Title: Halogen bonds in 2,5-dihalopyridine-copper(II) chloride complexes
Halogen Bonds in 2,5-Dihalopyridine-Copper(II) Chloride Complexes

Rakesh Puttreddy, a,b Carolina von Essen, c Anssi Peuronen, c Manu Lahtinen c and Kari Rissanen a,b

Ten coordination complexes obtained through a facile reaction between 2,5-dihalopyridines and copper(II) chloride (CuCl2) are characterized using single crystal X-ray diffraction. Two series of dihalopyridine complexes based on 2-chloro-5-X-pyridine and 2-bromo-5-X-pyridine (X = F, Cl, Br and I) were prepared to analyze the C···X2/X5–Cl–Cu halogen bonds (XB). The influence of X2- and X5-substituents on the respective interactions was examined by comparing them to the X2/X3–Cl–Cu XB found in mono-substituted halopyridine complexes, [n-X-pyridine]2-CuCl2 (n = 2, 3 and X = Cl, Br and I). Varying the X5 halogens in [2,5-(dihalopyridine)]2-CuCl2, the C5-X5–Cl–Cu XB follows the order F5<Cl5<Br5<I5 for X2 = Cl and Cl5<Br5<I5 for X2 = Br. The C2–X2–Cl–Cu XB distances did not follow any particular trends, and are slightly longer compared to corresponding distances in [2-(halopyridine)]2-CuCl2 complexes due to the competition of X2 and X5-halogen based halogen bonds. The C3–X3–Cl–Cu contacts in [3-(halopyridine)]2-CuCl2 have R2 values > 1 and they cannot be considered as halogen bonds. This proves the polarization effect of X2- to X5- rather than X5- to X2-halogen, and the introduction of second halogen substituent in para-position to X5- triggers C2–X2–Cl–Cu and C5–X5–Cl–Cu XB interactions.

Introduction

Halogen bonding, recently defined by IUPAC as a highly directional non-covalent interaction,1 is an efficient new tool in crystal engineering.2 Halogens at the aromatic ring (C(Ar)-X groups, C(Ar) = aromatic carbon and X = halogen) are capable of forming a variety of non-covalent interactions, e.g. halogen-halogen interactions, hydrogen bonds (HBs) and halogen bonds (XBs).3 The halogens at the organic ring are polarized due to the conjugation with the π-system and subsequently the interaction of nucleophiles with C(Ar)-X groups is more pronounced than with their C(Ar)-H analogues. Due to the polarization, the high electron density around the halogen atom is unequally distributed in the direction perpendicular to C-X bonds, and an electron deficient site is formed parallel to the covalent C(Ar)-X bond, called a-hole.4 The ability of the halogen atoms to function as XB-donors is dependent on their polarizability which increases in the order F<Cl<Br<I and is affected by the neighbouring covalently bound electron-withdrawing atoms/groups.4 In the solid-state, these polarized halogens are capable of forming a large variety of complex XBs of the type C–X...A–C or A...X...A (X = XB donor, A = XB acceptor).5

Nitrogen containing compounds, especially pyridines, are important ligands in coordination chemistry and have been reported for numerous applications in various fields.6 Over the past few years, mono-substituted halopyridines acting as ligands in coordination complexes have gained significant interest also within the halogen bonding research community.7 In combination with metal halides [MAx, M = metal ion, A = metal bound halide], two main interactions have been studied and modulated for crystal engineering applications viz. (a) C–X...A–M (halogen bonding) and (b) M–A...A–M (halogen-halogen interaction). These Interactions have gained more interest due to their potential applications in magnetic and semiconductor materials.8 Brammer et al. have studied complexes of the type M(LX)2A (LX = 2-, 3- and 4-X-pyridines) in solid state, with A acting as XB acceptor and X as XB donor.7a,b In these compounds, halopyridines coordinate in trans-arrangement to form C–X...A–M XBAs. The metal to pyridine nitrogen coordination activates the aromatic ring system and, subsequently, the halogen substituent for the formation of XBAs. Alternatively, the XB character in halopyridines can be enhanced by protonation of the nitrogen, leading to complexes of the type [LH][MAx].7a,b,c During the last years, we have successfully applied neutral pincer type [2,6-bis(di-tert-butylyphosphino)-methyl]-phenyl]PdY (Y = Cl, Br and I) and (terpyridine)[Me3Ptl complexes in XB chemistry. The metal bound halogen acts as the XB acceptor for donors viz. iodine and perfluoriodobenzene, respectively.8

Recently, we reported C–X...Br–Cu XBAs in [2,5-(dihalopyridine)]2-CuBr2 coordination compounds, in which X2- and X5-halogen act as XB donors and Cu-coordinated bromides as the XB acceptors.8 We utilized two series of 2,5-dihalopyridines based on 2-chloro- and 2-bromo-pyridine skeleton, varying the substituent in CS-position as shown in Fig. 1. We have shown that, in complexes based on 2-chloro-5-X-pyridine (X = Cl, Br and I), only C5–X5–Br–Cu XBAs are formed and these are electronically influenced by the C2-chlorine, which resides close to the Cu(II) coordination sphere. In contrast, in (2-bromo-5-X-pyridine)2-CuBr2 complexes, both X2 and X5-substituents form XBAs to the formally negatively charged bromide.
The corresponding XB distances are nearly similar due to the competition between X2- and X5-halogens forming C=X2/X5···Br–Cu XB.

![Diagram of XB interactions](image)

**Fig. 1.** Chemical structures of 2,5-dihalopyridines: 2-chloro-5-fluoropyridine (1), 2,5-dichloropyridine (2), 5-bromo-2-chloropyridine (3), 2-chloro-5-iodopyridine (4), 2-bromo-5-fluoropyridine (5), 2-bromo-5-chloropyridine (6), 2,5-dibromopyridine (7) and 2-bromo-5-iodopyridine (8).

In the present work, we utilize the same set of 2,5-dihalopyridines in combination with copper(II) chloride (CuCl2) to explore the C–X2/X5···Cl–Cu interactions. We anticipate that the more electronegative chloride bound to Cu(II) leads to stronger XBs compared to bromide. The results based on solid state structures are compared with previously reported structures of (2-X2pyridine)2CuCl2 (X = Cl and Br) and (3-Xpyridine)2CuCl2 (X = F, Cl, Br and I). In the present context, the abbreviations 2ClPy, 2BrPy, 3ClPy, 3Fpy and 3Ipy are used for 2-chloropyridine, 3-bromopyridine and 3-chloropyridine, respectively. The crystallographic data for (2ClPy)2CuCl2, (2BrPy)2CuCl2, (3ClPy)2CuCl2 and (3BrPy)2CuCl2 were extracted from CSD database, while (3Ipy)2CuCl2 is part of the current investigation (reported in the Supporting Information, Fig. S1).

**Results and discussion**

The complexes were synthesized by mixing a 2:1 molar ratio of 2,5-dihalopyridine and CuCl2·2H2O in acetonitrile at room temperature (See Supporting Information for more details). Slow evaporation of the resulting solution provides single crystals suitable for X-ray crystallographic analysis. A total of ten (2,5-dihalopyridine)2CuCl2 coordination compounds, obtained from 2,5-dihalopyridine + CuCl2 combinations, are discussed. With 2-chloro-5-iodopyridine (4), two types of structures, the dimeric (4.1)2{CuCl2}2 and monomeric (4.2)2{CuCl2}2, isolated as blue and green coloured crystals from the bulk sample, could be obtained. For (4.1)2{CuCl2}2 and (4.2)2{CuCl2}2 structures, the respective Cu(II) coordination geometries are square-pyramidal and see-saw. To determine the structural correlation between the measured single crystals and the crystalline bulk powders, powder X-ray diffraction data of each sample was collected and indexed with the unit cell parameters of corresponding single crystal structures using Pawley whole pattern fitting method. The results show that the solid state structures of bulk samples are consistent with single crystal data and that the bulk of the product from 4 + CuCl2 corresponds to the dimeric species, (4.1)2{CuCl2}2, and for 5 + CuCl2 to the monomer, (5.2)2{CuCl2}2. (See supporting information for more details).

All (1)2{CuCl2}2, (2)2{CuCl2}2, (3)2{CuCl2}2 and (4.1)2{CuCl2}2 are dimeric complexes with 4:2 ligand:metal ratio. In these complexes the coordination sphere of Cu(II) contains two N-atoms of the dihalopyridine and three chlorine ions, of which one is Cu–Cl–Cu bridging as shown in Fig. 2a-d, and is abbreviated as Cu–(μCl). The X2- and X5-substituents are in syn-arrangement in contrast to our previously published complexes. In that study, the trans-C2–C2···Cu contacts of ca. 3.0 Å in (2-chloro-5-X-pyridine)2CuBr2 complexes were shown to be dependent on X5-substituent. This encouraged us to investigate the same contacts in (2-chloro-5-X-pyridine)2CuCl2 complexes for X5-substituent effects. The presence of Cu–(μCl) in (1)2{CuCl2}2, (2)2{CuCl2}2, (3)2{CuCl2}2 and (4.1)2{CuCl2}2 leads to a deviation of N–Cu–N angles from linearity to 172.84(14)°, 169.35(5)°, 172.34(12)° and 171.84(4)°, respectively. For this reason, the C2–C2–Cu distances [ca. >3.20 Å] are longer compared to (2-chloro-5-X-pyridine)2CuBr2 complexes. The centrosymmetric dimers, (1)2{CuCl2}2 and (2)2{CuCl2}2, contain two crystallographically independent dihalopyridine ligands coordinated to the Cu(II) centre. In both complexes, one of the two X5-halogens does not showXBs, thus referred as XB passive (see Fig. 2a and 2b indicated using red arrow), while the other X5-halogen acts as a bifurcated XB acceptor. The structures exhibit similar but subtly different C2–C2–X5···Cu XBs interactions to form 1-D polymers between X5-halogen and Cu-chlorines (Fig 2a, Table 1). For example, in (1)2{CuCl2}2, the bifurcated C5-fluorine forms weak C2–C2···F5–Cu bonds (Fig 2b). With 2ClPy, (2)2{CuCl2}2, the C5-fluorine forms similar bifurcated XB bonds [Fig 2b] with C2–C2···Cl5–Cu and C2–CuCl2···I5–Cl5 distances of R{B} = 0.97 [3.121 Å, see Ref 12 for R{B} definition] and R{AB} = 0.98 [3.160 Å], respectively. The C2–C2···F5 angles [173.6°] are more linear and closer to the ideal value of XB angles compared to C2–C2···Cl5 [158.9°]. In (2)2{CuCl2}2, the C5-fluorine forms similar bifurcated XB bonds (Fig 2b) with C2–C2···Cl5–Cu and C2–C2···I5–Cl5 distances of R{B} = 0.99 [3.480 Å] and R{AB} = 0.97 [3.393 Å]. The C3-substituent in (3ClPy)2CuCl2 is XB passive. However, in (1)2{CuCl2}2 and (2)2{CuCl2}2, the presence of para-C2-chlorines provides F5- and Cl5-substituents an opportunity to form C2–C2···X5–Cu XB. The Cu–(μCl) and Cu–Cl in (1)2{CuCl2}2 and (2)2{CuCl2}2 are XB passive to X2- and X5-substituents. Nevertheless, short Cu–(μCl)···H and Cu–Cl···H interactions can be observed in the 3-D crystal lattice as shown in Fig 2a,b.

The complexes (3)2{CuCl2}2 and (4.1)2{CuCl2}2 are isostuctural and isomorphous, and crystallize in the monoclinic space group I2/m. The asymmetric units contain one 2,5-dihalopyridine ligand on general position coordinated to a CuCl2 residing on the mirror plane. Unlike (1)2{CuCl2}2 and (2)2{CuCl2}2, the Cu–(μCl) and Cu–Cl are bifurcated XB acceptors for either syn-oriented X2- or X5-substituents. Both (3)2{CuCl2}2 and (4.1)2{CuCl2}2 as discrete complexes form 1-D polymers through C2–C2···Cl–CuX2 XB distances with R{B} = 0.96 [3.420 Å] and R{AB} = 0.96 [3.474 Å]. These 1-D polymers are connected via C5–X5–CuX2 (X = Br and I) contacts to a 3-D network as shown in Fig. 2c-d. The C5–Br5–CuX2 XB in (3)2{CuCl2}2 [R{B} = 0.95] are shorter compared to (3BrPy)2CuCl2 [R{B} = 1.03, not XB]. Complex (4.2)2CuCl2 and our previously reported (4)2CuBr2 are isostuctural and isomorphous.9 The monomeric, discrete 21 ligand:metal complex extend into a 1-D polymer connected by C5–I5–Cl–Cu contacts as shown in Fig. 3. In contrast to (4.1)2{CuCl2}2, the Cu–Cl in (4.2)2CuCl2 is a monodentate XB acceptor. As a result, the C5–I5–Cl–Cu distances in (4.2)2CuCl2 [R{AB} = 0.90] are shorter compared to (4.1)2{CuCl2}2 [R{AB} = 0.93] and Cl3–I3–Cl–Cu XB in (3Ipy)2CuCl2 [R{AB} = 0.93].

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$R_{	ext{w}} = 0.92$ (see Supporting information, Fig S2). The $R_{	ext{w}}$ value of 0.90 is the smallest value observed for XBs in (2,5-dihalopyridine)$_2$-Cu(II) complexes. The relatively short contacts in (4.2)$_2$-CuCl$_2$ can further be a result of Cu(II) geometry, the presence of C2-chlorine and crystal packing interactions.

Fig. 2. Section of 3-D crystal packing displaying halogen bond and hydrogen bond interactions in (a) (1)$_2$-[CuCl$_2$], (b) (2)$_2$-[CuCl$_2$], (c) (3)$_2$-[CuCl$_2$] and (d) (4.1)$_2$-[CuCl$_2$]. Black dotted lines represent the halogen bonds, and red dotted lines represent hydrogen bonds.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Motif</th>
<th>$d$ (K2--Cl$_2$), Å</th>
<th>$\angle$C2--K2--Cl$_2$ (°)</th>
<th>$R_{	ext{w}}$</th>
<th>Motif</th>
<th>$d$ (K5--Cl), Å</th>
<th>$\angle$C5--K5--Cl (°)</th>
<th>$R_{	ext{w}}$</th>
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<tr>
<td>(1)$_2$-[CuCl$_2$]</td>
<td>C2’–Cl2’–F5–C5</td>
<td>131.2$^\text{a}$</td>
<td>173.6$^\text{a}$</td>
<td>0.97$^\text{b}$</td>
<td>C5–F5–C2–C2</td>
<td>136.0$^\text{a}$</td>
<td>158.9$^\text{a}$</td>
<td>0.98$^\text{b}$</td>
</tr>
<tr>
<td>(2)$_2$-[CuCl$_2$]</td>
<td>C2’–Cl2’–C15–C5’</td>
<td>3.480 [3.399]$^\text{a}$</td>
<td>174.7 [177.3]$^\text{a}$</td>
<td>0.99 [0.97]$^\text{a}$</td>
<td>C5’–C15’–C2–C2</td>
<td>3.393 [3.734]$^\text{a}$</td>
<td>160.1 [158.5]$^\text{a}$</td>
<td>0.97 [1.06]$^\text{a}$</td>
</tr>
<tr>
<td>(3)$_2$-[CuCl$_2$]</td>
<td>C2’–Cl2–Cl–Cu</td>
<td>3.371</td>
<td>161.3</td>
<td>0.96</td>
<td>Cu–Br–Cl–Cl–Cu</td>
<td>3.430 [3.675]$^\text{a}$</td>
<td>169.2 [157.7]$^\text{a}$</td>
<td>0.95 [1.03]$^\text{a}$</td>
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<tr>
<td>(4.1)$_2$-[CuCl$_2$]</td>
<td>C2’–Cl2–Cl–Cu</td>
<td>3.462</td>
<td>162.3</td>
<td>0.99</td>
<td>C5–I5–Cl–Cu</td>
<td>3.474 [3.413]$^\text{a}$</td>
<td>161.3 [170.1]$^\text{a}$</td>
<td>0.93 [0.92]$^\text{a}$</td>
</tr>
<tr>
<td>(4.2)$_2$-CuCl$_2$</td>
<td>C2’–Cl2–Cl–Cu</td>
<td>3.559</td>
<td>161.9</td>
<td>1.02</td>
<td>C5–I5–Cl–Cu</td>
<td>3.374 [3.413]$^\text{a}$</td>
<td>172.8 [170.1]$^\text{a}$</td>
<td>0.90 [0.92]$^\text{a}$</td>
</tr>
<tr>
<td>(5.1)$_2$-[CuCl$_2$]</td>
<td>C2’–Br2–Cl–Cu</td>
<td>3.459 [3.358]$^\text{b}$</td>
<td>170.1 [167.9]$^\text{b}$</td>
<td>0.99 [0.93]$^\text{b}$</td>
<td>C5–F5 passive</td>
<td>3.274 [3.143]$^\text{b}$</td>
<td>172.8 [170.1]$^\text{b}$</td>
<td>0.90 [0.92]$^\text{b}$</td>
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<tr>
<td>(5.2)$_2$-CuCl$_2$</td>
<td>C2’–Br2–Cl–Cu</td>
<td>3.459 [3.358]$^\text{b}$</td>
<td>148.4 [169.7]$^\text{b}$</td>
<td>0.99 [0.93]$^\text{b}$</td>
<td>C5–F5 passive</td>
<td>3.274 [3.143]$^\text{b}$</td>
<td>172.8 [170.1]$^\text{b}$</td>
<td>0.90 [0.92]$^\text{b}$</td>
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<tr>
<td>(6)$_2$-CuCl$_2$</td>
<td>C2’–Cl2–Cl–Cu</td>
<td>3.352 [3.358]$^\text{b}$</td>
<td>166.0 [167.9]$^\text{b}$</td>
<td>0.93 [0.93]$^\text{b}$</td>
<td>C5–I5–Cl–Cu</td>
<td>3.426 [3.734]$^\text{a}$</td>
<td>170.0 [158.5]$^\text{a}$</td>
<td>0.98 [1.06]$^\text{a}$</td>
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<tr>
<td>(7)$_2$-CuCl$_2$</td>
<td>C2’–Br2–Cl–Cu</td>
<td>3.380 [3.358]$^\text{b}$</td>
<td>165.1 [167.9]$^\text{b}$</td>
<td>0.94 [0.93]$^\text{b}$</td>
<td>C5–I5–Cl–Cu</td>
<td>3.372 [3.675]$^\text{a}$</td>
<td>171.5 [157.7]$^\text{a}$</td>
<td>0.94 [1.03]$^\text{a}$</td>
</tr>
<tr>
<td>(8)$_2$-CuCl$_2$</td>
<td>C2’–Br2–Cl–Cu</td>
<td>3.482 [3.358]$^\text{b}$</td>
<td>165.5 [167.9]$^\text{b}$</td>
<td>0.97 [0.93]$^\text{b}$</td>
<td>C5–I5–Cl–Cu</td>
<td>3.407 [3.413]$^\text{b}$</td>
<td>171.5 [170.1]$^\text{b}$</td>
<td>0.91 [0.92]$^\text{b}$</td>
</tr>
</tbody>
</table>

*Values in parentheses are C2- and C3-halogen based Xb bond parameters in (n-X-pyridine)$_2$-CuCl$_2$ [n = 2 and 3, X = Cl, Br and I] complexes; The normalized interaction ratio, $R_{\text{w}}$, is defined as $\frac{R_{\text{wa}} \times d_{Xb}(Xa)}{\sum d_{Xb}(Xb)}$, where $d_{Xb}$ (Å) is the distance between the donor atom (X) and the acceptor atom (B), and divided by the sum of vdW radii (Å) of X and B. The van der Waals distance determined by Bondi were used to calculate $R_{\text{wa}}$ values.$^\text{1,1}$; $^\text{1}$Crystal structure of 3-fluoropyridine + CuCl$_2$ not available for comparison.$^\text{3}$The values represent C2–Cl2–C2–Cl Xbs in (2ClPy)$_2$-CuCl$_2$ (CCDC No. PMALAS)$^\text{3}$; No Xbs observed in (3ClPy)$_2$-CuCl$_2$ (CCDC No. VEPKUX)$^\text{3}$, and the observed C3–Cl3–Cl–Cu short contacts are shown only as reference; $^\text{4}$No Xbs observed in (3BrPy)$_2$-CuCl$_2$ (CCDC No. VEPLAE)$^\text{3}$ and the C3–Br3–Cl–Cu contacts are shown only as reference; $^\text{5}$Part of current study, see SI Fig. S2 for X-ray crystal structure; $^\text{6}$The values are for C2–Br2–Cl–Cu Xbs in (2BrPy)$_2$-CuCl$_2$ (CCDC No. YENKOF)$^\text{3}$. $^\text{b}$

Fig. 3. Halogen bonded 1-D polymeric structure in (4.2)$_2$-CuCl$_2$. Black broken lines represent the halogen bonds.

In structures based on 2-bromo-5-X-pyridine, monomeric and dimeric complexes can be observed. Reaction of 5 with CuCl$_2$ resulted in two types of structures, the dimeric (5.1)$_2$-[CuCl$_2$] and monomeric (5.2)$_2$-CuCl$_2$, isolated as green and colourless crystals, respectively, from the bulk sample. Ligands 6 - 8 form monomeric complexes of the type (6)$_2$-CuCl$_2$, (7)$_2$-CuCl$_2$ and (8)$_2$-CuCl$_2$. In (5.1)$_2$-[CuCl$_2$], the X2- and X5-substituents are in syn-arrangement similar to (2-chloro-5-X-pyridine)$_2$-CuCl$_2$ complexes. The F5-substituent is both HB and XB passive, therefore, the dimers only extend to form 1-D polymers via C2–Br2–Cl–Cu Xbs. The Cu–(µ–Cl) does not form any halogen bonds to X2/X5-substituents. However, the 1-D self-assembly of dimers by bifurcated C2–Br2–Cl–Cu [R$_{\text{wa}}$ = 0.99, 3.459 Å] Xbs leads to relatively short Cu–(µ–Cl)···Cl–(µ–Cl)···Cu...
contacts \( R_{\text{Cu}} = 0.97, 3.395 \text{ Å} \), as shown in Fig. 4a. In \( \{5.2\}_2\cdot\text{CuCl}_2 \), the X2- and X5-substituents’ anti-arrangement and the square planar coordinated Cu(II) are similar to reported (2,5-dihalopyridine)_2–CuBr_2 complexes.\(^9\) The complex extends into a 1-D polymeric structure via C2–Br2···Cl–Cu contacts \( R_{\text{Cu}} = 0.99, 3.578 \text{ Å} \), as shown in Fig. 4b. Similar to \( \{5.1\}_2\cdot\text{CuCl}_2 \), the F5-substituent is XB passive but eight membered rings formed through C5–F5–H4–C4 HBs between adjacent 1-D polymers can be found in the 3-D crystal packing. A closer inspection of the crystal packing in \( \{5.2\}_2\cdot\text{CuCl}_2 \) also reveals weak C2–Br2···Cu contacts at distances of ca. 3.13 Å which are longer compared to \( \{5.1\}_2\cdot\text{CuBr}_2 \) (ca. 3.0 Å).\(^1\) The C2–Br2···Cl–Cu distances in \( \{5.1\}_2\cdot\text{CuCl}_2 \) and \( \{5.2\}_2\cdot\text{CuCl}_2 \) are longer than in \( \{2\text{BrPy}\}_2\cdot\text{CuCl}_2 \) indicating the electron withdrawing effect is opposite to electronegativity of F5-substituent.

Complexes \( \{6\}_2\cdot\text{CuCl}_2 \), \( \{7\}_2\cdot\text{CuCl}_2 \) and \( \{8\}_2\cdot\text{CuCl}_2 \) are isostructural and isomorphous [Fig. 5b–d], with Cu(II) centres in see-saw coordination geometries.\(^1\) These complexes exhibit C2–Br2···Cl–Cu XBs forming 1-D polymers, with C5–X5···Cl–Cu (X = Cl, Br and I) XBs extending into 2-D sheets. The electronegativity of halogens decreases in the order F>Cl>Br>I. It would be expected, that the strength of C2–Br2···Cl–Cu XBs, influenced by X5-substituents, would follow the same order. However, despite fluoride being more electronegative and XB passive, the C2–Br2···Cl–Cu contacts in \( \{5\}_2\cdot\text{CuCl}_2 \) \( R_{\text{Cu}} = 0.99 \) are longer compared to \( \{6\}_2\cdot\text{CuCl}_2 \) \( R_{\text{Cu}} = 0.93 \). When X2 and X5 are bromines in \( \{7\}_2\cdot\text{CuCl}_2 \), both C2–Br2···Cl–Cu and C5–Br5···Cl–Cu contacts are in same magnitude with \( R_{\text{Cu}} \) values of 0.94. Generally it is known that iodine is a better XB donor than bromine. As a consequence, the \( R_{\text{Cu}} \) values for C5–I5···Cl–Cu XBs in \( \{8\}_2\cdot\text{CuCl}_2 \) \( R_{\text{Cu}} = 0.91 \) are shorter than C2–Br2···Cl–Cu \( R_{\text{Cu}} = 0.97 \). The C5–X5···Cl–Cu (X = Cl, Br and I) XBs in \( \{2\text{bromo-5-X-pyridine}\}_2\cdot\text{CuCl}_2 \) complexes are shorter compared to corresponding C3–X3···Cl–Cu XBs in (3-halopyridine)_2–CuCl. On the other hand, in \( \{2\text{bromo-5-X-pyridine}\}_2\cdot\text{CuCl}_2 \) complexes, the C2–Br2···Cl–Cu XBs are longer compared to C2–Br2···Cl–Cu XBs in \( \{2\text{BrPy}\}_2\cdot\text{CuCl}_2 \) due to the competitive nature of X2–X5-halogen forms XBs with copper-coordinated chloride. Despite the C5–X5···Cl–Cu XBs follow the anticipated order, i.e. F5<Cl5<Br5<15 for X2 = Cl and Cl5<Br5<15 for X2 = Br, these bond distances influenced by X2-substituents (X=Br and Cl) are shorter compared to (3-halopyridine)_2–CuCl_2 complexes. This suggests the influence of substitution effect of X2- on X5-halogen and vice versa.

![Fig. 5 Section of crystal packing to display the halogen bonded 1-D polymeric structures in (a) \( \{6\}_2\cdot\text{CuCl}_2 \), (b) \( \{7\}_2\cdot\text{CuCl}_2 \), and (c) \( \{8\}_2\cdot\text{CuCl}_2 \).](image)

The substitution effect of X2/X5-halogen for donor-acceptor property can further be supported by comparing C5–X5···Cl–Cu XBs in \( (2,5\text{-dihalopyridine})_2\cdot\text{CuCl}_2 \) with C3–X3···Cl–Cu in \( (3\text{-halopyridine})_2\cdot\text{CuCl}_2 \) complexes. For example, although C3–Br in \( \{3\text{BrPy}\}_2\cdot\text{CuCl}_2 \) can be a good XB donor, particularly towards negatively charged Cu-chloride, the C3–X3···Cl–Cu distances have \( R_{\text{Cu}} = 1.03 \). The C3–X3···Cl–Cu in \( \{3\text{XPy}\}_2\cdot\text{CuCl} \) \( X = F \) and Cl) complexes have similar \( R_{\text{Cu}} \) values. The bond parameters shown in Table 1 suggest that the presence of X2-substituents in 2,5-dihalopyridines triggers both X2- and X5-halogen to form XBs compared to monosubstituted \( (n-X\text{-Py})_2\cdot\text{CuCl} \) complexes \( n = 2 \) and \( 3, X = F, Cl \) and Br).

**Conclusions**

The halogen bonds in complexes formed by 2,5-dihalopyridine and copper(II) chloride revealed a diverse palette of C-X2/X5···Cu interactions. This is due to flexible coordination sphere of Cu(II) in these complexes compared to our previously reported 2,5-dihalopyridine-copper(II) bromide complexes. The C5–X5···Cl–Cu halogen bonds follow the order F5<Cl5<Br5<15 for X2 = Cl and Cl5<Br5<15 for X2 = Br. In presence of C2-chlorine, even the less-polarisable C15 and F5-atoms exhibit true halogen bond contacts. In case of 3-halopyridine-copper(II) chloride complexes, no C3–X3···Cl–Cu XB contacts can be observed at all. The longer C2–X2···Cl–Cu contacts in case of 2,5-dihalopyridine-copper(II) chloride complexes, compared to 2-halopyridine-copper(II) chloride complexes, are a result of the competition between X2 and X5 in forming halogen bonds.
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References


