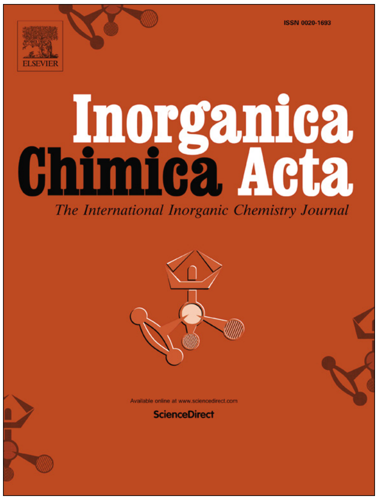


Construction of Heterometallic and Mixed-Valence Copper(I/II) Chloride π-Complexes with 1,2,4-Triazole Allyl-Derivative

Oleh R. Hordiichuk, Yurii I. Slyvka, Vasyl V. Kinzhybalo, Evgeny A. Goreshnik, Tamara J. Bednarchuk, Oleksandr Bednarchuk, Jarosław Jedryka, Iwan Kityk, Marian G. Mys'kiv

PII: S0020-1693(19)30666-8
DOI: https://doi.org/10.1016/j.ica.2019.119012
Article Number: 119012
Reference: ICA 119012

To appear in: *Inorganica Chimica Acta*

Received Date: 14 May 2019
Revised Date: 8 July 2019
Accepted Date: 10 July 2019

Please cite this article as: O.R. Hordiichuk, Y.I. Slyvka, V.V. Kinzhybalo, E.A. Goreshnik, T.J. Bednarchuk, O. Bednarchuk, J. Jedryka, I. Kityk, M.G. Mys'kiv, Construction of Heterometallic and Mixed-Valence Copper(I/II) Chloride π-Complexes with 1,2,4-Triazole Allyl-Derivative, *Inorganica Chimica Acta* (2019), doi: https://doi.org/10.1016/j.ica.2019.119012

Construction of Heterometallic and Mixed-Valence Copper(I/II) Chloride *π*-Complexes with 1,2,4-Triazole Allyl-Derivative

Oleh R. Hordiichuk[a], Yurii I. Slyvka[a], Vasyl V. Kinzhybalo[b], Evgeny A. Goreshnik[c], Tamara J. Bednarchuk[b], Oleksandr Bednarchuk[b], Jarosław Jedryka[d], Iwan Kityk[d,e], Marian G. Mys'kiv[a,*]

[a]*Department of Inorganic Chemistry, Ivan Franko National University of Lviv, Kyryla I Mefodiya 6, 79005 Lviv, Ukraine*

[b]*Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Okólna 2, 50-422 Wrocław, Poland*

[c]*Department of Inorganic Chemistry and Technology,"Jožef Stefan" Institute, Jamova 39, 1000, Ljubljana, Slovenia*

[d]*Institute of Optoelectronics and Measuring Systems, Faculty of Electrical Engineering, Czestochowa University of Technology, Czestochowa, Poland*

[e]*Institute of Solid State Physics, Eastern European University, Voli 6, Lutsk, Ukraine*

*Corresponding author. Tel.: +380322394506; e-mail: marian.myskiv@lnu.edu.ua (M. G. Mys'kiv)

Highlights:

- A family of heterometallic and mixed-valence copper(I) π-complexes studied
- New synthetic routes explored & crystal structures construction details discussed
- Magnetic properties of coordination compounds studied and discussed
- Laser stimulated non-linear optics studied

Abstract: Copper(I) coordination compounds with allyl-derivatives of various heterocycles are the interesting subject of current research, however, the possibility of exploiting a second metal cation (*i.e.* obtaining heterobimetallic complexes) as a tool for crystal engineering of copper(I) π-complexes was virtually uninvestigated. In this work we report the synthesis, structure, magnetic and non-linear optical properties of a family of heterometallic ($Cu^I – Ag^I$, $Cu^I – Zn^{II}$, $Cu^I – Fe^{II}$) and mixed-valence ($Cu^I – Cu^{II}$) copper(I) η^2-π-complexes with an 3-allylsulfanyl-4-allyl-5-phenyl-4*H*-1,2,4-triazole (**L**). The structures of obtained complexes can be considered as consisting of two subunits: cationic organometallic moiety formed by Cu(I) ions, and anionic inorganic fragments. The anionic part, formed by the second metal cation, determines the dimensionality of a crystal structure – it either connects two copper(I) ions in a bridging mode within the organometallic moiety leading to the 0D structure (in the case of Cu^{I} – Zn^{II} & Cu^{I} – Fe^{II}), or links cationic organometallic dimers into the 1D ladder (Cu^{I} – Ag^{I} & Cu^{I} – Cu^{II}). Magnetic properties of mixed-valence Cu(I/II) and heterometallic Cu(I)/Fe(II) coordination compounds were studied and discussed. Separate studies have been done for the laser stimulated nonlinear optics.

Keywords: copper(I); η^2-interaction; heterometallic; 1,2,4-triazole; allyl derivative; crystal structure.

1. Introduction

Copper(I) π-coordination compounds with allyl-derivatives of various heterocycles are becoming more and more appealing objects for modern interdisciplinary research in view of catalytic, anticancer, photoluminescent, ferroelectric and nonlinear optical properties of such compounds [1–12]. Adding the conformationally flexible allyl group (which forms the strongly directed Cu(I)–(C═C) interaction) into a rigid heterocyclic core enables both chelating and bridging functions for a ligand simultaneously and creates vast opportunities for crystal structure engineering. By virtue of new synthetic approaches, based on allyl-substituted azoles, a number of π-complexes with unknown or unstable in a free state Cu(I) salts ($CuHSO_4$, Cu_2SiF_6, $Cu(NH_2SO_3)$ *etc*) have been obtained and unique inorganic fragments (such as the first case of Cu(I) – F(SiF_6^{2-}) interaction) have been discovered [13–18].

We wondered whether it would be possible to incorporate other metal-based fragments into the structure while preserving π-coordination of Cu(I). This would enrich possibilities for purposeful control of composition and crystal structure through the choice of a metal cation with an appropriate electronic configuration and coordination geometry [19–21]. Obviously, the presence of a second metal ion in a structure can lead to distinct from such of monometallic Cu(I) π-complexes properties, which might emerge either due to the nature of an ion (*e.g.* paramagnetism of Fe ions), or because of the ion's structural role in a complex. There are numerous literature reports on the exceptional properties of heterometallic complexes which rely on the interplay between distinct coordination centers formed by different metal ions [21–25]. However, heterometallic Cu(I) π-complexes remain virtually unexplored, while they might be of a significant importance in view of catalytic, optical and biological properties.

Organometallic complexes containing Cu are particularly interesting for the laser stimulated nonlinear optical properties [26, 27]. Organometallic compounds are fundamentally different from typical organic NLO chromophores because of a variety of possible optical transitions they may exhibit: charge transfers from ligand to metal and from metal to ligand, intra-molecular charge transfer, and *d*-*d* electronic transitions [28]. These transitions as well as transitions present in an organic system depend on the interaction of metal *d*-orbitals with the electronic system of the ligand. In the end, it leads to an enhancement of the third order susceptibility ($\chi(3)$) and optimization of a chromophore for NLO applications [29].

We succeeded to obtain and to study a series of unique heterobimetallic Cu^I – Ag^I, Cu^I – Zn^{II}, Cu^I – Fe^{II} and mixed-valence Cu^I – Cu^{II} complexes with an 1,2,4-triazole allyl-derivative: $[Cu_2(\mathbf{L})_2Ag_2Cl_4]$ (**1**), $[Cu^I{}_2(\mathbf{L})_2Cu^{II}{}_2Cl_6]$ (**2**), $[Cu_2(\mathbf{L})_2ZnCl_4]\cdot 2CH_3CN$ (**3**) and $[Cu_2(\mathbf{L})_2FeCl_4]\cdot 2CH_3CN$ (**4**) (were **L** – is 3-allylsulfanyl-4-allyl-5-phenyl-4*H*-1,2,4-triazole). According to the Cambridge Structural Database, there have been no π-complexes of Cu(I) with any allyl-derivatives containing silver or zinc and there has been only one structure containing iron chloride [30]. The compound **2** is the first example of mixed-valence Cu^I – Cu^{II} complexes with 1,2,4-triazole allyl-derivatives.

In this report, we demonstrate how the incorporation of a second metal ion into the Cu(I) π-complex leads to the rearrangement of the crystal structure and thus can be used as a tool for crystal engineering. The influence of the second metal ion on physical properties is illustrated by magnetic and non-linear optical properties of the complexes.

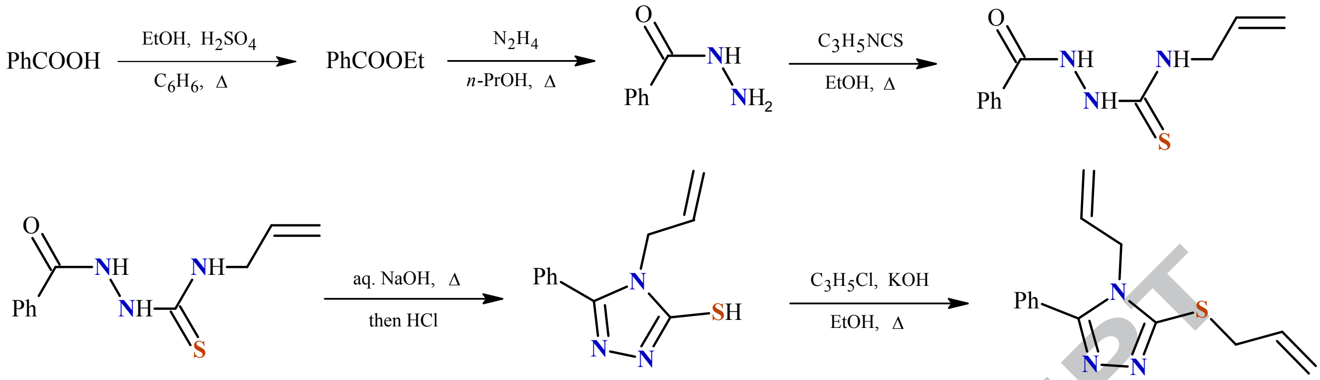
2. Experimental section

2.1. Materials and instrumentation

Unless mentioned otherwise, all chemicals were obtained from commercial sources and used without further purification. The NMR experiments: ^{1}H NMR (500 MHz), ^{13}C{^{1}H} NMR (125 MHz) for 1,2,4-triazole **L** were recorded on a Bruker Avance 500 MHz NMR spectrometer. The chemical shifts are reported in ppm relative to the residual peak of the deuterated CD_3CN for the ^{1}H and ^{13}C{^{1}H} NMR spectra. The infrared (IR) spectra were recorded on the Bruker IFS-88 spectrometer for **2-4** and on FT-IR Spectrum BX-II (Perkin Elmer) for **L** in nujol mulls. EDS analyses for **3** and **4** were performed using Tecnai G^2 F20 X-TWIN equipment (see supplementary materials). Diffraction data for **2** were collected on an Agilent Gemini A four-circle diffractometer equipped with an Atlas CCD detector. Diffraction data for **1**, **3** & **4** were collected on an Agilent Xcalibur four-circle diffractometer equipped with an Atlas CCD detector.

2.2. Synthesis of the Organic Ligand

Ligand **L** (3-allylsulfanyl-4-allyl-5-phenyl-4*H*-1,2,4-triazole) was obtained in several steps in accordance with the reported method [31] as described on Scheme 1. 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

*2.3. Synthesis of the [Cu_2(**L**)$_2Ag_2Cl_4$] (**1**)*

Crystals of the heterometallic complex **1** were obtained under conditions of the alternating-current electrochemical technique starting from the acetonitrile solution of **L** and copper(II) chloride on silver electrodes. A solution of **L** (3.0 mmol, 0.771 g) and $CuCl_2 \cdot 2H_2O$ (1.0 mmol, 0.171 g) in 3.0 mL of acetonitrile was prepared. The prepared green solution was placed into a small 3 mL test-tube and then silver-plates electrodes in cork were inserted. By the application of alternating current (frequency 50 Hz) of 0.55 V for 3-4 days good quality colourless single crystals of **1** in a very small amount appeared on silver electrodes.

*2.4. Synthesis of the [Cu^I_2(**L**)$_2Cu^{II}_2Cl_6$] (**2**)*

Crystals of the mixed-valence complex **2** were obtained by slow evaporation of the acetonitrile solution of ligand **L** and copper(II) chloride. For this, the solution of **L** (1.79 mmol, 0.46 g) and $CuCl_2 \cdot 2H_2O$ (1.79 mmol, 0.305 g) in 5.0 mL of acetonitrile was prepared. By slow evaporation of the obtained solution for 3 days good quality black crystals of **2** appeared. The yield was 89%. M.p. 166 ºC.

IR (Nujol, cm^{-1}): 410w, 413w, 419w, 425vw, 430w, 433vw, 440w, 442w, 451w, 472w, 486w, 491vw, 495vw, 497w, 502w, 512w, 527vw, 543w, 546w, 548w, 556w, 564w, 580w, 585w, 588w, 595w, 597w, 605w, 632vw, 645vw, 661w, 666w, 669w, 672w, 687w, 699s, 704s, 718m, 740m, 769m, 783s, 802w, 877m, 879m, 887m, 907m, 918s, 942s, 956m, 965m, 990m, 1011m, 1036w, 1075m, 1161w, 1187w, 1197w, 1214m, 1247m, 1264m, 1292m, 1331m, 1333m, 1368m, 1400m, 1413m, 1418m, 1446s, 1483s, 1544m, 1577w, 1606m, 1609m, 1632m, 1638m, 1646m, 1649m.

*2.4. Synthesis of the [Cu_2(**L**)$_2ZnCl_4$]·$2CH_3CN$ (**3**)*

Method A: Crystals of **3** were obtained starting from acetonitrile solution of the same organic ligand and the mixture of copper(II) and zinc(II) chlorides. For this the solution of **L** (3.0 mmol, 0.771 g) and $CuCl_2·2H_2O$ (1.0 mmol, 0.171 g) and $ZnCl_2$ (1.0 mmol, 0.136 g) in 5.4 mL of acetonitrile was prepared. 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 solution. Synthesis was performed using alternating current of 50 Hz, voltage (0.60 V) was applied to both wire electrodes. Colourless crystals of compound **3** appeared on the electrodes) in a dozen of minutes. The yield was about 90%. M.p. 147 ºC.

Method B: Crystals of **3** were obtained starting from acetonitrile solution of the **L** and the copper(II) chlorides on zinc electrodes. For this the solution of **L** (3.0 mmol, 0.771 g) and $CuCl_2·2H_2O$ (1.0 mmol, 0.171 g) in 5.4 mL of acetonitrile was prepared. Two zinc plates were inserted in a cork and immersed in the above-mentioned solution. Synthesis was performed using alternating current of 50 Hz, voltage (0.15 V) was applied to both wire electrodes. Colorless crystals of compound **3** appeared on the electrodes in one day. The yield was about 78%. M.p. 146-147ºC.
IR (Nujol, cm^{-1}): 408w, 414w, 416w, 428w, 444w, 447w, 449w, 460w, 478w, 481w, 490w, 499vw, 506w, 512m, 519w, 522w, 539w, 544w, 550vw, 561vw, 570w, 578w, 580m, 583m, 586w, 594w, 602w, 604w, 642w, 645w, 661w, 665w, 673w, 683w, 689m, 701s, 720m, 735m, 766m, 771m, 785s, 793m, 813w, 853w, 872m, 893m, 927s, 949m, 961m, 990m, 1013m, 1035w, 1057w, 1073w, 1100w, 1145m, 1160m, 1194m, 1215m, 1241m, 1255m, 1295m, 1327m, 1355m, 1365s, 1401m, 1414s, 1429s, 1446s, 1486s, 1546m, 1577w, 1610w, 1637w, 1641w, 1644m.

*2.4. Synthesis of the [Cu_2(**L**)$_2FeCl_4$]·$2CH_3CN$ (**4**)*

Crystals of **4** were obtained under the similar to **3** reaction conditions, using $FeCl_3$ instead of $ZnCl_2$. For this a solution of **L** (2.0 mmol, 0.514 g) and $CuCl_2·2H_2O$ (1.0 mmol, 0.171 g) and $FeCl_3·6H_2O$ (1.5 mmol, 0.346 g) in 5.4 mL of acetonitrile was prepared. With the application of alternating current (frequency 50 Hz) of 0.56 V for 12 hours good-quality colourless crystals of **4** appeared on the copper electrodes. The yield was about 85%. M.p. 165 ºC.

IR (Nujol, cm^{-1}): 410w, 414vw, 416vw, 422w, 430w, 435w, 445w, 449vw, 460w, 466w, 472w, 484w, 491w, 499vw, 506w, 513w, 518w, 528w, 536w, 542w, 550vw, 560w, 565w, 570w, 573w, 577w, 582m, 599m, 602m, 690m, 700s, 722m, 737m, 764m, 785s, 792m, 873m, 893m, 927s, 945m, 962m, 988m, 994s, 1008w, 1012m, 1075w, 1100w, 1149m, 1159m, 1192m, 1242m, 1250m, 1257m, 1295m, 1325m, 1352m, 1367m, 1399m, 1415m, 1420m, 1425m, 1439s, 1446s, 1486s, 1536m, 1546m, 1578w, 1610m, 1640w, 1632m, 1645m.

2.5. Single crystal X-ray diffraction studies

The collected diffraction data for **1**-**4** were processed with CrysAlis Pro [32] program. The structures were solved by ShelXT and refined by least squares method on F^2 by ShelXL with the following graphical user interface of OLEX^2 [33–35]. In **3** and **4** structure, bonded allyl group (C23 and C24) as well as Cu(2) atom are disordered over two sites with the occupancy ratios of 0.534(6) : 0.466(6) (**3**) and 0.521(6) : 0.479(6) (**4**), while uncoordinated allyl group (C26, C27 and C28) is disordered over two sites with an occupancy ratio of 0.850(7) : 0.150(7) (**3**) and 0.804(7) : 0.196(7) (**4**). Atomic displacements for non-hydrogen atoms (except disordered carbon atoms of uncoordinated allyl group with lower s.o.f. and the atoms of disordered solvent molecules in **3** & **4**) were refined using an anisotropic model. Hydrogen atoms were placed on geometrically calculated positions and refined as riding atoms with relative isotropic displacement parameters. The crystal parameters, data collection, and the refinement are summarized in Table 1.

Table 1. Selected crystal data and structure refinement parameters of **1-4**

Crystal data	**1**	**2**	**3**	**4**
CCDC number	1914906	1914892	1914893	1914894
Empirical formula	$C_{28}H_{30}Ag_2Cl_4Cu_2N_6S_2$	$C_{28}H_{30}Cl_6Cu_4N_6S_2$	$C_{28}H_{30}Cl_4Cu_2N_6S_2Zn$, $2(C_2H_3N)$	$C_{28}H_{30}Cl_4Cu_2N_6S_2Fe$, $2(C_2H_3N)$
F. w. (g·mol^{-1})	999.32	981.56	931.06	921.54
Crystal system,	triclinic, $P\bar{1}$	monoclinic,	monoclinic,	monoclinic,

space group		$P2_1/c$	$P2_1/n$	$P2_1/n$
a (Å)	8.948(3)	9.485(3)	10.775(4)	10.795(4)
b (Å)	9.680(3)	10.042(4)	15.452(5)	15.510(6)
c (Å)	10.165(4)	19.001(5)	23.266(6)	23.233(8)
α (º)	93.25(3)	90.0	90.0	90.0
β (º)	101.26(3)	103.34(3)	92.70(3)	92.70(3)
γ (º)	95.72(3)	90.0	90.0	90.0
V ($Å^3$)	856.6(5)	1761.0(10)	3869(2)	3886(2)
Z	1	2	4	4
μ (mm^{-1})	2.815	2.988	2.124	1.871
F(000)	492	980	1888	1872
Crystal size (mm)	0.48 × 0.26 × 0.21	0.45 × 0.23 × 0.19	0.62 × 0.39 × 0.33	0.45 × 0.36 × 0.21
Crystal color	colourless	black	colourless	colourless
Calculated density, g/cm^3	1.937	1.851	1.598	1.575
Data collection				
Radiation type, wavelength, λ(Å)	Mo *Ka*, 0.71073	Mo *Ka*, 0.71073	Mo *Ka*, 0.71073	Mo *Ka*, 0.71073
Temperature, *K*	100	150	100	100
Used in refinement reflections	4500	4213	9934	10156
$R[F^2 > 2\sigma(F^2)]$	0.0313	0.0254	0.0320	0.0328
$wR(F^2)$	0.0861	0.0584	0.0749	0.0788
GooF = S	1.067	1.047	1.059	1.053
$\Delta\rho_{max}/\Delta\rho_{min}$ (e $Å^3$)	1.541/-0.863	0.478/-0.567	0.716/-0.522	0.703/-0.713

3. Results and discussion

3.1. Peculiarities of synthesis

Compounds reported herein are unique of their kind, therefore there has been no standard algorithm for their synthesis. Widely used approach for Cu(I) π-complexes synthesis is the alternating current electrochemical method [15,31,36] which is based on the reduction of Cu(II) to Cu(I) on copper electrodes in a solution in the presence of a ligand. Since the method had proved to be highly effective and yielding high-quality single crystals, we decided to try to adapt it to synthesize heterometallic Cu(I) π-complexes. In order to obtain the Cu^I – Ag^I complex [Cu_2(**L**)$_2$$Ag_2Cl_4$] (**1**) copper electrodes were replaced by silver ones and electrochemical alternating current reduction of $CuCl_2$ in the acetonitrilic solution of the ligand **L** was carried out. A few high-quality single crystals appeared on the electrodes in several days. To synthesize the Cu^I – Zn^{II} complex [Cu_2(**L**)$_2$$ZnCl_4$]·2$CH_3CN$ (**3**) two alternative synthetic routes may be used. According to the first method, $ZnCl_2$ was dissolved in acetonitrile together with $CuCl_2$ and the ligand **L**, and alternating current was applied to copper electrodes. The complex **3** crystallized in a dozen of minutes with a high yield. By the second route, zinc electrodes instead of copper ones were used and the acetonitrilic solution contained only $CuCl_2$ and ligand **L**. In the case of Cu^I – Fe^{II} joint electrochemical reduction of Cu(II) and Fe(III) chlorides was carried out in the acetonitrilic solution of the corresponding salts in the presence of the ligand **L** and copper electrodes. After applying alternating current the solution became colourless in several minutes and a large amount of crystals [Cu_2(**L**)$_2$$FeCl_4$]·2$CH_3CN$ grew shortly. The mixed-valence complex [Cu^I_2(**L**)$_2$$Cu^{II}_2Cl_6$] (**2**) was obtained by slow evaporation of the acetonitrilic solution of ligand **L** and copper(II) chloride. Particularly interesting is the fact that the reduction of Cu(II) to Cu(I) occurs spontaneously in the air even in the absence of metallic copper, what indicates a large driving force towards formation of the Cu(I) organometallic units which are discussed in the next paragraph.

3.2. Crystal structures descriptions

Structures of the complexes **1**-**4** may be considered as consisting of two subunits – the cationic organometallic core and an anionic inorganic fragment. The two parts are joined via the μ_2-Cl ion (Fig. 1, 3 & 4). The organometallic part in all complexes is represented by the {Cu_2(**L**)$_2$}$^{2+}$ dimers which are formed due to the chelating-bridging coordination behavior of the ligand **L**. The formation of similar organometallic moieties has been previously observed in copper(I) halides π-complexes with the ligand **L** [31]. Only the 3-thioallyl group of the ligand **L** is coordinated, while the second one (4-allyl, N-bounded) remains inactive with respect to Cu(I) but has some contribution to the structure formation due to the weak interactions. Two possible reasons for why the second allyl group is noncoordinated – electronic and steric ones – have been proposed [31]. The dimeric moieties contain a six-membered ring comprised of two pairs of *[–N–N–]* triazole fragments and two Cu(I) cations. In all complexes the π-coordinated Cu(I) cation adopts a close to a trigonal pyramidal coordination environment (2N, (C=C) + Cl) (Tables 2 & 3). The corresponding four-coordinate geometry indexes τ_4 [37] are 0.87 (**1**), 0.80 (**2**), 0.83/0.83 (**3**) and 0.84/0.83 (**4**). The basal plane of the coordination arrangement consists of two N(*tr*) atoms and the η^2-allyl group. The axial site is occupied by a Cl ion that is part of anionic inorganic fragments which are different for every complex and are described below. The C=C bond of the η^2-allyl group is elongated because of π-coordination in accordance with the Dewar – Chatt – Duncanson model [38,39].

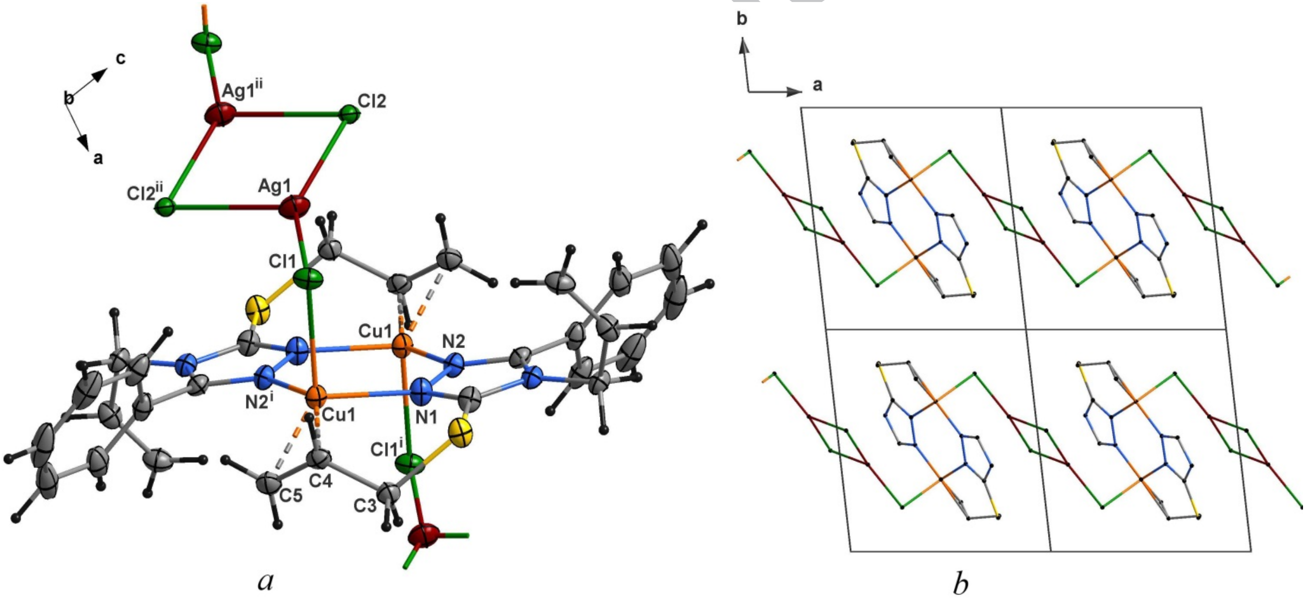


Figure 1. The part of crystal (*a*) and infinite organometallic chains (*b*) in **1** structure. Symmetry codes: (*i*) 1–*x*, 1–*y*, 1–*z*; (*ii*) 2–*x*, 1–*y*, 1–*z*.

In the structure of **1** inorganic part is represented by almost flat and centrosymmetric $\{Ag_2Cl_4\}$ subunit (Fig. 1), which is apically bonded to the two copper(I) ions through bridging Cl1 ions. Thus, $\{Cu_2(\mathbf{L})_2\}$ dimers are stitched through $\{Ag_2Cl_4\}$ bridges into the infinite ladder-like chain extended in [100] crystallographic direction. The heterometallic complex **1** is isostructural to a previously studied copper(I) bromide π-complex $[Cu_2(\mathbf{L})_2Cu_2Br_4]$ with the same ligand **L** [31], thus revealing the crystallochemical interchangeability of the anionic inorganic fragments (silver(I) chloride and copper(I) bromide moieties) (Fig. 2). Interestingly, in the case of copper(I) chloride π-complex with the ligand **L** of the same stoichiometry, the anionic inorganic part is organized differently, leading to a 0D structure [31]. The distance between steps within the chain in [100] direction makes up 6.261(1) Å in the case of **1**, which is much smaller than the same step length (6.616(1) Å) in the earlier studied isostructural copper(I) bromide [Cu_2(**L**)$_2Cu_2Br_4$] π-complex [31] (Fig. 2).

Table 2

Selected interatomic distances and angles for crystals **1** & **2**.

Distance	(Å)	(Å)	Distance	(Å)	(Å)
	1	**2**		**1**	**2**
Cu1—Cl1	2.501(1)	2.819(1)	Ag1—Cl1	2.426(1)	
Cu1—N1	2.048(3)	1.977(2)	Ag1—Cl2	2.480(1)	
Cu1—N2^{i}	2.005(2)	1.982(2)	Ag1—Cl2^{ii}	2.688(1)	
Cu1—m [a]	1.993(3)	1.936(2)	Cu2—Cl1		2.1982(7)
C4—C5	1.370(4)	1.365(3)	Cu2—Cl2		2.235(1)
N1—N2	1.394(3)	1.391(2)	Cu2—Cl3		2.2712(9)
N1—C2	1.315(4)	1.315(2)	Cu2—Cl3^{ii}		2.326(1)
Angle	(º)	(º)	Angle	(º)	(º)
	1	**2**		**1**	**2**
N1—Cu1—N2^{i}	109.71(10)	111.37(6)	Cu1—Cl1—Ag1	98.40(4)	
N1—Cu1—Cl1	95.09(8)	94.40(6)	Cl1—Ag1—Cl2	114.94(4)	
N2^{i}—Cu1—Cl1	100.15(8)	91.42(6)	Cu1—Cl1—Cu2		105.68(2)
N1—Cu1—m	111.0(1)	115.99(8)	Cl1—Cu2—Cl2		96.94(3)
N2^{i}—Cu1—m	126.9(1)	131.24(8)	Cl1—Cu2—Cl3		94.04(3)
Cl1—Cu1—m	108.7(1)	95.89(6)	Cl2—Cu2—Cl3		159.17(2)

[a] m – middle point of C4=C5 bond.

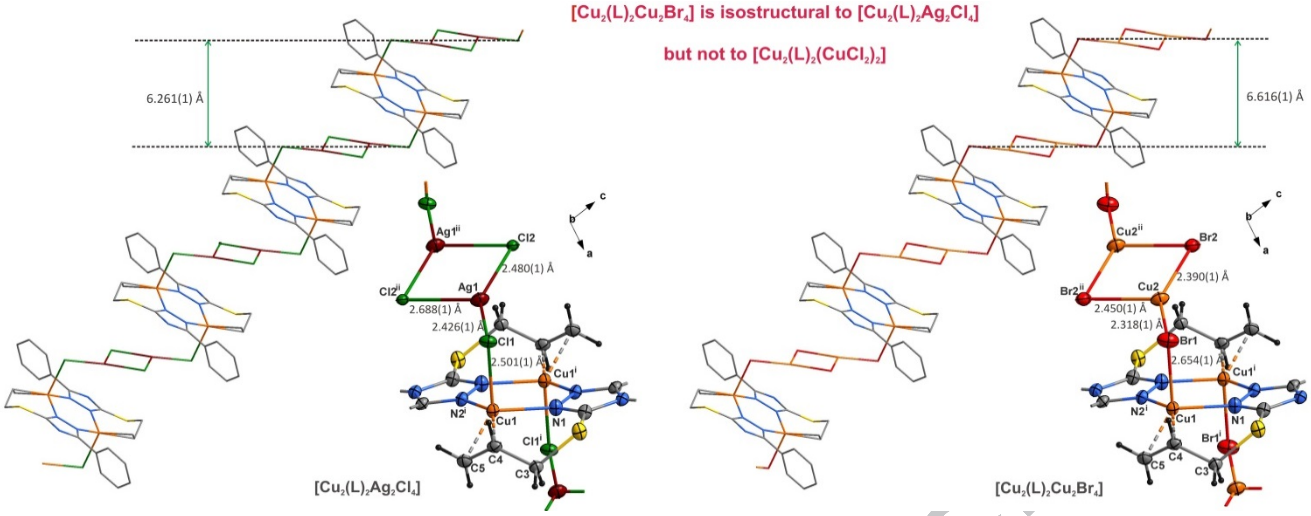


Figure 2. Two isostructural copper(I) π-complexes: heterometallic [Cu$_2$(L)$_2$Ag$_2$Cl$_4$] (**1**) and [Cu$_2$(L)$_2$Cu$_2$Br$_4$] [31].

Replacement of a monovalent metal in the anionic $\{Me_2Cl_4\}^{2-}$ fragment by copper(II) ion leads to a modification of the inorganic subunit due to an appearance of the distorted square environment (τ_4 = 0.31) of Cu(II) ion by inclusion of one more terminal chloride ion to the metal surrounding in structure **2**. Despite some modification of inorganic part, the centrosymmetric $\{Cu_2Cl_6\}^{2-}$ anion is apically bonded through μ_2-Cl ions to Cu(I) of the dimers, forming similar 1D-ladder (Fig. 3). The terminal Cl2 ion is remote from the nearest metallic center by 3.488(1) Å, which is too long for Cu—Cl interaction [40].

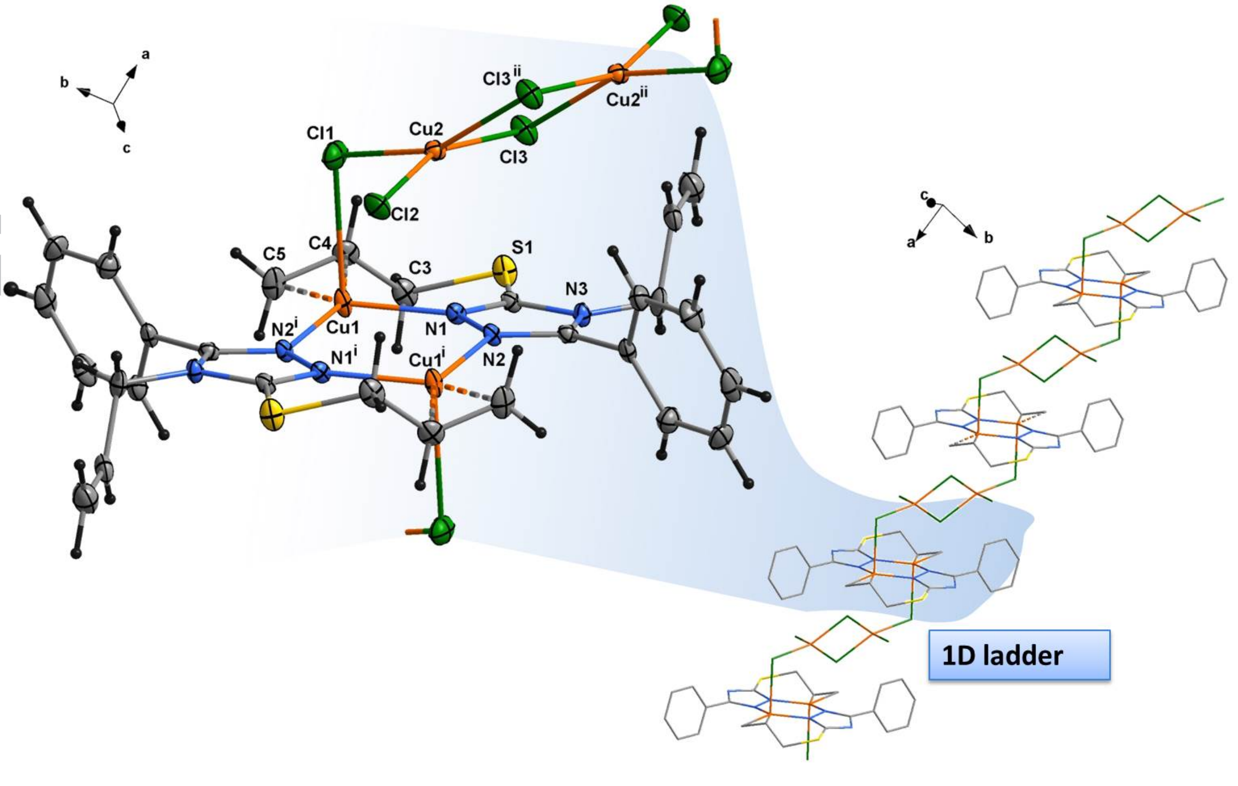


Figure 3. The structure of heterovalent π-complex **2**. Symmetry codes: (*i*) 1–*x*, –*y*, 1–*z*; (*ii*) 2–*x*, 1–*y*, 1–*z*.

π-Complexes **3** and **4** are isostructural. The structures of these compounds implement a different construction principle - the inorganic part is represented by a tetrahedral anion $\{MeCl_4\}^{2-}$ (*Me* = Zn(II) or Fe(II)), which binds two copper(I) ions of the $\{Cu_2(\mathbf{L})_2\}^{2+}$ dimer in a bridging mode. Copper(I) ion adopts close to a trigonal pyramid coordination environment. The tendency of **L**, like allylsubstituted 1,3,4-thiadiazole [18], to form centrosymmetric $\{Cu_2(\mathbf{L})_2\}^{2+}$ fragments leads to disordering of Cu2 ion and π-bonded to it allyl group over two sites (Fig. 4). One of the chlorine ion of the $\{MeCl_4\}^{2-}$ anion presumably interacts with the electron deficient aromatic system of the 1,2,4-triazole ring via the anion-π-interaction [41] with a distance of 3.514(2) Å. The anion-π-interactions may have a directing effect on the mutual orientation of the anionic inorganic $\{MeCl_4\}^{2-}$ part with respect to the organometallic cationic dimeric $\{Cu_2(\mathbf{L})_2\}^{2+}$ moiety.

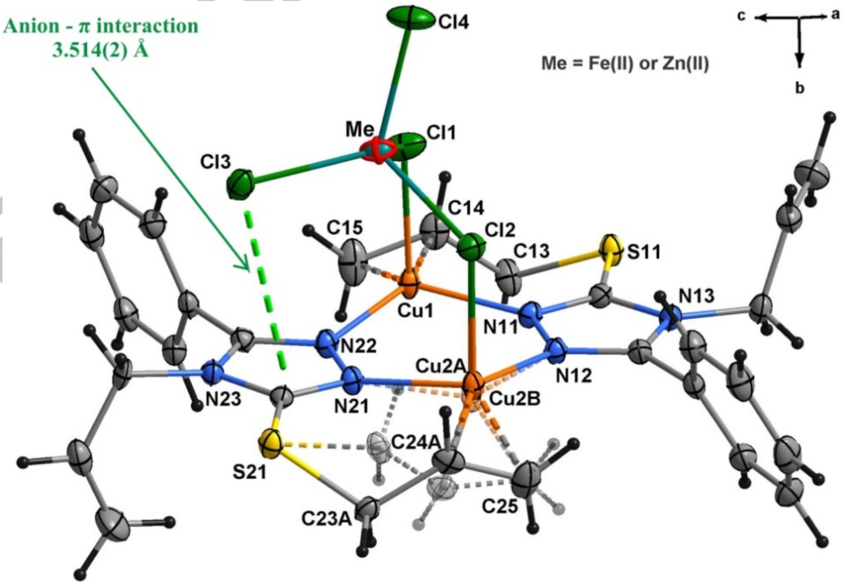


Figure 4. The molecular structure of heterometallic π-complexes **3** & **4**. Disordered noncoordinated allyl groups with lower s.o.f. are omitted for clarity.

Table 3

Selected interatomic distances and angles for crystals **3** & **4**.

Distance	(Å)	(Å)	Distance	(Å)	(Å)
	3	**4**		**3**	**4**
Cu1—Cl1	2.4878(9)	2.483(1)	Cu2A—*m*2A [a]	1.965(6)	1.972(6)
Cu1—N11	2.008(2)	2.011(2)	C24A—C25A	1.351(6)	1.341(6)
Cu1—N22	1.985(2)	1.985(2)	Cu2B—Cl2	2.815(4)	2.817(6)
Cu1—*m*1 [a]	1.953(2)	1.954(2)	Cu2B—*m*2B	1.959(6)	1.953(6)
C14—C15	1.367(3)	1.371(3)	*Me*—Cl1 [b]	2.297(1)	2.338(1)
Cu2A—Cl2	2.540(4)	2.531(4)	*Me*—Cl2	2.3040(7)	2.3444(8)
Cu2A—N12	2.018(6)	2.018(6)	*Me*—Cl3	2.2586(9)	2.294(1)
Cu2A—N21	2.043(6)	2.039(6)	*Me*—Cl4	2.2679(9)	2.304(1)
Angle	(°)	(°)	Angle	(°)	(°)
	3	**4**		**3**	**4**
N11—Cu1—N22	110.68(7)	110.59(7)	N21—Cu2A—Cl2	98.5(2)	98.8(2)
N11—Cu1—Cl1	97.42(5)	97.51(5)	N12—Cu2A—*m*2A	129.3(3)	128.7(3)
N22—Cu1—Cl1	95.61(6)	96.14(6)	N21—Cu2A—*m*2A	113.4(3)	113.7(3)
N11—Cu1—*m*1	114.48(6)	114.34(6)	Cl2—Cu2A—*m*2A	102.6(3)	102.5(3)
N22—Cu1—*m*1	128.16(6)	127.86(6)	Cu1—Cl1—*Me*	118.62(4)	117.56(4)
Cl1—Cu1—*m*1	102.40(6)	102.76(6)	Cl1—*Me*—Cl2	107.69(3)	107.05(3)
N12—Cu2A—N21	108.1(2)	108.4(2)	Cu2A—Cl2—*Me*	111.69(4)	111.00(4)
N12—Cu2A—Cl2	98.4(2)	98.6(2)	Cl1—*Me*—Cl3	110.74(4)	111.46(4)

[a] *m*1, *m*2A and *m*2B – middle points of C14=C15, C24A=C25A and C24B=C25B bonds; [b] *Me* – Zn(II) or Fe(II).

Considering the design of the copper(I) chloride π-complexes with **L**, it is also advisable to take into account the two previously studied structures: $[Cu_2(\mathbf{L})_2Cl_2]$ and $[Cu_2(\mathbf{L})_2(ClCuCl)_2]$ [31]. The complex $[Cu_2(\mathbf{L})_2Cl_2]$ with two terminal chloride ions may be regarded as the main building block (MB). An addition of two CuCl units to this block leads to a formation of 0D $[Cu_2(\mathbf{L})_2(ClCuCl)_2]$ complex with two linear ClCuCl subunits (Fig. 5). In the case of incorporation of two $CuCl_2$ units to the MB, the last ones are connected by copper(II) chloride linkers into 1D-ladder. The addition of two AgCl units to the MB has similar effect. The inclusion of $ZnCl_2$ or $FeCl_2$ units to the MB leads to the loss of MB's centrosymmetry and tetrahedral $\{MeCl_4\}^{2-}$ anions serve as a bridge between the Cu(I) centers of MB.

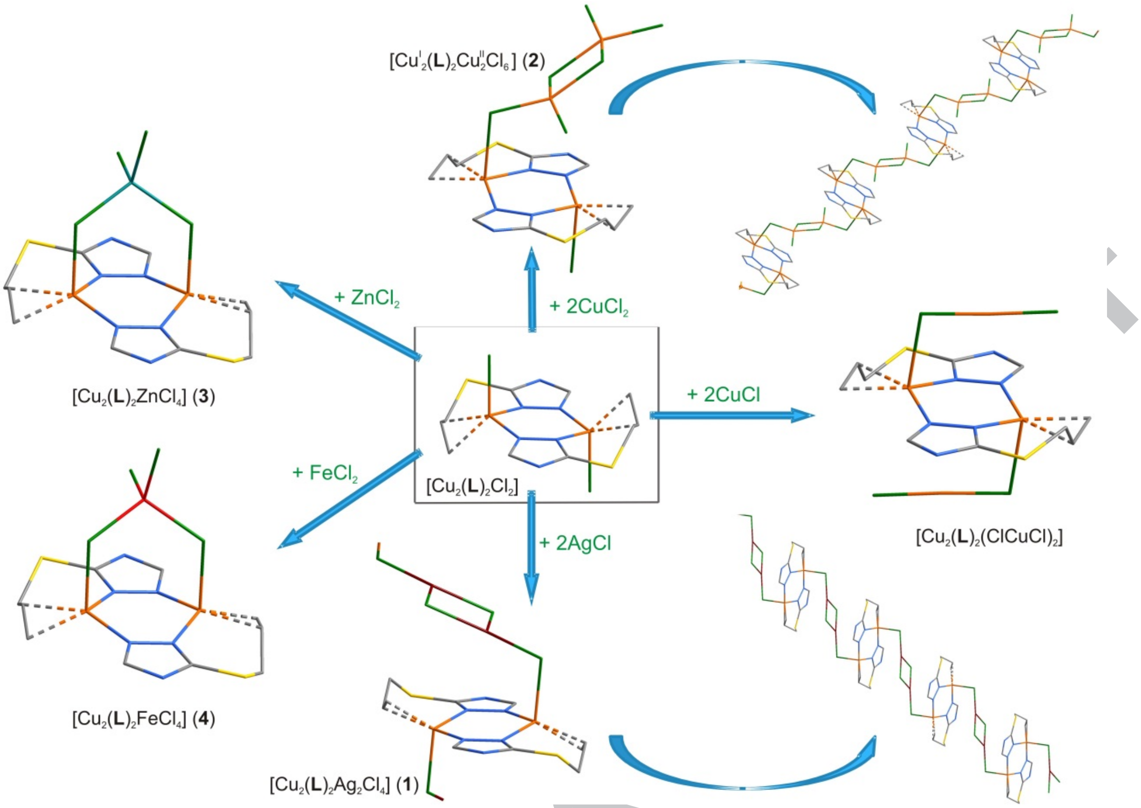


Figure 5. The construction principles of copper(I) π-complexes with **L.**

3.3. Magnetic properties measurements.

Magnetic measurements were performed using commercial Quantum design MPMS 5 SQUID magnetometer setup. Measurements performed on a sufficient amount of single crystals of substances **2** and **4** stuffed and tightly sealed in a gelatin capsule. Magnetic susceptibility curves were recorded within the 1.8 – 300 K temperature range and magnetic fields of 0.5 T for complex **2** and 0.1 T for complex **4**, respectively. Magnetization curves at the lowest T = 1.72 K for both samples were recorded in fields up to 5 T.

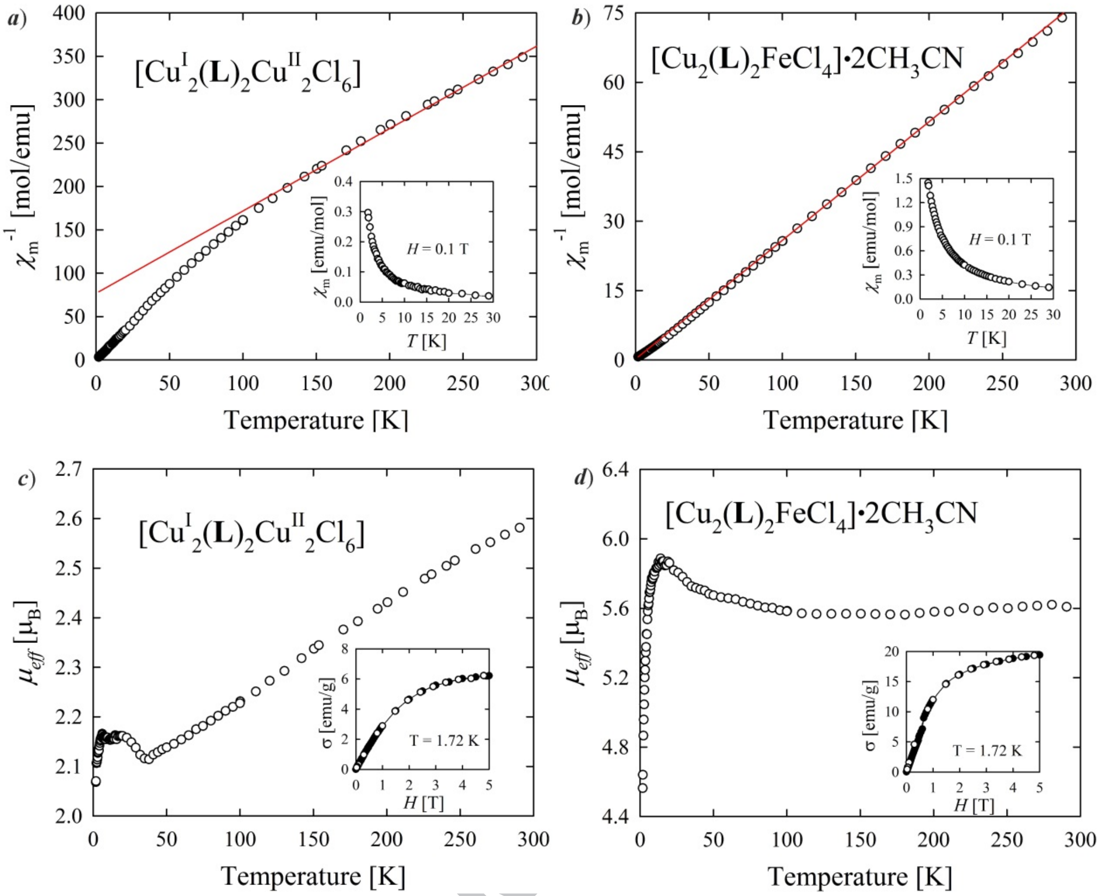


Figure 6. Temperature variation of inverse molar magnetic susceptibility (panels **a** and **b**) and the effective magnetic moment (panels **c** and **d**) for complexes **2** and **4**. Solid lines were obtained from the modified Curie-Weiss equation. Insets show low temperature magnetic susceptibility (insets to panels **a** and **b**) and magnetization isotherms at 1.72 K (panels **c** and **d**). Full and empty symbols in the latter insets represent data points in increasing (full) and decreasing (empty) magnetic field measurement sequences.

Temperature dependent inverse magnetic susceptibilities $\chi^{-1}(T)$ of complexes **2** and **4** are depicted in Fig.6.(**a,b**). As expected for both compounds $\chi^{-1}(T)$ decreases with T in congruence with Curie-Weiss (CW) theory for compound **4,** while for **2** there is a significant departure from linearity in $\chi^{-1}(T)$ below 150 K, possibly caused by the CEF splitting. To include these deviations, a modified CW equation $\chi(T) = \frac{C}{T-\theta_p} + \chi_0$ was used to fit the experimental data (see solid line in Fig.6.(**a,b)**) with the following parameters μ_{eff} = 2.52 μ_B and 5.58 μ_B; θ_p = 0.2 K and 0.8 K for the substance **2** and **4**, respectively. Both values of θ_p hint on a very weak ferromagnetic character of magnetic interactions. The values of effective moment μ_{eff}

are in good correspondence with those reported in the literature 5.1 μ_B for tetrahedral Fe(II) complexes [38, 39] and 2.54 μ_B for the case of divalent copper ion in tetrahedral coordination environment [44]. In temperatures below 30 K χ(T) dependencies for both compounds show immense increase due to the increasing strength of short range interactions or possible magnetic impurities. The variation of the effective moment ($\mu_{eff} = \sqrt{8\chi T}$) with temperature is shown in panels **c,d** to Fig.6. It is apparent that the magnetic moment for the Fe(II) complex is nearly independent of temperature and remains close to the expected $d^6(e^3t_2^3)$ state with a perceptible orbital contribution. Temperature change of μ_{eff} for complex **2** shows a monotonous decrease with T, changing from 2.6 μ_B at RT to 2.1 μ_B at 35 K, due to continuous change of the ligand environment on the contraction of the crystal lattice upon cooling. This might be especially the case, since the tetrahedral environment of Cu(II) ion is distorted at room temperature. Moreover, the shortest distance between magnetic Cu(II) ions is approximately 3.42 Å and these ions are connected in a Cu2-Cl3-Cu2 chain that could bridge the exchange interactions. In order to check on any metamagnetic behavior, magnetization isotherms were recorded at 1.8 K (see insets to panels **c,d**). Experimental data collected in magnetic fields of growing and diminishing strength showed typical paramagnetic behavior and did not reveal any anomalies or hysteretic behavior up below H= 5 T.

3.4. Nonlinear optical effects

Fig. 7 shows the dependences of the THG for complexes **3** and **4** versus the laser stimulated two beam coherent power densities treatment at wavelength 1064 nm using 7 ns pulse laser duration with pulse frequency repetition about 10 Hz. More details are described in the ref. [45].

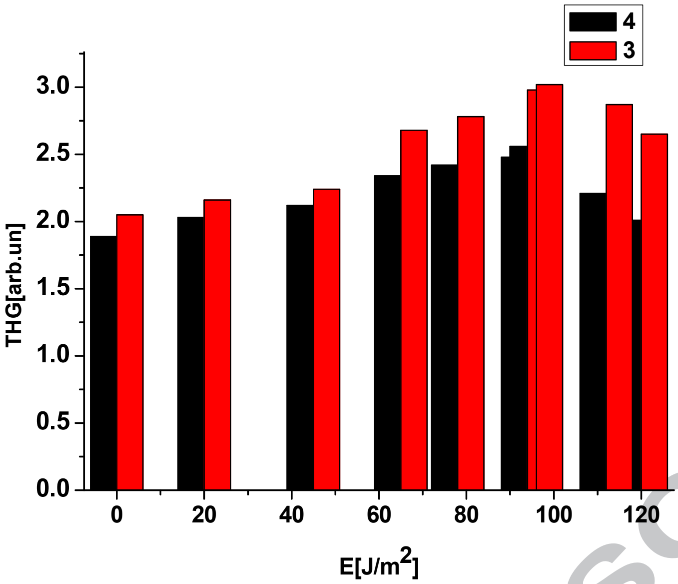


Figure 7. Dependence of the THG versus the photoinducing energy density at fundamental wavelength 1064 nm.

The photoinduced regime was carried out up to 3 min. by two coherent beams split in the space at power density tuned continuously up to 110 J/m^2. At power densities about 120 J/m^2 there occurs some sample's destruction. The existing NLO maxima were achieved almost at the same photoinduced energy densities. After they decreased drastically at higher energy densities. This may be caused by the excitations of a higher level and partial overheating which favors the sample heating up to 20 K. Below this energy density, the THG magnitudes relaxed to initial states within 2-3 min. without a significant irreversible changes. So, there appears a very good opportunity to operate by tripling of the initial frequency. One can see that for the compound **3** (without iron) the THG signal is higher comparing to the compound **4**. This difference may be attributed to the fact that the 3*d*-localized Fe states might be an additional source of the third order hyperpolarizabilities due to the high localization of Fe states. They also have a huge potential for the good nonlinear optics [46], however they are more sensitive to the coordination by ligands than Cu. This may be a principal goal of further research.

4. Conclusions

To sum up, we presented a family of novel Cu(I) heterobimetallic $[Cu_2(\mathbf{L})_2Ag_2Cl_4]$ (**1**), $[Cu_2(\mathbf{L})_2ZnCl_4]\cdot 2CH_3CN$ (**3**), $[Cu_2(\mathbf{L})_2FeCl_4]\cdot 2CH_3CN$ (**4**) and mixed-valence $[Cu^{I}_2(\mathbf{L})_2Cu^{II}_2Cl_6]$ (**2**) π-coordination compounds. We developed a new approach for the synthesis of heterometallic copper(I) π-complexes based on the alternating-current electrochemical method used for copper(I)-olefine compounds. Mixed-valence complex **2** crystallized from the acetonitrile solution of **L** and copper(II) chloride during the spontaneous reduction of Cu(II) to Cu(I) in the air even in the absence of metallic copper or another reducing agent. This fact confirms a large motive force towards the formation of copper(I) organometallic moieties with the ligand **L**, and hence a high stability of Cu(I) towards oxidation in this coordination environment. The structures of **1**-**4** can be represented as being constructed from two subunits: the cationic organometallic moiety $\{Cu^{I}_2(\mathbf{L})_2\}^{2+}$, which is formed by two η^2-π-coordinated copper(I) ions and two pairs of N atoms of triazole cycles, and an anionic inorganic fragment. In all complexes, the second metal cation is incorporated in the form of anionic halide fragments without perturbing significantly the organometallic core. At the same time, the dimensionality of the discussed crystal structures is determined exactly by this anionic subunit. Tetrahedral $ZnCl_4^{2-}$ or $FeCl_4^{2-}$ anion joins two copper(I) ions in a bridging mode within the organometallic moiety leading to 0D structures (**3** & **4**), while in the case of **1** & **2**, $\{Ag_2Cl_4\}^{2-}$ and $\{Cu^{II}_2Cl_6\}^{2-}$ fragments connect $\{Cu^{I}_2(\mathbf{L})_2\}^{2+}$ cations into 1D ladder. Comparison of the presented herein heterometallic complexes with previously studied copper(I) π-complexes with the ligand **L** reveals the crystallochemical interchangeability of anionic inorganic fragments (silver(I) chloride and copper(I) bromide moieties). We have discovered also laser stimulated third order NLO maxima that were achieved almost at the same photoinduced energy densities. After they decreased drastically at higher energy densities. Magnetic properties studies of mixed-valence Cu(I/II) (**2**) and heterometallic Cu(I)/Fe(II) (**4**) coordination compounds yielded the following parameters $\mu_{eff} = 2.52\ \mu_B$ ($\theta_p = 0.2$ K) and $\mu_{eff} = 5.58\ \mu_B$ ($\theta_p = 0.8$ K), respectively; both values of paramagnetic Curie temperatures hint on very weak character of magnetic interactions of ferromagnetic (positive) type. The THG signal is higher for **3**, than for **4**, that may be attributed to the fact that the 3*d*-localized Fe states might be an additional source of the third order hyperpolarizabilities. In the conclusion, the interplay between copper(I), other metals and organic ligands may serve as a powerful tool for tuning magnetic and non-linear optical properties, and its study may be a subject of future research.

Appendix A. Supplementary data

CCDC 1914906, **1914892**, **1914893** and **1914894** contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge filling the corresponding form on https://www.ccdc.cam.ac.uk/structures/? page of CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

5 References

[1] G.-X. Wang, Z. Xing, L.-Z. Chen, G.-F. Han, A ferroelectric olefin–copper(I) organometallic polymer with flexible organic ligand (R)-MbVBP, J. Mol. Struct. 1091 (2015) 16–19. doi:10.1016/j.molstruc.2015.02.043.

[2] E. Cariati, E. Lucenti, C. Botta, U. Giovanella, D. Marinotto, S. Righetto, Cu(I) hybrid inorganic–organic materials with intriguing stimuli responsive and optoelectronic properties, Coord. Chem. Rev. 306 (2016) 566–614. doi:10.1016/j.ccr.2015.03.004.

[3] Y. Slyvka, E. Goreshnik, G. Veryasov, D. Morozov, A.A. Fedorchuk, N. Pokhodylo, I. Kityk, M. Mys'kiv, The novel copper(I) π,σ-complexes with 1-(aryl)-5-(allylthio)-1H-tetrazoles: Synthesis, structure characterization, DFT-calculation and third-order nonlinear optics, J. Coord. Chem. 72 (2019) 1049–1063. doi:10.1080/00958972.2019.1580699.

[4] A.A. Fedorchuk, Y.I. Slyvka, E.A. Goreshnik, I.V. Kityk, P. Czaja, M.G. Mys'kiv, Crystal structure and NLO properties of the novel tetranuclear copper(I) chloride π-complex with 3-allyl-2-(allylimino)-1,3-thiazolidin-4-one, J. Mol. Struct. 1171 (2018) 644–649. doi:10.1016/j.molstruc.2018.06.017.

[5] X.-S. Wang, H. Zhao, Y.-H. Li, R.-G. Xiong, X.-Z. You, Olefin-copper(I) complexes and their properties, Top. Catal. 35 (2005) 43–61. doi:10.1007/s11244-005-3812-6.

[6] Q. Ye, X.-S. Wang, H. Zhao, R.-G. Xiong, Highly stable olefin–Cu(I) coordination oligomers and polymers, Chem. Soc. Rev. 34 (2005) 208–225. doi:10.1039/B407253G.

[7] L.M. Stanley, M.P. Sibi, Enantioselective copper-catalyzed 1,3-dipolar cycloadditions, Chem. Rev. 108 (2008) 2887–2902. doi:10.1021/cr078371m.

[8] N. Yoshikai, E. Nakamura, Mechanisms of nucleophilic organocopper(I) reactions, Chem. Rev. 112 (2012) 2339–2372. doi:10.1021/cr200241f.

[9] C. Santini, M. Pellei, V. Gandin, M. Porchia, F. Tisato, C. Marzano, Advances in copper complexes as anticancer agents, Chem. Rev. 114 (2014) 815–862. doi:10.1021/cr400135x.

[10] Q. Ye, M.-L. Liu, Z.-Q. Chen, S.-W. Sun, R.-G. Xiong, Solvothermal syntheses and physical properties of noncentrosymmetric olefin–copper(I) coordination compounds, Organometallics. 31 (2012) 7862–7869. doi:10.1021/om300343j.

[11] Y. Slyvka, A.A. Fedorchuk, E. Goreshnik, G. Lakshminarayana, I.V. Kityk, P. Czaja, M. Mys'kiv, Synthesis, structural and NLO properties of the novel copper(I) *p*-toluenesulfonate π-complex with 1-allyloxybenzotriazole, Chem. Phys. Lett. 694 (2018) 112–119. doi:10.1016/j.cplett.2018.01.041.

[12] Y.I. Slyvka, A.A. Fedorchuk, N.T. Pokhodylo, T. Lis, I.V. Kityk, M.G. Mys'kiv, A novel copper(I) sulfamate π-complex based on the 5-(allylthio)-1-(3,5-dimethylphenyl)-1H-tetrazole ligand: Alternating-current electrochemical crystallization, DFT calculations, structural and NLO properties studies, Polyhedron. 147 (2018) 86–93. doi:10.1016/j.poly.2018.03.015.

[13] E.A. Goreshnik, Y.I. Slyvka, M.G. Mys'kiv, The first example of a direct Cu^+–SiF_6^{2-} bond. Synthesis and crystal structure of two closely related copper(I) hexafluorosilicate π-complexes with 1-allylbenzotriazole of $[Cu_2(C_6H_4N_3(C_3H_5))_2(H_2O)_2SiF_6]\cdot 2H_2O$ and $[Cu_2(C_6H_4N_3(C_3H_5))_2(CH_3OH)_2(H_2O)_2]SiF_6$ comp, Inorganica Chim. Acta. 377 (2011) 177–180. doi:10.1016/j.ica.2011.08.008.

[14] E.A. Goreshnik, A.A. Vakulka, Y.I. Slyvka, M.G. Mys'kiv, Isomer-selective complexation of copper(I) ionic salts towards 1- and 2-allylbenzotriazoles. Synthesis and characterization of $CuBF_4\cdot$2-all-bta$\cdot H_2O$, $CuClO_4\cdot$2-all-bta,

$CuClO_4$·1-all-bta·2-all-bta and $CuHSO_4$·2-all-bta – The first known example of $CuHSO_4$ π-com, J. Organomet. Chem. 710 (2012) 1–5. doi:10.1016/j.jorganchem.2012.02.024.

[15] Y. Slyvka, E. Goreshnik, O. Pavlyuk, M. Mys'kiv, Copper(I) π-complexes with allyl derivatives of heterocyclic compounds: structural survey of their crystal engineering, Open Chem. 11 (2013). doi:10.2478/s11532-013-0323-3.

[16] E.A. Goreshnik, G. Veryasov, D. Morozov, Y. Slyvka, B. Ardan, M.G. Mys'kiv, Solvated copper(I) hexafluorosilicate π-complexes based on $[Cu_2(amtd)_2]^{2+}$ (amtd = 2-allylamino-5-methyl-1,3,4-thiadiazole) dimer, J. Organomet. Chem. 810 (2016) 1–11. doi:10.1016/j.jorganchem.2016.03.001.

[17] A.A. Fedorchuk, V. V. Kinzhybalo, Y.I. Slyvka, E.A. Goreshnik, T.J. Bednarchuk, T. Lis, M.G. Mys'kiv, Unexpected complexation of allylpseudothiohydantoin hydrochlorides towards CuX (X = Cl, NO_3, ClO_4, BF_4, 1/2SiF_6). The first known examples of joint $Cu^I(Cl,ClO_4)$ and $Cu^I(Cl,BF_4)$ π-complexes, J. Coord. Chem. 70 (2017) 871–884. doi:10.1080/00958972.2017.1286012.

[18] B. Ardan, V. Kinzhybalo, Y. Slyvka, O. Shyyka, M. Luk`yanov, T. Lis, M. Mys`kiv, Ligand-forced dimerization of copper(I)–olefin complexes bearing a 1,3,4-thiadiazole core, Acta Crystallogr. Sect. C Struct. Chem. 73 (2017) 36–46. doi:10.1107/S2053229616018751.

[19] Z.-P. Deng, Z.-Y. Zhang, L.-H. Huo, S.W. Ng, H. Zhao, S. Gao, Syntheses, crystal structures and properties of transition metal coordination polymers based on isophthalic acid and flexible bis(pyridyl) ligand with unsymmetrical spacer: influence of metal cations, ligand conformations and coordination modes, CrystEngComm. 14 (2012) 6548. doi:10.1039/c2ce25339a.

[20] H. Tamaki, Z.J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto, H. Okawa, Design of metal-complex magnets. Syntheses and magnetic properties of mixed-metal assemblies $\{NBu_4[MCr(ox)_3]\}_x$ (NBu_4^+ = tetra(*n*-butyl)ammonium ion; ox^{2-} = oxalate ion; M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}), J. Am. Chem. Soc. 114 (1992) 6974–6979. doi:10.1021/ja00044a004.

[21] Boris I. Kharisov, ed., Direct synthesis of metal complexes, 1 edition, Elsevier, 2018.

[22] Z. Lei, Q.-M. Wang, Homo and heterometallic gold(I) clusters with hypercoordinated carbon, Coord. Chem. Rev. 378 (2019) 382–394. doi:10.1016/j.ccr.2017.11.001.

[23] W.-X. Gao, H.-N. Zhang, G.-X. Jin, Supramolecular catalysis based on discrete heterometallic coordination-driven metallacycles and metallacages, Coord. Chem. Rev. 386 (2019) 69–84. doi:10.1016/j.ccr.2019.01.023.

[24] N. Gauthier, G. Argouarch, F. Paul, L. Toupet, A. Ladjarafi, K. Costuas, J.-F. Halet, M. Samoc, M.P. Cifuentes, T.C. Corkery, M.G. Humphrey, Electron-rich iron/ruthenium arylalkynyl complexes for third-order nonlinear optics: redox-switching between three states, Chem. - A Eur. J. 17 (2011) 5561–5577. doi:10.1002/chem.201003427.

[25] Y.-Y. Zhang, W.-X. Gao, L. Lin, G.-X. Jin, Recent advances in the construction and applications of heterometallic macrocycles and cages, Coord. Chem. Rev. 344 (2017) 323–344. doi:10.1016/j.ccr.2016.09.010.

[26] J.P. Morrall, G.T. Dalton, M.G. Humphrey, M. Samoc, Organotransition Metal Complexes for Nonlinear Optics, in: 2007: pp. 61–136. doi:10.1016/S0065-3055(07)55002-1.

[27] N.J. Long, Organometallic Compounds for Nonlinear Optics—The Search for En-light-enment!, Angew. Chemie Int. Ed. English. 34 (1995) 21–38. doi:10.1002/anie.199500211.

[28] X.Q. Wang, Q. Ren, J. Sun, H.L. Fan, T.B. Li, X.T. Liu, G.H. Zhang, L.Y. Zhu, D. Xu, Preparation, crystal growth, characterization, thermal and third-order nonlinear optical properties of ethyltriphenylphosphonium bis(2-thioxo-1,3-dithiole-4,5-dithiolato)aurate(III) for all-optical switching, J. Cryst. Growth. 324 (2011) 124–129. doi:10.1016/j.jcrysgro.2011.03.035.

[29] T. Huang, Z. Hao, H. Gong, Z. Liu, S. Xiao, S. Li, Y. Zhai, S. You, Q. Wang, J. Qin, Third-order nonlinear optical properties of a new copper coordination compound: A promising candidate for all-optical switching, Chem. Phys. Lett. 451 (2008) 213–217. doi:10.1016/j.cplett.2007.12.001.

[30] C.R. Groom, I.J. Bruno, M.P. Lightfoot, S.C. Ward, The Cambridge Structural Database, Acta Crystallogr. Sect. B Struct. Sci. Cryst. Eng. Mater. 72 (2016) 171–179. doi:10.1107/S2052520616003954.

[31] O.R. Hordiichuk, 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, J. Organomet. Chem. 838 (2017) 1–8. doi:10.1016/j.jorganchem.2017.03.022.

[32] Agilent (2014). CrysAlis PRO. Agilent Technologies Ltd, Yarnton, Oxfordshire, England., (n.d.).

[33] G.M. Sheldrick, Crystal structure refinement with SHELXL, Acta Crystallogr. Sect. C Struct. Chem. 71 (2015) 3–8. doi:10.1107/S2053229614024218.

[34] G.M. Sheldrick, SHELXT – Integrated space-group and crystal-structure determination, Acta Crystallogr. Sect. A Found. Adv. 71 (2015) 3–8. doi:10.1107/S2053273314026370.

[35] O. V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2 : a complete structure solution, refinement and analysis program, J. Appl. Crystallogr. 42 (2009) 339–341. doi:10.1107/S0021889808042726.

[36] Y. Slyvka, E. Goreshnik, G. Veryasov, D. Morozov, M. Luk'yanov, M. Mys'kiv, The first copper(I)-olefin complexes bearing a 1,3,4-oxadiazole core: Alternating-current electrochemical crystallization, X-ray experiment and DFT study, Polyhedron. 133 (2017) 319–326. doi:10.1016/j.poly.2017.05.052.

[37] L. Yang, D.R. Powell, R.P. Houser, Structural variation in copper(I) complexes with pyridylmethylamide ligands: structural analysis with a new four-coordinate geometry index, τ_4, Dalt. Trans. (2007) 955–964. doi:10.1039/B617136B.

[38] M.J.S. Dewar, A review of π-complex theory, Bull. Soc. Chim. Fr. C71 (1951).

[39] J. Chatt, L.A. Duncanson, 586. Olefin co-ordination compounds. Part III. Infra-red spectra and structure: attempted preparation of acetylene complexes, J. Chem. Soc. (1953) 2939. doi:10.1039/jr9530002939.

[40] S. Alvarez, A cartography of the van der Waals territories, Dalt. Trans. 42

(2013) 8617. doi:10.1039/c3dt50599e.

[41] B.L. Schottel, H.T. Chifotides, K.R. Dunbar, Anion-π interactions, Chem. Soc. Rev. 37 (2008) 68–83. doi:10.1039/B614208G.

[42] E.J. Hawrelak, W.H. Bernskoetter, E. Lobkovsky, G.T. Yee, E. Bill, P.J. Chirik, Square planar vs tetrahedral geometry in four coordinate iron(II) complexes, Inorg. Chem. 44 (2005) 3103–3111. doi:10.1021/ic048202+.

[43] N.S. Gill, 680. Complex halides of the transition metals. Part II. Tetrahedral iron complexes, J. Chem. Soc. (1961) 3512. doi:10.1039/jr9610003512.

[44] K. Ito, T. Ito, Magnetic moments of copper(II) complexes, Aust. J. Chem. 11 (1958) 406. doi:10.1071/CH9580406.

[45] A. Antony, P. Poornesh, K. Ozga, P. Rakus, A. Wojciechowski, I.V. Kityk, G. Sanjeev, V.C. Petwal, V.P. Verma, J. Dwivedi, An electron beam induced study in fluorine doped ZnO nanostructures for optical filtering and frequency conversion application, Opt. Laser Technol. 115 (2019) 519–530. doi:10.1016/j.optlastec.2019.03.003.

[46] M. Fuentealba, L. Toupet, C. Manzur, D. Carrillo, I. Ledoux-Rak, J.-R. Hamon, Pentamethylcyclopentadienyl organoiron(II) hydrazone complexes: Synthesis, spectroscopic characterization, and second-order nonlinear optical properties. X-ray crystal structure of, J. Organomet. Chem. 692 (2007) 1099–1109. doi:10.1016/j.jorganchem.2006.11.008.