# Copper(I) π-Complexes with Guanidine Allyl Derivatives: Synthesis and Crystal Structures of [CH$_2$=CH–CH$_2$–NHC($=$NH$_2$)$_2$]CuCl$_{2-x}$Br$_x$ ($x$ = 0.516) and [CH$_2$=CH–CH$_2$–NHC($=$NH$_2$)$_2$]CuBr$_2$

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**Abstract**—Crystals of the [CH$_2$=CH–CH$_2$–NHC($=$NH$_2$)$_2$]CuCl$_{2-x}$Br$_x$ ($x$ = 0.516) (**I**) and [CH$_2$=CH–CH$_2$–NHC($=$NH$_2$)$_2$]CuBr$_2$ (**II**) compounds were prepared by ac electrochemical synthesis, and their crystal structures were determined (a DARCh diffractometer, Mo$K_\alpha$ radiation, 1018 and 1453 independent reflections with $F \geq 4\sigma(F)$, $R$ = 0.023 and 0.030 for **I** and **II**, respectively). The compounds are not isostructural. Parameters of **I**: space group $Pna2_1$, $a$ = 15.741(6), $b$ = 7.428(3), $c$ = 7.387(3) Å, $V$ = 864(1) Å$^3$, $Z$ = 4; parameters of **II**: space group $P\bar{1}$, $a$ = 8.142(3), $b$ = 7.819(4), $c$ = 7.067(2) Å, $\alpha$ = 84.39(4)°, $\beta$ = 86.86(3)°, $\gamma$ = 82.07(4)°, $V$ = 443.1(6) Å$^3$, $Z$ = 2. In both structures, the allylguanidinium ligand is coordinated to copper through the C=C bond, whose length is equal to 1.343(7) Å in **I** and 1.343(9) Å in **II**. The structure of complex **II** is very similar to those of the known copper(I) π-complexes with $S$-allylisothiouronium [CH$_2$=CH–CH$_2$–SC($=$NH$_2$)$_2$]CuX$_2$ (X = Cl$^-$ or Br$^-$).

Recent studies of the π-complexation of *N*-allyl-2-furylaldimine and *N*-allylbenzaldimine with copper(I) showed that the azomethine nitrogen atom exhibits pronounced σ-donating properties and effectively interacts, along with the C=C bond, with Cu(I) to give molecular π,σ-complexes [1]. Because of hydrolysis, attempts at obtaining the ionic copper(I) π-complexes involving nitrogen-protonated Schiff bases resulted in copper(I) allylammonium π-complexes, e.g., previously known [C$_3$H$_5$NH$_3$]CuCl$_2$ [2]. It was of interest to study the ionic copper(I) π-complexes with unsaturated azomethine derivatives, in particular, with allyl-substituted guanidinium salts. Besides, the allylguanidinium complexes are intermediates between the copper(I) azomethine π-complexes and complexes with thiourea *N*- and *S*-allyl derivatives [3, 4]. For this purpose, copper(I) halide π-complexes with an allylguanidinium ligand, [CH$_2$=CH–CH$_2$–NHC($=$NH$_2$)$_2$]CuCl$_{2-x}$Br$_x$ ($x$ = 0.516) (**I**) and [CH$_2$=CH–CH$_2$–NHC($=$NH$_2$)$_2$]CuBr$_2$ (**II**), were synthesized and their crystal structures were studied.

## EXPERIMENTAL

Allylguanidinium (AGU) bromide was synthesized from *S*-ethylisothiouronium bromide (obtained from thiourea and ethyl bromide according to [5]) and allylamine by a modified procedure [6]. Complexes **I** and **II** were obtained as colorless well-edged prisms by ac electrochemical reduction of Cu(II) to Cu(I) on copper electrodes in an ethanol solution of CuCl$_2$ · 2H$_2$O or CuBr$_2$ and AGU bromide. Rather air-stable crystals of compounds **I** and **II** grew over 24 h.

The structures were solved using diffraction data collected on a single-crystal DARCh diffractometer. Intensities of reflections were corrected for Lorentz and polarization effects. Absorption correction was applied using the DIFABS program. Crystallographic data and summary of data collection are reported in Table 1.

The structures were solved by direct methods, the light and hydrogen atoms being located from difference Fourier syntheses. Full-matrix anisotropic refinement for all the non-hydrogen atoms (isotropic for the hydrogen atoms) was performed using the CSD program package [7].

Atomic coordinates and thermal parameters for structures **I** and **II** are listed in Table 2. Bond lengths and angles and torsion angles are presented in Table 3.

## RESULTS AND DISCUSSION

Similar to the *S*-allylisothiouronium ligand (AITU) [4], the cationic form [CH$_2$=CH–CH$_2$–NH–C$^+$($=$NH$_2$)$_2$] cannot exhibit σ-donating properties with respect to Cu(I). Indeed, the copper atom in compounds **I** and **II** is coordinated only by the C=C bond of AGU. The trigonal-pyramidal coordination of the metal atom is completed by three halogen atoms. The Cu–(axial ligand) distances are longer than those in the [AITU]CuCl$_2$

**Table 1.** Crystallographic data and summary of data collection for complexes **I** and **II**

| Parameter | I | II | Parameter | I | II |
|---|---|---|---|---|---|
| $M$ | 257.5 | 323.5 | Radiation | $MoK_\alpha$ | $MoK_\alpha$ |
| $F(000)$ | 509 | 308 | Diffractometer | DARCh | DARCh |
| Space group | $Pna2_1$ | $P\bar{1}$ | Scan mode | $\theta/2\theta$ | $\theta/2\theta$ |
| $a$, Å | 15.741(6) | 8.142(3) | Number of reflections: | | |
| $b$, Å | 7.428(3) | 7.819(4) | measured | 1074 | 1669 |
| $c$, Å | 7.387(3) | 7.067(2) | independent with $F \geq 4\sigma(F)$ | 1018 | 1453 |
| $\alpha$, deg | 90 | 84.39(4) | $2\theta_{max}$, deg | 63 | 63 |
| $\beta$, deg | 90 | 86.86(3) | Number of refined parameters | 131 | 131 |
| $\gamma$, deg | 90 | 82.07(4) | $R$ | 0.023 | 0.030 |
| $V$, Å$^3$ | 864(1) | 443.1(6) | $R_w$ | 0.024 | 0.032 |
| $Z$ | 4 | 2 | Weighing scheme | $[\sigma(F_o)^2 + 0.0004F_o^2]^{-1}$ | $[\sigma(F_o)^2 + 0.0007F_o^2]^{-1}$ |
| $\rho$(calcd), g/cm$^3$ | 1.980(2) | 2.425(3) | GOOF | 0.98 | 1.04 |
| $\mu_{Mo}$, cm$^{-1}$ | 55.34 | 120.36 | | | |

**Table 2.** Atomic coordinates and thermal parameters* for structures **I** and **II**

| Atom | $x$ | $y$ | $z$ | $B$, Å$^2$ | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|
| | | | **I**** | | | | **II** | |
| Cu | 0.51287(3) | 0.80710(7) | 0 | 2.80(1) | 0.51718(8) | 0.78364(9) | 0.06834(9) | 2.92(2) |
| X(1) | 0.52789(4) | 0.07782(9) | 0.1555(1) | 2.61(1) | 0.42871(6) | 0.91688(6) | −0.23723(7) | 2.56(1) |
| X(2) | 0.64809(5) | 0.7128(1) | −0.0681(1) | 3.55(2) | 0.80457(6) | 0.66263(7) | 0.03490(7) | 2.64(1) |
| N(1) | 0.2757(2) | 0.7166(4) | 0.2743(5) | 2.64(8) | 0.0277(5) | 0.8375(6) | 0.3443(6) | 2.7(1) |
| N(2) | 0.2776(2) | 0.7674(6) | 0.5800(6) | 4.0(1) | 0.0960(6) | 0.7268(6) | 0.6462(6) | 3.2(1) |
| N(3) | 0.1556(2) | 0.6786(5) | 0.4428(6) | 3.46(9) | −0.1579(6) | 0.7014(8) | 0.5385(7) | 4.3(2) |
| C(1) | 0.4344(3) | 0.5837(6) | −0.0059(8) | 3.5(1) | 0.4278(8) | 0.6320(8) | 0.3013(9) | 3.3(2) |
| C(2) | 0.3888(3) | 0.7237(5) | 0.0554(6) | 2.65(9) | 0.2968(6) | 0.7184(7) | 0.2099(7) | 2.5(1) |
| C(3) | 0.3662(3) | 0.7545(6) | 0.2496(6) | 2.9(1) | 0.1936(6) | 0.8746(6) | 0.2779(7) | 2.7(1) |
| C(4) | 0.2374(2) | 0.7224(5) | 0.4328(7) | 2.50(9) | −0.0094(6) | 0.7551(6) | 0.5101(6) | 2.5(1) |
| H(1.1) | 0.466(3) | 0.501(6) | 0.087(8) | 4(1) | 0.463(7) | 0.683(7) | 0.397(9) | 3(1) |
| H(1.2) | 0.440(3) | 0.558(6) | −0.135(7) | 2.8(9) | 0.477(8) | 0.529(8) | 0.272(9) | 4(1) |
| H(2.1) | 0.367(3) | 0.772(5) | −0.009(7) | 3(1) | 0.268(8) | 0.667(8) | 0.122(9) | 5(1) |
| H(3.1) | 0.400(4) | 0.663(8) | 0.33(1) | 7(1) | 0.172(7) | 0.947(6) | 0.202(8) | 3(1) |
| H(3.2) | 0.377(3) | 0.863(5) | 0.292(6) | 2.6(8) | 0.249(5) | 0.918(5) | 0.375(6) | 1.4(9) |
| H(1) | 0.249(3) | 0.710(5) | 0.180(8) | 3(1) | −0.022(6) | 0.843(6) | 0.266(7) | 2(1) |
| H(2) | 0.322(2) | 0.800(5) | 0.575(7) | 3(1) | 0.187(8) | 0.760(7) | 0.646(9) | 4(1) |
| H(3) | 0.254(3) | 0.775(5) | 0.65(1) | 4(1) | 0.076(8) | 0.680(7) | 0.732(9) | 4(1) |
| H(4) | 0.141(2) | 0.687(4) | 0.362(5) | 0.3(6) | −0.21(1) | 0.73(1) | 0.45(1) | 8(2) |
| H(5) | 0.129(3) | 0.678(6) | 0.531(9) | 4(1) | −0.188(9) | 0.684(9) | 0.68(1) | 6(2) |

* For non-hydrogen atoms, $B_{eq} = 1/3 \sum_i \sum_j B_{ij} a_i^* a_j^* \vec{a}_i \vec{a}_j$ .

** In **I**, X(1) = 0.726(3)Cl + 0.274(3)Br; X(2) = 0.758(3)Cl + 0.242(3)Br.

**Table 3.** Bond lengths and angles in structures **I**\* and **II**

| Bond** | d, Å | | Angle** | ω, deg | |
|---|---|---|---|---|---|
| | **I** | **II** | | **I** | **II** |
| Cu–X(1) | 2.328(3) | 2.407(3) | X(1)CuX(1)' | 102.2(1) | 99.3(1) |
| Cu–X(1)' | 2.760(3) | 2.827(4) | X(1)CuX(2) | 106.1(2) | 108.3(1) |
| Cu–X(2) | 2.297(6) | 2.408(3) | X(1)'CuX(2) | 96.2(1) | 96.6(1) |
| Cu–C(1) | 2.069(6) | 2.091(7) | X(1)Cu$m$(12) | 122.4(2) | 121.8(2) |
| Cu–C(2) | 2.090(7) | 2.106(6) | X(1)'Cu$m$(12) | 94.4(2) | 103.0(2) |
| Cu–$m$(12) | 1.968(7) | 1.988(6) | X(2)Cu$m$(12) | 126.5(3) | 121.3(2) |
| | | | C(1)CuC(2) | 37.7(2) | 37.3(2) |
| C(1)–C(2) | 1.343(7) | 1.343(9) | C(2)C(1)H(1.1) | 119(3) | 116(4) |
| C(1)–H(1.1) | 1.04(5) | 0.90(6) | C(2)C(1)H(1.2) | 122(3) | 123(4) |
| C(1)–H(1.2) | 0.98(5) | 0.88(6) | H(1.1)C(1)H(1.2) | 119(4) | 121(6) |
| C(2)–C(3) | 1.495(7) | 1.489(8) | C(1)C(2)C(3) | 124.7(5) | 123.7(5) |
| C(2)–H(2.1) | 0.68(5) | 0.83(6) | C(1)C(2)H(2.1) | 116(4) | 114(4) |
| | | | C(3)C(2)H(2.1) | 118(4) | 122(4) |
| C(3)–N(1) | 1.463(8) | 1.464(7) | C(2)C(3)N(1) | 108.7(5) | 111.5(5) |
| C(3)–H(3.1) | 1.04(6) | 0.75(5) | N(1)C(3)H(3.1) | 108(4) | 100(4) |
| C(3)–H(3.2) | 0.88(4) | 0.95(4) | N(1)C(3)H(3.2) | 109(3) | 112(3) |
| | | | C(2)C(3)H(3.1) | 108(4) | 115(4) |
| | | | C(2)C(3)H(3.2) | 116(3) | 109(3) |
| | | | H(3.1)C(3)H(3.2) | 108(4) | 109(5) |
| N(1)–C(4) | 1.318(7) | 1.321(7) | C(3)N(1)C(4) | 123.4(5) | 125.4(5) |
| N(1)–H(1) | 0.82(6) | 0.70(5) | C(3)N(1)H(1) | 114(3) | 109(4) |
| | | | C(4)N(1)H(1) | 122(3) | 123(4) |
| C(4)–N(2) | 1.302(8) | 1.307(7) | N(1)C(4)N(2) | 121.8(5) | 121.3(5) |
| C(4)–N(3) | 1.330(8) | 1.332(8) | N(1)C(4)N(3) | 119.0(5) | 119.0(5) |
| | | | N(2)C(4)N(3) | 119.1(5) | 119.7(5) |
| N(2)–H(2) | 0.75(4) | 0.82(6) | C(4)N(2)H(2) | 120(3) | 127(4) |
| N(2)–H(3) | 0.62(7) | 0.70(6) | C(4)N(2)H(3) | 114(5) | 120(5) |
| | | | H(2)N(2)H(3) | 124(6) | 113(6) |
| N(3)–H(4) | 0.64(4) | 0.77(8) | C(4)N(3)H(4) | 105(3) | 111(6) |
| N(3)–H(5) | 0.78(6) | 1.02(8) | C(4)N(3)H(5) | 125(4) | 111(4) |
| | | | H(4)N(3)H(5) | 126(5) | 133(7) |

Torsion angles

| Angle | φ, deg | | Angle | φ, deg | |
|---|---|---|---|---|---|
| | **I** | **II** | | **I** | **II** |
| X(1)'CuX(1)Cu' | −142.2 | 0.0 | C(1)C(2)C(3)N(1) | −107.3 | −110.3 |
| X(2)CuX(1)Cu' | −117.6 | −100.2 | C(2)C(3)N(1)C(4) | 176.4 | −77.8 |
| X(2)CuX(1)'Cu' | 88.9 | 109.9 | C(3)N(1)C(4)N(2) | 1.8 | 13.0 |
| CuC(1)C(2)C(3) | 102.9 | 102.9 | C(3)N(1)C(4)N(3) | 177.3 | −167.6 |

\* The ratios of the Br and Cl atoms are given in the footnote to Table 2.
\*\* $m$(12) is the midpoint of the C(1)=C(2) bond.

(**III**) and [AITU]CuBr$_2$ (**IV**) complexes: 2.760(3) and 2.827(4) Å in **I** and **II**, respectively; 2.634(1) and 2.748(3) Å in **III** and **IV**, respectively. Such an elongation is consistent with the fact that the copper atoms in **I** and **II** are offset from the plane of equatorial ligands by 0.29 and 0.37 Å, respectively. This is somewhat lesser than in structures **III** and **IV** (0.32 and 0.39 Å, respectively). The τ angle between the plane of equatorial ligands and the C=C bond is equal to 8° in **I** and 0° in **II**. Despite the effective Cu–(C=C) interaction [the Cu–(midpoint of the C=C bond) distance is equal to 1.968(7) Å in **I** and 1.988(6) Å in **II**], the coordinated olefinic C(1)=C(2) bond is only slightly elongated [to 1.343(7) Å in **I** and 1.343(9) Å in **II**], evidencing a comparatively small contribution of the (M ⟶ L)$_\pi$-component to the Cu(I)–(C=C) interaction [8]. By contrast, the π-dative component of the Cu(I)–(C=C) bond in **III** and **IV** is more pronounced, and the C=C bond is elongated to 1.357(6) Å in **III** and 1.362(9) Å in **IV**.

Complexes **I** and **II** are close in their composition and geometry of the Cu(I) coordination sphere (Table 3), but differ structurally. In **I**, the helical polymeric fragments $(CuX_2)_n^{n-}$ are formed about the $2_1$ axis. In these fragments, the halogen atom X(1) serves as a bridge, while the X(2) atom is terminal and lies in the equatorial plane. Structure **II** is constructed from the centrosymmetric Cu$_2$Br$_4$(AGU)$_2$ dimers formed due to the elongated Cu···Br contacts [2.827(4) Å]. The fragments are linked together by the hydrogen bonds, of which the most important are given in Table 4.

**Table 4.** Geometry of hydrogen bonds in structures **I**\* and **II**

| A–H···B bond | Distances, Å | | AHB angle, deg |
|---|---|---|---|
| | H···B | A–H | |
| **I** | | | |
| C(3)–H(3.1)···X(2) | 3.00(6) | 1.04(6) | 128(4) |
| C(3)–H(3.2)···X(1) | 3.03(4) | 0.88(4) | 121(3) |
| N(1)–H(1)···X(2) | 2.49(5) | 0.82(6) | 161(4) |
| N(2)–H(2)···X(1) | 2.59(4) | 0.75(4) | 164(4) |
| N(2)–H(3)···X(2) | 2.69(7) | 0.62(7) | 176(6) |
| N(3)–H(5)···X(1) | 2.73(5) | 0.78(6) | 141(5) |
| **II** | | | |
| C(1)–H(1.1)···Br(1) | 3.29(6) | 0.90(6) | 157(5) |
| C(1)–H(1.2)···Br(2) | 3.31(7) | 0.88(6) | 163(5) |
| C(2)–H(2.1)···Br(2) | 3.05(6) | 0.83(6) | 151(5) |
| C(3)–H(3.2)···Br(1) | 3.17(4) | 0.95(4) | 159(3) |
| N(1)–H(1)···Br(2) | 2.81(5) | 0.70(5) | 146(5) |
| N(2)–H(2)···Br(1) | 2.66(6) | 0.82(6) | 158(5) |
| N(3)–H(5)···Br(2) | 2.49(8) | 1.02(8) | 166(6) |

\* The ratios of the Cl and Br atoms are given in the footnote to Table 2.

In structure **I**, the guanidinium moiety of the AGU cation, whose C=C bond is coordinated by the copper atom of one $(CuX_2)_n^{n-}$ fragment, is firmly bonded to one bridging and two terminal halogen atoms of
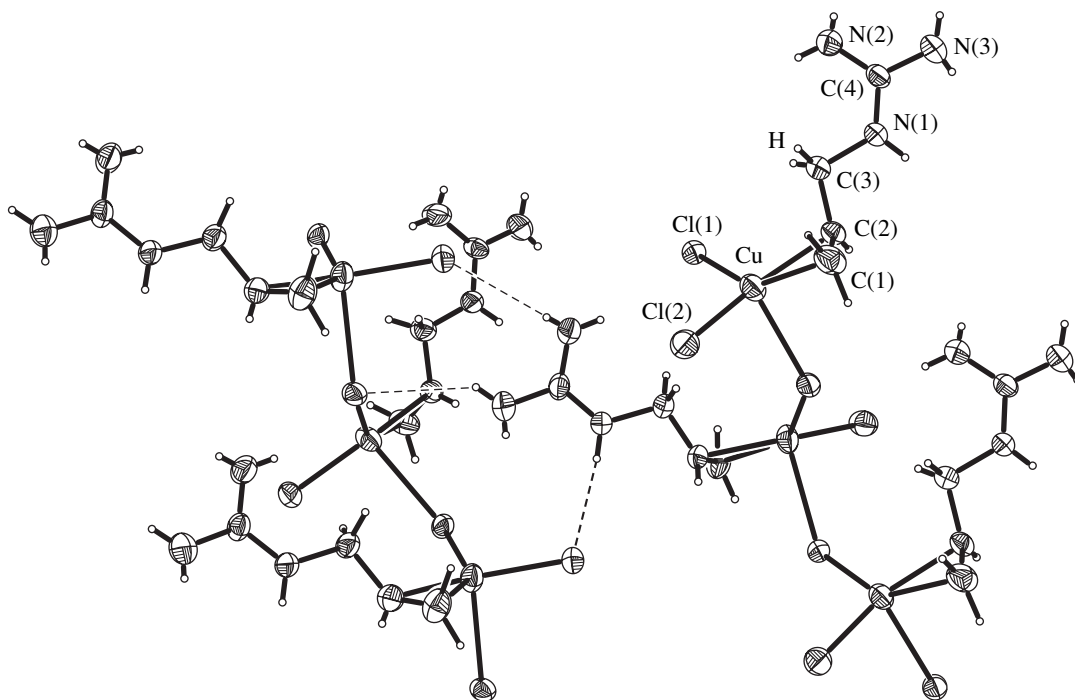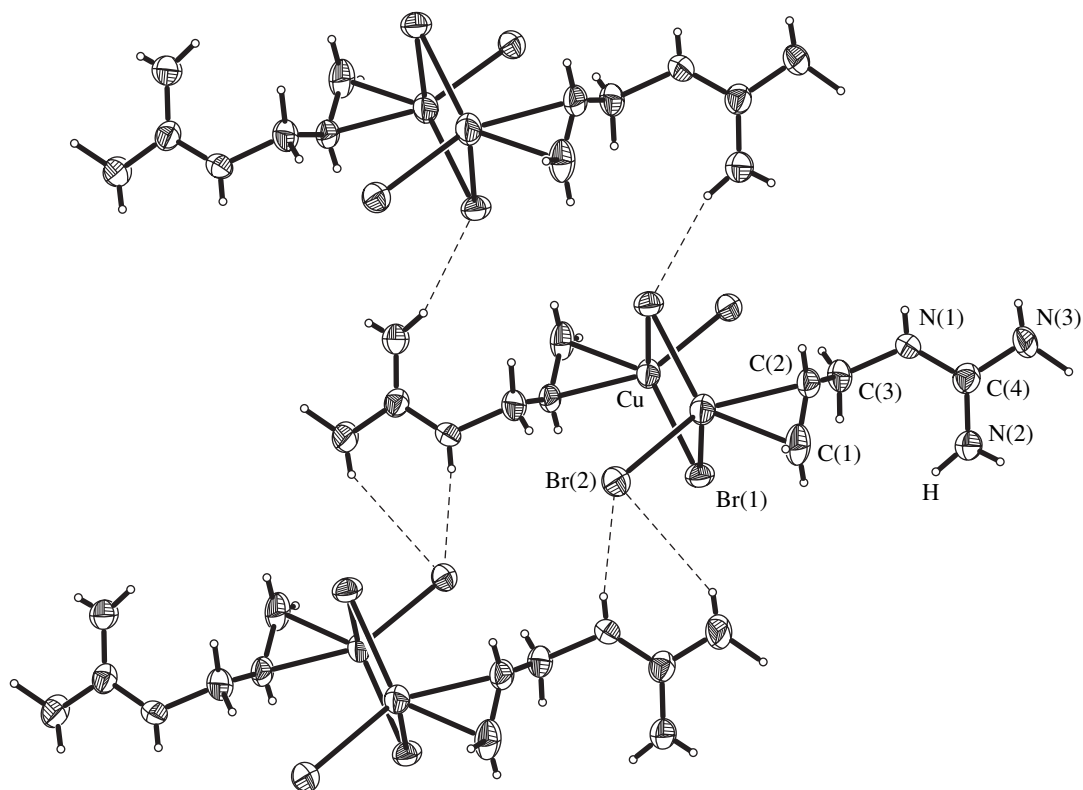


**Fig. 1.** Fragment of structure **I**.

**Fig. 2.** Layers of the $Cu_2Br_4(AGU)_2$ dimers in structure **II**.

another $(CuX_2)_n^{n-}$ fragment via the N–H⋯X hydrogen bonds (Fig. 1). Thus, each polymeric $[(AGU)CuX_2]_n$ fragment is bonded to four analogous fragments. In structure **II**, the $Cu_2Br_4(AGU)_2$ dimers are combined by the N–H⋯X contacts into layers lying in the (010) plane (Fig. 2). The layers are joined by the van der Waals forces and hydrogen bonds of the C–H⋯Br type. Complex **II** is structurally close to *S*-allylisothiouronium π-complexes **III** and **IV**, but somewhat differs in the geometry of its organic cation.

Calculations performed with the HYPERCHEM program using a modified version of the iterative SCF MO LCAO method in the INDO approximation [9] showed that, due to the Cl–Cu $p$–$d_\pi$ interaction, a small effective charge ($-0.04\,\bar{e}$) occurs on the copper atom in complex **I** [a contribution from the Br atoms to the occupancy of the $G(X_i)$ positions was neglected in the calculations (see footnote to Table 2)]. A considerable negative charge on both nitrogen [$-0.24\,\bar{e}$ for N(1) and $-0.39\,\bar{e}$ for N(2) and N(3)] and chlorine [$-0.52\,\bar{e}$ for Cl(1) and $-0.67\,\bar{e}$ for Cl(2)] atoms is due to the secondary polarization of these atoms upon the formation of the N–H⋯Cl hydrogen bonds.

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