table 3). Although the $NH_2SO_3^-$ anion is able to be bound to Cu(I) simultaneously by N and O atoms [17, 46], the hydroxyl group of the methanol molecule appeared to be more favorable in **4**. The last fact may be caused by a significant role of N–H···O–S hydrogen contacts involving NH₂SO₃ fragments (table 4). The S–O···H–O hydrogen contacts between the sulfamate anion and hydroxyl group of methanol together with N–H···O–S bonding connect individual [Cu(*Tfmatht*)(NH₂SO₃)(MeOH)] complex fragments into infinite chains.

One may note that the efficiency of Cu(I)–(C=C) interaction in 1, 2 and 4 is confirmed by rather short Cu–*m* (*m* – a middle point of the C=C bond) distances and rather large C–Cu–C angles (figure captions 1-4). The fact that Cu(I) deviates from the base of the trigonal pyramid by 0.36 Å (1), 0.19 Å (2) and 0.44 Å (4) (as well as the angle between the C=C bond and base plane is 24.1° (1), 10.8° (2) and 5.4° (4)) also confirms this conclusion [2].

3.2. Computational results

In order to get deeper insight into the molecular structures of **1-4**, calculations at B3LYP/ccpVDZ level were performed. The experimental molecular geometries were utilized as an initial point for geometry optimization. The optimized structures are shown in figures S1-S4, Supplementary Materials, and selected geometrical parameters for every compound in comparison to the experimental ones are provided below each figure. Equilibrium geometries appeared to be very close to the experimental values; so, for **1** and **2** at equilibrium point CuN4Cu hexagon is slightly bent towards chair conformation in the way that Cu atoms protrude from the plane formed by four nitrogen atoms, giving dihedral angles $N3^iN4N3Cu$ and $N4^iN3N4Cu^i$ of 13.0° and 12.7° in **1** and 9.3° and 9.6° in **2**.

The first HOMO/LUMO orbitals are represented in figure 5. There is very interesting difference related to the localization of the latter. In 1 and 2, the HOMOs are located mostly along the π -bond between the allyl groups and Cu atoms and ligands/anions bounded to metal

centers, whereas the LUMOs are situated on the tetrazole and aromatic rings. The same distribution is preserved in **4**, where most of the HOMO is located around the $SO_3NH_2^-$ anion. A rather different case is observed for **3**, where the HOMO is predominately localized on the tetrazole, sulphur atom, allyl group and copper, and the LUMO is predominately localized on π -bonds between allyl groups and copper atom indicating lack of electron density on these atoms, which allows for further substitution of a *Tfmatht* ligand by another σ -donor ligand. The HOMO-LUMO gaps for all the compounds have high values of at least 4.68 eV (**2**) (see figure 5), indicating that these compounds could adsorb light in UV diapason. The equilibrium geometries were utilized for calculation of the Raman spectra; absence of the imaginary frequencies confirmed the optimizations convergence to real minimum.

3.3. Raman spectra

The Raman spectra of 1-3 are shown in figure 6, this of 4 was not possible to collect due to too intense fluorescence. The band assignments were made on the basis of computed Raman spectra (see tables S1-S4). The bands due to BF_4^- anions in 1 and 3 were assigned in agreement with the literature sources [47].

The computed and experimental spectra appeared to be in good agreement with the exception of **2**, where discrepancies in relative intensities appeared. Presumably, the difference is caused by lattice contribution to resulting polarizability tensor in the experiment, whereas this effect is not taken into account while calculating bands of a single molecule. The allyl v(C=C) band, which is most frequently considered to be characteristic for these compounds, is found to appear at 1537, 1528 and 1591 cm⁻¹ in the spectra of **1**, **2** and **3**, respectively. Apparently, the bond Cu–(C=C) in **3** is the weakest among these compounds, as a significant red shift is expected in a case of strong bonding [15, 48].

3.4. Nonlinear optical properties

The results of third order nonlinear optical studies are presented in figure 7. Well-known BiB_3O_6 crystals were applied as a standard; the observed THG signal intensity appeared to comprise about 30% with respect to BiB_3O_6 . The other samples show very similar magnitudes and the difference between them is within the experimental errors. Among the compounds investigated, the intensity of THG follows the order 3>4>1 in all the ranges of pump laser powers.

Presumably, monomeric Cu(I) units are more favorable targets for THG studies. It might be suggested that by means of optimization of π , σ -donating ligands, better performance might be achieved.

4. Conclusion

The utilization of alternating-current electrochemical technique allowed us to prepare and isolate single crystals of copper(I) π,σ -coordination compounds containing 1-(4-methylphenyl)- (*Matht*), (*Chmatht*) and 1-[2-(trifluoromethyl)phenyl]- (*Tfmatht*) 1-(3-chloro-4-methylphenyl)-5-(allylthio)-1*H*-tetrazoles. The coordination environment of Cu(I) was found to be affected by presence of electron acceptor group in a ligand and by the nature of anion/ligands according to Pearson's HSAB principles. These factors promote a complete change of the Cu(I) surrounding, leading to either dimeric complexes or to monomeric in a case of $[Cu(Tfmatht)_2]BF_4$ and [Cu(*Tfmatht*)(NH₂SO₃)(MeOH)]. The geometries and HOMO/LUMO orbitals were analyzed by means of *ab initio* DFT calculations. Detailed analysis of the Raman spectra of the compounds was made on the basis of computed vibrational spectra. The conclusions of this work open new avenues for intentional preparation of Cu(I) compounds with predetermined geometry, which might be suitable for further investigation of nitrogen-rich compounds. The studied samples possess the THG efficiency equal to about 30% with respect to the well-known BiB₃O₆ crystals.

Supporting information

CCDC 1857210, 1857211, 1857212 and 1857213 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).

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Table 1. Crystal data and structure refinement for 1-4.

	1	2	3	4
CCDC number	1857210	1857211	1857212	1857213
Empirical formula	$C_{22}H_{28}B_2Cu_2F_8N_8O_2S_2$	$C_{22}H_{22}Cl_4Cu_2N_8O_8S_2$	$C_{22}H_{18}BCuF_{10}N_8S_2$	$C_{12}H_{15}CuF_3N_5O_4S_2$
Formula weight (g/mol)	801.34	859.47	722.94	477.95
Temperature, K	200(2)	200(2)	200(2)	200(2)
Wavelength (Å)	0.71069	0.71069	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>C</i> 2/ <i>c</i>	$P2_1/a$	<i>C2/c</i>	P-1
Unit cell dimensions (Å, °)				
a, Å	20.431(6)	9.000(3)	12.681(4)	7.241(3)
b, Å	7.659(3)	14.959(4)	10.474(4)	8.213(3)
<i>c</i> , Å	20.896(6)	11.870(4)	21.402(6)	16.215(5)
α, °	90	90	90	75.03(3)
β, °	97.70(3)	96.42(3)	96.93(3)	79.09(3)
γ, °	90	90	90	78.59(3)
$V, Å^3$	3240.3(19)	1588.0(9)	2821.9(16)	903.4(6)
Ζ	4	2	4	2
Calculated density (g/cm ³)	1.643	1.797	1.702	1.757
Absorption coeff. (mm ⁻¹)	1.523	1.866	1.019	1.500
F(000)	1616	864	1448	484
Crystal size (mm)	$0.11 \times 0.1 \times 0.06$	$0.14 \times 0.12 \times 0.1$	0.12 imes 0.1 imes 0.1	$0.11 \times 0.08 \times 0.07$
Color	Colorless	Colorless	Colorless	Colorless
Theta range for data collection (°)	2.0 - 27.7	1.7 – 28.4	1.9 - 29.3	2.6 - 29.1
Measured reflections	6251	6213	3091	8770
Used in refinement	3125	3027	3091	3776
Free parameters	243	208	210	248
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.0622, 0.1941, 1.115	0.0579, 0.1813, 1.129	0.0522, 0.1563, 0.966	0.0464, 0.1289, 1.121

Bond	1	2	Angle	1	2
Cu–N3 ⁱ	1.988(4)	1.968(4)	C3CuC4	38.4(2)	38.8(2)
Cu–N4	2.013(4)	1.975(4)	m–Cu–N3 ^{i}	127.6(2)	130.0(2)
Cu-O1	2.217(4)	2.397(4)	<i>m</i> –Cu–N4	114.6(2)	116.7(2)
Cu–m	1.946(5)	1.923(5)	N3 ⁱ -Cu-N4	107.9(2)	110.4(2)
C3–C4	1.353(7)	1.353(8)	N3 ⁱ –Cu–O1	92.9(1)	87.6(2)

Table 2. Selected bond distances (Å) and angles (°) in **1** and **2**.

m – a mid-point of C3–C4 double bond. Symmetry code: (i) 1–x, 1–y, 1–z.

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3					
Cu–N4	2.059(3)	C3–Cu–C4	35.4(1)		
Cu–m	2.068(3)	m –Cu– m^i	124.1(2)		
C3–C4	1.321(5)	<i>m</i> –Cu–N4	108.7(2)		
		m–Cu–N4 ^{i}	105.4(2)		
		N4–Cu–N4 ⁱ	102.6(2)		
4					
Cu–N4	2.020(3)	C3–Cu–C4	38.5(1)		
Cu–N5	2.055(3)	<i>m</i> –Cu–N4	117.1(1)		
Cu–O4	2.160(3)	N4–Cu–N5	96.8(1)		
Cu–m	1.944(3)	N4–Cu–O4	95.5(1)		
C3–C4	1.358(5)	N5–Cu–O4	102.0(1)		

Table 3. Selected bond distances (Å) and angles (°) in 3 and 4.

m – is a mid-point of C3–C4 double bond. Symmetry code: (i) 1–x, y, 0.5–z.

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Atoms involved	Symmetry	D	Angle, deg			
D–H…A		D····H	H···A	D····A	D−H…A	
		1				
O1–H1A…F4	1- <i>x</i> , 2- <i>y</i> , 1- <i>z</i>	0.86(1)	1.89(1)	2.748(5)	174(6)	
O1-H1B…F1A		0.86(1)	2.36(5)	3.12(2)	148(8)	
O1−H1B…F2A		0.86(1)	2.21(4)	3.01(1)	154(8)	
O1−H1B…F1B		0.86(1)	2.06(5)	2.85(2)	151(8)	
		4			X	
O4−H4…O1	1-x, -y, 1-z	0.87	1.84	2.699(4)	169	
N5−H5A…O2	1-x, 1-y, 1-z	0.91	2.35	3.194(3)	154	
N5-H5B…O3	1-x, -y, 1-z	0.91	2.26	3.159(3)	172	
Acepted Manus						

Table 4. Geometry of selected hydrogen bonds in 1 and 4.

Graphical Abstract



Figure captions



Figure 1. Cationic $[Cu_2(Matht)_2(H_2O)_2]^{2+}$ dimer in crystal structure 1. Symmetry code: (*i*) 1–*x*, 1–*y*, 1–*z*.

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Figure 2. Molecular fragment of crystal structure **2**. Symmetry code: (i) -x, 1-y, 1-z.



Figure 3. Fragment of crystal structure 3. Symmetry code: (i) 1-x, y, 0.5-z. One of the two disordered positions of a fluorine atom with lower s.o.f. value is shown in semitransparent mode.

RcceR



Figure 4. Molecular fragment of crystal structure **4** (*a*) and a part of polymeric chain of earlier studied complex $[Cu(C_{12}H_{14}N_4S)NH_2SO_3]_n$ [17] (*b*).

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Figure 5. HOMO (left) and LUMO (right) orbitals of compounds 1-4. For the clarity of representation, only cation of compound 1 is shown. HOMO-LUMO band gaps have the values of 4.94 eV (1), 4.68 eV (2), 5.17 eV (3) and 5.87 eV (4).



Figure 6. Raman spectra of compounds 1-3. Detailed band lists and assignments are provided in Supplementary Materials.

, C C K



Figure 7. Dependence of the THG versus the fundamental power energy.

