Cent. Eur. J. Chem. • 11(12) • 2013 • 1875-1901
DOI: 10.2478/s11532-013-0323-3

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Central European Journal of **Chemistry**

# Copper(I) π-complexes with allyl derivatives of heterocyclic compounds: structural survey of their crystal engineering

**Review Article**

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**Received 26 April 2013; Accepted 18 July 2013**

**Abstract:** In this review an exhaustive crystallochemical analysis of copper(I) π-complexes with allyl derivatives of heterocyclic compounds has been performed. Structural genesis of inorganic constituents starting from the simplest units to the most complicated aggregates was considered taking into account the specific role of Cu-(C=C) interaction, the construction of the organic ligands, the basicity and nucleophilic activity of their heteroatoms, as well as olefin Cu(I) π- complex preparation route.

**Keywords:** *π-Complex • Copper(I) • Structure • Heterocyclic Allyl Derivatives • Crystal Engineering*



## 1. Introduction

More than one century has passed since Berthelot [1], Manchot and Brandt [2] have performed first studies on ethylene absorption with copper(I) chloride solution and which started an intensive development of Cu(I) π-coordination chemistry. Presently, copper alkene complexes are known to play a key role in biochemistry [3,4] and have been found to be important as catalysts in organic syntheses [5-10], as an effective instrument in crystal engineering of metal-organic frameworks [11-13], for their fluorescent activity [14,15], and many other useful properties [16-21]. The elaboration of new copper(I) π-complexes synthetic techniques has allowed to obtain the compounds with unknown (or less-stable) in a free state copper(I) salts: $CuClO_4$ [22], $CuBF_4$ [23], $CuNO_3$ [24], Cu(HCOO) [25], $CuOOCCF_3$ [26], $CuSO_3NH_2$ [27], $Cu(CF_3COCHCOCF_3)$ [28], $Cu_2SiF_6$ [29], $CuPF_6$ [30], $Cu_2SO_4$ [31] *etc*. A formation of copper(I) π-complexes is caused with a specific role of a directed Cu(I)-(C=C) interaction in a presence of σ-donor (such as N, O, S) atoms as well as Cl, Br, O, N, F ones from various anions. To study Cu(I)-(C=C) interaction peculiarities and their efficiency, near 400 copper(I) π-complexes with C=C-containing ligands have been synthesized and X-ray structurally investigated during the last three decades.

In 2005 Xi-Sen Wang *et al*. published a review on olefin copper(I) complexes [21], where brief characteristics of the main coordination types of copper(I) π-complexes were described without emphasizing the role of ligand donor atoms, their number, nature of an anion and influence of medium in a formation of Cu(I) coordination junction. To fill the gaps mentioned above, Cu(I) π-complexes with allyl derivatives of heterocyclic compounds which unite rigid building moieties – heterocyclic cores as well as conformational-flexible allyl groups (which provide simultaneously ligand chelate and bridged-chelate behavior), are attractive from the viewpoint of crystal structure engineering [32,33] and should be considered. In recent years, specific attention has been paid to the syntheses and investigation of copper(I) π-complexes with allylic derivatives of heterocyclic compounds since

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a combination of heterocyclic core and C=C bond plays an exclusively important role in the formation of the unique inorganic fragments [34,35]. Contrary, a systematic search of new π-ligands for the synthesis of Cu(I) compounds with outstanding properties requires to be made periodically for a precise analysis of the accumulated structural information on the Cu(I)-(C=C) interaction.

In this review we attempted to analyze widely the coordination behavior of heterocyclic compounds allyl derivatives regarding diverse Cu(I) salts – halides and ionic ones (taking into consideration all hitherto known π-complex structures). An influence of the heterocyclic core, its basicity, structure, number of heteroatoms on a formation of a certain fragment type, as well as a role of hydrogen bonds (only superficially) in a creation of coordination frameworks will also be considered.

## 2. Aspects of Cu-(C=C) interaction in Cu(I) π-complexes with allyl derivatives of selected organic compounds

According to Pearson`s HSAB theory [36] a C=C bond, as a soft base, should readily react with a soft acid Cu(I). However, a presence of the other donor atoms – N, S, O *etc.* which successfully compete for a coordination place in the metal surrounding makes certain for stereochemical perturbations in a structural organization of the compounds to be discussed. We should apply the Dewar-Chatt-Duncanson concept [37,38] to reveal the influence of the above σ-ligand atoms (in a presence of anions from the Cu(I) salts) on the behavior of allyl derivatives (aromatic or nonaromatic, cyclic or acyclic compounds) regarding copper(I). According to this theory, (Cu-C=C)-bond includes the mutually reversible $(Cu\leftarrow C{=}C)_{\sigma}$ and $Cu\rightarrow(C{=}C)_{\pi}$ components. In the olefine π-complex, the contribution from the π-dative $(Cu\rightarrow C{=}C)_{\pi}$ component (meaning $d_{x^2-y^2} \rightarrow \pi^*$ donation) of a Cu(I)-olefin bond to the tetrahedral ligand field leads to a splitting of the copper atom *d* orbitals, which are arranged in a organized series of decreasing energy: $d_{z^2}$, $d_{x^2-y^2}$, and $d_{xy}$, $d_{xz}$, $d_{yz}$. This brings about a considerable deformation of the initial tetrahedral copper(I) environment (typical for it [39]), which is accompanied by the change of L–Cu–L angles, an elongation of the Cu–$L_{ap}$ link as compared to the Cu–$L_{eq}$ and Cu–(C=C) bonds. The distortion of a tetrahedron towards a trigonal pyramid is caused both by a difference in spatial orientation of the 3*d*-orbitals and a certain deficiency of electron density in the $d_{x^2-y^2}$ orbital (due to π-dative $(Cu\rightarrow C{=}C)_{\pi}$ interaction). Therefore, a Cu–$L_{eq}$ bond shortening should be accompanied by an increase in the deformation of the copper(I) tetrahedral environment due to an increase in the π-dative component contribution to the Cu–(C=C) bond. The degree of the polyhedron distortion of a copper coordination environment relates also with other factors, such as the structure of the inorganic moiety, the conformation rigidity of the organic ligand, and the strength of the Cu – anion interaction.

A more objective evaluation parameter is the correlation between the degree of a trigonal-pyramidal distortion of the initial tetrahedral copper environment (defined by a value of the deviation of the copper atom from the polyhedron base plane (Δ)) and the distance from the copper atom to the apical ligand *d*(Cu–$L_{ap}$). The values of Δ and *d*(Cu–$L_{ap}$) are inversely proportional: a decrease in Δ is accompanied by an increase in *d*, *i.e.*, due to Cu–$L_{ap}$ bond weakening. From this dependence one can derive the utmost Cu-$L_{ap}$ value (formal limit distance of Cu and $L_{ap}$ interaction, Fig. 1) response to copper(I) position in a hypothetical place at the equatorial ligands plane (Δ=0). So, a limit distance Cu-$Cl_{ap}$ is equal to 3.15Å, and Cu-$Br_{ap}$ - 3.25 Å (Figs. 1a, 1b), which corresponds to a sum of van-der-Vaals radii of the atoms.

Minimal deviations from the above values might be observed in a range of 3.07-3.15 Å for chlorine atoms and 3.22-3.25 Å for bromine ones. For $SO_4^{2-}$, $HSO_4^-$, $NH_2SO_3^-$, $CF_3COO^-$ anions maximal Cu-$O_{ap}$ equals 2.45 Å (Fig. 1c), but for $NO_3^-$ anion this distance increases to 2.63 Å. Taking into account a marked hardness of the fluorine atom in $BF_4^-$ and especially $SiF_6^{2-}$ Cu–F contacts rarely occur. Therefore, only six points on Fig. 1d of the appropriate π-compounds represent a similar dependence which specifies 2.82 Å as a limit of the Cu-$F_{ap}$ distance (it declines negligibly from 2.87 Å − sum of copper and fluorine van-der-Vaals radii).

A pyramidal distortion degree of the copper(I) coordination environment relates to other factors as well, such as a structure of an inorganic fragment, a conformation rigidity of an organic ligand, *etc.*

In general, the set of geometrical parameters of π-coordinated copper(I) cores, *e.g.* the Cu–(C=C) and Cu–$L_{ap}$ distances, the elongation of the coordinated double C=C bond, parameter Δ and angle value of the C=C line deviation from the base plane of a trigonal pyramid (*τ*) as well as C-Cu-C and C-C=C angles are very useful for the analysis of the efficiency of the Cu–(C=C) interaction in a crystalline π-complex. The corresponding parameters of Cu(I) π-core in the structures of copper(I) π-complexes with allyl derivatives of heterocyclic compounds are listed in Tables 1 and 2.

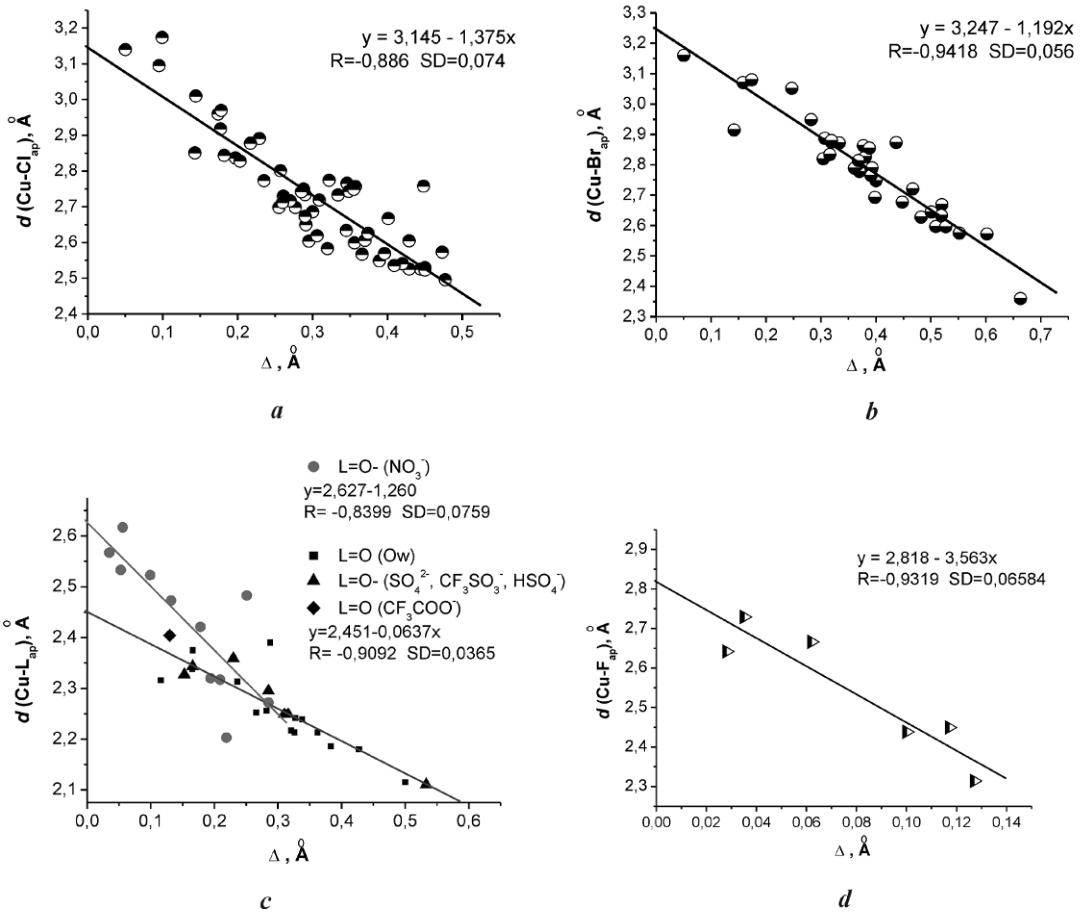



**Figure 1.** Plot of *Δ versus d*(Cu-$L_{ap}$) for Cu(I) π-complexes: *a* - $L_{ap}$= Cl (for 56 compounds), *b* - $L_{ap}$= Br (for 37 compounds), *c* - $L_{ap}$= O (for 32 compounds), *d* - $L_{ap}$= F. Some acyclic ligands have been included for comparison.

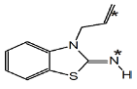
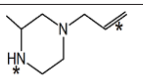
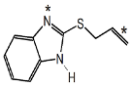
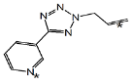
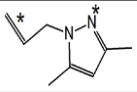
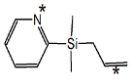
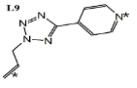
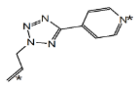
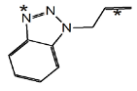
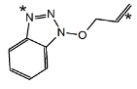
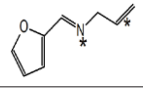
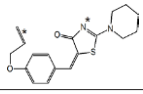
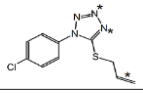
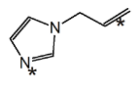
# 3. Crystallochemical survey of Cu(I) π-complexes with allylic derivatives of heterocyclic compounds

## 3.1. Molecular copper(I) halide π-complexes

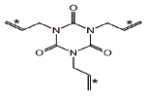
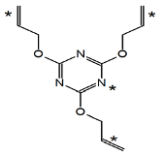
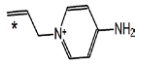
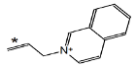
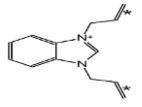
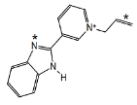
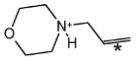
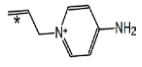
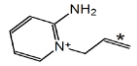
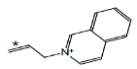
Because of a high ability of Cu(I) and Cl atoms to form a covalent bond, they are readily combined into a polymeric structure (a first example is the structure of CuCl itself) or oligomeric fragments of various nuclearity. A structure of such topological units depends on a composition and a charge of an inorganic fragment $Cu_xCl_y^{-(y-x)}$ (where y ≥ x), the nature of donor centers (O, N, S atoms *etc.*) attached to the metal, atom donor centers (O, N, S atoms *etc.*), and the ligand coordination (chelating or bridging) mode. Typically, coordination of Cu(I) by a relatively soft olefin C=C bond does not cause a formation of the isolated π-bonded CuCl moiety. So, among the structures of Cu(I) π-complexes with allyl derivatives of heterocyclic compounds one can depict only two cases where π-coordinated copper(I) is bound to the only chlorine atom (compounds **1** and **2**).

In compound **1,** the chelate bridging mode of N-allyl-2-iminobenzothiazole (**L1**, C=C bond and N atom of 2-imino-group) results in a formation of an isolated CuCl unit **C1a** (Fig. 2) [40]. The inability for ligand to form stable cyclic fragments of a chelate type as demonstrated in N-allyl-3-methylpiperazine **L2** does not prevent a stabilization of isolated CuCl units, π-bonded to the allyl group [41]. So, in the crystal structure of complex **2,** organic moiety plays only a bridging role (**C1b**), the closest distance from the metal atom to the chlorine one of an adjacent inorganic fragment being 3.70Å. Obviously, the compliant participation of a strong nucleophylic center, which is a nitrogen atom of a piperazine ring, and a double C=C bond, provides a significant increase of Cu(I) $d_{z^2}$-orbital energy which

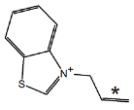
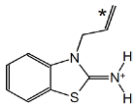
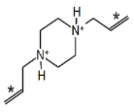
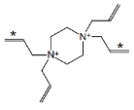
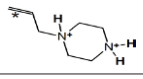
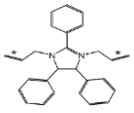
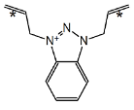
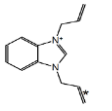
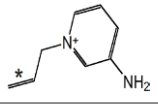
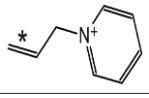
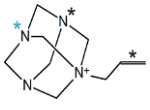
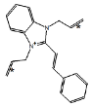
**Table 1.** Geometric parameters of Cu(I) π-core in the structures of copper(I) halide π-complexes.

| | Ligand [a] | | Composition (*preparation method*) [b] | Fragment | Cu-m[c], Å<br>C=C, Å | C=C-C, deg | Δ[d], Å | τ [e], deg | C-Cu-C, deg<br>φ(C=CCX)[f], deg | Cu-$X_{ap}$ [g], Å | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | **L1** |  | [(**L1**)CuCl] *(e.c.)* | **C1a** | 1.920(5)<br>*1.374(7)* | 123.2 | 0.04 | 17.5 | 39.4(2)<br>*145.2* | - | [40] |
| 2 | **L2** |  | $[(\mathbf{L2})CuCl]_n$ *(d.r.)* | **C1b** | 1.891<br>*1.368* | 123.9 | 0.01 | 9.9 | 39.8<br>*146.8* | 3.70 [h] | [41] |
| 3 | **L3** |  | [(**L3**)CuCl] *(e.c.)* | **C2a** | 1.96(2)<br>*1.35(3)* | 127(2) | 0.14 | 14.9 | 38.0(8)<br>*150.9* | 3.031(4) | [42] |
| 4 | | | [(**L3**)CuBr] *(e.c.)* | **C2a** | 1.961(4)<br>*1.354(5)* | 124.2(4) | 0.32 | 13.4 | 38.1(2)<br>*150.2* | 2.875(1) | [42] |
| | | | | | 1.97(1) [i,j]<br>*1.40(1)* | 125(1) | 0.21 | 17.0 | 39.1(4)<br>*155.6* | 2.986(1) | |
| 5 | **L4** |  | $[(\mathbf{L4})CuCl]_n$ *(d.r.)* | **C2b** | 1.917(3)<br>*1.364(5)* | 123.7(4) | 0.05 | 10.1 | 39.2(1)<br>*105.3* | 3.136(1) | [43] |
| 6 | | | $[(\mathbf{L4})CuBr]_n$ *(d.r.)* | **C2b** | 1.933(3)<br>*1.361(4)* | 123.7(3) | 0.08 | 8.8 | 38.8(1)<br>*104.4* | 3.158(1) | [44] |
| 7 | **L5** |  | $[(\mathbf{L5})_2Cu_2Cl_2]$ | **C3a** | 2.031<br>*1.338* | 122.9 | 0.44 | 21.1 | 36.4<br>*117.0* | 2.526 | [45] |
| 8 | **L6** |  | $[(\mathbf{L6})_2Cu_2I_2]$ *(d.r.)* | **C3a** | 2.01(2)<br>*1.10* [k] | 155.5 | 0.497 | 28.5 | 30.5(1)<br>*102.4* | 2.881(3) | [46] |
| 9 | **L9** |  | $[(\mathbf{L9})_2Cu_2Cl_2]_n$ *(d.r.)* | **C3b** | 1.949(3)<br>*1.351(4)* | 121.1(3) | 0.42 | 26.6 | 38.2(1)<br>*97.7* | 2.537(1) | [47] |
| 10 | **L9** |  | $[(\mathbf{L9})_2Cu_2Br_2]_n$ *(d.r.)* | **C3b** | 1.965(4)<br>*1.351(5)* | 122.0(4) | 0.51 | 33.9 | 37.9(1)<br>*98.9* | 2.597(1) | [48] |
| 11 | **L7_1** |  | $[(\mathbf{L7\_1})_2Cu_2Cl_2]_n$ *(e.c.)* | **C3b** | 1.965(1)<br>*1.36(1)* | 124.4(7) | 0.29 | 8.2 | 38.2(4)<br>*87.9* | 2.673(3) | [11] |
| 12 | | | $[(\mathbf{L7\_1})_2Cu_2Cl_{1.7}Br_{0.3}]_n$ *(e.c.)* | **C3b** | 1.972(7)<br>*1.348(9)* | 124.1(7) | 0.26 | 4.34 | 37.7(3)<br>*168.9* | 2.831(2) | [49] |
| 13 | **L8** |  | $[(\mathbf{L8})_2Cu_2Cl_2]_n$ *(e.c.)* | **C3b** | 1.922(6)<br>*1.331(9)* | 122.4(5) | 0.20 | 1.36 | 38.2(2)<br>*98.2* | 2.754(2) | [50] |
| 14 | | | $[(\mathbf{L8})_2Cu_2Br_2]_n$ *(e.c.)* | **C3b** | 1.979(4)<br>*1.359(8)*<br>2.038(4)<br>*1.34(1)* | 123.9(5)<br>124.6(5) | 0.32<br>0.52 | 0.58<br>16.89 | 37.9(2)<br>*103.5*<br>36.3(3)<br>*104.1* | 2.834(1)<br>2.6337(9) | [51] |
| 15 | | | $[(\mathbf{L8})Cu_2Cl_2]_n$ *(e.c.)* | **C4** | 1.936(6)<br>*1.285(9)* | 123.5(5) | 0.16 | 5.66 | 36.7(3)<br>*105.3* | 2.276(2) | [51] |
| 16 | **L10** |  | $[(\mathbf{L10})_2Cu_4Cl_4]$ *(e.c.)* | **C5** | 1.946(5)<br>*1.366(7)* | 122.9(5) | 0.09 | 2.76 | 38.7(2)<br>*146.9* | 3.578(3)[h] | [52] |
| 17 | | | $[(\mathbf{L10})_2Cu_4Br_4]$ *(e.c.)* | **C5** | 1.991(9)<br>*1.35(1)* | 124.5(9) | 0.03 | 0.99 | 37.4(3)<br>*149.4* | 3.346(6)[h] | [53] |
| 18 | **L11** |  | $[(\mathbf{L11})_2Cu_4Cl_4]_n$ *(e.c.)* | **C6** | 1.977(7)<br>*1.351(8)* | 125.0(5) | 0.05 | 1.41 | 37.7(2)<br>*7.9* | - | [54] |
| 19 | **L12** |  | $[(\mathbf{L12})_2Cu_6Cl_6]_n$ *(e.c.)* | **C7** | 1.977(9)<br>*1.34(1)* | 123.8(9) | 0.36 | 19.23 | 37.4(3)<br>*149.9* | 2.552(4) | [55] |
| 20 | **L13** |  | $[(\mathbf{L13})_2Cu_4Cl_4]_n$ *(d.r.)* | **C8** | 1.934(4)<br>*1.374(6)* | 121.5(4) | 0.27 | 8.16 | 39.11(17)<br>*93.3* | 2.824(1) | [56] |
| 21 | | | $[(\mathbf{L13})_2Cu_4Br_4]_n$ *(d.r.)* | **C8** | 1.956(11)<br>*1.372(13)* | 122.2(11) | 0.31 | 8.3 | 38.6(4)<br>*91.5* | 2.887(2) | [56] |

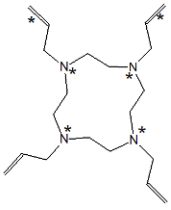
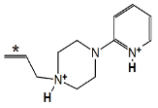
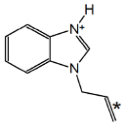
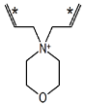
Continued **Table 1.** Geometric parameters of Cu(I) π-core in the structures of copper(I) halide π-complexes.

| | Ligand [a] | | Composition (*preparation method*) [b] | Fragment | Cu-m[c], Å C=C, Å | C=C-C, deg | Δ[d], Å | τ [e], deg | C-Cu-C, deg φ(C=CCX)[f], deg | Cu-$X_{ap}$[g], Å | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 22 | **L14** |  | $[(\mathbf{L14})_2Cu_4Br_4]_n$ *(d.r.)* | **C9** | 1.968<br>*1.401*<br>1.952<br>*1.347* | 121.0<br>121.9 | 0.01<br>0.26 | 2.7<br>12.6 | 39.2<br>*135.0*<br>38.2<br>*101.8* | 3.378[h]<br>2.952 | [57] |
| 23 | | | $[(\mathbf{L14})_2Cu_6Br_6]_n$ *(d.r.)* | **C10** | 2.047<br>*1.336* | 123.5 | 0.52 | 10.3 | 36.1<br>*110.6* | 2.669 | [57] |
| 24 | **L15** |  | $[(\mathbf{L15})_2Cu^{II}Cu_2Cl_4]_n$ *(e.c.)* | **C11** | 1.926(8)<br>*1.363(9)* | 122.18(1) | 0.17 | 6.843 | 39.0(2)<br>*84.93(1)* | 2.962(7) | [58] |
| 25 | | | $[(\mathbf{L15})_2Cu^{II}Cu_6Cl_8]_n$ *(e.c.)* | **C12** | 1.946(3)<br>*1.361(5)*<br>1.968(4)<br>*1.363(4)* | 122.1(3)<br>123.4(3) | 0.28<br>0.26 | 8.39<br>3.83 | 38.6(1) *102.2*<br>38.2(1)<br>*103.5* | 2.889(1)<br>2.698(1) | [12] |
| 26 | | | $[(\mathbf{L15})_2Cu^{II}Cu_6Cl_{1.52}Br_{6.48}]_n$ *(e.c.)* | **C12** | 1.99(3)<br>*1.36(4)*<br>2.00(3)<br>*1.331(4)* | 126(5)<br>121(5) | 0.44<br>0.36 | 9.41<br>3.57 | 37.7(11)<br>*103.1*<br>36.7(12)<br>*107.9* | 2.873(6)<br>2.788(6) | [59] |
| 27 | | | $[(\mathbf{L15})_2Cu_8Cl_8]_n$ *(e.c.)* | **C13** | 1.968(4)<br>*1.348(6)*<br>1.976(5)<br>*1.357(7)*<br>1.920(4)<br>*1.387(6)* | 121.6(4)<br>120.8(4)<br>124.8(4) | 0.40<br>0.58<br>0.02 | 14.8<br>37.2<br>2.7 | 37.8(2)<br>*101.8*<br>37.9(2) *104.7*<br>39.7(2)<br>*32.9* | 2.668(1)<br>2.404(1)[f]<br>- | [12] |
| 28 | **{L16}$^+$** |  | $[(\mathbf{L16})CuCl_2]$ *(e.c.)* | **C14** | 1.950(6)<br>*1.343(6)* | 125.6(4) | 0.07 | 6.1 | 38.0(2)<br>*24.7* | - | [60] |
| 29 | **{L17}$^+$** |  | $[(\mathbf{L17})CuBr_2]$ *(e.c.)* | **C14** | 1.931(1)<br>*1.364(4)* | 123.2(2) | 0.03 | 2.9 | 39.11(9)<br>*89.2* | - | [61] |
| 30 | **{L18}$^+$** |  | $[(\mathbf{L18})Cu_2Cl_3]_n$ *(e.c.)* | **C15** | 1.89(2)<br>*1.32(2)* | 127(1) | 0.10 | 13.1 | 38.5(6)<br>*104.1* | 3.090(9) | [62] |
| 31 | **{L19}$^+$** |  | $[(\mathbf{L19})_2Cu_4Cl_2Br_4]$ *(d.r.)* | **C16** | 1.937<br>*1.376* | 122.9 | 0.00 | 7.8 | 39.1<br>*100.2* | 3.422[h] | [19] |
| 32 | **L20 (H$^+$)** |  | $[\{\mathbf{L20}(H^+)\}_2Cu_2Cl_4]$ *(e.c.)* | **C17b** | 1.97(1) *1.30(2)*<br>1.94(1)<br>*1.36(2)* | 124.3(14)<br>121.9(12) | 0.29<br>0.13 | 14.4<br>6.7 | 36.5(6)<br>*142.7*<br>38.5(8)<br>*97.7* | 2.743(3)<br>3.072(4) | [63] |
| 33 | **{L16}$^+$** |  | $[(\mathbf{L16})_2Cu_2Br_4]\cdot 2H_2O$ *(e.c.)* | **C17b** | 2.007(1)<br>*1.332(6)* | 122.7(3) | 0.39 | 1.4 | 36.9(2)<br>*110.3* | 2.790(1) | [60] |
| 34 | | | $[(\mathbf{L16})_2Cu_2Cl_{2.7}Br_{1.3}]\cdot 2H_2O$ *(e.c.)* | **C17b** | 1.994(6)<br>*1.349(6)* | 122.9(5) | 0.36 | 3.3 | 37.4(2)<br>*112.4* | 2.756(1) | [60] |
| 35 | **{L21}$^+$** |  | $[(\mathbf{L21})_2Cu_2Cl_4]$ *(e.c.)* | **C17b** | 1.968(3)<br>*1.357(5)* | 123.0(3) | 0.43 | 6.3 | 38.1(1)<br>*108.8* | 2.5260(8) | [64] |
| 36 | | | $[(\mathbf{L21})_2Cu_2Cl_{1.8}Br_{2.2}]$ *(e.c.)* | **C17b** | 1.981(3)<br>*1.341(6)* | 123.7(3) | 0.46 | 4.8 | 37.4(2)<br>*108.7* | 2.561(4) | [64] |
| 37 | **{L17}$^+$** |  | $[(\mathbf{L17})_2Cu_2Cl_2]\cdot 2H_2O$ *(e.c.)* | **C17b** | 1.98(1)<br>*1.35(2)* | 123(1) | 0.35 | 5.2 | 37.7(5)<br>*115.4* | 2.733(3) | [65] |
| 38 | | | $[(\mathbf{L17})_2Cu_2Cl_{2.86}Br_{1.14}]\cdot 2H_2O$ *(e.c.)* | **C17b** | 1.950(8)<br>*1.35(1)* | 124.5(7) | 0.33 | 6.3 | 38.3(3)<br>*114.9* | 2.743(4) | [65] |
| 39 | | | $[(\mathbf{L17})_2Cu_2Br_4]\cdot 2H_2O$ *(e.c.)* | **C17b** | 1.985(1)<br>*1.364(4)* | 123.1(3) | 0.39 | 0.8 | 37.9(1)<br>*117.1(3)* | 2.7645(9) | [61] |

Continued **Table 1.** Geometric parameters of Cu(I) π-core in the structures of copper(I) halide π-complexes.

| | | Ligand [a] | Composition (*preparation method*) [b] | Fragment | Cu-m[c], Å C=C, Å | C=C-C, deg | Δ[d], Å | τ [e], deg | C-Cu-C, deg φ(C=CCX)[f], deg | Cu-$X_{ap}$[g], Å | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 40 | {**L22**}$^+$ |  | [(**L22**)$_2$Cu$_2$Cl$_4$]·2H$_2$O *(e.c.)* | **C17b** | 1.94(1)<br>*1.37(1)* | 121.8(8) | 0.36 | 10.9 | 38.9(4)<br>*109.8* | 2.695(2) | [66] |
| 41 | | | [(**L22**)$_2$Cu$_2$Cl$_{2.12}$Br$_{1.88}$]·2H$_2$O *(e.c.)* | **C17b** | 1.966(7)<br>*1.381(9)* | 124.0(5) | 0.40 | 7.8 | 38.6(2)<br>*108.3* | 2.750(1) | [66] |
| 42 | **L1**<br>**(H$^+$)** |  | [{**L1**(H$^+$)}$_2$Cu$_2$Cl$_4$] *(e.c.)* | **C17b** | 1.983(8)<br>*1.361(10)* | 123.8 | 0.40 | 7.61 | 37.9(3)<br>*113.4* | 2.577(2) | [40] |
| 43 | | | [{**L1**(H$^+$)}$_2$Cu$_2$Br$_4$] *(e.c.)* | **C17b** | 2.013(7)<br>*1.34(1)* | 125.4 | 0.45 | 4.84 | 36.9(3)<br>*115.8* | 2.677(1) | [40] |
| 44 | **L24**<br>**(2H$^+$)** |  | [{**L24**(2H$^+$)}Cu$_2$Cl$_4$]$_n$ *(e.c.)* | **C17a** | 1.936(6)<br>*1.386(8)* | 121.2(5) | 0.24 | 2.7 | 39.4(2)<br>*90.0* | 2.774(3) | [67] |
| 45 | {**L25**}$^{2+}$ |  | [(**L25**)Cu$_2$Cl$_4$]$_n$ (12.2%) [n] *(e.c.)* | **C17a** | 1.920(5)<br>*1.339(5)* | 126.7(3) | 0.50 | 57.3 | 37.1(2)<br>*74.7* | 2.58(1) [l] | [68] |
| | | | [(**L25**)Cu$_2$Cl$_4$] (87.8%) *(e.c.)* | **C14** | 1.941(5)<br>*1.339(5)* | 126.7(3) | 0.01 | 19.6 | 38.0(2)<br>*74.7* | 3.746(2) [h] | |
| 46 | **L26**<br>**(2H$^+$)** |  | [{(**L26**(2H$^+$)}$_2$Cu$_4$Cl$_8$] *(e.c.)* | **C18** | 1.94(1)<br>*1.35(2)* | 125(1) | 0.27 | 11.6 | 38.3(5)<br>*108.4* | 2.717(5) | [67] |
| 47 | {**L27**}$^+$ |  | [(**L27**)$_2$Cu$_2$Br$_3$]$_n$ *(d.r.)* | **C19** | 2.027<br>*1.327*<br>1.989(8)<br>*1.34(1)* | 122.6<br>122.5 | 0.38<br>0.28 | 3.1<br>0.3 | 36.2<br>37.2<br>*103.7* | 2.863<br>2.984 | [69] |
| 48 | {**L28**}$^+$ |  | [(**L28**)$_2$Cu$_2$Br$_3$]$_n$ *(e.c.)* | **C19** | 2.001(7)<br>*1.332(9)*<br>1.98(2)<br>*1.33(2)*[j] | 125.4(6)<br>124(1) | 0.28<br>0.49 | 10.0<br>6.6 | 36.8(3)<br>37.2(5) | 2.949(1)<br>2.683(2) | [70] |
| 49 | {**L18**}$^+$ |  | [(**L18**)$_2$Cu$_4$Cl$_{2.8}$Br$_{3.2}$]$_n$ *(e.c.)* | **C20** | 1.934<br>*1.346* | 124.4 | 0.15 | 4.0 | 37.4(5)<br>*83.5* | 3.067 | [71] |
| 50 | | | [(**L18**)$_2$Cu$_4$Cl$_{1.34}$Br$_{4.66}$]$_n$ *(e.c.)* | **C20** | 1.958(7)<br>*1.37(1)* | 119.4(6) | 0.16 | 6.9 | 38.6(3)<br>*85.6* | 3.071(2) | [72] |
| 51 | | | [(**L18**)$_2$Cu$_4$Br$_6$]$_n$ *(e.c.)* | **C20** | 1.954<br>*1.326* | 121.8 | 0.18 | 7.1 | 37.4(5)<br>*85.7* | 3.078 | [71] |
| 52 | {**L29**}$^+$ |  | [(**L29**)$_2$Cu$_4$Cl$_6$]$_n$ *(e.c.)* | **C20** | 1.943(5)<br>*1.344(7)* | 122.8(4) | 0.07 | 7.1 | 38.2(2)<br>*93.4* | 3.201(1)[f] | [73] |
| 53 | {**L30**}$^+$ |  | [(**L30**)$_2$Cu$_4$Cl$_6$]$_n$ *(e.c.)* | **C21** | 1.936(1)<br>*1.376(2)* | 122.1(1) | 0.18 | 8.1 | 39.11(5)<br>*102.6* | 2.9646(3) | [13] |
| 54 | {**L31**}$^+$ |  | [(**L31**)$_2$Cu$_4$Cl$_6$]$_n$ *(e.c.)* | **C22** | 1.964(5)<br>*1.371(6)* | 124.6(4) | 0.40 | 2.0 | 38.5(2)<br>*91.1* | 2.470(5) | [74] |
| 55 | | | [(**L31**)$_2$Cu$_4$Cl$_6$]$_n$ *(e.c.)* | **C23** | 1.988(7)<br>*1.37(1)* | 121.3(6) | 0.37 | 7.8 | 37.7(3)<br>*104.5* | 2.567(3) | [74] |
| 56 | {**L32**}$^+$ |  | [(**L32**)$_2$Cu$_6$Br$_4$Cl$_4$]$_n$ *(d.r.)* | **C24** | 1.962<br>*1.341*<br>1.983<br>*1.341* | 123.0<br>125.0 | 0.48<br>0.18 | 10.8<br>1.2 | 37.7<br>*112.4*<br>37.4<br>*115.5* | 2.692<br>2.990 | [75] |

**Continued Table 1.** Geometric parameters of Cu(I) π-core in the structures of copper(I) halide π-complexes.

| | Ligand [a] | Composition (*preparation method*) [b] | Fragment | Cu-m[c], Å<br>C=C, Å | C=C-C, deg | Δ[d], Å | τ [e], deg | C-Cu-C, deg<br>φ(C=CCX)[f], deg | Cu-$X_{ap}$[g], Å | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| 57 | **L33**  | $[\{(\mathbf{L33})NiCl\}_2\{Cu_6Cl_8\}]_n \cdot 2nCH_3CN$<br>*(d.r.)* | **C25** | 1.969<br>*1.387*<br>1.955<br>*1.373* | 123.0<br>122.5 | 0.43<br>0.20 | 3.2<br>3.0 | 38.8(3)<br>*104.7*<br>38.7(3)<br>*100.9* | 2.605(2)<br>2.837(2) | [76] |
| 58 | **L34**<br>**($2H^+$)**  | $[\{\mathbf{L34}(2H^+)\}_2Cu_6Cl_{10}]$<br>*(e.c.)* | **C26** | 1.967(4)<br>*1.38(7)* | 125(4) | 0.20 | 5.9 | 39(1)<br>*134.4* | 2.831(12) | [77] |
| 59 | **L35**<br>**($H^+$)**  | $[\{\mathbf{L35}(H^+)\}_2Cu_6Cl_8]_n$<br>*(e.c.)* | **C27** | 1.966(4)<br>*1.335(11)* | 124.29 | 0.258 | 8.3 | 37.8(2)<br>*119.8* | 2.801(2) | [78] |
| 60 | **{L36}$^+$**  | $[(\mathbf{L36})_2Cu_8Cl_{10}]_n$<br>*(e.c.)* | **C28** | 1.985(5)<br>*1.341(7)*<br>1.948(6)<br>*1.350(7)* | 123.5(4)<br>123.4(5) | 0.39<br>0.35 | 0.5<br>8.5 | 37.3(2)<br>*105.7*<br>38.2(2)<br>*97.0* | 2.677(1)<br>2.578(1) | [79] |

*[a] asterisk indicates "active" as to the Cu(I) coordination ligand site; [b] method of preparation: alternating current electrochemical (e.c.) and direct (d.r.) (dominant solvothermal) techniques; [c] m - a middle point of C=C bond, [d] – a distance value of copper(I) deviation from the base plane of a trigonal pyramid, [e] – angle between C=C line and trigonal pyramid base plane, [f] – torsion angle of allyl C=C-C-X group (X – any element), [g] – a distance from the copper(I) to the apical ($L_{ap}$) donor atom, [h] - a distance from the copper(I) to the nearest hypothetically apical $L_{ap}$ halogen atom, [i] – data for other crystallographic independent Cu(I), [g] – data for one of two disordered C=C bond positions, [k] – allylic C=C bond probably disordered, [l] - coordination polyhedron of the atom is preferably tetrahedral, [n] – site occupation probability of disordered CuCl moieties*

excludes other halogen atom coordination. For **C2,** a display of the steric hindrance due to an appearance of a peculiar zigzag coordination chain in **2** should not be excluded (Fig. 2). The architecture of another molecular complex **3** is caused by the chelate role of S-allyl-benzimidazole-2-thiol (**L3**), where both the olefinic C=C bond of the allyl group and the N atom of the imidazole ring are combined by a Cu(I) atom into the six-membered organometallic cycles [42]. Moreover, the lower nucleophilic activity of the heterocyclic N atom and a large lability of the S-allyl group in **3**, favor a formation of a pseudodimeric centrosymmetric fragment $[(\mathbf{L3})_2Cu_2Cl_2]$ (**C2a**), in which current Cu ... Cl contacts at adistance of 3.03Å between different π-coordinated CuCl units, fit in a hypothetical scope of the Cu(I)-$Cl_{ap}$ interaction (Fig. 1a). The reaction of **L3** with CuBr leads to a formation of an acentric $[(\mathbf{L3})_2Cu_2Br_2]$ fragment with Cu-$Br_{ap}$ and distances of 2.88 and 2.99 Å. A decrease of the Cu-$X_{ap}$ distance in replacing a chlorine atom by a bromine atom can be explained by a lesser polarizing ability of the Br atom accompanied by a Cu(I) deviation from the base plane of a trigonal pyramid up to $\Delta$ = 0.32 Å (Table 1).

N-Allyl-5-(3-pyridyle)-2*H*-tetrazole **L4**, which contains five potential nucleophilic nitrogen atoms in the crystal structure of **5** and **6,** is coordinated to Cu(I) atoms only through the C=C bond of the allyl group and the most nucleophilic nitrogen atom of the pyridyle ring [43,44]. Thus, a significant space separation of the active donor center and the allylic C=C bond does not affect a $d_{z^2}$ -orbital energy increase and leads to a formation of inorganic pseudodimeric $\{Cu_2Hal_2\}$ (Hal = Cl (**5**), Br (**6**)) **C2b** fragment, in which CuHal moieties are isolated from each other by the Cu-X distance of 3.14 Å (**5**) and 3.16 Å (**6**) respectively.

A cyclic $Cu_2Cl_2$ fragment appears to be favorable also in the crystal structure of **7**-**14**, in which organic molecules play a role of bidentate ligands (Fig. 3). Only two ligands **L5** and **L6** are attached to the copper(I) center in a chelate mode (forming five- (**7**) and six-membered (**8**) organometallic cycles (C3a) via the allylic C=C group and heterocyclic N atom), whereas the others (**L7**-**L10**) – are bound to Cu(I) atoms in a bridged manner.

An increase in the nucleophilic activity of N-allyl-5-(4-pyridyle)-2*H*-tetrazole **L9**, in comparison with

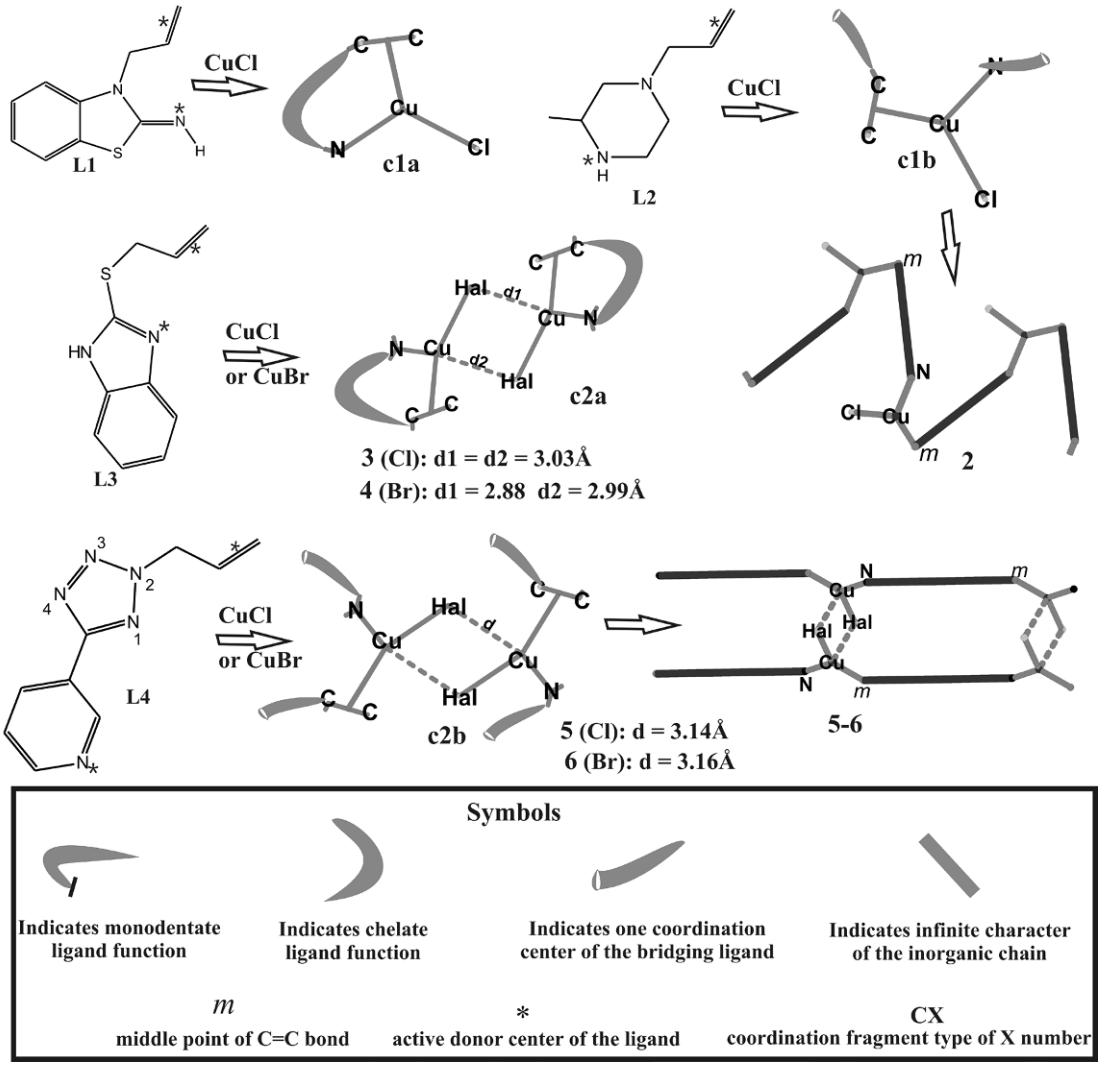



**Figure 2.** Structural genesis of **C1** and **C2** fragments in **1-6** compounds.

3-pyridyle analogue **L4**, accompanied by a decrease of $d_{z^2}$ -orbital energy, leads to an effective Cu(I)-Hal$_{ap}$ interaction (Cu-Cl$_{ap}$ 2.54 and Cu-Br$_{ap}$ 2.60Å), resulting in the infinite dimeric {[(**L9**)$_2$Cu$_2$Hal$_2$]}$_n$ chains of **9** [47] and **10** [48]. Taking into account a general structural motif, organometallic chains **5** and **6** can be considered virtually as isomorphic to **9** and **10**.

Some other type of ligand, 1-allyloxybenzotriazole **L8,** by means of the C=C bond and the most nucleophilic N3 atom of the triazole ring, in the presence of Br atoms links metal centers to the similar infinite {[(**L8**)$_2$Cu$_2$Br$_2$]}$_n$ chains **14** [51]; a presence of Cl leads to a formation of the polymer structure **13** [50]. Both a similar structure of the inorganic fragment **C3** and different dimensionality of organometallic chains in **13** and **14** indicate the steric hindrance of the benzotriazole core as a limiting factor formation (Fig. 3). This statement is confirmed by the fact that 1-allylbenzotriazole **L7_1** under similar conditions reacts with CuCl and CuBr and results in the 2D-coordionation polymeric **11** and **12** formations. It should be noted, that a mixture of two isomers 1- (**L7_1**) and 2-allylbenzotriazole (**L7_2**) with a molar ratio of 1:1, was used for the preparation of the **13** and **14** compounds; under alternating current (*ac*-) electrochemical conditions, the CuHal unit selectively coordinates only **L7_1** isomer.

At less **L8**: CuCl ratio more complicated [(**L8**)Cu$_2$Cl$_2$] (**15**) structure appeared, in which two crystallographically independent metal atoms are characterized by different coordination environments: π-coordinated Cu(I) atom possesses trigonal (formed by the allylic C=C bond and two Cl atoms) and σ-coordinated – tetrahedral (formed by N3 atom of the triazole ring and three chlorine atoms) surroundings [51]. Consequently Cu$_2$Cl$_2$

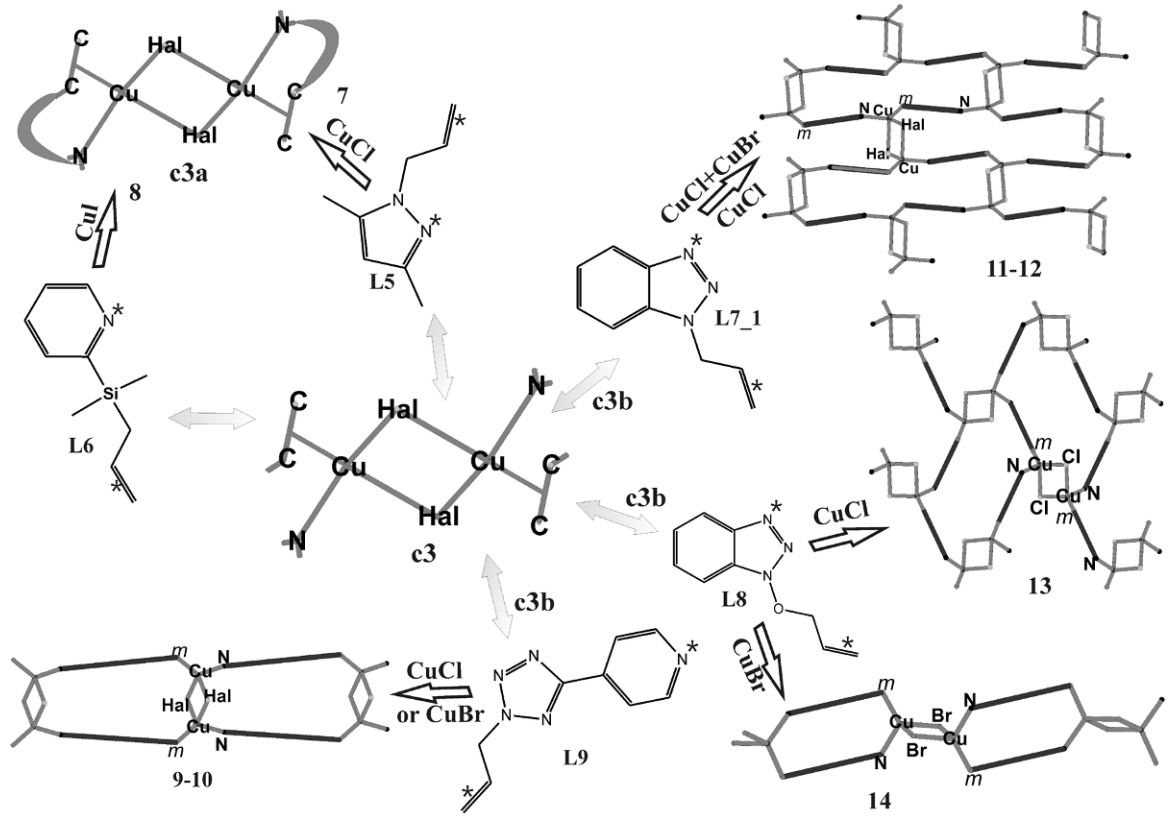



**Figure 3.** Structural genesis of **C3** fragment in **7-14** compounds.

fragments are linked into infinite inorganic chains $\{Cu_2Cl_2\}_n$ (**C4**), which, in turn, are connected by bridged 1-allyloxibenzotriazole molecules in the 3D-framework **15** (Fig. 4). N-allylfurylaldimine **L10** is unable to form cyclic organometallic fragments in a chelate mode with one metal center, therefore two independent Cu(I) atoms and cyclic $\{Cu_4Hal_4\}$ fragments (**C5**) in the twist-configuration appear (Fig. 4).

In **16** and **17** structures, both π- and σ-attached to **L10** Cu(I) atoms have a trigonal environment; in **16**, however, the coordination of the σ-bound Cu(I) center may be regarded as trigonal-pyramidal due to a presence of a Cu-O contact with the furyl ring [52,53]. The elongated Cu(2)-O (2.79 A) bond as well as a OCu(2)N (70.8(1)°) angle indicate a presence of a fourth coordination environment participant due to a packing effect. An analog twisted $\{Cu_4Hal_4\}$ skeleton was found in the copper(I) π-complex with N-allylbenzaldimine [52], dibenzo[a,e]cyclooctatetraene [80] and allyl alcohol [81]. The reaction of another azomethine type of heterocyclic **L11** ligand with CuCl leads to a formation of similar eight-membered $\{Cu_4Cl_4\}$ cycles (**C6**) which in the structure of **18** are linked into stairs-like coordination polymers [54], due to both significant donor center space separation and specific ligand rigidity (Fig. 4).

The 5-(allylthio)-1-(4-chlorophenyl)-1H-tetrazole (**L12**) in the structure of **19** almost fully realizes its coordination abilities (**C7**) by means of two N (N3 and N4) atoms of the tetrazole ring as well as the olefin C=C bond (Fig. 5). Its behavior regarding CuHal moiety considerably differs from that of the 5-pyridyle derivatives of tetrazoles **L4** and **L9**. Thus, the **L12** molecule plays a role of tridentate chelate-bridging ligand connecting two Cu(I) atoms into centrosymmetric $[(\mathbf{L12})_2Cu_2]^{2+}$ dimers (with one six-membered almost planar $Cu_2N_4$ cycle and two seven-membered $CuNC_4S$ organometallic rings), while the chlorine atom occupies the apical position ($Cu\text{-}Cl_{ap}$ 2.55Å) of the metal coordination polyhedron. The above conditions lead to an oligomerization of CuCl units into infinite anionic $\{Cu_2Cl_3^-\}_\infty$ chains, which link $[(\mathbf{L12})_2Cu_2]^{2+}$ dimers into 2D polymeric layers **19** (Fig. 5) [55].

An increase in nucleophilic activity of the N-donor center and a decrease in the number of active sites in the ligand as well as heterocyclic core radius, in the presence of Cu(I) π-bonded allyl group, make its specific contributions to the polynuclear inorganic fragment construction. For example, in the structure of **20** and **21** (prepared by solvothermal reaction), bidentate N-allylimidazole **L13** provides a combination

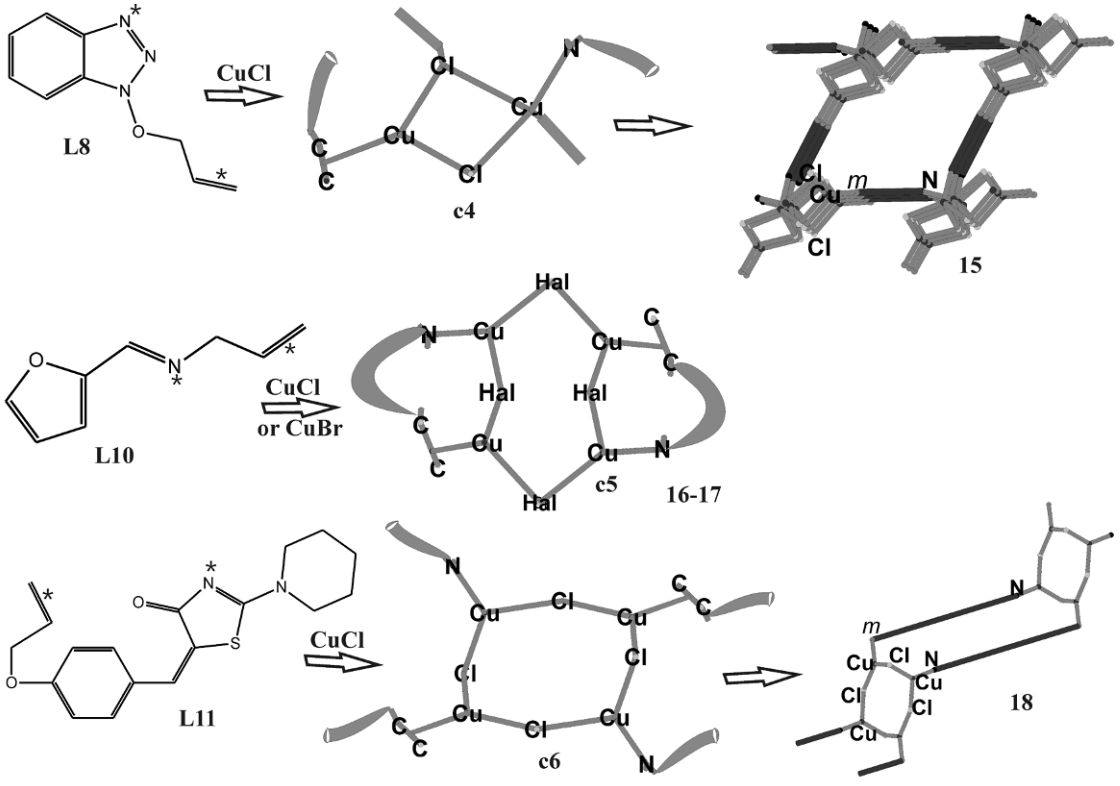



**Figure 4.** Structural genesis of **C5** and **C6** fragments in **15-18** compounds.

of CuHal (Hal = Cl(**20**), Br(**21**)) moieties into infinite fragments $\{(Cu_2Hal_2)_2\}_n$, within which only one of the two independent metal atom is π-coordinated and adopts a trigolal-pyramidal environment with a Cu-$Hal_{ap}$ distance of 2.82 (**20**) and 2.89 Å (**21**). Thus, the **C8** architecture may be represented by two **C1** fragments, symmetrically united by two bridging CuHal moieties; $\{(Cu_2Hal_2)_2\}_n$ chains are linked by bridging **L13** molecules into a 3D-framework. It should be noted, that **20** and **21** are the first 3D copper(I)-olefin coordination polymers synthesized by direct method [56].

As it was stated in [57], triallyl-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione **L14** in the reaction with CuBr of a 1:2 and 1:3 molar ratio (under solvothermal condition) affords two types of $[(\mathbf{L14})_2Cu_4Br_4]$ (**22**) and $[(\mathbf{L14})_2Cu_6Br_6]$ (**23**) π-complexes. So, in the structure of **22** the organic molecule uses only two of the three available allyl groups (these two active olefinic bonds have *trans*-location relatively of the triazine plane). Due to such **L14** behaviour the eight-membered $Cu_4Br_4$ fragment (**C9**) with an open-cubane arrangement appears (only few Cu(I) π-complexes with inorganic particle of cubane (or open cubane) topology [82-85] are known, while cubane $Cu_4Cl_4$-core was found in a number of Cu(I) σ-complexes with N- and P-donor ligands [86-89]). Two of the independent metal centers are π-bonded to allylic C=C bonds: they possess different trigonal and trigonal-planar environments respectively ((Cu(2)-$Br_{ap}$ 2.95 Å). The bridged ligand **L14** connects isolated $Cu_4Br_4$ units into a polymeric chain **22**.

In the **23** crystal structure all three allyl groups of the same organic molecule **L14** participate in copper(I) coordination. The increase in the number of active C=C sites results in an aggregation of CuBr units into the distorted hexagonal-prismatic 12-membered $\{Cu_6Br_6\}$ (**C10**) fragment (Fig. 6) [57]. Each Cu(I) in this cluster has a distorted tetrahedral environment composed of one C=C bond and three bromine atoms; in its turn, Br atom is linked to the three metals center, while each $\{Cu_6Br_6\}$ fragment is bonded to six **L14** molecules. As a result **L14** molecules are coordinated to three different clusters $\{Cu_6Br_6\}$ and form 2D coordination network **23**.

A role of isomeric 2,4,6-triallyloxy-1,3,5-triazine **L15** in regard to CuHal appears to be similar to that of **L14** relating to the inorganic fragment construction, despite a participation of a N atom in the metal coordination. By means of the *ac*-electrochemical technique at a molar ratio of $CuCl_2$ and **L15** 3:1.6 compound **24** was isolated from the ethanol solution [58]. The latter complex is built up of the cyclic (like twice open-cubane arrangement) tetrameric $\{Cu_4Cl_4\}$ units (**C11**) of a "bath" conformation. Due to -4, symmetrical Cu-Cl distances are equal to

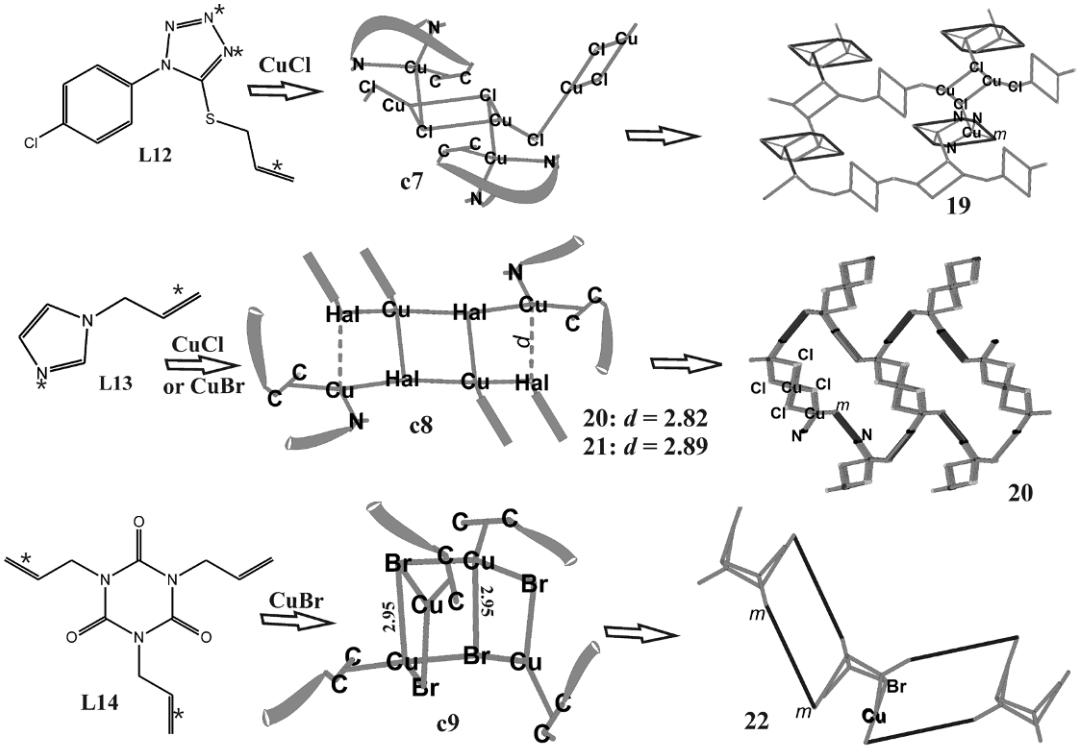



**Figure 5.** Structural genesis of **C7-C9** fragments in **19-22** compounds.

2.256 and 2.260 Å, and each $Cu_4Cl_4$ unit is linked to four **L15** molecules. One more included Cu(II) atom forms its own square coordination $\{Cu^{II}Cl_2(N\text{-})_2\}$ environment (also found in $[(\mathbf{L15})_2Cu^{II}Cl_2]$ structure [12]), and is coordinated with the ligand by means of two active N atoms of two different **L15** molecules. As a result, the bridging $Cu^{II}Cl_2$ fragments connect π-coordinated copper atoms (Cu-$Cl_{ap}$ 2.96 Å) of adjacent $Cu_4Cl_4$ clusters into $\{[Cu^{II}Cu_2Cl_4]\}_n$ 3D inorganic framework, which are stitched by **L15** ligands. It should be noted that **L15** molecule in the structure of **24** is coordinated to the metal atoms only by two active sites (allylic C=C bond and opposite N triazine atom), while the π-coordinated allyl group and one adjacent free (not bonded) C=C bond are on the same side of the triazine ring, and the third, also free $C_3H_5$-group, on the triazine plane.

Under *ac*-electrochemical conditions, starting from a water-ethanol solution of $CuCl_2$ and **L15** a π-complex $[(\mathbf{L15})_2Cu^{II}Cu_6Cl_8]$ (**25**) of 1:1.2 molar stoichiometry was obtained [12]. This compound and the described above **23** complex are very similar in terms of $Cu_6Hal_6$ construction, but in the latter, $Cu_6Cl_6$ units were united by means of $\{Cu^{II}Cl_2(N\text{-})_2\}$ linkers (Cu-Cl 2.30 Å) into endless inorganic $\{[Cu^{II}Cu_6Cl_8]\}_n$ chains, combined by three active sites (two C=C and one N atom) of **L15** in the 3D coordination framework. In this case each **L15** molecule was bonded by two donor centers (N and C=C) to one inorganic chain, and the third (C=C) – to the neighbouring chains. These π-coordinated allyl groups were situated in trans-coordination mode (located at triazine ring opposite sides), and the free one – in the plane of a heterocyclic core. In general, **C12** architecture in **25** can be derived from **C11** by incorporating two CuCl units, with an increase in active C=C bonds (two coordinated C=C bonds). Mix-halogen $\{[(\mathbf{L15})2Cu^{II}Cu_6Cl_{1.52}Br_{6.48}]\}$ (**26**) complex is isostructural to **25** [59]. Further *ac*-electrochemical treatment of mother liquor containing crystals of **25** during 96h, favored a reduction of the remaining Cu(II) (occurred in **25**) to Cu(I) and caused an appearance of $[(\mathbf{L15})_2Cu_8Cl_8]$ (**27**) π-complex (Fig. 6) [12]. This process was accompanied by a transformation of a bridging $\{Cu^{II}Cl_2(N\text{-})_2\}$ fragment into a terminal $\{Cu^{I}Cl(N\text{-})(C{=}C\text{-})\}$ one and finally forming an $\{[Cu_6Cl_6(CuCl)_2]\}$ aggregate. Thus, in **27** the organic ligand **L15** fully realizes its π-coordinating abilities and combines the inorganic subunits into a three-dimensional framework (corresponds to **C13** fragment, Fig. 6).

## 3.2. Zwitterionic copper(I) halide π-complexes

The simplest representatives of this class of π-complexes are the halide π-compounds of $[(\mathbf{L}^+)CuHal_2]$ ($\mathbf{L}^+$ - N-allyl-4-aminopyridinium ($\mathbf{L16}^+$) (**28**) [60] or N-allylisoquinolinium $\mathbf{L17}^+$ (**29**) [61]) composition with

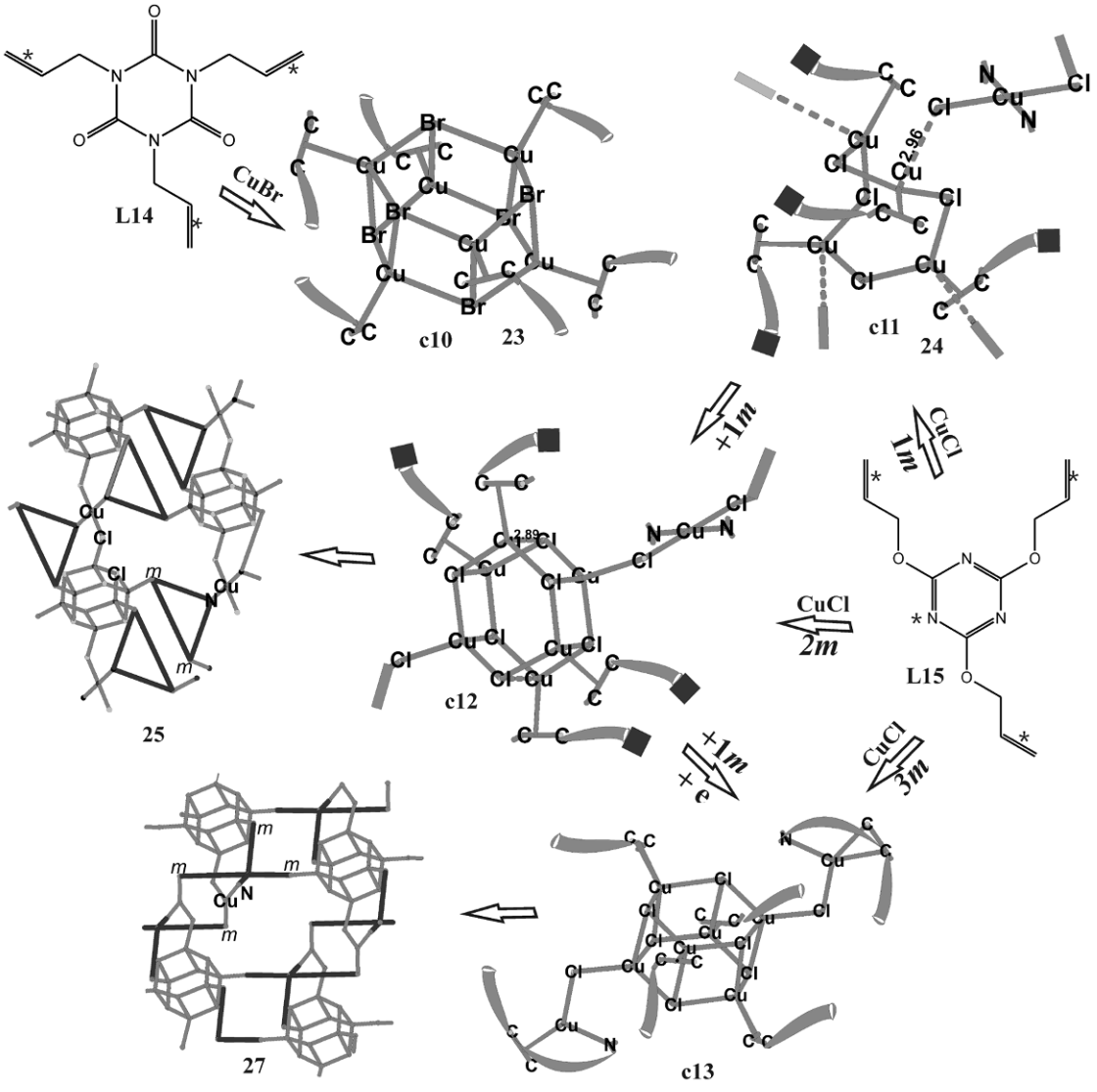



**Figure 6.** Structural genesis of **C10-C13** fragments in **23-27** compounds.

a **C14** fragment. It is of importance to note that cation **L16**$^+$ promotes a formation of $\{CuHal_2\}^-$ unit (**C14**) in a presence of only chloride ions (Fig. 7), while chlorine by bromine substitution leads to the other $\{Cu_2Hal_2\}^-$ fragment (**C17**). It is obvious that **C14** architecture of **28** is caused probably by the participation of an amino group of the ligand **L16**$^+$ in effective N-H...Cl hydrogen bonds construction. This effect is less pronounced in the case of Br atoms in **33** and **34**. So, N-allylisoquinolinium **L17**$^+$, which is unable to form N-H..X (X=Cl or Br) hydrogen bonds, leads to the predominant $Cu_2Hal_4^{2-}$(**C17b**) construction; but $Cu_2Br_4^{2-}$, when kept [(**L17**)CuBr]·$H_2O$ (**39**) in the mother liquor for six months, transformed into [(**L17**)$CuBr_2$] (**29**) with $CuBr_2^-$ unit (**C14**) [61].

Diallylbenzimidazolium (**L18**$^+$) cation, due to a presence of two coordinated active allyl groups, governs a formation of a $\{Cu_2Cl_3\}^-$ unit (**C15**) through the combination of two π-bonded CuCl moieties with one bridging $Cl^-$ anion (Fig. 7). In this, the bond length between CuCl units (Cu-$Cl_{ap}$ 3.09 Å) is found within an acceptable hypothetical scope of copper(I)-chlorine interaction (Fig. 1). As a result, in the structure of **30** bridging **L18**$^+$ moieties connect $Cu_2Cl_3^-$ fragments into an infinite chain [62]. The other cation **L19**$^+$, 2-(3-pyridil) derivative of benzimidazole, in the structure of **31** acts as a bidentate ligand forming similar $\{Cu_2ClBr_2\}^-$ unit (**C16**) with the absence of any interaction between two CuHal moieties (the second nearest halogen atom is located at 3.32 and 3.42 Å from the metal center). Both copper atoms here possess different coordination environments: first Cu(I) is π-bonded and the second one - σ-bonded to N pyridyl atoms, resulting in {(**L19**)

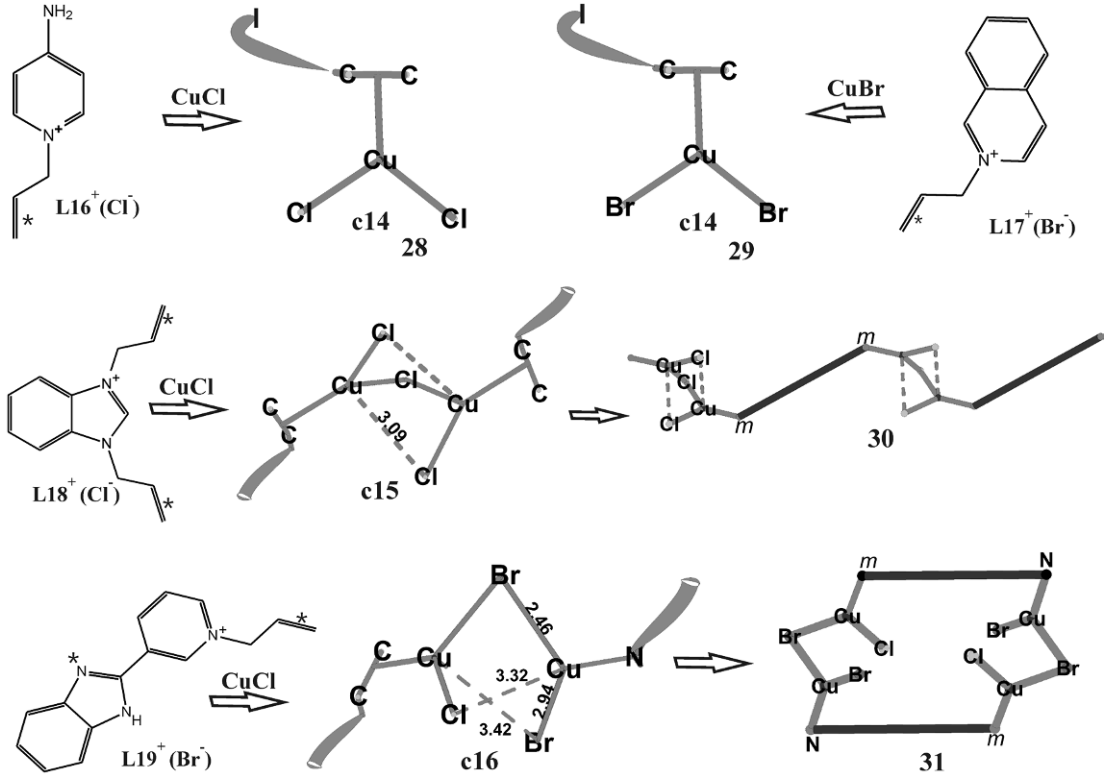



**Figure 7.** Structural genesis of **C14-C16** fragments in **28-31** compounds.

$Cu_2ClBr_2\}_2$ dimer **31** [19]. A similar $\{Cu_2Hal_3\}^-$ fragment construction in **30** and **31** may be caused by a specific geometry of the benzimidazole core.

All the ligands shown in Fig. 8 contain an allyl group, directly bound to a quaternary N atom of heterocyclic core. π-Compounds **33**-**43** possess centrosymmetrical $[Cu_2Hal_4]^{2-}$ (**C17b**) fragment with two π-attached allylic C=C bonds; the only exception – **32** where acentric $[Cu_2Cl_4]^{2-}$ anion occurred [63]. It should be noted, that similar **C17b** architecture was found earlier in $[(CH_2{=}CH\text{-}CH_2\text{-}NH_3)CuX_2)$ (X=Cl, Br) [91,92] π-compounds. The Cu(I) center in **32**-**42** structures possesses a trigonal-pyramidal coordination environment with the bridging apical halogen atoms. The acentric $[Cu_2Cl_4]^{2-}$ ion ($Cu(1)\text{-}Cl_{ap}$ 2.74 and $Cu(2)\text{-}Cl_{ap}$ 3.07 Å) which occurred in a **32** π-complex may arise due to the existence of asymmetrical (N)H...Cl contacts. These appear among protonated nitrogen atoms of two **L20(H+)** cations and only one $Cu(1)Cl_2$ moiety, while the other independent $Cu(2)Cl_2$ unit does not participate in hydrogen bonds formation.

As mentioned above, **L16**$^{+\cdot}$(Br$^-$), **L17**$^+$(Cl$^-$) and **L17**$^+$(Br$^-$) react with CuBr or CuCl to form a $Cu_2Hal_4^{2-}$ anion (**33**, **34**, **37**-**39**, Fig. 8), which corresponds to the **C17b** fragment (Fig. 8). In contrast to 1-allyl-4-aminopyridinium chloride in **28**, with monomeric anion $CuCl_2^-$ (fragment **C14**, Fig. 7), isomeric 1-allyl-2-aminopyridinium chloride or bromide (**L21**$^+$(Cl$^-$) or **L21**$^+$Br$^-$) due to (N)-H...X contacts of less efficiency, behaves as **L16**$^{+\cdot}$(Br$^-$) producing π-complexes of [(**L21**)$CuX_2$] composition with the inorganic fragment **C17b** (Fig. 8) [64].

A difference in the N-allylquinolinium **L35**$^+$ behavior, which does not form copper-halide π-compounds[1] [65,93], and N-allylisoquinolinium **L17**$^+$, which produces zwitterionic copper(I) halide π-complexes, can also be explained by a different $pK_a$ value of origin for quinoline (4.90) and isoquinoline (5.40). The lowest $pK_a$ value of quinoline, among the compounds under consideration, reflects on the allyl group electron density distribution making it inert to π-coordination. Nevertheless, **C17** architecture was found in **40** and **41** π-compounds [66], in which origin benzothiazole **L22** has a much lower $pK_a$ value of 2.44. It is interesting to note that **L1(H**$^+$**)** (Br$^-$) under *ac*-electrochemical conditions in an ethanol solution reacts with CuCl and CuBr to give the same $Cu_2Hal_4^{2-}$ fragments (**42**, **43**), while in an acetonitrile solution, **L1(H**$^+$**)** (Br$^-$) loses the HBr molecule resulting in [(**L1**)CuCl] (**1**) complex with a **C1a** fragment.

[1]Allylquinolinium as well allylisoquinolinium cations form copper(II) salts of the composition $(L^+)_2[Cu^{II}Cl_4]$ [93].

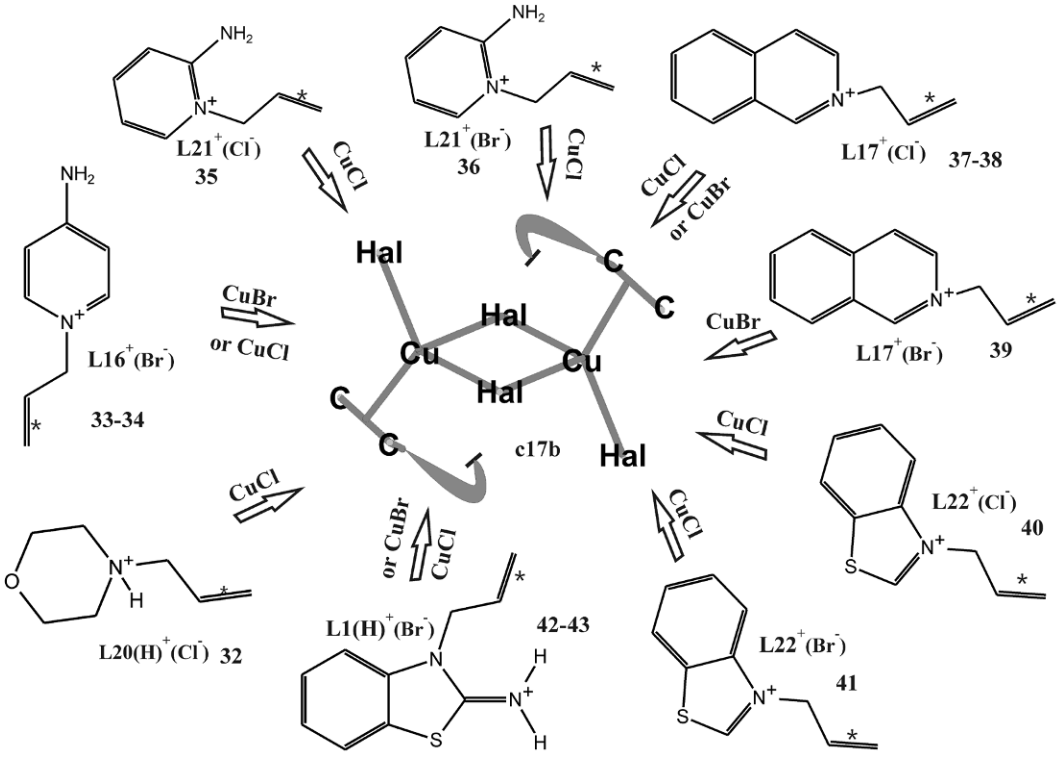



**Figure 8.** Structural genesis of **C17** fragment in **32-43** compounds.

In Fig. 9 one can see that diallylpiperazinium {**L24(2H$^+$)**}$^{2+}$ and tetraallylpiperazinium **L25**$^{2+}$ cations, containing the same piperazine core, react with CuCl and result in centrosymmetrical inorganic $\{Cu_2Cl_4\}^{2-}$ fragments (**C17a,** Fig. 9). In this case they are connected by π-bridging cations into coordination polymers **44** [67] and **45** [68]. In the last structures both organic cations act as the bidentate ligand (despite the presence of four allyl group in **L25**$^{2+}$) and π-bonded allyl groups are related by the center of the symmetry of the piperazine ring (it should be noted, that **C17a** architecture in **45** is one of two disordered modes of $CuCl_2^-$ π-coordination, the second CuCl unit with 87% occupation probability causes a realization of isolated $\{CuCl_2\}^-$ fragment with trigonal Cu(I) surrounding). In general, it can be concluded, that $\{(\text{-}CH_2)_2N(R)C_3H_5\}^+$ (R=H, $C_3H_5$) organic linkers (belonging to **L20(H)**$^+$, {**L24(2H**$^+$**)**}$^{2+}$, **L25**$^{2+}$) in the crystal structure of **32**, **44** and **45** appear to be a guiding building factor in $Cu_2Cl_4^{2-}$ construction.

A tendency of $\{(\text{-}CH_2)_2N(R)C_3H_5\}^+$ organic linkers to form a $\{Cu_nCl_{2n}\}^{2-}$ unit is also displayed in a formation of more complicated centrosymmetric $Cu_4Cl_8^{2-}$ fragments (**C18**) in **46** [67]. The last anion can be considered to be a broken π-bonded $\{Cu_2Cl_4\}^{2-}$ unit (due to a higher (number of active sites)/(ligand charge) ratio). Geometric parameters of piperazine core (chair conformation) in **44**, **45** and **46** are basically the same.

Some more examples – diallylisoamarinium **L27**$^+$ and diallylbenzotriazolium **L28**$^+$, containing similar, but spatially separated by {C-N-X-N$^+$-C} (X=C or N) linker active C=C bonds, form infinite anionic $\{Cu_2Br_3^-\}_n$ chains (**C19**), in which one can also depict a dimeric $\{Cu_2Br_4\}$ unit (Fig. 9). Similar **C18** architecture was found earlier in the $[(C_3H_5)_2NH_2]Cu_2Br_3$ π-complex with a diallylammonium cation [94]. The bridging bidentate **L27** and **L28**$^+$ moieties bind $\{Cu_2Br_3^-\}_n$ chains into isomorphous two-dimensional grids (Fig. 9). Inorganic parts in **47** [69] and **48** [70] contain two crystallographically independent Cu(I) atoms belonging to two neighboring $Cu_2Br_3$ units. It should be noted, that only isoamarine (in which phenyl rings, in 5 and 6 positions, are in *trans*-configuration) derivative **L27**$^+$ is able to give Cu(I) π-compounds. On the contrary to the above amarine (possessing the *cis*-configuration of phenyl rings), due to a steric hindrance, produces (diallylamarinium)$[Cu_2Br_4]$ salt only [69]. Corresponding Cu-$Br_{ap}$ distance within the anion in **48** equals to 2.98 Å for Cu(1) and 2.86 Å for Cu(2).

The reaction of diallylbenzimidazolium (**L18**$^+$) bromide with CuCl or CuBr under the *ac*-electrochemical conditions produces two mix-halogen $[(\mathbf{L18})Cu_2Hal_3]$ (**49**, **50**) (with a molar ratio Br:Cl of 1.6:1.4 (1.14)) and one bromine $[(\mathbf{L18})Cu_2Br_3]$ (**51**) π-compounds with more complicated fragments built in **C20** [71,72]. Transformation of **C19** into **C20** (keeping the same [(**L**)

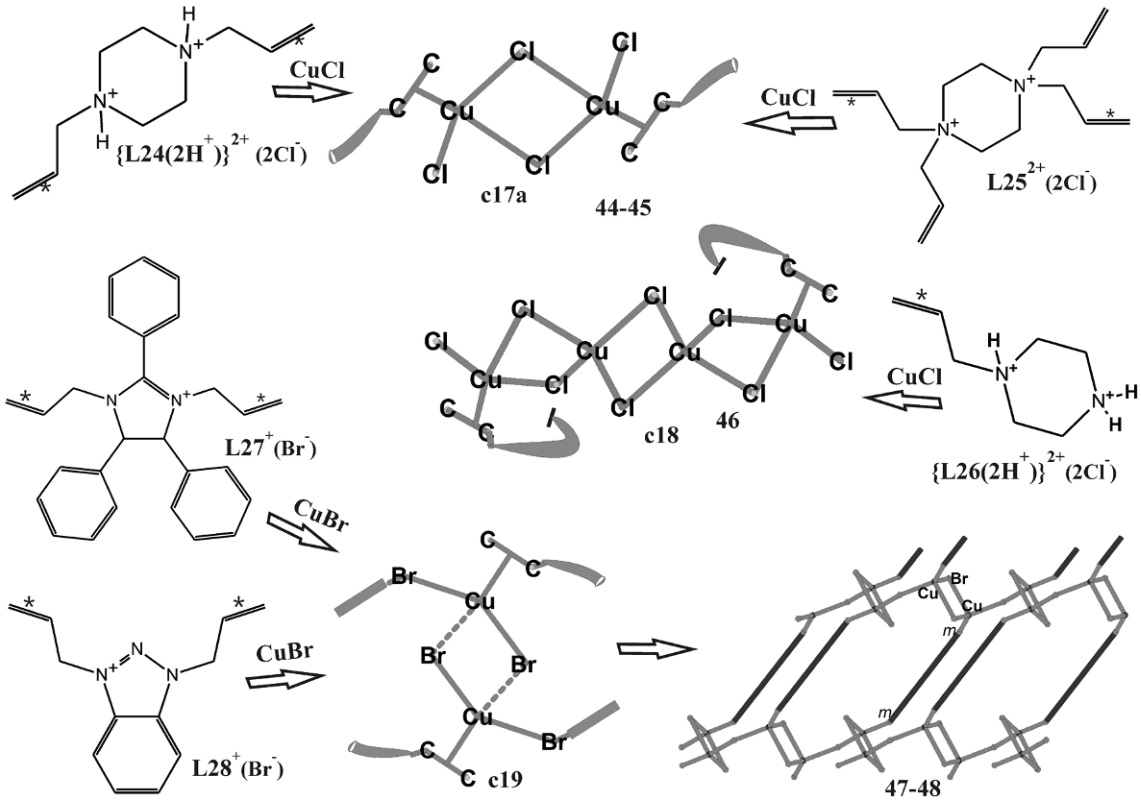



**Figure 9.** Structural genesis of **C17-C19** fragments in **44-48** compounds.

$Cu_2Br_3$] composition) may be caused by a significantly higher $pK_a$ value of original benzimidazole (5.53, basicity) in comparison with benzotriazole (<0, basicity), that reflects an electrostatic interaction between **L18**$^+$ and the inorganic anion. The inorganic part in **49**-**51** consists of two independent copper(I) atoms with a different coordination environment: trigonal-pyramidal for π-bonded Cu(I) and tetrahedral with the only halogen atoms for the other copper(I) atom. As a result, the infinite $\{Cu_2Hal_3^-\}_n$ chains in **C20** possess two different subunits – eight-membered cycle $Cu_4Hal_4$ of chair conformation and a square $Cu_2Hal_2$ cycle, which are cross-linked into a 1D polymer by nodal metal atoms (Fig. 10). Within $Cu_4Hal_4$ cycles, the apical position of an π-coordinated Cu(I) polyhedron is occupied by an opposite halogen atom of the ring at a distance of 3.07 (**49**) [71], 3.07 (**50**) [72] and 2.99 Å (**51**) [71]).

The same **C20** fragment formation in N-allyl-3-aminopyridinium **L29**$^+$ also relates to a $pK_a$ value of original 3-aminopyridine (5.98), which is less than the corresponding $pK_a$ value of 2- (6.86) and 4-aminopyridine (9.25) (see above). The $Cl_{ap}$ atoms in $Cu_4Hal_4$ ring of **52** are remote from Cu(I) up to 3.2Å (due to more covalent character of Cu-$Cl_{eq}$ bonds, accompanied by effective Cu-(C=C) interaction) and therefore eight-member cycles appear to be more distorted.

A lower $pK_a$ value (5.22) of pyridine (compared with those of its amino derivatives) and its inability to form effective hydrogen bonds may explain the very complicated architecture (**C21**) of the inorganic chain which arises due to the interaction of CuCl and N-allylpyridinium **L30**$^+$ chloride [13]. Thus, one may regard the resulting inorganic $\{Cu_4Cl_6^{2-}\}$ fragment (the simplest composition is $\{Cu_2Cl_3^{2-}\}$) in a structure of **53** as Cu(I) tetrahedra, connected by a common edge Cl(3)-Cl(3) in pairs, and simultaneously - by opposite vertices Cl(2)-Cl(2), and combined into endless chains, whereas the π-coordinated Cu(I) plays a bridge role between Cl(3) atoms in **C21** architecture (Fig. 10).

It is worth noting that N-allylhexamethylenetetraminium **L31**$^+$ can play a role of bidentate or tridentate ligand due to its participation in the metal coordination by means of the allylic C=C bond and one (or two) N-atoms from the heterocyclic core. Applying the *ac*-electrochemical technique, the reaction of CuCl with (**L31**$^+$)($Cl^-$) in water-ethanol solution results in a **54** structure with a **C22** architecture, while under similar conditions from the corresponding solution, acidified by formic acid to pH 4.5, the π-complex **55** with **C23** fragment was found (Fig. 11) [74].

The structure of **54** is built of original centrosymmetric insular $\{Cu_4Cl_6\}^{2-}$ fragments (**C22**) which are composed

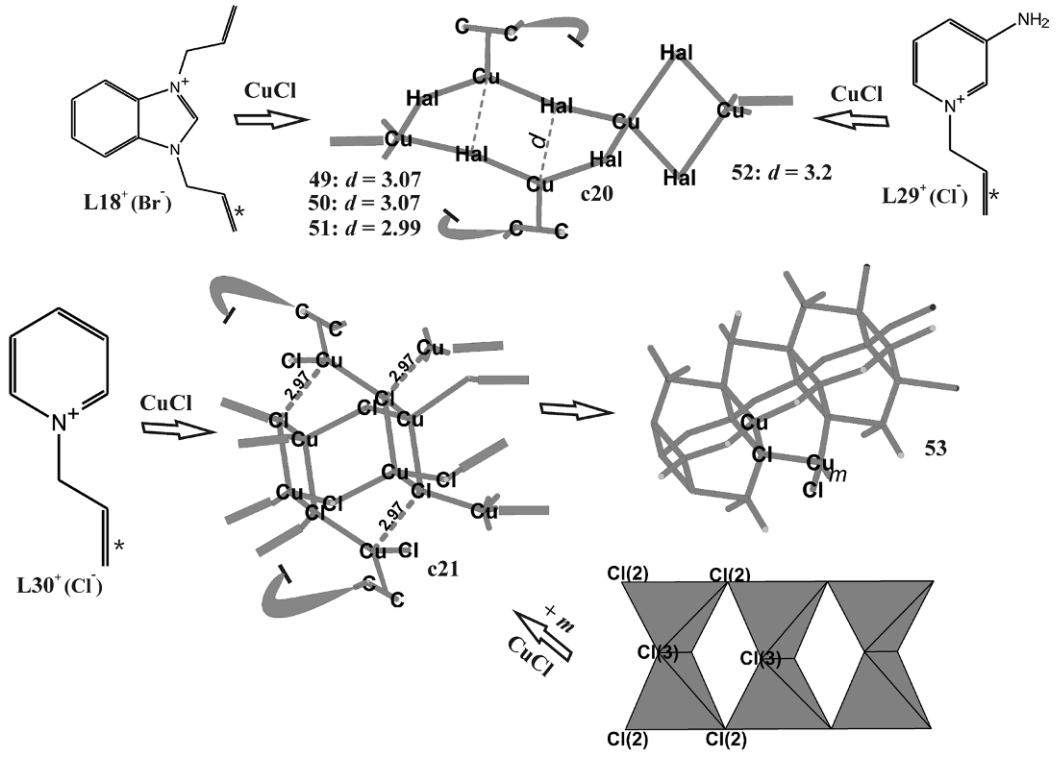



**Figure 10.** Structural genesis of **C20** and **C21** fragments in **49-53** compounds.

of two CuCl moieties with **C1b** π-coordination mode and are linked by dimeric bridged $Cu_2Cl_4^{2-}$ anion. All Cu(I) atoms in **C22** are connected with one N atom of the heterocyclic core. Thus, each inorganic anion is bound with six **L31**$^+$ cations (by means of C=C bond and two nucleophilic N atoms) into a 2D-layer **54**.

A decrease in donor activity of **L31**$^+$ upon acidifying **L31**$^+$, leads to the infinite $\{Cu_2Cl_3^-\}_n$ chain (**C23** mode) formation in **55**. The inorganic part can be considered as derived from **C22** by recombination of π-coordinated CuCl moieties (due to passivation of the second ligand`s nucleophilic nitrogen atom) in the $\{Cu_2Cl_2\}$ fragment united, in turn, by bridging $Cu_2Cl_4^{2-}$ anions into a 2D coordination polymer $\{(\mathbf{L31}^+)_2Cu_4Cl_6^{2-}\}_n$ (**55**). Under similar synthetic conditions from the corresponding solution, acidified by strong hydrochloric acid to pH~3, only the σ-compound [(**L31**$^+$)$CuCl_2$] was also isolated [74].

The N-allyl derivative of 2-styrylbenzimidazol (**L32**$^+$)($Br^-$) due to solvothermal reaction with CuCl in methanol solution gives π-complex **56** with $\{Cu_6Cl_4Br_4\}^-$ (**C24**) anion [75], built up of two uncompleted (without one metallic vertex) and slightly distorted cubane units, united by bridging Cu-Cl bonds (Fig. 12). Both independent π-bonded copper(I) atoms within the $\{Cu_3Cl_2Br_2\}$ subunit have a trigonal-pyramidal coordination environment with different Cl/Br statistics. For Cu(1) the apical position of coordination polyhedron is occupied by $Cl_{ap}$ atoms, and equatorial plane possesses two $Br_{eq}$ and C=C bond, while for Cu(2) – $Br_{ap}$ and only $Cl_{eq}$ correspondingly. The bidentate **L32**$^+$ cations by means of two allylic C=C bonds connect $\{Cu_6Cl_4Br_4\}^-$ fragments into coordination layers **56**. It should be noted that under the same conditions (**L32**$^+$)($Br^-$) reacts with CuBr giving (**L32**) $[Cu_2Br_3]$ compound with only electrostatic interaction among the particles.

In heterometallic π-compound **57** [76] organic ligand **L33** demonstrates a distinguishing coordination behavior relating to Cu(I) and Ni(II) atoms. Four N atoms of **L33** are linked to the Ni(II) atom from the isolated $NiCl^+$ unit to form a complex cation [**L33**NiCl]$^+$. The latter produces with the π-coordinated CuCl unit and $CuCl_2^-$ anion the centrosymmetrical $\{Cu_6Cl_8^{-2}\}$ fragment **C25** with three independent metal atoms (two of them are π-bonded). Thus, each $\{Cu_6Cl_8\}^{-2}$ anion is attached to four different **L33** molecules, which in **57** have only two active allyl groups, connecting the complex anions in the polymeric bimetallic chain (Fig. 12).

In contrast to the piperazine containing structures **44** and **45** with centrosymmetrical $Cu_2Cl_4^{2-}$ (**44** and **45**) and $Cu_4Cl_8^{4-}$ (**46**) anions, in the structure of **58** also centrosymmetrical $Cu_6Cl_{10}^{4-}$ fragment (**C26**) of higher nuclearity appears (Fig. 13) [77]: it can be considered as two π-bonded CuCl units attached to

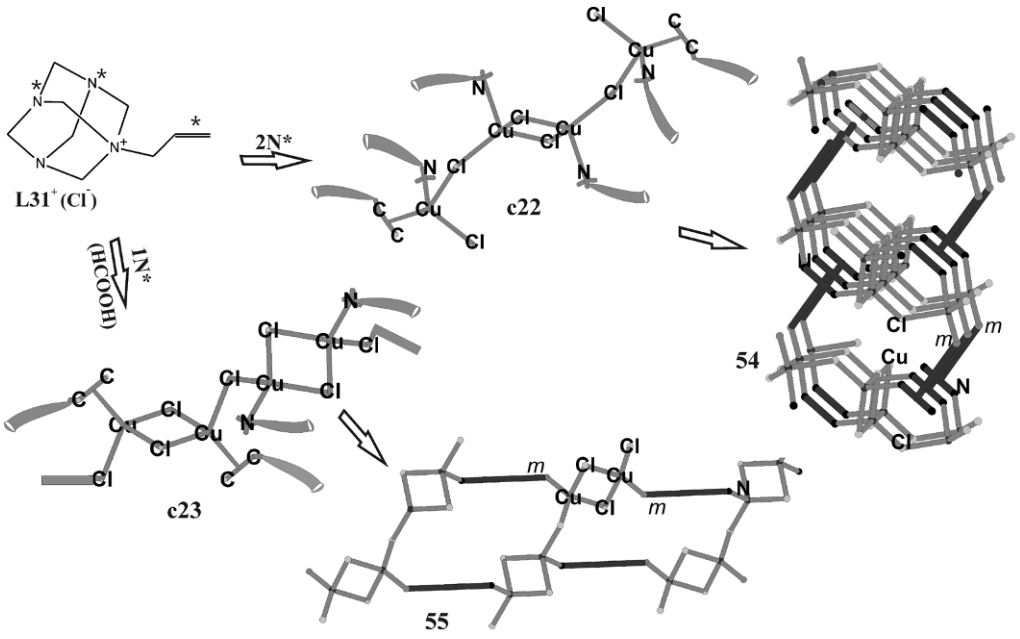



**Figure 11.** Structural genesis of **C22** and **C23** fragments in **54** and **55** compounds.

$\{Cu_4Cl_8^{4-}\}$ anion composed, in turn, by two $\{Cu_2Cl_4^{2-}\}$ moieties.

Protonated allylbenzimidazole **{L35(H+)}** in π-complex **59** forms the infinite $\{Cu_3Cl_4^{-}\}_n$ chains (**C27**). The trigonally surrounded Cu(I) atoms are disordered into two sites with 50% probability.

In contrast to N-allylmorpholinium chloride **L20(H+)** ($Cl^-$), which react with CuCl forming dimeric $\{Cu_2Cl_4^{2-}\}$ (**C17b**) inorganic unit (Fig. 8), N,N-diallylmorpholinium chloride (**L36+**)($Cl^-$) under the same conditions causes a formation of a markedly complicated $\{Cu_8Cl_{10}^{2-}\}_n$ (**C28**) anion (Fig. 13). The last fragments in the structure of **60** are united in rather thick layers, containing four- and six-membered small, as well as twenty-membered large, copper-halide cycles. As a result, bridged **L36+** cations by means of allylic C=C bonds connect $\{Cu_8Cl_{10}^{2-}\}_n$ chains into a 3D-framework (Fig. 13). Contrary to the above, in the presence of $Br^-$ anions **{L20(H+)}+** gives only two crystalline salts (**L36**) $[CuCl_{0.59}Br_{1.41}]$ and (**L37**)$[CuBr_2]$ without any Cu(I)-(C=C) interaction.

## 3.3. π-Complexes with ionic copper(I) salts

The review of this class of π-complexes should be started from the compounds containing nitrate anion It is known, $NO_3^-$ ion possesses an intermediate position among halide and other anions, and therefore it acts very often as a bridged pseudo-halide particle.

The first representative of $CuNO_3$ π-compounds is complex **61** [95], in which N,N`-diallylpiperazinium cation **{L24(2H+)}2+** acts as a bidentate π-ligand, connecting inorganic $\{Cu(NO_3)_2H_2O^-\}$ units in the centrosymmetrical island $\{Cu(NO_3)_2H_2O$-**L24**$(2H^+)$-$Cu(NO_3)_2H_2O\}$ complex. The trigonal-pyramidal Cu(I) environment in **61** includes allylic C=C bond, one O atom of water, and two O atoms from two different $NO_3^-$, one of which is located at the apical position of the metal coordination polyhedron (**C29**, Fig. 14).

The N heterocyclic atom of N-allylhexamethylenetetraminium cation (**L31+**) and O-$NO_2^-$ as well as C=C bond and $H_2O$ molecule form a Cu(I) coordination sphere in **62** which possesses a structure fragment **C30** (Fig. 14). Thus, in the structure of **62** bidentate **L31+** cations combine inorganic $\{CuNO_3(H_2O)\}$ fragments into infinite metal-organic chains. The $CuNO_3$ substitution by $CuBF_4$ does not affect on the bidentate **L31+** coordination mode and, due to more hardness of the fluorine atom in $BF_4^-$, two other positions of the metal polyhedron in **63** are occupied by $H_2O$ molecules (**C31**) [95].

An absence of any donor atoms, except the C=C bond in N-allylquinolinium **L37+** cation, complicates the inorganic topological moieties and due to bridging function of $O_{ap}(NO_3^-)$ atom in **64**, leads to the dimeric centrosymmetric $\{(\mathbf{L37})Cu(NO_3)_2\}_2$ unit (**C32**) (Fig. 14) [96]. N-allylquinolinium nitrate, contrary to the corresponding halide salts, is more tolerant to form a Cu(I) π-compound. Structural similarity of $\{(\mathbf{L37})Cu(NO_3)_2\}_2$ **64** [96] and halide $\{(\mathbf{L17})_2Cu_2Hal_4\}$ complexes **38, 39** [61, 65] (Fig. 8) displays a pseudohalide behavior of a $NO_3^-$ anion.

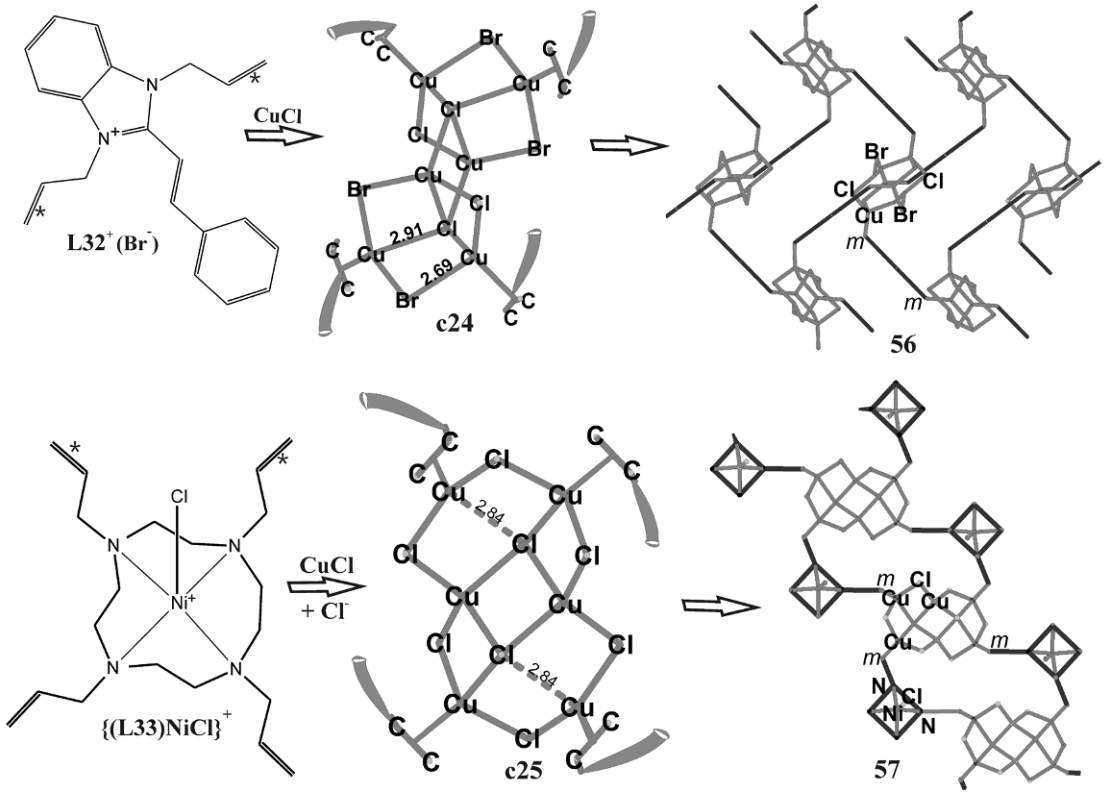



**Figure 12.** Structural genesis of **C24** and **C25** fragments in **56** and **57** compounds.

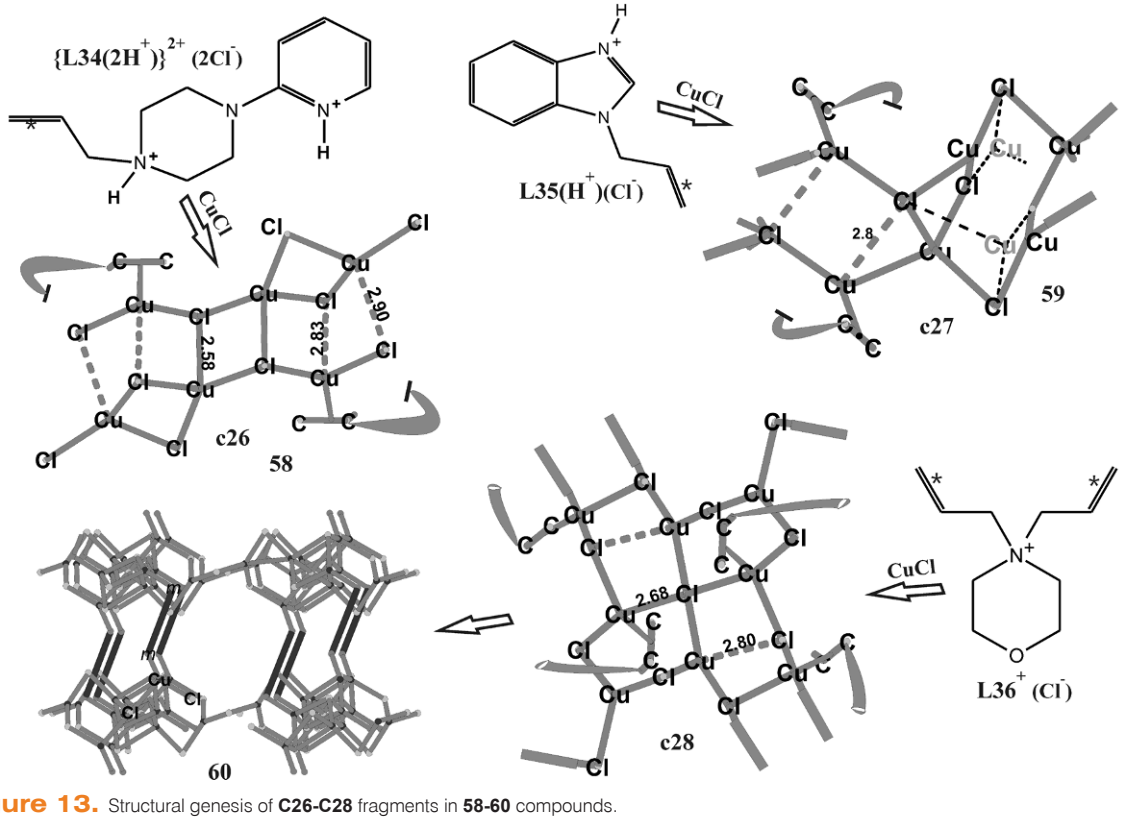



**Figure 13.** Structural genesis of **C26-C28** fragments in **58-60** compounds.

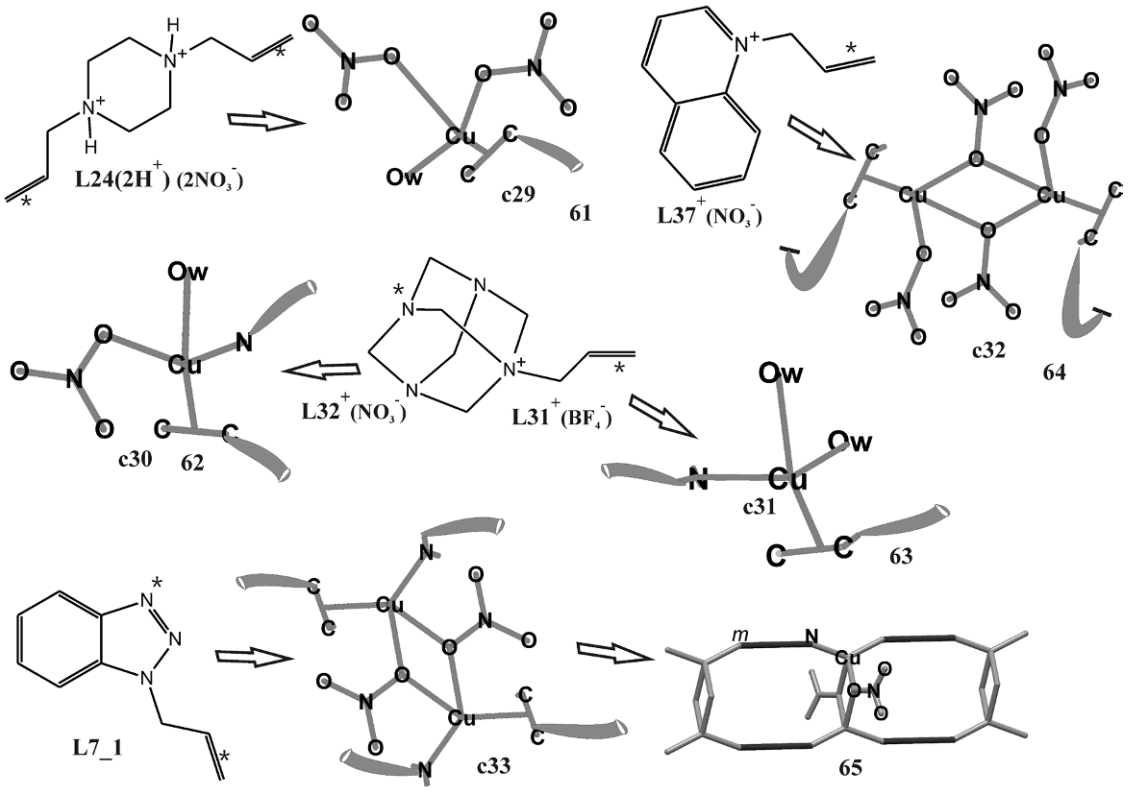



**Figure 14.** Structural genesis of **C29-C33** fragments in **61-65** compounds.

Molecular N-allyl-1H-benzotriazole **L7_1** reacts selectively[2] with $CuNO_3$ to give a dimeric $\{Cu_2(NO_3)_2\}$ moiety (**C33**) which resembles the halide $\{Cu_2Hal_2\}$ fragment occurred in **11** and **12** (Fig. 3). But in contrast to the last structures with a 2D-coordination network, in π-complex of **65** [97], ligand **L7_1** connects inorganic $\{Cu_2(NO_3)_2\}$ units into the double polymeric chains (Fig. 14).

5-(Allylthio)-1-(4-chlorophenyl)-1*H*-tetrazole **L12** reacts with $CuNO_3$ [55] as well as 5(allylthio)-1-phenyl-1*H*-tetrazole **L38** with $CuBF_4$ to give dimeric cationic $\{(L)_2Cu_2(H_2O)_2\}^{2+}$ moieties (**C34**) [98], in which the organic molecule plays a role of a N,N,(C=C)-tridentate chelate-bridging ligand (Fig. 15). The apical positions of the metal coordination polyhedra in **66** and **67** are occupied by water molecules, which, in turn, through $(Ow)H...O(NO_3^-)$ or $(Ow)H...O(BF_4^-)$ hydrogen bonds act as a bridge between Cu(I) and the corresponding anions. It should be noted that cationic $\{(L)_2Cu_2\}^{2+}$ fragment, as is the case of the 5-(allylthio)-1*H*-tetrazole derivative, appears to be a stable building block, which is able to incorporate into 2D polymeric layers in a chloride complex $[(\mathbf{L12})_2Cu_3Cl_3]$ (**19**) through the bridging of $Cl_{ap}$ (Fig. 5) or to form island cations $\{(L)_2Cu_2(H_2O)_2\}^{2+}$ with the $H_2O$ apical molecules (**66** and **67**) (Fig. 15).

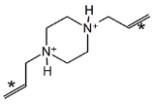
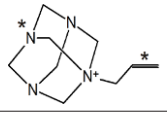
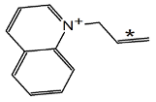
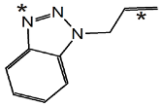
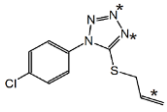
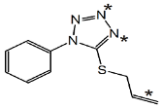
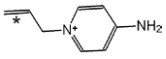
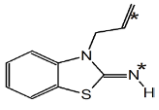
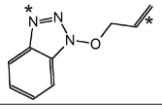
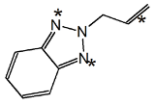
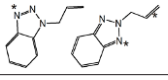
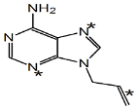
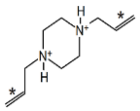
A mixed-anion π-complex **68** was isolated under *ac*-electrochemical reduction of a $Cu(NO_3)_2$ ethanol solution in the presence of 1-allyl-4-aminopyridinium chloride ($\mathbf{L16}^+$)($Cl^-$) (Fig. 15, **C35**) [96]. The last structure is built of the infinite $\{(\mathbf{L16})_2Cu_3Cl_3(NO_3)_2\}_n$ coordination polymers, in which π-bonded Cu(I) possesses a trigonal-pyramidal environment and is surrounded by C=C bond, O nitrate atom and two bridging chlorine atoms: $Cl_{eq}$ (with Cu-Cl-Cu angle 102.4°) and $Cl_{ap}$ (belonging to a linear bridging $\{CuCl_2\}$ fragment).

Use of an ethanol solution of $Cu(NO_3)_2 \cdot 3H_2O$ and the mixture of N-allyl-2-iminobenzothiazole **L1** and original 2-aminobenzothiazole (**ambthia)**), *ac*-electrochemical technique, mixed ligand Cu(I) π-complex **69** with **C36** fragment was isolated [99]. The N atom and C=C bond of the chelate **L1** ligand occupy two equatorial positions of the metal polyhedron, while the N atom of **ambthia** is on the third corresponding site. Participation of the latter N-atom influences the removal of $O_{ap}$ ($NO_3^-$) from Cu(I) up to 2.48 Å (it corresponds to a point that lies above the line plot (c) on Fig. 1).

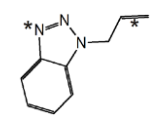
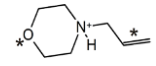
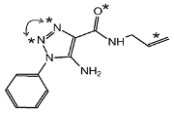
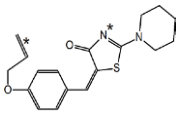
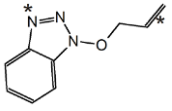
One more example of two ligand molecules coordinating to one Cu(I) center is π-complex **70** [26], in which bidentate N-allyloxybenzotriazole

[2]In all the cases the mixture of two isomeric 1- and 2-allylbenzotriazole in molar ratio of 1:1 was used as the started reagent for Cu(I) π-complex preparation [35].

**Table 2.** Geometric parameters of Cu(I) π-core in the structures of complexes with ionic copper(I) salts.

| | Ligand [a] | Composition (preparation method) [b] | Fragment | Cu-m[c], Å<br>C=C, Å | C=C-C, deg | Δ[d], Å | τ [e], deg | C-Cu-C, deg<br>φ(C=CCX)[f], deg | Cu-$X_{ap}$ [g], Å | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|
| 61 | **L24(2H⁺)**  | [{**L24**(2H⁺)}$Cu_2(H_2O)_2$·$(NO_3)_4$]·2$H_2O$ *(e.c.)* | **C29** | 1.884(4)<br>*1.379(3)* | 122.5 | 0.05 | 9.8 | 40.19(8)<br>*95.7* | 2.241(3) | [95] |
| 62 | **{L31}⁺**  | {[(**L31**)Cu$(NO_3)(H_2O)$]}$_n$ $(NO_3)_n$·n$H_2O$ *(e.c.)* | **C30** | 1.917(3)<br>*1.368(5)* | 122.3(1) | 0.33 | 3.5 | 39.7(1)<br>*98.8* | 2.241(3) | [95] |
| 63 | | {[(**L31**)Cu$(H_2O)_2$]}$_n$·$(BF_4)_{2n}$·n$H_2O$ *(e.c.)* | **C31** | 1.921(4)<br>*1.374(5)* | 121.8 | 0.25 | 2.9 | 39.5(1)<br>*94.0* | 2.174(3) | [95] |
| 64 | **{L37}⁺**  | [(**L37**)$_2$$Cu_2(NO_3)_4$] *(e.c.)* | **C32** | 1.890(2)<br>*1.382(3)* | 122.01 | 0.06 | 6.0 | 40.2(1)<br>*96.7* | 2.617(2) | [96] |
| 65 | **L7_1**  | [(**L7_1**)$_2$$Cu_2(NO_3)_2$]$_n$ *(e.c.)* | **C33** | 1.912(5)<br>*1.356(6)* | 123.2 | 0.19 | 1.3 | 39.1(2)<br>*81.1* | 2.319(3) | [97] |
| 66 | **L12**  | [$Cu_2$(**L12**)$_2$$(H_2O)_2$]$(NO_3)_2$×<br>×$C_2H_5OH$ *(e.c.)* | **C34** | 1.944(9)<br>*1.37(5)*<br>1.953(9)<br>*1.33(4)* | 122(4)<br><br>123.5(9) | 0.32<br><br>0.39 | 21.6<br><br>24.4 | 38.9(4)<br>*150.9*<br>37.6(4) *147.0* | 2.217(7)<br><br>2.188(7) | [55] |
| 67 | **L38**  | [$Cu_2$(**L38**)$_2$$(H_2O)_2$]$(BF_4)_2$ *(e.c.)* | **C34** | 1.935(5)<br>*1.368(6)* | 122.1(4) | 0.27 | 11.3 | 38.9(2)<br>*156.5* | 2.252(4) | [98] |
| 68 | **{L16}⁺**  | [(**L16**)$_2$$Cu_2Cl_3(NO_3)_2$]$_n$ *(e.c.)* | **C35** | 1.954(4)<br>*1.371(6)*<br>1.942(4)<br>*1.360(6)* | 122.1<br><br>123.6 | 0.31<br><br>0.29 | 9.9<br><br>12.8 | 38.7(2)<br>*151.3*<br>38.6(2)<br>*146.4* | 2.620(2)<br><br>2.651(2) | [97] |
| 69 | **L1(H⁺)**  | [(**L1**)(*abthia*)Cu$(NO_3)$][h] *(e.c.)* | **C36** | 1.932(3)<br>*1.365(5)* | 122.8 | 0.25 | 7.2 | 38.9(1)<br>*147.2* | 2.486(3) | [99] |
| 70 | **L8**  | {[(**L8**)$_2$$Cu(H_2O)$]}$_n$$(BF_4)_n$ *(e.c.)* | **C37** | 1.953<br>*1.40(1)* | 122.2 | 0.50 | 17.0 | 39.5(4)<br>*103.8* | 2.115(9)<br>tetr | [26] |
| 71 | **L7_2**  | {[(**L7_2**)Cu$(H_2O)$]}$_n$$(BF_4)_n$ *(e.c.)* | **C38** | 2.007(4)<br>*1.329* | 123.5 | 0.43 | 21.7 | 37.3(2)<br>*115.3* | 2.166(3) | [35] |
| 72 | | [(**L7_2**)Cu$(ClO_4)$]$_n$ *(e.c.)* | **C38** | 2.025(6)<br>*1.348* | 123.5 | 0.38 | 17.2 | 36.8(3)<br>*119.9* | 2.234(5) | [35] |
| 73 | | [(**L7_2**)Cu$(HSO_4)$]$_n$ *(e.c.)* | **C39** | 2.040(8)<br>*1.363(9)* | 120.9 | 0.53 | 13.1 | 36.9(3)<br>*119.5* | 2.111(4) | [35] |
| 74 | **L7_1**<br>**L7_2**  | [(**L7_1**)(**L7_2**)Cu$(ClO_4)$]$_n$ *(d.r.)* | **C40** | 1.962(7)<br>*1.353(6)* | 124.7 | 0.27 | 18.4 | 38.1(2)<br>*117.5* | 2.452(4) | [35] |
| 75 | **L39**  | {[(**L39**)Cu$(H_2O)$]}$_n$$(ClO_4)_n$ *(d.r.)* | **C38** | 1.911(3)<br>*1.368* | 121.8 | 0.29 | 10.0 | 37.9(2)<br>*139.2* | 2.394(2) | [100] |
| 76 | | {[(**L39**)Cu$(CH_3CN)$]}$_n$$(ClO_4)_n$ *(d.r.)* | **C38** | 1.980(5)<br>*1.360(7)* | 123.0 | 0.47 | 2.7 | 39.4(1)<br>*143.1* | 2.111(4) | [100] |
| 77 | **L24(2H⁺)**  | [{**L24**(2H⁺)}<br>$Cu_2(SO_3NH_2)_4$]·2$H_2O$ *(e.c.)* | **C41** | 1.919(4)<br>1.368(6) | 121.3 | 0.13 | 5.1 | 39.2(1)<br>92.8 | 2.574(3) | [101] |
| 78 | | {*pip*(2H⁺)}[{**L24**(2H⁺)}<br>$Cu_2(SO_3NH_2)_6$]×$H_2O$[i] *(e.c.)* | **C42** | 1.962(9)<br>1.29(2) | 124.4(9) | 0.46 | 5.2 | 36.4(4)<br>91.4 | 2.295(6) | [101] |
| 79 | | [{**L24**(2H⁺)}$Cu_2(H_2O)_6$]<br>$(SiF_6)$·$H_2O$ *(e.c.)* | **C43** | 1.89(1)<br>1.32(2) | 124.6 | 0.17 | 4.0 | 38.5(5)<br>99.8 | 2.375(2) | [102] |

Continued **Table 2.** Geometric parameters of Cu(I) π-core in the structures of complexes with ionic copper(I) salts.

| | Ligand [a] | | Composition (preparation method) [b] | Fragment | Cu-m[c], Å C=C, Å | C=C-C, deg | Δ[d], Å | τ [e], deg | C-Cu-C, deg φ(C=CCX)[f], deg | Cu-$X_{ap}$[g], Å | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 80 | L7_2 |  | $\{[(\mathbf{L7\_1})_2Cu_2(CH_3OH)_2(H_2O)_2]\}_n(SiF_6)_n$ *(e.c.)* | C44 | 1.935(5)<br>1.366(6) | 121.3 | 0.38 | 10.8 | 38.9(2)<br>160.3 | 2.186(3) | [34] |
| 81 | | | $\{[(\mathbf{L7\_1})_2Cu_2(H_2O)_2(SiF_6)]\}_n \cdot 2nH_2O$ *(e.c.)* | C45 | 1.920(5)<br>1.368(6) | 122.0 | 0.11 | 11.1 | 39.2(3)<br>160.3 | 2.439(2) | [34] |
| 82 | L20(H⁺) |  | $\{[\{\mathbf{L20}(H^+)\}Cu(H_2O)_2]\}_n(SiF_6)_n \cdot nH_2O$ *(e.c.)* | C46 | 1.894(8)<br>1.38(1) | 122.8 | 0.22 | 5.9 | 40.1(3)<br>89.1 | 2.436(5) | [103] |
| 83 | L40 |  | $\{[(\mathbf{L40})Cu(NO_3)]\}_n \cdot 0.5nH_2O$ *(e.c.)* | C47 | 1.970(4)<br>1.363(5) | 123.8 | 0.47 | 9.0 | 38.2(1)<br>145.1 | 2.159(3) | [30] |
| 84 | | | $[(\mathbf{L40})Cu(CF_3COO)]_n$ *(e.c.)* | C47 | 1.913(5)<br>1.339(8) | 126.3 | 0.28 | 6.8 | 38.6(2)<br>12.6 | 2.325(3) | [30] |
| 85 | L11 |  | $[(\mathbf{L11})_2Cu_2(CF_3COO)_2]$ *(e.c.)* | C48 | 1.905(7)<br>1.385(9) | 120.1 | 0.08 | 6.8 | 39.9(3)<br>110.9 | - | [104] |
| 86 | L8 |  | $[(\mathbf{L8})_2Cu_2(CF_3COO)_2]_n$ *(e.c.)* | C49 | 1.90(1)<br>1.37(2) | 123.8 | 0.13 | 11.9 | 39.5(5)<br>88.5 | 2.404(8) | [26] |

*[a] asterisk indicates an active Cu(I) coordination ligand site; [b] method of preparation: alternating current electrochemical (e.c.) and direct (d.r.) techniques; [c] m - a middle point of C=C bond, [d] – a distance value of a deviation of copper(I) atom from the trigonal pyramid base plane, [e] – angle value of the C=C line deviation from the base plane of a trigonal pyramid, [f] – torsion angle of allyl C=C-C-X group (X – any element), [g] – a distance from the copper(I) to the apical ($L_{ap}$) donor atom, [h] abthia – 2-aminobenzothiazole molecule; [i] pip – piperazine.*

**L8** connects the metal atoms into infinite cationic $\{((\mathbf{L8})Cu(H_2O))^+\}_n$ (**C37**) chains (by means of allylic C=C bond and the most nucleophilic N3 triazole atom). The fourth position of a distorted tetrahedral Cu(I) environment is occupied also by a N3 atom of the other **L8** molecule, acting as a σ-ligand only (Fig. 15).

The reaction of a mixture of isomeric N-allyl-1*H*- (**L7_1**) and N-allyl-2*H*- benzotriazole (**L7_2**) with $CuBF_4$, $CuClO_4$ and $CuHSO_4$ in an alcohol solution (acidified by corresponding acid to pH ~ 4) under *ac*-electrochemical conditions results in π-compounds **71**-**73** with the selective **L7_2** participation in the metal coordination [35]. In the structure of these compounds, the organic ligand is coordinated to Cu(I) simultaneously in the chelate and bridge fashions by means of all three available active center (N1 and N3 triazole atoms and allylic C=C bond). Thus, **C38** and **C39** infinite chains differ only by the apical position of the Cu(I) trigonal-pyramidal arrangement: $H_2O$ molecule in **71** (due to marked hardness of fluorine atom in $BF_4^-$) and O atoms from the anions in **72** and **73** (Fig. 16).

Under the same (as in **71** and **72**) initial conditions without applying *ac*-tension, , the crystals of complex **74** grew on a copper-wire during one month. It is interesting to note, that **74** represents the unusual mixed ligand-isomers coordination compound. The metal coordination includes a C=C bond, a N1 atom of 2-allylbenzotriazole (**L7_2**) and a N3 atom of 1-allylbenzotriazole isomer (**L7_1**) (Fig. 16, **C40**). The last molecule **L7_1** in the structure of **74** plays only a role of σ-ligand (allylic C=C bond does not participate in the metal coordination). In summary, this circumstance causes the significant $d_{z^2}$ -orbital energy increase and elongation of Cu(I)-O($ClO_4$) distance up to 2.45 Å (Table 2) (driving this extremal point above the line plot (c) on Fig. 1). So, the selective complexation of Cu(I) with two N-allylbenzotriazole isomers causes a formation of discrete [(**L7_1**)(**L7_2**)$Cu(ClO_4)$] moieties (**74**, Fig. 16) [35].

In **75** and **76** π-complexes 9-allyladenine **L39** is attached to Cu(I) in **C39** manner, and an apical position of the metal trigonal-pyramidal environment is occupied by a neutral molecule - $H_2O$ (**75**) or $CH_3CN$ (**76**) [100]. Chelate function of **L39** is realized by means of the allylic C=C bond and N3 atom of the adenine core, while second bridging N7 atom connects the metal centers into cationic $\{[(\mathbf{L39})CuX]^+\}_n$ chains (**75**). Also, due to a higher nucleophilic activity of $CH_3CN$ moiety, in **76** the deviation of a copper atom from the base plane of the polyhedron increases to 0.47 Å, compared to the analogous metal deviation in **75** – 0.29 Å (Fig. 16).

A reaction of $\{\mathbf{L24}(2H^+)\}(SO_3NH_2)_2$ with $Cu(SO_3NH_2)$ under the *ac*-electrochemical conditions leads to the

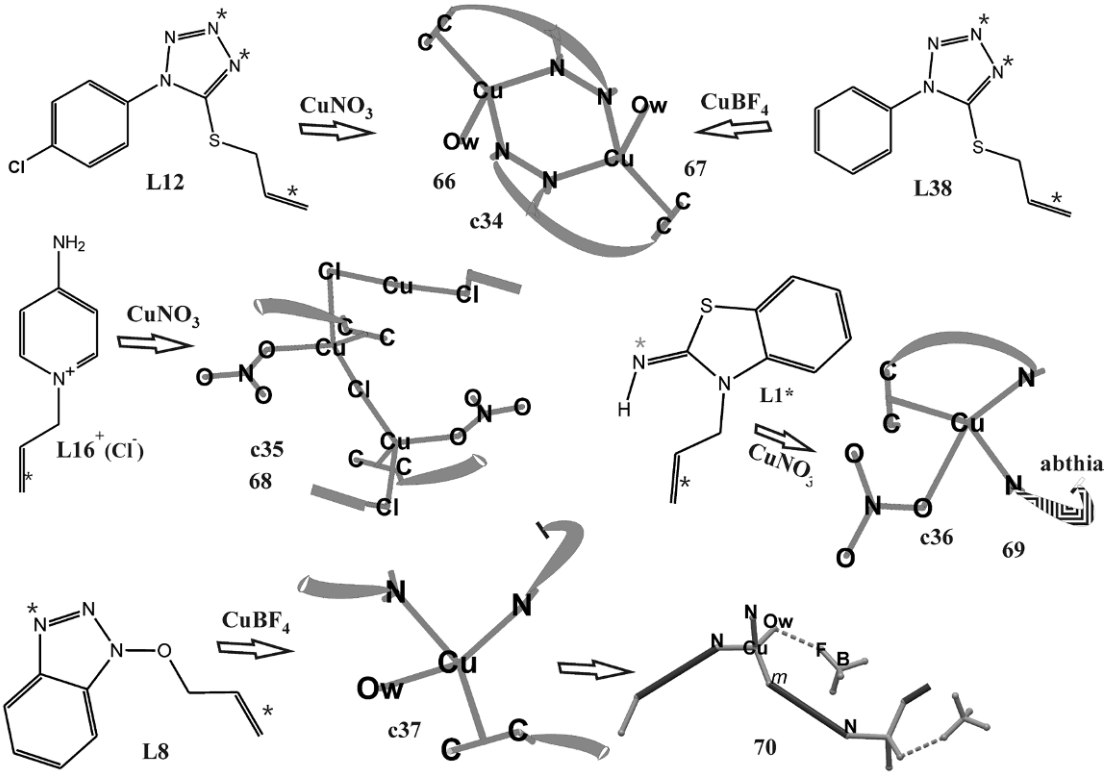



**Figure 15.** Structural genesis of **C34-C37** fragments in **66-70** compounds.

polymeric **77** compound formation (Fig. 17). Due to cationic status, {**L24**$(2H^+)$}$^{2+}$ acts as a bidentate π-ligand, connecting two inorganic {$Cu_2(SO_3NH_2)_4$}$^{2-}$ fragments into the centrosymmetric [(**L24**$(2H^+)Cu_2(SO_3NH_2)_4$] units, while the oxygen atom of the sulfamate anion (occupying an apical position of the metal polyhedron) plays a bridge role between the above units, linking them into 1D-polymer **77** (fragment **C41**) [101].

Under the same synthetic conditions, starting from an ethanol solution of monoallylpiperazinium sulfamate, the latter transforms into N,N`-diallypiperazinium sulfamate {{**L24**$(2H)$}$^{2+}$}$(NH_2SO_3^-)_2$ and piperazinium sulfamate {{*pip*$(2H^+)$}$^{2+}$}$(NH_2SO_3^-)_2$ , which react with $Cu(SO_3NH_2)$ giving **78** – a rare anionic Cu(I) π-compound of (*pip*$(2H^+)$) [(**L24**$(2H^+)Cu_2(SO_3NH_2)_6$]•$H_2O$ composition [101]. The centrosymmetric {**L24**$(2H)$}$^{2+}$ cation in **78** acts only as bidentate π-ligand linking {$Cu(SO_3NH_2)_3$}$^-$ fragments into discrete {**L24**$(2H^+)$)$Cu_2(SO_3NH_2)_6$}$^{2-}$ anions, within which Cu(I) environment includes, except C=C bond, the three N atoms of three $NH_2SO_3^-$ anions (Fig. 17, **C42**).

The replacement of $NH_2SO_3^-$ anion by "rigid" $SiF_6^{2-}$ moiety does not change the {**L24**$(2H^+)$}$^{2+}$ coordination behavior, but water molecules participation (**C43**) in Cu(I) coordination in the structure **79** [102] modifies the discrete cation to [(**L24**$(2H^+)Cu_2(H_2O)_4$]$^{2+}$ unit (Fig. 17).

In a presence of $SiF_6^{2-}$ anion from water-methanol solution of two isomers mixture **L7_1** and **L7_2** (previously acidified by $H_2SiF_6$ to pH~3) only the **L7_1** isomer selectively participates in the Cu(I) π-coordination, and keeps the same (C=C),N-bidentate function (**C44**) as in the **65** compound. Thus, in the **80** crystal structure **L7_1** forms the infinite {(**L7_1**)$Cu(H_2O)_2$}$_n$ chains, in which $H_2O$ molecules (as well as in **79**) play a bridged role between Cu(I) and $SiF_6^{2-}$ by means of branched (Ow)H...F hydrogen bonds [34].

Under a similar synthetic condition, starting from a water-methanol mixture of two isomers **L7_1** and **L7_2**, in a presence of small excess of $H_2SiF_6$, one more π-complex **81** was obtained, which appears to be the first known example representing the direct $Cu^+$... $FSiF_5^{2-}$ interaction. Similarly to **80**, in this structure bidentate **L7_1** molecules connect Cu(I) atoms into infinite {(**L7_1**)$Cu(H_2O)$}$_n$ chains, in which only one $H_2O$ molecule is coordinated to the metal center, while the apical position of copper(I) polyhedron is occupied by F atom of the bridging $SiF_6^{2-}$ anion (Cu-F 2.439(2) Å). Thus, centrosymmetrical hexafluorosilicate anions link {(**L7_1**)$Cu(H_2O)$}$_n$ chains in the corrugated layers **81** (Fig. 17, fragment **C45**).

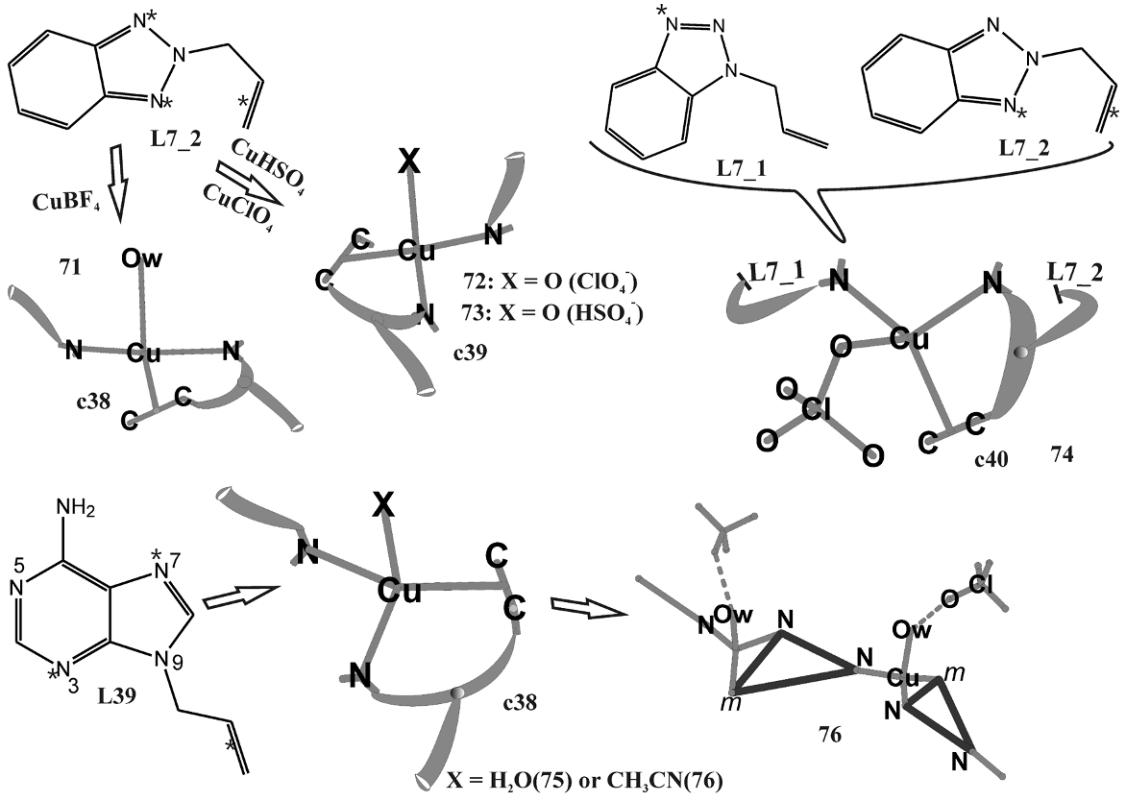



**Figure 16.** Structural genesis of **C38-C40** fragments in **71-76** compounds

N-Allylmorpholinium cation $\{\mathbf{L20}(H^+)\}^+$ in a presence of $SiF_6^{2-}$ anions forms the infinite cationic $\{[(\mathbf{L20}(H^+))Cu(H_2O)_2]^+\}_n$ chains (**82**) with equatorial C=C bond and two water molecules [103]. The fourth (apical) position of the metal polyhedron (**C46**) is occupied by bridging O atom of morpholine core of $\{\mathbf{L20}(H^+)\}^+$ (Fig. 18). Contrary to this, in a presence of halide anions, O atom of heterocyclic core is unable to compete with $Hal^-$ in the metal coordination (Fig. 8, **C17b**).

The triazole ring of ligand **L40** shows excellent coordination behavior (**C47**) with the $CuNO_3$ (**83**) and $CuOOCCF_3$ (**84**) [30]. The organic molecule acts as (C=C), N,O-tridentate chelate-bridging ligand by means of allylic C=C bond, one triazole N atom and O atom of the amide group. It is interesting to note, that two triazole N atoms and O amide are coordinated in **83** and **84** in different modes: participation of N2 triazole atom and O atom of C=O group in the metal coordination allows $NO_3^-$ to use its O-atom as the axial ligand; this increases the Δ distance up to 0.47 Å (**84**), while the participation of an axial O-atom of $CF_3COO^-$ and N3 triazole atom in Cu(I) coordination causes the essential lowering of Cu(I) to the basal plane (Δ = 0.28 Å) (**84**). The involvement of the hetero-ring **L40** nitrogen atoms with different nucleophility into Cu(I) coordination in **83** and **84** is likely caused by a formation of asymmetric hydrogen bonds (N)H…O(=C), (N)H…O($NO_2$) (**83**) and (N)H…O($OCCF_3$) (**84**) with **L40** amino group, $NO_3^-$ and $CF_3COO^-$ anions, and O atom of the amide group of the ligand. In both **83** and **84** cases, **L40** molecules link inorganic fragments into the 1D polymers.

A bulky **L11** molecule plays a role of (C=C), N-bidentate bridging ligand which is coordinated to Cu(I) through an allylic C=C bond and N thiazole atom (**C48**). So, in the **85** crystal structure, two **L11** molecules connect two $CuOOCCF_3$ units into the insular $\{(\mathbf{L11})Cu(OOCCF_3)\}_2$ fragment [104], containing 24-membered cycle. As it was mentioned in [104], under the same synthetic conditions, **L11** reacts with $CuBF_4$ to give only the σ-complex $[(\mathbf{L11})_2Cu]BF_4$ in which the Cu(I) atom is coordinated with two organic molecules (by means of two N thiazole atoms) in a linear manner.

In the structure of **86,** in presence of $CF_3COO^-$ anions, organic molecules of allyloxybenzotriazole **L8** (by means of C=C bond and N3 triazole atom) connect Cu(I) atoms in the cationic $\{(\mathbf{L8})Cu)^+\}_n$ chains [26]. In **86** the $CF_3COO^-$ anion plays the same role as $NO_3^-$ as is in the case of 1-allylbenzotriazole (**C33**, Fig. 14), connecting $\{[\mathbf{L8})Cu]^+\}_n$ by bridging carboxylic group into the doubled chains (**C49**, Fig. 18).

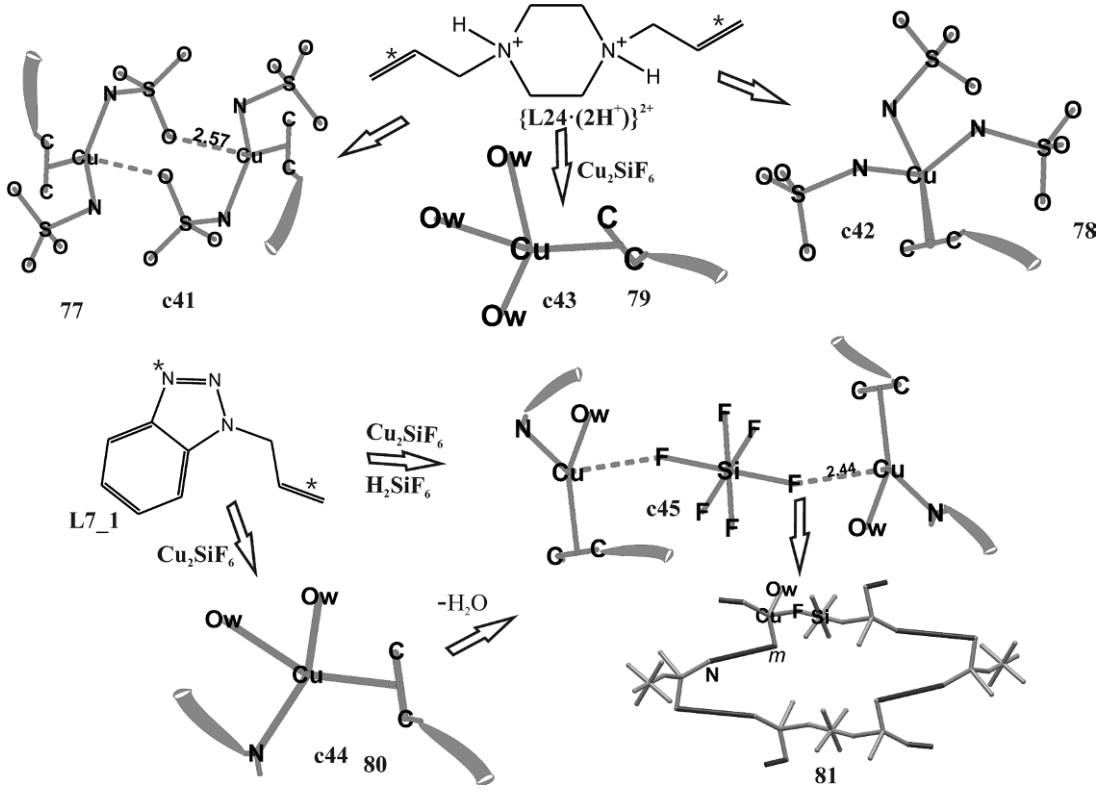



**Figure 17.** Structural genesis of **C41-C45** fragments in **77-81** compounds.

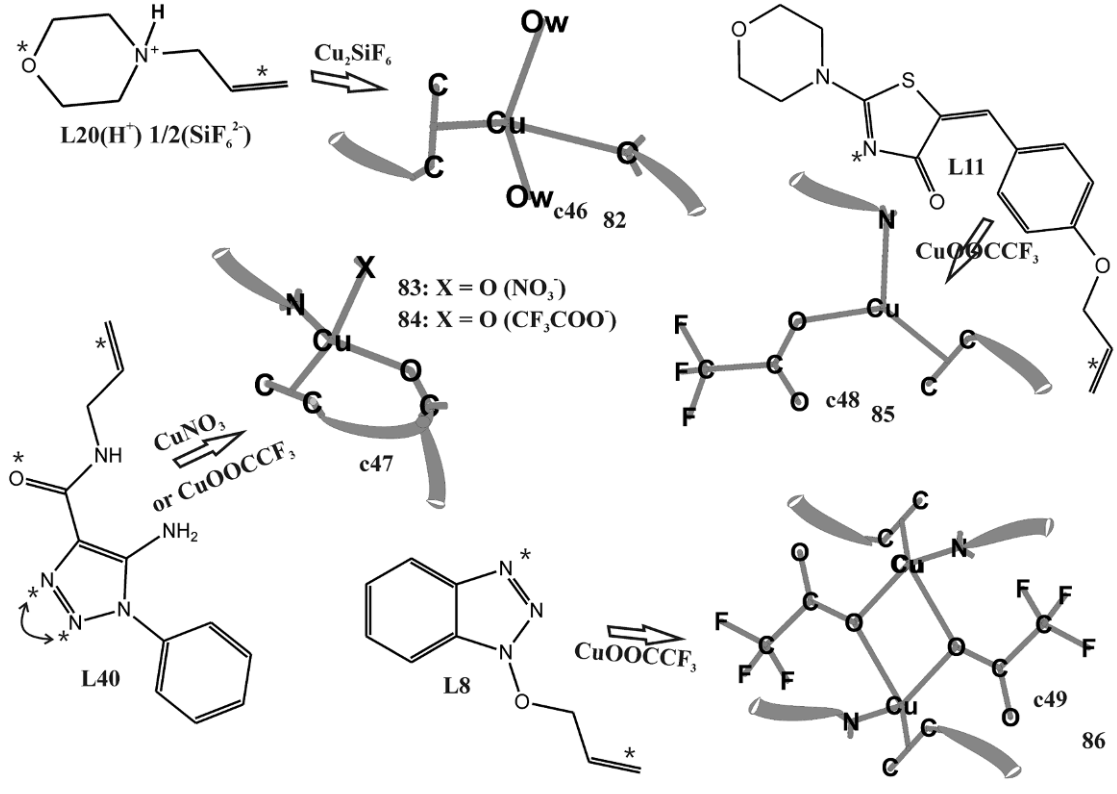



**Figure 18.** Structural genesis of **C46-C49** fragments in **82-86** compounds.

## 4. Conclusions

An efficiency rise of Cu(I)–(C=C) interaction in the complexes under consideration is accompanied with an elongation of the coordinated C=C bond as well as an increase in Cu(I)-L(apical) distance.

Due to a strongly directed Cu(I)–(C=C) interaction, a variety of structural inorganic fragments of different dimensionality may be derived.

A certain architecture of building blocks depends on a form of organic ligand, numbers of π- and σ-active coordination centers as well as a type of the copper(I) salts anion ($Cl^-$, $Br^-$, $NO_3^-$, $NH_2SO_3^-$, $SO_4^{2-}$, $BF_4^-$, $ClO_4^-$, $SiF_6^{2-}$, $CF_3COO^-$ *etc.*)

The type of a mixed π, σ-coordinating mode (bridged, chelate, chelate-bridged) of an organic ligand depends on the basicity and nucleophilic activity of its heteroatoms as well as the allylic groups flexibility.

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