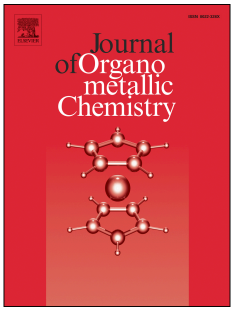

Influence of apical ligands on Cu–(C=C) interaction in Copper(I) halides (Cl^{-}, Br^{-}, I^{-}) π-complexes with an 1,2,4-triazole allyl-derivative: Syntheses, crystal structures and NMR spectroscopy

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PII: S0022-328X(17)30170-5

DOI: 10.1016/j.jorganchem.2017.03.022

Reference: JOM 19856

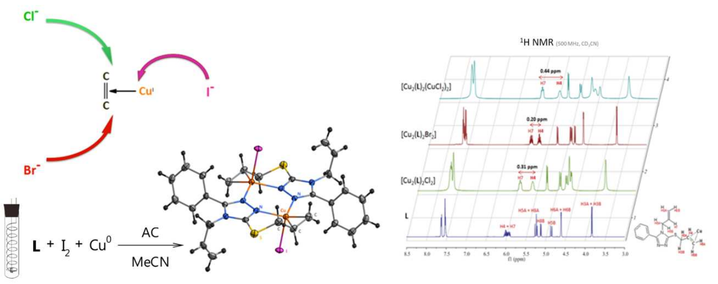
To appear in: *Journal of Organometallic Chemistry*

Received Date: 16 December 2016

Revised Date: 7 March 2017

Accepted Date: 9 March 2017

Please cite this article as: O.R. Hordiychuk, V.V. Kinzhybalo, E.A. Goreshnik, Y.I. Slyvka, M.S. Krawczyk, M.G. Mys'kiv, Influence of apical ligands on Cu–(C=C) interaction in Copper(I) halides (Cl^{-}, Br^{-}, I^{-}) π-complexes with an 1,2,4-triazole allyl-derivative: Syntheses, crystal structures and NMR spectroscopy, *Journal of Organometallic Chemistry* (2017), doi: 10.1016/j.jorganchem.2017.03.022.


Cl⁻
Br⁻
I⁻
C
C
Cuᴵ
L + I₂ + Cu⁰
AC
MeCN
¹H NMR (500 MHz, CD₃CN)
[Cu₂(L)₂(CuCl₂)₂]
0.44 ppm
[Cu₂(L)₂Br₂]
0.20 ppm
[Cu₂(L)₂Cl₂]
0.31 ppm
L
H7
H8
f1 (ppm)

Influence of Apical Ligands on Cu–(C═C) Interaction in Copper(I) Halides (Cl^-, Br^-, I^-) π-Complexes with an 1,2,4-Triazole Allyl-Derivative: Syntheses, Crystal Structures and NMR Spectroscopy

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ABSTRACT: New multifunctional 1,2,4-triazole based allyl-derivative as the ligand **L** (3-allylsulfanyl-4-allyl-5-phenyl-4*H*-1,2,4-triazole) revealed an ability to form stable binuclear copper(I) π-complexes. A series of related Cu(I) halides π-complexes, $[Cu_2(\mathbf{L})_2X_2]$ (X = Cl, **1a**; Br, **1b**; I, **1c**), $[Cu_2(\mathbf{L})_2I_2]_2$ (**1c'**), $[Cu_2(\mathbf{L})_2(CuCl_2)_2]$ (**2**), $[Cu_2(\mathbf{L})_2Cu_2Br_4]$ (**3**) was obtained by alternating-current electrochemical synthesis, starting from acetonitrile solutions of the ligand **L** and CuX_2 (in the case of **1a**, **1b**, **2**, **3**) or I_2 (**1c**, **1c'**). This is the first notice of using iodine being reduced at copper electrodes under alternating current in the presence of a ligand for copper(I) iodide complexes synthesis. The crystal structures were determined by means of single crystal X-ray diffraction. The organic ligand acts as multidentate chelating σ,π-donor using triazole *(tr)* and η^2-allyl moieties, resulting in a formation of the dimeric $\{Cu_2N_4\}$ core with a trigonal-pyramidal (2N, C=C + X) environment of the Cu atom. Packing polymorphism was revealed for the iodine complex. In the case of **2** and **3** the Cu centers participate in a formation of both – metal-organic cations and copper(I)halide anions. In structure **3**, the copper(I)-halide subunit is organized in the $Cu_2(\mu_2\text{-}Br)_2Br_2$ cluster that links organometallic moieties leading to a 1D ladder fragment. High inertia of complexes in acetonitrile solutions enabled a comparative evaluation of a strength of the Cu(I)–(C═C) interaction by means of ^1H NMR spectra. NMR spectroscopic studies are consistent with the structural analysis.

KEYWORDS: Copper(I); η^2-Interaction; Electrochemical synthesis; ^1H NMR spectra; Allyl Derivatives; 1,2,4-Triazole.

1. Introduction

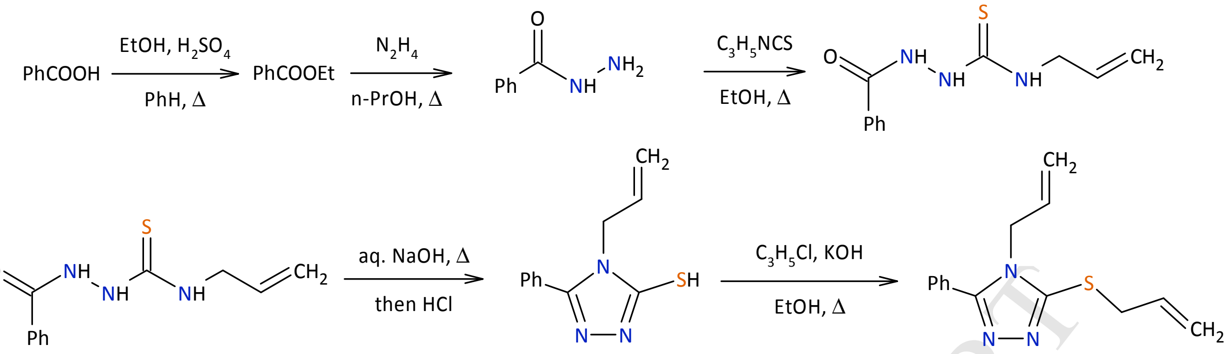
A formation of copper(I) π-complexes is caused by a specific role of a directed Cu(I)-(C═C) interaction. Usually unstable copper – olefin adducts could be stabilized in a presence of σ-donor atoms, for example from heterocyclic cores. Interaction with various anions (except the case of weakly bonded ones) also presents in such compounds and influences strongly on the copper – olefin interaction. Synergy of a conformationally rigid heterocyclic core and the flexible allyl group plays an exclusively important role in a formation of the unique fragments [1,2,3], resulting in complexes that exhibit a range of useful properties [4,5]. Recent researches on copper(I) π-complexes have been devoted considerably to catalytic [6,7], biological [8], photoluminescence [9] and optoelectronic [10] properties of these compounds as well as to their application as an effective instrument in crystal engineering of metal-organic frameworks [11,12]. It was shown that among copper(I) halides, copper(I) iodide demonstrates the highest activity in catalysis of some organic synthesis reactions due to the formation of key Cu(I)-olefin complexes that is facilitated by the directing effect of the group that contains the σ-donor atom [13,14]. On the other hand only four structures of copper(I) iodide – olefin π-complexes can be found in the Cambridge Structural Database (5.37 – May 2016).

In recent years copper(I) π-complexes with a wide range of nitrogen-containing heterocyclic ligands were obtained by virtue of new synthetic approaches[1]. In particular, many such complexes with 1,2,3-triazole derivatives have been studied [15–17], and we herein introduce copper(I) π-complexes with a 1,2,4-triazole (*tr*) allyl derivative. 1,2,4-Triazole derivatives are well-known ligands successfully used as tectones in crystal engineering [18,19]. They are also potential antibacterial agents [20]. Nevertheless, there is no information on copper(I) π-complexes with 1,2,4-triazole allyl-derivatives in the Cambridge Structural Database. Therefore, we obtained copper(I) chloride, bromide and iodide π-complexes to study the coordination behavior of this ligand and particularly the influence of coordination surrounding of copper(I) on the effectiveness of Cu(I)-(C═C) interaction. The results are represented in this report.

2. Material and Methods

2.1. Synthesis of the Organic Ligand

The ligand **L** was obtained in several steps as shown in Scheme 1. Benzhydrazide was prepared in two steps from benzoic acid by a typical procedure. Then a solution of allyl isothiocyanate (1.98 g, 20 mmol) in 10 mL of ethanol was added dropwise to the hot solution of benzhydrazide (2.72 g, 20 mmol) in 25 mL of ethanol. The prepared mixture was heated under reflux for 4 hours and than ice-cooled. The obtained white precipitate was filtered off and then recrystallized from the ethanol to give N-allyl-2-benzoylhydrazinecarbothioamide as white needles. Yield: 4.0 g (85 %), m.p. 185 °C. This synthon was subjected to alkaline cyclization similarly to the described procedure [21]. A solution of 27.3 g. (0.116 mol) of N-allyl-2-benzoylhydrazinecarbothioamide and 4.8 g. (0.12 mol) of sodium hydroxide in 35 ml. of water in a round-bottomed flask is heated on a steam bath for 1 hour. The solution is cooled for 30 minutes in an ice bath and then is treated with 11 ml. of concentrated hydrochloric acid. The reaction mixture is cooled in an ice bath for 2 hours, and the product that precipitates is collected by suction filtration, washed with ice-water and air-dried overnight. The 3-thiol-4-allyl-5-phenyl-4*H*-1,2,4-triazole weighs 20.1 g. (50%) and melts at 119–120°. After that, the 1,2,4-triazole derivative was alkylated by allyl chloride in ethanol solution of KOH. To the solution of 3-thiol-4-allyl-5-phenyl-4*H*-1,2,4-triazole (17.44 g, 0.080 mol) in ethanol (50 mL) KOH was added (5.20 g, 0.093 mol). The pH value of the solution was 10. Fresh-distilled allyl chloride (6.30 g, 0.082 mol) was added with drip funnel. The reaction mixture was stirred and heated at 65 ^{o}C during 15 h. After cooling to rt the precipitate of KCl was filtered off and an residual solution was evaporated. 14.3 g (70 %) of the ligand **L** (3-allylsulfanyl-4-allyl-5-phenyl-4*H*-1,2,4-triazole) was obtained that melts at 49 ^{o}C. Ligand (**L**): ^{1}H NMR (CD_3CN, 500 MHz) δ_H 7.68 – 7.58 (2H, m), 7.58 – 7.47 (3H, m), 6.05 – 5.86 (2H, m), 5.32 – 5.16 (2H, m), 5.11 (1H, d, *J* = 10.1 Hz), 4.85 (1H, d, *J* = 17.2 Hz), 4.65 – 4.54 (2H, m), 3.83 (2H, d, *J* = 7.1 Hz). ^{13}C NMR (CD_3CN, 126 MHz) δ_C 155.8, 150.8, 133.4, 132.4, 130.2, 128.9, 128.5, 128.4, 127.4, 118.1, 117.4, 116.9, 46.6, 36.2. IR (Nujol, cm^{-1}): 411w, 432w, 475w, 495w, 530m, 563m, 587m, 603m, 700vs, 770vs, 855w, 877m, 920s, 936s, 979m, 996m, 1024m, 1075m, 1108w, 1137w, 1160w, 1201s, 1232m, 1257w, 1285w, 1298w, 1324m, 1353m, 1371m, 1387m, 1424vs, 1438m, 1460vs, 1475s, 1525w, 1580m, 1605m, 1635m, 1651m, 1702m, 1773vw, 1821vw, 1847w, 1897w, 1960w, 1980vw, 2024vw, 2341w, 2362w, 2548vw, 2612vw, 2711vw, 2853w, 2932m, 2976m, 3010m, 3082m.



Scheme 1. The ligand **L** synthesis

2.2. Synthesis of the Coordination Compounds

General Procedure for Synthesis. High-quality single crystals of all compounds were obtained by alternating current electrochemical synthesis [22,23] in acetonitrile. Solutions containing copper(II) halide (for **1a**, **1b**, **2,3** compounds) or iodine (for **1c**, **1c'**) and the ligand were placed in small test-tubes. The volume of the solvent was ~5.5 mL. A copper wire was wrapped into a spiral of ~1 cm diameter. A straight copper wire was placed inside the spiral. These copper electrodes were inserted in a cork and immersed in the above mentioned solutions. Syntheses were performed using alternating current of 50 Hz, voltage was applied to both wire electrodes. Colorless crystals of compounds appeared on the electrodes.

$[Cu_2(L)_2Cl_2]$ ***(1a)***. The solution of $CuCl_2{\cdot}2H_2O$ (0.171 g, 1.0 mmol) and ligand **L** (0.771 g, 3.0 mmol) was prepared. Voltage – 0.75 V. Crystals appeared after one day. ^{1}H NMR (CD_3CN, 500 MHz) δ_H 8.00 – 7.23 (5H, m), 6.04 – 5.74 (1H, m), 5.69 – 5.45 (1H, m), 5.23 (1H, d, J = 10.4 Hz), 4.90 (1H, d, J = 17.1 Hz), 4.82 – 4.47 (4H, m), 3.76 (2H, s). IR (Nujol, cm^{-1}): 452w, 578m, 653vw, 700s, 717s, 728m, 788s, 872m, 898s, 916m, 931m, 947w, 971m, 991m, 1005w, 1026w, 1072w, 1092vw, 1159w, 1181w, 1214w, 1236m, 1257m, 1304w, 1334m, 1375s, 1416s, 1458vs, 1533m, 1664w, 1796vw, 1937vw, 1999vw, 2020vw, 2020vw, 2337vw, 2361vw, 2724vw, 2854vs, 2927vs, 3046w, 3088vw.

$[Cu_2(L)_2Br_2]$ ***(1b)***. $CuBr_2$ (0.224 g, 1.0 mmol) and ligand **L** (0.771 g, 3.0 mmol) were dissolved in acetonitrile. Applied voltage was 0.50 V. After one day, colorless crystals appeared on the electrodes. ^{1}H NMR (CD_3CN, 500 MHz) δ_H 7.68 – 7.48 (5H, m), 5.98 – 5.82 (1H, m), 5.78 – 5.61 (1H, m), 5.25 (1H, d, J = 10.6 Hz), 4.90 (2H, dd, J = 16.8, 8.2 Hz), 4.81 (1H, d, J = 9.7 Hz), 4.64 – 4.53 (2H, m), 3.75 (2H, d, J = 6.7 Hz). IR (Nujol, cm^{-1}): 407w, 469w, 516w, 560m, 603w, 618w, 650w, 667vw, 706s, 729m, 766m, 784s, 855w, 879m, 908s, 939s, 972m, 1003m, 1038w, 1062m, 1073m, 1100w, 1157m, 1197m, 1214m, 1249m, 1260m, 1294w, 1381s, 1404s, 1462vs, 1541m, 1575w, 1605w, 1643m, 1815w, 1839vw, 1881w, 1914vw, 1941vw, 1991vw, 2018vw, 2487vw, 2725vw, 2854vs, 2935vs, 3043vw, 3073vw.

$[Cu_2(L)_2I_2]$ ***(1c)***. The initial solution in acetonitrile contained ligand **L** (0.771 g, 3.0 mmol), I_2 (0.127 g, 0.5 mmol) and CsF (0.304 g, 2.0 mmol). The last component was added in attempt to obtain copper(I) fluoride complex, but it resulted in the structure of **1c** formation. Voltage was 0.40 V. The crystalline product formed after 12h. IR (Nujol, cm^{-1}): 407w, 471w, 505w, 548m, 559m, 603m, 647w, 700s, 725m, 773s, 870m, 899m, 937s, 963m, 977m, 996m, 1030w, 1074m, 1096vw, 1120vw, 1158m, 1206s, 1246m, 1261m, 1288m, 1347m, 1379s, 1400m, 1431m, 1441m, 1462vs, 1480s, 1542m, 1577m, 1607m, 1643w, 1804w, 1877w, 1976vw, 2349w, 2365w, 2890m, 2912vw, 2951m, 2975w, 2989w, 3032w, 3087vw.

$[Cu_2(L)_2I_2]_2$ ***(1c')***. Ligand **L** (0.771 g, 3.0 mmol) and I_2 (0.254 g, 1.0 mmol) were dissolved in acetonitrile. Applied voltage – 0.55 V. Colorless crystals appeared on the electrodes in one day. IR (Nujol, cm^{-1}): 468w,

504w, 548m, 559m, 605m, 647w, 698s, 725m, 701s, 725m, 773s, 817w, 866m, 899m, 939s, 963m, 976w, 994s, 1032m, 1074m, 1096w, 1122vw, 1157m, 1204s, 1246m, 1261m, 1288m, 1347m, 1376s, 1400m, 1415m, 1431m, 1443m, 1461vs, 1480s, 1538m, 1577m, 1604m, 1645m, 1696vw, 1806w, 1881w, 1987vw, 2340w, 2359w, 2890m, 2950m, 2973w, 2987w, 3031w, 3073vw, 3086vw.

*$[Cu_2(\mathbf{L})_2(CuCl_2)_2]$ (**2**).* The solution of $CuCl_2{\cdot}2H_2O$ (0.171 g, 1.0 mmol) and ligand **L** (0.386 g, 1.5 mmol) was prepared. Voltage – 0.75 V. Crystals appeared after two days. ^1H NMR (500 MHz, CD_3CN) δ 8.01 – 7.35 (5H, m), 6.03 – 5.77 (1H, m), 5.68 – 5.33 (1H, m), 5.25 (1H, d, *J* = 10.4 Hz), 5.06 – 4.80 (1H, m), 4.79 – 4.17 (4H, m), 3.72 (2H, s). IR (Nujol, cm^{-1}):405m, 546vw, 579m, 605vw, 667vw, 700vs, 724m, 784vs, 850vw, 890m, 905m, 930s, 945s, 984m, 998m, 1010m, 1033vw, 1058vw, 1075w, 1103w, 1143w, 1197m, 1208m, 1254m, 1303m, 1318m, 1377s, 1415m, 1466vs, 1543m, 1578vw, 1607m, 1648w, 1824vw, 1902vw, 1979vw, 2007vw, 2362vw, 2724vw, 2854vs, 2926vs, 3084w.

*$[Cu_2(\mathbf{L})_2Cu_2Br_4]$ (**3**).* The solution of ligand **L** (0.400 g, 1.56 mmol), $CuBr_2$ (0.224 g, 1.0 mmol) was prepared. The mixture of 4 mL acetonitrile and 2 mL of ethanol was used as a solvent. Voltage – 0.6 V. After 12h crystals of **3** were formed. IR (Nujol, cm^{-1}): 479vw, 550w, 607w, 663vw, 701m, 722m, 771m, 874w, 923m, 963w, 990m, 1007vw, 1064vw, 1079vw, 1160vw, 1206w, 1243w, 1261vw, 1296vw, 1347w, 1378s, 1400w, 1466vs, 1534m, 1647w, 2726vw, 2854vs, 2925vs, 3092vw.

2.3. Measurements

IR spectra (400 – 4000 cm^{-1}) were collected on a Bruker Vertex 70 FTIR and Bruker IFS-88 spectrometers in Nujol mull. ^1H NMR spectra were recorded on a Bruker Avance 500 MHz NMR spectrometer. Hirshfeld surfaces of the complexes and fingerprint plots were produced by CrystalExplorer software [24,25].

X-ray Crystallography. Diffraction data for **1a** and **1c** crystals were collected on an Agilent Xcalibur four-circle diffractometer with Mo *K*α radiation (λ = 0.71073 Å) equipped with Ruby or Atlas CCD detectors, respectively. Diffraction data for **1b** and **3** crystals were collected on Kuma KM4CCD diffractometer with Mo *K*α radiation (λ = 0.71073 Å). Diffraction data for **1c'** and **3** crystals were collected on an Agilent Gemini A four-circle diffractometer with Mo *K*α radiation (λ = 0.71073 Å) and Atlas CCD detector. The collected diffraction data for all compounds were processed with the CrysAlis PRO program [26]. The structures were solved by direct methods using SHELXS or SHELXT programs and refined by least squares method on F^2 by SHELXL software with the following graphical user interfaces of OLEX^2 [27,28]. Atomic displacements for non-hydrogen atoms were refined using an anisotropic model. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters.

The crystal parameters, data collection and the refinement are summarized in Table S1 in SI. The crystallographic material can also be obtained from the CCDC, the deposition numbers being CCDC 1518836, 1518837, 1518838 (for **1a**, **1b**, **1c**, respectively), 1519365 (for **1c'**), 1518839 and 1518840 (for **2** and **3**, respectively).

3. Results and Discussion

3.1. Synthesis and Crystal Structures of Coordination Compounds

Copper(I) chloride (**1a**, **2**) and bromide (**1b**, **3**) π-complexes were synthesized by a known alternating current electrochemical method [22]. First, when acetonitrile solutions of Cu^{2+} salt and the ligand **L** are mixed, a σ-complex of Cu^{2+} and **L** forms that is evidenced by a color change. Then alternating current is applied to copper electrodes resulting in the reduction of Cu(II) to Cu(I) and ensuing crystallization of a π-complex. The method enables obtaining of chloride and bromide complexes but is unusable for iodide complexes due to instability of

CuI_2 in any solvents. To solve this problem, we use iodine in a solution of an organic ligand as a source of I^{-} and as an oxidant that is reduced at copper electrodes [23]. Applying alternating (but not direct) current enhances crystals quality and prevents the possible destruction of a ligand. By this method, we obtained the iodine complexes as high-quality single crystals with a high yield.

Complexes **1a-1c** may be regarded as isotypical. The organic ligand plays chelating - bridging role that results in the formation of the dimeric moiety, containing six-membered ring built of two pairs of [-N-N-] triazole fragments and two Cu atoms (Figure 1). The torsion Cu1–N2–N1–Cu1' angle is about 20° indicating the $\{Cu_2N_4\}$ moiety is not perfectly planar. There is one crystallographically independent Cu atom adopting a trigonal pyramidal (τ_4 = 0.83; 0.88 and 0.87 for **1a**, **1b** and **1c** respectively, where τ_4 is the four-coordinate geometry index [29]) environment (2N, (C═C) + *X*). The basal plane of the coordination arrangement is comprised of two conjugated N(*tr*) atoms and the η^2-allyl group. The axial site is occupied by a halide ion. For **1a-1c**, there is the clear tendency to the decrease of the Cu–N bonds length and to the increase of the Cu–*m* (*m* is a mid-point of the C=C bond) distance accompanied by reduction of the C═C bond elongation (Table 1). This fact indicates an increase of strength of the Cu ion σ-coordination in equatorial plane. At the same time the efficiency of π-coordination from **1a** to **1c** decreases that is evidenced by alteration of the C═C bond length in accordance with the Dewar–Chatt–Duncanson model [30,31]. The Cu–X distance changes appropriately to the size of a halide ion. For this reason, it is hard to estimate the strength of the Cu(I) ion interaction with the axial ligand in comparison with the equatorial ones. The distance Δ between the Cu atom and the basal plane (N1', N2, *m*, where *m* is the mid-point of the C4═C5 bond) may be used as such characteristic [1]. In this context it is interesting that the Cu atom is the most remote from the basal plane in the **1a** structure (0.58 Å) despite a comparatively strong Cu–(C═C) interaction. The C═C bond is highly inclined to the basal plane of coordination polyhedron in **1a** (40.9°) and to a lesser degree in **1b** and **1c** (22.8° and 23.8°, respectively). Such high values of the angle between the C═C bond and the trigonal-pyramid basal plane are extremely unusual for copper(I) π-complexes with allyl derivatives of heterocyclic compounds [1].

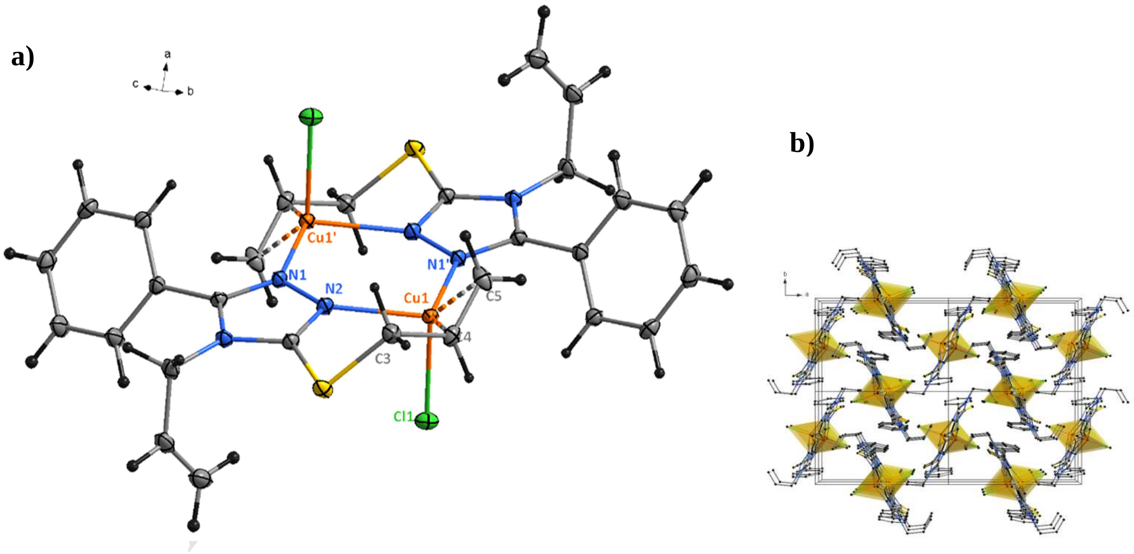


Figure 1. (a) The centrosymmetric dimer in complex **1a**. Compounds **1b** and **1c** have isotypical molecular structure. Thermal ellipsoids are drawn at 50 % probability. Symmetry code: (') –*x*, 1–*y*, 1–*z*. (b) Crystal packing of the complex units along the *c* axis in compound **1a** in which copper(I) coordination polyhedra are represented.

The **1c’** structure is built of dimeric moieties, which are similar to those in **1c**. However, in **1c’**, in contrast to the **1c** complex, the moiety is split into two independent dimers which are spaced at 9.725(1) Å (the distance between the centroids of {Cu_2N_4} rings) and mutually tilted by 36.6(1)° (Figure 2). Compounds **1c** and **1c’** are an example of packing polymorphism (Figure 3). Both Cu(I) coordination polyhedra in **1c’** differ from those in **1c** by stronger Cu–I and Cu–(C═C) binding. The first may be referred from shorter Cu–I distances and higher Δ values in **1c’**. More significant C=C bond elongations and higher C–Cu–C angle values indicate more effective Cu–(C═C) interactions. A compromise between the strong Cu–*X* bond accompanied by the Cu atom shift along the axial vector and the Cu–(C═C) bond in the basal plane leads to the similar situation as in **1a** – strong tilting of the C═C bond (29.4° for the Cu1 atom polyhedron and 35.3° for the Cu2 one) and the augmentation of the *m*–Cu–*X* angle (up to 10° in **1a** and **1c’** in comparison with **1b** and **1c**).

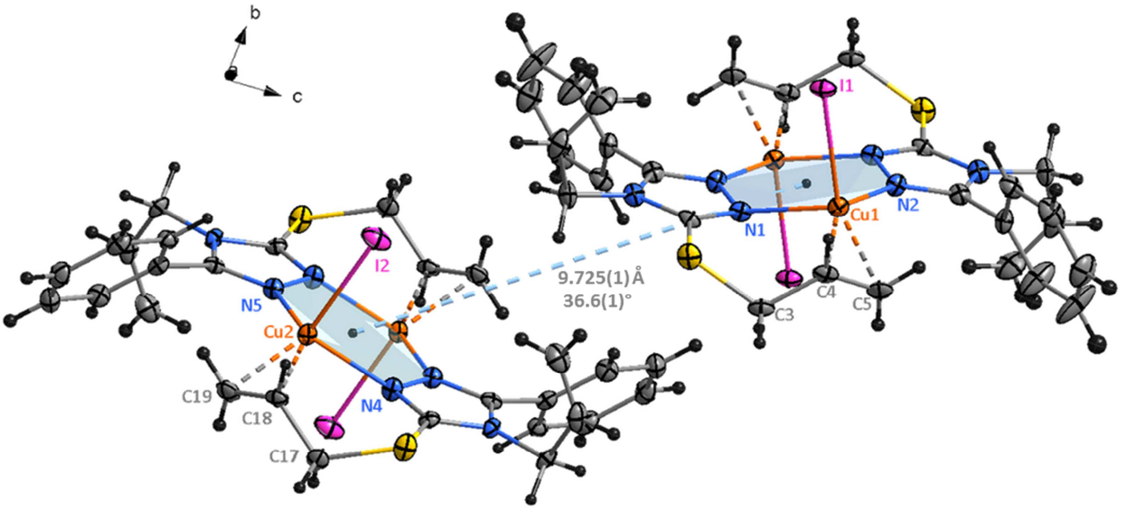


Figure 2. In the structure of **1c’**, the dimeric moiety is split into two independent ones both containing π-coordinated Cu(I) atoms. The distance between the {Cu_2N_4} mid-points and the angle between the {Cu_2N_4} hexagons are shown. Thermal ellipsoids are drawn at 50 % probability.

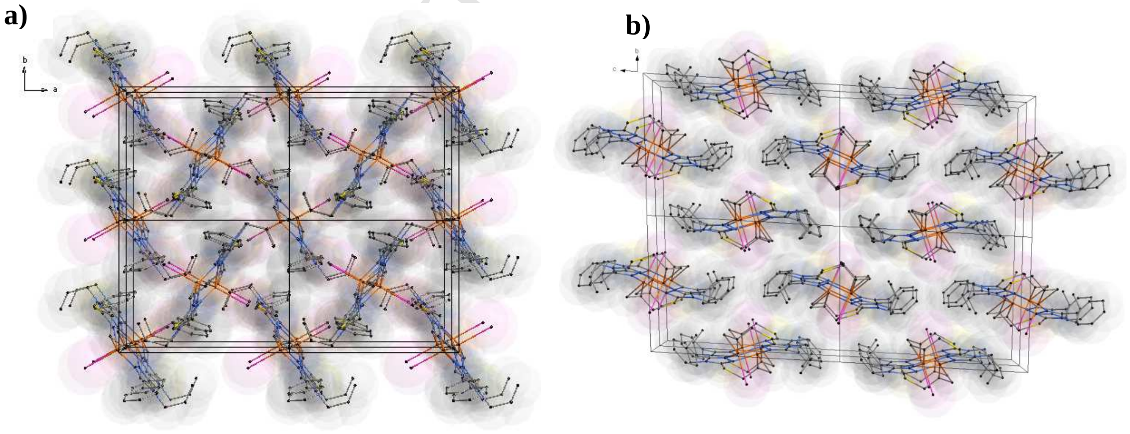


Figure 3. Packing polymorphism of the iodine complex. The crystal structure of **1c** (a) is described as monoclinic in the $P2_1/n$ space group, while **1c’** (b) as centrosymmetric triclinic.

In the case of **2** (Figure 4) and **3** (Figure 5), Cu*X* and the ligand **L** are self-assembled in structures built of two subunits – the cationic organometallic core and the anionic inorganic fragment. These two parts are joined *via* the μ_2-*X*1 bridge with the 101.58(3)° in **2** and 100.55(3)° in **3** Cu1–*X*1–Cu2 angle. It should be noted that the

Cu1 atom in **2** is located much closer to the equatorial coordination plane (two N(*tr*) atoms and the C═C bond) than in **1a** that is evidenced by smaller Cu1 atom shift Δ by 0.37 Å. This change is accompanied by weaker axial Cu1–Cl1 interaction in **2** (the distance is longer by 0.3 Å than in **1a**). At the same time the Cl2' atom also influences the Cu1 coordination centre. The interplay between the Cu1–Cl1 and Cu1–Cl2' oppositely directed vectors causes small Cu1 atom shift along the Cu1–Cl1 direction and gives trigonal bipyramidal features to the Cu1 atom coordination environment. The inorganic part in **2** is represented by the nearly linear (175.65(3)°) Cl1–Cu2–Cl2 fragment with almost equal Cu – Cl distances of 2.0989(8) and 2.0867(8) Å, respectively. The Cu2–Cl2'' (symmetry code: ('') –*x*, 2–*y*, 1–*z*) distance of 4.4541(9) Å between two $[Cu_2\mathbf{L}_2(CuCl_2)_2]$ units largely exceeds the sum of the van der Waals radii of Cu and Cl [32]. It follows that the units are isolated and interconnected by weak interactions only. Geometrical characteristics of the Cu1 atom coordination polyhedron in **3** adopt intermediate between **1a** and **2** values that are close to the ones in **1b** and **1c**.

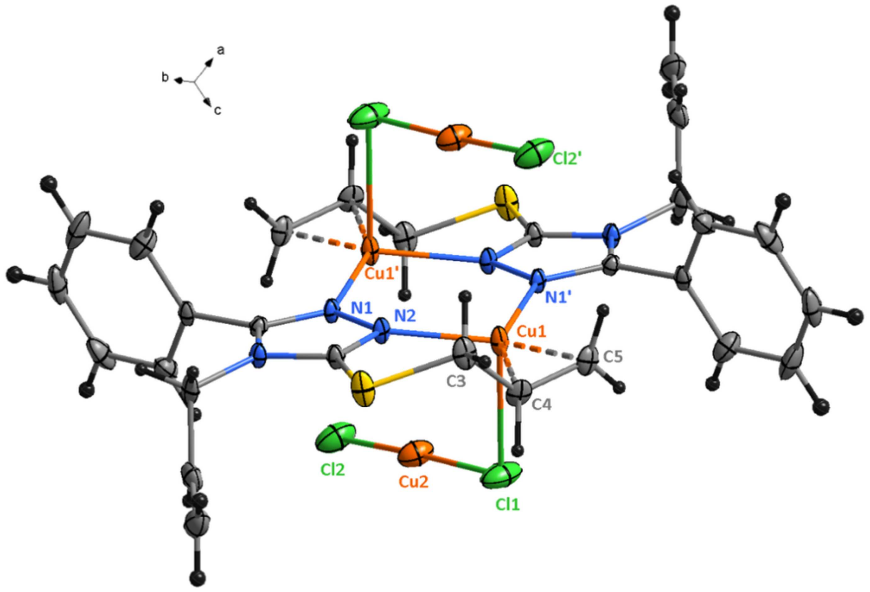


Figure 4. Two independent copper(I) atoms in the structure of **2**. The Cu1 atom forms the organometallic core while the Cu2 atom constitutes the inorganic linear $\{CuCl_2\}$ fragment. Symmetry code: (') 1–*x*, 2–*y*, 1–*z*. Thermal ellipsoids are drawn at 50 % probability.

In **3**, the copper(I)-halide subunit is organized in the centrosymmetric $Cu_2(\mu_2\text{-}Br)_2Br_2$ cluster with the direct Cu—Cu distance of 2.851(2) Å. The inorganic moiety serves as a linker connecting organometallic cores that results in a formation of the 1D ladder. Different from **2** organization of the anionic inorganic fragment in **3** causes a reduction of symmetry from the monoclinic $P2_1/c$ space group to triclinic $P\bar{1}$ one.

In all complexes 4-allyl (N-bound) group stays uncoordinated. This may be explained by taking into account two effects – electronic and steric ones. The 4-allyl group is bonded to the nitrogen atom of the highly electron-deficient triazole system. This has the electron-withdrawing effect on the allyl group and makes it less suitable for coordination with Cu(I). Moreover, in the case of Cu(I) coordination by 3-thioallyl group the six-membered $\{CuNCSCC_2\}$ ring is formed. The 4-Allyl group is not able to form such energetically favorable configuration in the present dimers.

The Hirshfeld surfaces were built for all dimeric moieties (except of the complex **3** because of its polymeric structure) to analyze intermolecular interactions in the crystal structures (Figure S1 in SI). Hydrogen

C–H···*X* bonds contribute the most to directed intermolecular interactions. The largest contribution of C–H···*X* contacts is present in the case of **2**.

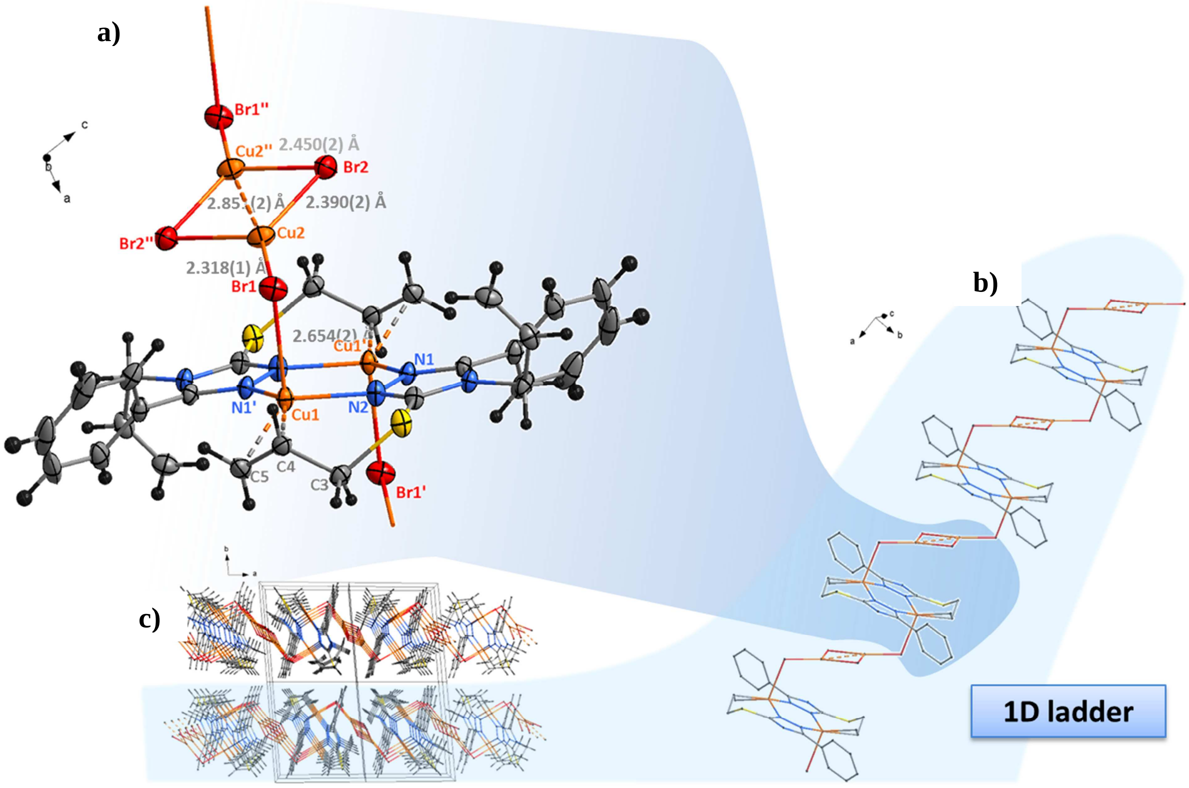


Figure 5. Organometallic dimers (a) in **3** are joined via the centrosymmetric μ_2-($Cu_2(\mu_2\text{-}Br)_2Br_2$) clusters leading to a 1D ladder formation (b). (c) Crystal packing of ladders along the *c* axis in **3**. Symmetry codes: (') 1–*x*, 1–*y*, 1–*z*; ('') –*x*, 1–*y*, 1–*z*. Thermal ellipsoids are drawn at 50 % probability.

3.2. The effectiveness of Cu–(C═C) bonding

According to the Table 1, the strongest Cu(I) π-coordination appears in **2**, then it decreases from **1a** to **1c'** with **3** adopting middle values. However, the C═C bond elongation is much stronger in the case of **1a**. At the same time the NMR data (Figure 6) also evidence of more effective Cu–(C=C) interaction in **2** than in **1a**. Referring to the Dewar–Chatt–Duncanson model [30,31], a formation of the Cu–(C=C) bond involves donation of the π-bond of the organic moiety to a vacant 4s and 4p metal orbital and back-donation from an occupied 3d metal orbital to a low-lying empty *π** orbital of the substrate. Recently Halbert and Gérard demonstrated that a good linear correlation was found between back-donation and the C═C bond distance. However, no correlation between the amount of donation and the C═C bond distance could be found [33]. Therefore, it may be presumed that the highest value of the C═C bond elongation in **1a** means the most substantial contribution of back-donation to the Cu–(C═C) bonding with little donation. Since the Cu–(C═C) distance is a measure of the sum *π*-interaction including both donation and back-donation, the lowest value in **2** indicates noticeable donation that compensates lack of back-donation to achieve the most effective Cu–(C═C) interaction.

Coordination environment of the Cu atom in the basal plane is formed of two N(*tr*) atoms and the C═C bond in all complexes. Therefore, the apical ligand is the only one factor that influences the Cu–(C═C) bond. In the case of **2**, the apical position is occupied by the μ_2-Cl atom while in **1a** – by the terminal Cl one. The bridging Cl atom is coordinated more weakly than the terminal one, that leads in the case of **2** to stronger Cu atom bonding with ligands in the basal plane and in particular with the C═C bond. In **1a**, the C═C bond is highly inclined (40.9°) to the basal plane that is accompanied by the large value (0.581 Å) of the Cu atom shift from the basal plane Δ. It may be suggested that in this way more effective back-donation can be achieved. The efficiency of the Cu–(C═C) interaction decreases from **1a** to **1c’**, i.e. from Cu(I) chloride to iodide complexes. This fact may be explained by an increase of the strength of Cu–*X* bonding from Cl to I in agreement with the HSAB concept – soft Cu(I) cation prefers soft iodide ion.

Table 1. Selected bond distances (Å) and angles (°) in the structures

bond/angle type	**1a**	**1b**	**1c**	**1c’**	**2**	**3**
Cu1 – N1’	2.0044(9)	1.998(2)	1.9967(17)	2.100(3) 2.113(3)	1.9776(19)	1.996(3)
Cu1 – N2	2.1288(9)	2.059(2)	2.0610(17)	2.004(3) 2.008(3)	2.0024(19)	2.044(3)
Cu1 – C4	2.1008(10)	2.100(2)	2.104(2)	2.122(4) 2.134(4)	2.057(2)	2.125(4)
Cu1 – C5	2.0759(12)	2.091(3)	2.100(2)	2.106(4) 2.092(4)	2.061(2)	2.088(4)
Cu1 – *m* [a]	1.9729(6)	1.982(1)	1.9907(7)	2.003(1) 2.001(1)	1.9447(3)	1.994(1)
Cu1 – *X*1 [b]	2.3294(7)	2.5283(8)	2.6997(8)	2.683(2) 2.656(2)	2.6305(10)	2.6535(11)
C4═C5	1.3698(14)	1.357(4)	1.348(3)	1.354(6) 1.359(6)	1.355(3)	1.359(6)
N1 – Cu1 – N2’	107.97(4)	107.71(8)	108.00(7)	107.94(13) 109.79(12)	110.06(8)	110.80(13)
N1’ – Cu1 – *m*	123.33(3)	125.28(6)	125.39(5)	107.59(9) 104.70(9)	131.45(6)	126.63(9)
N2 – Cu1 – *m*	104.56(3)	111.34(6)	110.94(5)	124.83(9) 123.78(9)	115.12(6)	111.54(9)
N2 – Cu1 – *X*1	96.25(3)	99.84(7)	97.52(5)	101.18(10) 100.24(10)	97.22(6)	94.10(11)
N1’ – Cu1 – *X*1	100.91(3)	98.84(7)	99.31(5)	94.00(10) 93.55(10)	92.48(6)	98.38(10)
***m* – Cu1 – *X*1**	120.19(2)	110.32(2)	111.67(2)	116.87(4) 120.63(4)	98.54(2)	109.33(3)
Cu1 – N2 – N1 – Cu1’	17.33(10)	24.4(3)	23.9(2)	25.5(4) 23.7(4)	25.1(3)	12.1(4)
C4 – Cu1 – C5	38.29(4)	37.79(11)	37.41(8)	37.35(17) 37.50(16)	38.41(9)	37.63(15)
Cu1 – C5 – C4 – C3	105.96(8)	101.7(2)	100.83(19)	102.5(4) 104.5(3)	98.3(3)	101.0(4)
τ [c]	40.9(1)	22.8(1)	23.8(1)	29.5(3) 35.4(3)	12.8(2)	27.9(3)
Δ [d]	0.5809(3)	0.463(1)	0.463(1)	0.524(1) 0.553(1)	0.208(1)	0.386(1)

[a] *m* – a middle point of C═C bond; [b] *X*1– Cl1 (for **1a**, **2**), Br1 (for **1b**, **3**) or I1 (for **1c**, **1c'**); [c] τ – angle between C═C line and trigonal pyramid base plane; [d] Δ – a distance value of copper(I) deviation from the base plane of a trigonal pyramid.

3.3. NMR measurements

Figure 6 shows the ^{1}H NMR spectra of the ligand **L** and **1a**, **1b**, and **2** complexes in acetonitrile at 25 °C. For the full spectra see Figure S2 in SI. For the ligand **L** two multiplets at 7.68 – 7.58 and 7.58 – 7.47 ppm with a total relative intensity of five correspond to the hydrogen atoms of the phenyl ring. This signal undergoes almost no changes in complexes and will not be further analyzed. An overlap of two signals from $–CH_2–C\underline{H}=CH_2$ hydrogen atoms of two allyl groups results in the multiplet at 6.05 – 5.86 ppm with a relative intensity of 2. These signals are high-priority because they are significantly altered in case of π-coordination. The multiplet at 5.32 – 5.16 ppm with a relative intensity of 2 occurs because of an overlap of the $–CH_2–CH=C\underline{H}_AH_B$ signals from 3-thioallyl and 4-allyl groups. The doublet at 5.11 ppm with a relative intensity of 1 was assigned to the $–CH_2–CH=CH_A\underline{H}_B$ atom of the 4-allyl group. The doublet at 4.85 ppm corresponds to the $–CH_2–CH=CH_A\underline{H}_B$ atom of the 3-thioallyl group. The $–CH_2–$ atoms of the 4-allyl group give multiplet at 4.65 – 4.54 ppm with a relative intensity of 2. The doublet at 3.83 ppm was assigned to the $–CH_2–$ atoms of the 3-thioallyl group. Signal assignment was accomplished by means of the ^{1}H – ^{13}C HSQC experiment.

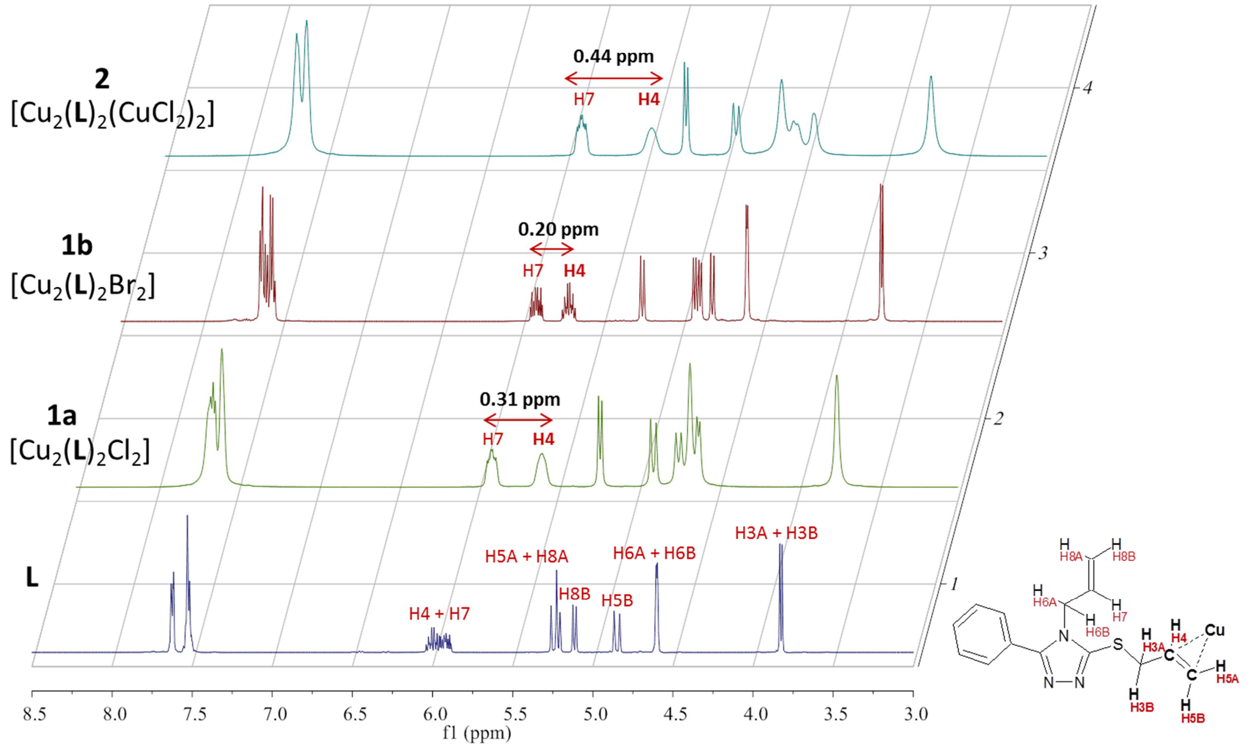


Figure 6. The ^{1}H NMR spectra of complexes **1a**, **1b** and **2** show a displacement of corresponding signals of the coordinated allyl group into the strong field region comparatively to the ligand **L**. The difference between shifts of the coordinated allyl group and the uncoordinated one may be a measure of the effectiveness of Cu(I)–(C═C) bonding.

The NMR spectra of complexes differ significantly by alteration of the 3-thioallyl group signals that is caused by η^2-coordination of the allyl-group to the Cu(I) atom. According to the Dewar–Chatt–Duncanson model [30,31], Cu(I)–(C═C) interaction tends to reduce the carbon-carbon bond order, leading to a displacement of corresponding signals into the strong field region. In the case of the ligand **L**, signals from the $–CH_2–$

C$\underline{H}$═CH$_2$ hydrogen atoms of two allyl-groups are overlapped. However, in complexes only one allyl-group (3-thioallyl) is coordinated while another one (4-allyl) has practically the same shifts of signals as in **L**. This fact enables the differentiation of the coordinated allyl-group from uncoordinated one and based on differences in –CH$_2$–C$\underline{H}$═CH$_2$ shifts the comparison of the strength of the Cu–(C═C) interaction in complexes. In **1a**, the 4-allyl group gives the signal at 6.04 – 5.74 ppm while the coordinated 3-thioallyl group gives the multiplet at 5.69 – 5.45 ppm. The difference is 0.31 ppm. The multiplets of two groups are nearly symmetric, that’s why the difference was measured between midpoints. The same approach was applied to remaining spectra. In the case of **1b**, the difference is 0.20 ppm, indicating less effective π-coordination than in **1a**. In **2**, the corresponding difference is 0.44 ppm. Therefore, the strongest Cu–(C═C) interaction is realized in **2**, then goes **1a**, and comparatively the weakest bonding is observed in the case of **1b**. The –CH$_2$–CH═C$\underline{H}_A\underline{H}_B$ hydrogen atoms are also influenced by π-coordination, but corresponding signals overlap with others, causing difficulties in their analysis. Signals from the methylene H atoms are also altered when the C═C bond is coordinated, but changes are too small to be an appropriate measure of a strength of the Cu–(C═C) interaction in the complexes. It is worthy of note that the NMR spectra of the π-complexes indicate complexes' inertia even to such affined to Cu(I) solvent as acetonitrile and evidence the high strength of Cu–(C═C) bonding.

4. Conclusions

Summarizing the above results, we have studied the coordination behavior of the 1,2,4-triazole allyl derivative in its first six π-complexes with copper(I) halides. The ligand serves as chelating-bridging π,σ-donor by N(*tr*) atoms and the η^2-allyl group that leads to the cationic dimers formation in all complexes. At the same time, an anionic inorganic part determines the way of the crystal structure construction – isolated dimers (**1a** – **1c**, **2**) or 1D ladder (**3**). Also an apical ligand reveals its influence on strength of Cu(I)–(C═C) bonding that was considered by means of the crystallochemical as well as by the ^{1}H NMR spectra analyses. The signals displacement of the coordinated allyl group may be used as a measure of the effectiveness of Cu(I)–(C═C) interaction. Large influence of an axial ligand on donation with less significant impact on back-donation was ascertained. The highest efficiency of Cu(I)–(C═C) bonding is realized in the case of weakest axial coordination, i.e. in complex **2**. Moreover, we have introduced herein a new easily and speedily carried out method for synthesis of copper(I) iodide complexes. By means of the method we obtained the copper(I) iodide π-complex, which featured packing polymorphism (**1c** and **1c’**).

Appendix A. Supplementary Data

Crystallographic data, experimental details for X-ray structural analyses, NMR spectra, the Hirshfeld surfaces and fingerplots. This material is available free of charge.

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- η^2-Interaction of copper(I) is preserved in complexes' acetonitrile solutions.
- Signals displacement at ^{1}H NMR spectra is used to estimate Cu(I)–(C═C) interaction.

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