

**This is a self-archived version of an original article. This version may differ from the original in pagination and typographic details.**

**Author(s):** Puttreddy, Rakesh; von Essen, Carolina; Peuronen, Anssi; Lahtinen, Manu; Rissanen, Kari

**Title:** Halogen bonds in 2,5-dihalopyridine-copper(II) chloride complexes

**Year:** 2018

**Version:** Accepted version (Final draft)

**Copyright:** © The Royal Society of Chemistry 2018

**Rights:** In Copyright

**Rights url:** <http://rightsstatements.org/page/InC/1.0/?language=en>

**Please cite the original version:**

Puttreddy, R., von Essen, C., Peuronen, A., Lahtinen, M., & Rissanen, K. (2018). Halogen bonds in 2,5-dihalopyridine-copper(II) chloride complexes. *CrystEngComm*, 20(14), 1954-1959.  
<https://doi.org/10.1039/C8CE00209F>

## Halogen Bonds in 2,5-Dihalopyridine-Copper(II) Chloride Complexes

Rakesh Puttreddy,<sup>\*a</sup> Carolina von Essen,<sup>a</sup> Anssi Peuronen,<sup>a</sup> Manu Lahtinen<sup>a</sup> and Kari Rissanen<sup>\*a</sup>

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Ten coordination complexes obtained through a facile reaction between 2,5-dihalopyridines and copper(II) chloride (CuCl<sub>2</sub>) 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–X<sub>2</sub>/X<sub>5</sub>–Cl–Cu halogen bonds (XB). The influence of X<sub>2</sub>- and X<sub>5</sub>-substituents on the respective interactions was examined by comparing them to the X<sub>2</sub>/X<sub>3</sub>–Cl–Cu XBs found in mono-substituted halopyridine complexes, (n-X-pyridine)<sub>2</sub>-CuCl<sub>2</sub> (n = 2, 3 and X = Cl, Br and I). Varying the X<sub>5</sub> halogens in (2,5-dihalopyridine)<sub>2</sub>-CuCl<sub>2</sub>, the C<sub>5</sub>-X<sub>5</sub>–Cl–Cu XBs follow the order F<sub>5</sub><Cl<sub>5</sub><Br<sub>5</sub><I<sub>5</sub> for X<sub>2</sub> = Cl and Cl<sub>5</sub><Br<sub>5</sub><I<sub>5</sub> for X<sub>2</sub> = Br. The C<sub>2</sub>–X<sub>2</sub>–Cl–Cu XB distances did not follow any particular trends, and are slightly longer compared to corresponding distances in (2-halopyridine)<sub>2</sub>-CuCl<sub>2</sub> complexes due to the competition of X<sub>2</sub> and X<sub>5</sub>-halogen based halogen bonds. The C<sub>3</sub>–X<sub>3</sub>–Cl–Cu contacts in (3-halopyridine)<sub>2</sub>-CuCl<sub>2</sub> have R<sub>XB</sub> values > 1 and they cannot be considered as halogen bonds. This proves the polarization effect of X<sub>2</sub>- to X<sub>5</sub>- rather than X<sub>5</sub>- to X<sub>2</sub>-halogen, and the introduction of second halogen substituent in *para*-position to X<sub>5</sub>- triggers C<sub>2</sub>-X<sub>2</sub>–Cl–Cu and C<sub>5</sub>-X<sub>5</sub>–Cl–Cu XB interactions.

### Introduction

Halogen bonding, recently defined by IUPAC as a highly directional non-covalent interaction,<sup>1</sup> is an efficient new tool in crystal engineering.<sup>2</sup> 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).<sup>3</sup> The halogens at the organic ring are polarized due to the conjugation with the  $\pi$ -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  $\sigma$ -hole.<sup>4</sup> 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.<sup>4</sup> In the solid-state, these polarized halogens are capable of forming a large variety of complex XBs of the type C–X $\cdots$ A–C or A $\cdots$ X $\cdots$ A [X = XB donor, A = XB acceptor].<sup>5</sup>

Nitrogen containing compounds, especially pyridines, are important ligands in coordination chemistry and have been reported for numerous applications in various fields.<sup>6</sup> 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.<sup>7</sup> In combination with metal halides [MA<sub>n</sub>, M = metal ion, A = metal bound halide], two main interactions have been studied and modulated for crystal engineering applications *viz.* (a) C–X $\cdots$ A–M (halogen bonding) and (b) M–A $\cdots$ A–M (halogen-halogen interaction). These Interactions have gained more interest due to their potential applications in magnetic and semiconductor materials.<sup>7</sup> Brammer *et al.* have studied complexes of the type M(LX)<sub>2</sub>A<sub>2</sub> [LX = 2-, 3- and 4-X-pyridines] in solid state, with A acting as XB acceptor and X as XB donor.<sup>7a,b</sup> In these compounds, halopyridines coordinate in *trans*-arrangement to form C–X $\cdots$ A–M XBs. The metal to pyridine nitrogen coordination activates the aromatic ring system and, subsequently, the halogen substituent for the formation of XBs. Alternatively, the XB character in halopyridines can be enhanced by protonation of the nitrogen, leading to complexes of the type [LH]<sup>+</sup>(MA<sub>n</sub>)<sup>–</sup>.<sup>7c–e</sup> During the last years, we have successfully applied neutral pincer type {2,6-bis[(di-*t*-butylphosphino)-methyl]-phenyl}PdY (Y = Cl, Br and I) and (terpyridine)Me<sub>3</sub>PtI complexes in XB chemistry. The metal bound halogen acts as the XB acceptor for donors *viz.* iodine and perfluoriodobenzene, respectively.<sup>8</sup>

Recently, we reported C–X $\cdots$ Br–Cu XBs in (2,5-dihalopyridine)<sub>2</sub>-CuBr<sub>2</sub> coordination compounds, in which X<sub>2</sub>- and X<sub>5</sub>-halogens act as XB donors and Cu-coordinated bromides as the XB acceptors.<sup>9</sup> We utilized two series of 2,5-dihalopyridines based on 2-chloro- and 2-bromopyridine skeleton, varying the substituent in C<sub>5</sub>-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 C<sub>5</sub>–X<sub>5</sub>–Br–Cu XBs are formed and these are electronically influenced by the C<sub>2</sub>-chlorine, which resides close to the Cu(II) coordination sphere. In contrast, in (2-bromo-5-X-pyridine)<sub>2</sub>-CuBr<sub>2</sub> complexes, both X<sub>2</sub> and X<sub>5</sub>-substituents form XBs to the formally negatively charged bromide.

<sup>a</sup>Rakesh Puttreddy, Carolina von Essen, Anssi Peuronen, Manu Lahtinen and Kari Rissanen

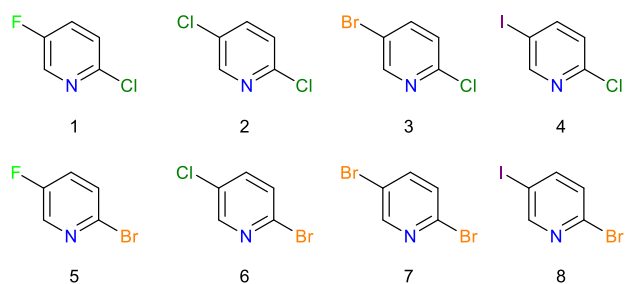
University of Jyväskylä, Department of Chemistry, Surfontie 9 B  
40014 Jyväskylä, Finland

Email rakesh.r.puttreddy@jyu.fi, kari.t.rissanen@jyu.fi

<sup>†</sup>Electronic Supplementary Information (ESI) available: [X-ray experimental details, powder X-ray diffraction data, CCDC 1821327–1821338].

See DOI: 10.1039/x0xx00000x

The corresponding XB distances are nearly similar due to the competition between X2- and X5-halogens forming C–X2/X5···Br–Cu XBs.



**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 ( $\text{CuCl}_2$ ) 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-X-pyridine) $_2\text{CuCl}_2$  (X = Cl and Br) and (3-X-pyridine) $_2\text{CuCl}_2$  (X = F, Cl, Br and I).<sup>7f–h</sup> In the ahead discussions, the following abbreviations 2ClPy, 2BrPy, 3ClPy and 3IPy are used for 2-chloropyridine, 2-bromopyridine, 3-chloropyridine and 3-iodopyridine, respectively. The crystallographic data for (2ClPy) $_2\text{CuCl}_2$ ,<sup>7f</sup> (2BrPy) $_2\text{CuCl}_2$ ,<sup>7g</sup> (3ClPy) $_2\text{CuCl}_2$ <sup>7h</sup> and (3BrPy) $_2\text{CuCl}_2$ <sup>7h</sup> were extracted from CSD database,<sup>10</sup> while (3IPy) $_2\text{CuCl}_2$  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  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  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) $_2\text{CuCl}_2$  coordination compounds, obtained from 2,5-dihalopyridine +  $\text{CuCl}_2$  combinations, are discussed. With 2-chloro-5-iodopyridine (**4**), two types of structures, the dimeric (**4.1**) $_4[\text{CuCl}_2]_2$  and monomeric (**4.2**) $_2\text{CuCl}_2$ , isolated as blue and green coloured crystals from the bulk sample, could be obtained. For (**4.1**) $_4[\text{CuCl}_2]_2$  and (**4.2**) $_2\text{CuCl}_2$  structures, the respective Cu(II) coordination geometries are square-pyramidal and see-saw.<sup>11</sup> 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** +  $\text{CuCl}_2$  corresponds to the dimeric species, (**4.1**) $_4[\text{CuCl}_2]_2$ , and for **5** +  $\text{CuCl}_2$  to the monomer, (**5.2**) $_2\text{CuCl}_2$  (See supporting information for more details).

All (**1**) $_4[\text{CuCl}_2]_2$ , (**2**) $_4[\text{CuCl}_2]_2$ , (**3**) $_4[\text{CuCl}_2]_2$  and (**4.1**) $_4[\text{CuCl}_2]_2$  are dimeric complexes with 4:2 ligand:metal ratio. In these complexes

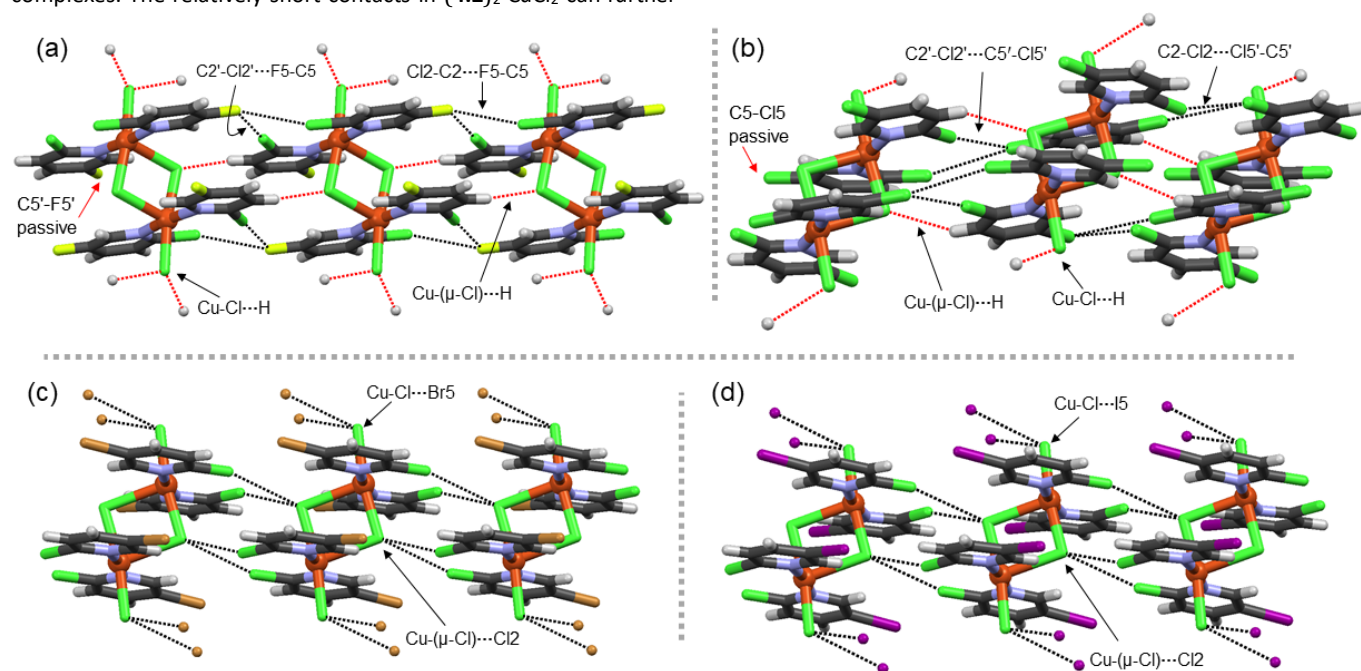
the coordination sphere of Cu(II) contains two N-atoms of the dihalopyridine and three chloride ions, of which one is Cu–Cl–Cu bridging as shown in Fig. 2a–d, and is abbreviated as Cu–( $\mu$ -Cl). The X2- and X5-substituents are in *syn*-arrangement in contrast to our previously reported square planar (2,5-dihalopyridine) $_2\text{CuBr}_2$  complexes.<sup>9</sup> In that study, the *trans*-C2–Cl2···Cu contacts of *ca.* 3.0 Å in (2-chloro-5-X-pyridine) $_2\text{CuBr}_2$  complexes were shown to be dependent on X5-substituent. This encouraged us to investigate the same contacts in (2-chloro-5-X-pyridine) $_2\text{CuCl}_2$  complexes for X5-substituent effects. The presence of Cu–( $\mu$ -Cl) in (**1**) $_4[\text{CuCl}_2]_2$ , (**2**) $_4[\text{CuCl}_2]_2$ , (**3**) $_4[\text{CuCl}_2]_2$  and (**4.1**) $_4[\text{CuCl}_2]_2$  leads to a deviation of N–Cu–N angles from linearity to adopt 172.84(14)°, 169.35(5)°, 172.34(12)° and 171.8(4)°, respectively. For this reason, the C2–Cl2···Cu distances [*ca.* >3.20 Å] are longer compared to (2-chloro-5-X-pyridine) $_2\text{CuBr}_2$  complexes.<sup>9</sup>

The centrosymmetric dimers, (**1**) $_4[\text{CuCl}_2]_2$  and (**2**) $_4[\text{CuCl}_2]_2$ , contain two crystallographically independent dihalopyridine ligands coordinated to the Cu(II) centre. In both complexes, one of the two X5-halogens does not show XBs, 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–Cl2···X5–C5 XB interactions to form 1-D polymers between X5-halogens and C2-chlorines [Fig 2a,b, Table 1]. For example, in (**1**) $_4[\text{CuCl}_2]_2$ , the bifurcated C5-fluorine forms weak C2'–Cl2'···F5–C5 and C2–Cl2···F5–C5 XB interactions at distances of  $R_{\text{XB}} = 0.97$  [3.121 Å, see Ref 12 for  $R_{\text{XB}}$  definition] and  $R_{\text{XB}} = 0.98$  [3.160 Å], respectively. The C2'–Cl2'···F5 angles [173.6°] are more linear and closer to the ideal value of XB angles compared to C2–Cl2···F5 [158.9°]. In (**2**) $_4[\text{CuCl}_2]_2$ , the C5-chlorine forms similar bifurcated XB bonds [Fig 2b] with C2'–Cl2'···Cl5'–C5' and C2–Cl2···Cl5'–C5' distances of  $R_{\text{XB}} = 0.99$  [3.480 Å] and  $R_{\text{XB}} = 0.97$  [3.393 Å]. The Cl3-substituent in (3ClPy) $_2\text{CuCl}_2$ <sup>7h</sup> is XB passive. However, in (**1**) $_4[\text{CuCl}_2]_2$  and (**2**) $_4[\text{CuCl}_2]_2$ , the presence of *para*-C2-chlorines provides F5- and Cl5-substituents an opportunity to form C2–Cl2···X5–C5 XBs. The Cu–( $\mu$ -Cl) and Cu–Cl in (**1**) $_4[\text{CuCl}_2]_2$  and (**2**) $_4[\text{CuCl}_2]_2$  are XB passive to X2- and X5-substituents. Nevertheless, short Cu–( $\mu$ -Cl)···H and Cu–Cl···H interactions can be observed in the 3-D crystal lattice as shown in Fig 2a,b.

The complexes (**3**) $_4[\text{CuCl}_2]_2$  and (**4.1**) $_4[\text{CuCl}_2]_2$  are isostructural 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  $\text{CuCl}_2$  residing on the mirror plane. Unlike (**1**) $_4[\text{CuCl}_2]_2$  and (**2**) $_4[\text{CuCl}_2]_2$ , the Cu–( $\mu$ -Cl) and Cu–Cl are bifurcated XB acceptors for either *syn*-oriented X2- or X5-substituents. Both (**3**) $_4[\text{CuCl}_2]_2$  and (**4.1**) $_4[\text{CuCl}_2]_2$  as discrete complexes form 1-D polymers through C2–Cl2···(–Cl– $\mu$ )–Cu XBs with distances of  $R_{\text{XB}} = 0.96$  [3.420 Å] and  $R_{\text{XB}} = 0.96$  [3.474 Å]. These 1-D polymers are connected *via* C5–X5···Cl–Cu (X = Br and I) contacts to a 3-D network as shown in Fig. 2c–d. The C5–Br5···Cl–Cu XBs in (**3**) $_4[\text{CuCl}_2]_2$  [ $R_{\text{XB}} = 0.95$ ] are shorter compared to (3BrPy) $_2\text{CuCl}_2$  [ $R_{\text{XB}} = 1.03$ , not XB].<sup>7h</sup> Complex (**4.2**) $_2\text{CuCl}_2$  and our previously reported (**4**) $_2\text{CuBr}_2$  are isostructural and isomorphous.<sup>9</sup> The monomeric, discrete 2:1 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**) $_4[\text{CuCl}_2]_2$ , the Cu–Cl in (**4.2**) $_2\text{CuCl}_2$  is a monodentate XB acceptor. As a result, the C5–I5···Cl–Cu distances in (**4.2**) $_2\text{CuCl}_2$  [ $R_{\text{XB}} = 0.90$ ] are shorter compared to (**4.1**) $_4[\text{CuCl}_2]_2$  [ $R_{\text{XB}} = 0.93$ ] and C3–I3···Cl–Cu XBs in (3IPy) $_2\text{CuCl}_2$  [ $R_{\text{XB}}$

= 0.92] (see Supporting information, Fig S2). The  $R_{XB}$  value of 0.90 is the smallest value observed for XBs in  $(2,5\text{-dihalopyridine})_2\text{-Cu(II)}$  complexes. The relatively short contacts in  $(\mathbf{4.2})_2\text{-CuCl}_2$  can further

be a result of Cu(II) geometry, the presence of C2-chlorine and crystal packing interactions.

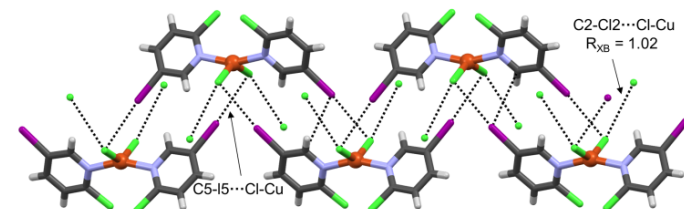


**Fig. 2.** Section of 3-D crystal packing displaying halogen bond and hydrogen bond interactions in (a)  $(\mathbf{1})_4\text{-[CuCl}_2\text{]}_2$ , (b)  $(\mathbf{2})_4\text{-[CuCl}_2\text{]}_2$ , (c)  $(\mathbf{3})_4\text{-[CuCl}_2\text{]}_2$  and (d)  $(\mathbf{4.1})_4\text{-[CuCl}_2\text{]}_2$ . Black dotted lines represent the halogen bonds, and red dotted lines represent hydrogen bonds.

**Table 1.** Solid-state X-ray crystallography bond parameters\* for complexes  $(\mathbf{1})_4\text{-[CuCl}_2\text{]}_2$  -  $(\mathbf{8})_2\text{-CuCl}_2$ .

| Complex                                     | Motif               | $d(\text{X}2\cdots\text{Cl})$ , Å | $\angle\text{C}2\text{-X}2\cdots\text{Cl}$ (°) | $R_{XB}^\dagger$         | Motif             | $d(\text{X}5\cdots\text{Cl})$ , Å | $\angle\text{C}5\text{-X}5\cdots\text{Cl}$ (°) | $R_{XB}^\dagger$         |
|---|---------------------|-----------------------------------|--|--------------------------|-------------------|-----------------------------------|--|--------------------------|
| $(\mathbf{1})_4\text{-[CuCl}_2\text{]}_2$   | C2'-Cl2'...F5-C5    | 3.121 <sup>a</sup>                | 173.6 <sup>a</sup>                             | 0.97 <sup>a</sup>        | C5-F5...Cl2-C2    | 3.160 <sup>a</sup>                | 158.9 <sup>a</sup>                             | 0.98 <sup>a</sup>        |
| $(\mathbf{2})_2\text{-[CuCl}_2\text{]}_2$   | C2'-Cl2'...Cl5'-C5' | 3.480 [3.399] <sup>b</sup>        | 174.7 [177.3] <sup>b</sup>                     | 0.99 [0.97] <sup>b</sup> | C5'-Cl5'...Cl2-C2 | 3.393 [3.734] <sup>c</sup>        | 160.1 [158.5] <sup>c</sup>                     | 0.97 [1.06] <sup>c</sup> |
| $(\mathbf{3})_2\text{-[CuCl}_2\text{]}_2$   | C2-Cl2...Cl-Cu      | 3.371                             | 161.3  | 0.96                     | C5-Br5...Cl-Cu    | 3.430 [3.675] <sup>d</sup>        | 169.2 [157.7] <sup>d</sup>                     | 0.95 [1.03] <sup>d</sup> |
| $(\mathbf{4.1})_4\text{-[CuCl}_2\text{]}_2$ | C2-Cl2...Cl-Cu      | 3.462                             | 162.3  | 0.99                     | C5-I5...Cl-Cu     | 3.474 [3.413] <sup>e</sup>        | 161.3 [170.1] <sup>e</sup>                     | 0.93 [0.92] <sup>e</sup> |
| $(\mathbf{4.2})_2\text{-CuCl}_2$            | C2-Cl2...Cl-Cu      | 3.559                             | 161.9  | 1.02                     | C5-I5...Cl-Cu     | 3.374 [3.413] <sup>e</sup>        | 172.8 [170.1] <sup>e</sup>                     | 0.90 [0.92] <sup>e</sup> |
| $(\mathbf{5.1})_4\text{-[CuCl}_2\text{]}_2$ | C2-Br2...Cl-Cu      | 3.459 [3.358] <sup>f</sup>        | 170.1 [167.9] <sup>f</sup>                     | 0.99 [0.93] <sup>f</sup> | C5-F5             | passive                           | passive  | passive                  |
| $(\mathbf{5.2})_2\text{-CuCl}_2$            | C2-Br2...Cl-Cu      | 3.459 [3.358] <sup>f</sup>        | 148.4 [167.9] <sup>f</sup>                     | 0.99 [0.93] <sup>f</sup> | C5-F5             | passive                           | passive  | passive                  |
| $(\mathbf{6})_2\text{-CuCl}_2$              | C2-Br2...Cl-Cu      | 3.352 [3.358] <sup>f</sup>        | 166.0 [167.9] <sup>f</sup>                     | 0.93 [0.93] <sup>f</sup> | C5-Cl5...Cl-Cu    | 3.426 [3.734] <sup>c</sup>        | 170.0 [158.5] <sup>c</sup>                     | 0.98 [1.06] <sup>c</sup> |
| $(\mathbf{7})_2\text{-CuCl}_2$              | C2-Br2...Cl-Cu      | 3.380 [3.358] <sup>f</sup>        | 165.1 [167.9] <sup>f</sup>                     | 0.94 [0.93] <sup>f</sup> | C5-Br5...Cl-Cu    | 3.372 [3.675] <sup>d</sup>        | 171.5 [157.7] <sup>d</sup>                     | 0.94 [1.03] <sup>d</sup> |
| $(\mathbf{8})_2\text{-CuCl}_2$              | C2-Br2...Cl-Cu      | 3.482 [3.358] <sup>f</sup>        | 165.5 [167.9] <sup>f</sup>                     | 0.97 [0.93] <sup>f</sup> | C5-I5...Cl-Cu     | 3.407 [3.413] <sup>e</sup>        | 171.5 [170.1] <sup>e</sup>                     | 0.91 [0.92] <sup>e</sup> |

\*Values in parentheses are C2- and C3-halogens based XB bond parameters in  $(n\text{-X-pyridine})_2\text{-CuCl}_2$  [ $n = 2$  and  $3$ ,  $X = \text{Cl}$ ,  $\text{Br}$  and  $\text{I}$ ] complexes; <sup>†</sup>The normalized interaction ratio,  $R_{XB}$ , is defined as  $(R_{XB} = d_{XB}/(X_{vdw} + B_{vdw}))^{12}$  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 radii determined by Bondi were used to calculate  $R_{XB}$  values.<sup>13</sup>; <sup>a</sup> Crystal structure of 3-fluoropyridine + CuCl<sub>2</sub> not available for comparison; <sup>b</sup> The values represent C2-Cl2...Cl2-C2 XBs in  $(2\text{ClPy})_2\text{-CuCl}_2$  (CCDC No. PAMLAS)<sup>7i</sup>; <sup>c</sup> No XBs observed in  $(3\text{ClPy})_2\text{-CuCl}_2$  (CCDC No. VEPKUX)<sup>7h</sup>, and the observed C3-Cl3...Cl-Cu short contacts are shown only as reference; <sup>d</sup> No XBs observed in  $(3\text{BrPy})_2\text{-CuCl}_2$  (CCDC No. VEPLAE)<sup>7h</sup> and the C3-Br3...Cl-Cu contacts are shown only as reference; <sup>e</sup> Part of current study, see SI Fig. S2 for X-ray crystal structure; <sup>f</sup> The values are for C2-Br2...Cl-Cu XBs in  $(2\text{BrPy})_2\text{-CuCl}_2$  (CCDC No. YENXOF).<sup>7g</sup>

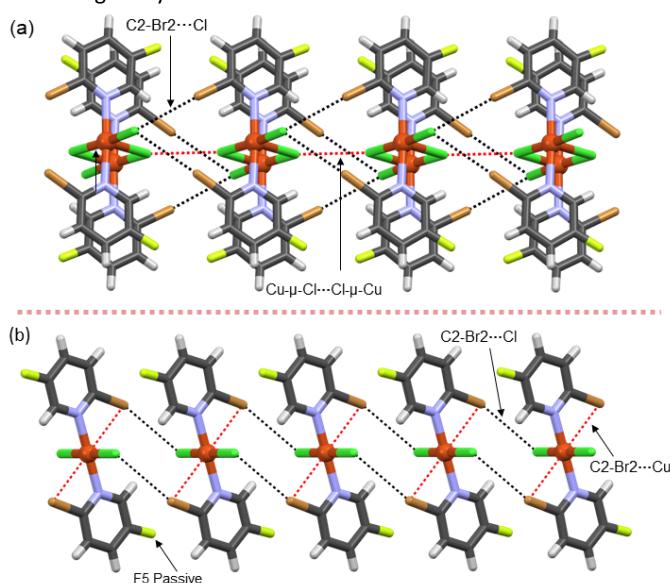


**Fig. 3.** Halogen bonded 1-D polymeric structure in  $(\mathbf{4.2})_2\text{-CuCl}_2$ . Black broken lines represent the halogen bonds.

In structures based on 2-bromo-5-X-pyridine, monomeric and dimeric complexes can be observed. Reaction of **5** with CuCl<sub>2</sub>

resulted in two types of structures, the dimeric  $(\mathbf{5.1})_4\text{-[CuCl}_2\text{]}_2$  and monomeric  $(\mathbf{5.2})_2\text{-CuCl}_2$ , isolated as green and colourless crystals, respectively, from the bulk sample. Ligands **6** - **8** form monomeric complexes of the type  $(\mathbf{6})_2\text{-CuCl}_2$ ,  $(\mathbf{7})_2\text{-CuCl}_2$  and  $(\mathbf{8})_2\text{-CuCl}_2$ . In  $(\mathbf{5.1})_4\text{-[CuCl}_2\text{]}_2$ , the X2- and X5-substituents are in *syn*-arrangement similar to  $(2\text{-chloro-5-X-pyridine})_2\text{-CuCl}_2$  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 [ $R_{XB} = 0.99$ , 3.459 Å] XBs leads to relatively short Cu-(μ-Cl) ... (Cl-μ)-Cu

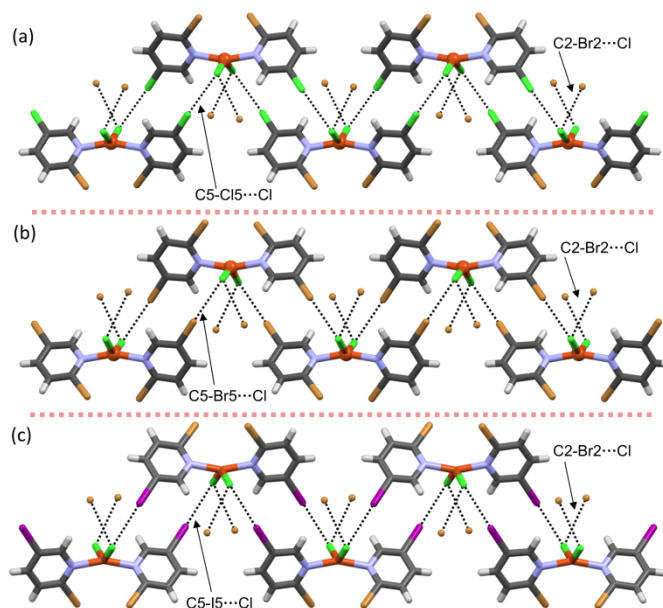
contacts [ $R_{XB} = 0.97, 3.395 \text{ \AA}$ ], as shown in Fig. 4a. In  $(\mathbf{5.2})_2 \cdot \text{CuCl}_2$ , the X2- and X5-substituents' *anti*-arrangement and the square planar coordinated Cu(II) are similar to reported (2,5-dihalopyridine) $_2$ ·CuBr $_2$  complexes.<sup>9</sup> The complex extends into a 1-D polymeric structure via C2–Br2···Cl–Cu contacts [ $R_{XB} = 0.99, 3.578 \text{ \AA}$ ], as shown in Fig. 4b. Similar to  $(\mathbf{5.1})_4 \cdot [\text{CuCl}_2]_2$ , 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  $(\mathbf{5.2})_2 \cdot \text{CuCl}_2$ , also reveals weak C2–Br2···Cu contacts at distances of *ca.* 3.13 Å which are longer compared to  $(\mathbf{5})_2 \cdot \text{CuBr}_2$  [*ca.* 3.0 Å].<sup>9</sup> The C2–Br2···Cl–Cu distances in  $(\mathbf{5.1})_4 \cdot [\text{CuCl}_2]_2$  and  $(\mathbf{5.2})_2 \cdot \text{CuCl}_2$  are longer than in  $(2\text{BrPy})_2 \cdot \text{CuCl}_2$  indicating the electron withdrawing effect is opposite to electronegativity of F5-substituent.



**Fig. 4** Section of crystal packing to display the halogen bonded 1-D polymeric structures in (a)  $(\mathbf{5.1})_4 \cdot [\text{CuCl}_2]_2$  and (b)  $(\mathbf{5.2})_2 \cdot \text{CuCl}_2$ .

Complexes  $(\mathbf{6})_2 \cdot \text{CuCl}_2$ ,  $(\mathbf{7})_2 \cdot \text{CuCl}_2$  and  $(\mathbf{8})_2 \cdot \text{CuCl}_2$  are isostructural and isomorphous [Fig. 5b–d], with Cu(II) centres in see-saw coordination geometries.<sup>11</sup> 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  $\text{F} > \text{Cl} > \text{Br} > \text{I}$ . 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  $(\mathbf{5})_2 \cdot \text{CuCl}_2$  [ $R_{XB} = 0.99$ ] are longer compared to  $(\mathbf{6})_4 \cdot [\text{CuCl}_2]_2$  [ $R_{XB} = 0.93$ ]. When X2 and X5 are bromines in  $(\mathbf{7})_2 \cdot \text{CuCl}_2$ , both C2–Br2···Cl–Cu and C5–Br5···Cl–Cu contacts are in same magnitude with  $R_{XB}$  values of 0.94. Generally it is known that iodine is a better XB donor than bromine. As a consequence, the  $R_{XB}$  values for C5–I5···Cl–Cu XBs in  $(\mathbf{8})_2 \cdot \text{CuCl}_2$  [0.91] are shorter than C2–Br2···Cl–Cu [0.97]. The C5–X5···Cl–Cu (X = Cl, Br and I) XBs in (2-bromo-5-X-pyridine) $_2$ ·CuCl $_2$  complexes are shorter compared to corresponding C3–X3···Cl–Cu XBs in (3-halopyridine) $_2$ ·CuCl $_2$ . On the other hand, in (2-bromo-5-X-pyridine) $_2$ ·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-halogens forming XBs with copper-coordinated chloride. Despite the C5–X5···Cl–Cu XBs follow the

anticipated order, *i.e.*  $\text{F5} < \text{Cl5} < \text{Br5} < \text{I5}$  for X2 = Cl and  $\text{Cl5} < \text{Br5} < \text{I5}$  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)  $(\mathbf{6})_4 \cdot [\text{CuCl}_2]_2$ , (b)  $(\mathbf{7})_2 \cdot \text{CuCl}_2$  and (c)  $(\mathbf{8})_2 \cdot \text{CuCl}_2$ .

The substitution effect of X2-/X5-halogens for donor-acceptor property can further be supported by comparing C5–X5···Cl–Cu XBs in (2,5-dihalopyridine) $_2$ ·CuCl $_2$  with C3–X3···Cl–Cu in (3-halopyridine) $_2$ ·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  $R_{XB} = 1.03$ . The C3–X3···Cl–Cu in  $(3\text{XPy})_2 \cdot \text{CuCl}_2$  (X = F and Cl) complexes have similar  $R_{XB}$  values. The bond parameters shown in Table 1 suggest that the presence of X2-substituents in 2,5-dihalopyridines triggers both X2- and X5-halogens to form XBs compared to monosubstituted ( $n\text{-X-Py}$ ) $_2$ ·CuCl $_2$  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···Cl–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  $\text{F5} < \text{Cl5} < \text{Br5} < \text{I5}$  for X2 = Cl and  $\text{Cl5} < \text{Br5} < \text{I5}$  for X2 = Br. In presence of C2-chlorine, even the less-polarisable Cl5 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.

## Acknowledgements

The authors gratefully acknowledge financial support from the Academy of Finland (RP: grant no. 298817, ML: grant no. 277250) and the University of Jyväskylä.

## References

- G. R. Desiraju, P. S. Ho, L. Kloo, A. C. Legon, R. Marquardt, P. Metrangolo, P. Politzer, G. Resnati and K. Rissanen, *Pure Appl. Chem.* 2013, **85**, 1711–1713.
- (a) L. C. Gilday, S. W. Robinson, T. A. Barendt, M. J. Langton, B. R. Mullaney, P. D. Beer, *Chem. Rev.* 2015, **115**, 7118–7195; (b) H. Wang, W. Wang, W. J. Jin, *Chem. Rev.* 2016, **116**, 5072–5104; (c) G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev.* 2016, **116**, 2478–2601.
- (a) A. M. Maharramov, K. T. Mahmudov, M. N. Kopylovich, A. J. L. Pombeiro, *Non-Covalent Interactions in the Synthesis and Design of New Compounds*, Hoboken, New Jersey: Wiley-VCH, 2016; (b) R. W. Troff, T. Mäkelä, F. Topić, F. A. Valkonen, A. K. Raatikainen, K. Rissanen, *Eur. J. Org. Chem.* 2013, **2013**, 1617–1637; (c) K. Rissanen, *CrystEngComm* 2008, **10**, 1107–1113; (d) L. Brammer, *Chem. Soc. Rev.* 2004, **33**, 476–489.
- (a) K. Riley, J. Murray, J. Fanfrlík, J. Řezáč, R. Solá, M. Concha, F. Ramos, P. Politzer, *J. Mol. Model.* 2011, **17**, 3309–3318; (b) P. Politzer, J. S. Murray, *ChemPhysChem* 2013, **14**, 278–294; (c) P. Politzer, J. S. Murray, T. Clark, *Phys. Chem. Chem. Phys.* 2013, **15**, 11178–11189; (d) P. Politzer, J. S. Murray, T. Clark, *Phys. Chem. Chem. Phys.* 2013, **15**, 11178–11189; (e) T. Clark, P. Politzer, J. S. Murray, *Wiley Interdiscip. Rev. Comput. Mol. Sci.* 2015, **5**, 169–177; (f) P. Politzer, K. E. Riley, F. A. Bulat, J. S. Murray, *Comput. Theor. Chem.* 2012, **998**, 2–8.
- (a) A. Abate, M. Brischetto, G. Cavallo, M. Lahtinen, P. Metrangolo, T. Pilati, S. Radice, G. Resnati, K. Rissanen and G. Terraneo, *Chem. Commun.* 2010, **46**, 2724–2726; (b) N. K. Beyeh, F. Pan, K. Rissanen, *Angew. Chem., Int. Ed.* 2015, **54**, 7303–7307; (c) F. Pan, N. K. Beyeh, K. Rissanen, *J. Am. Chem. Soc.* 2015, **137**, 10406–10413; (d) F. Topic, K. Rissanen, *J. Am. Chem. Soc.* 2016, **138**, 6610–6616; (e) L. Turunen, U. Warzok, R. Puttreddy, N. K. Beyeh, C. A. Schalley, K. Rissanen, *Angew. Chem. Int. Ed.* 2016, **55**, 14239–14242; (f) L. Turunen, A. Peuronen, S. Forsblom, E. Kalenius, M. Lahtinen, K. Rissanen, *Chem. Eur. J.* 2017, **23**, 11714–11718; (g) F. Topić, R. Puttreddy, J. M. Rautiainen, H. M. Tuononen, K. Rissanen, *CrystEngComm* 2017, **19**, 4960–4963; (h) L. Turunen, U. Warzok, C. A. Schalley, K. Rissanen, *Chem* 2017, **3**, 861–869; (i) L. Turunen, F. Pan, N. K. Beyeh, J. F. Trant, R. H. A. Ras and K. Rissanen, *Crystal Growth Des.* 2018, **18**, 513–520.
- R. Hernandez-Molina, A. Mederos, J. A. McCleverty and T. J. Meyer, *Comprehensive Coordination Chemistry II*, Newnes, Elsevier Pergamon, 2004.
- (a) F. Zordan, L. Brammer, P. Sherwood, *J. Am. Chem. Soc.* 2005, **127**, 5979–5989; (b) F. Zordan, L. Brammer, *Cryst. Growth Des.* 2006, **6**, 1374–1379; (c) F. Zordan, S. L. Purver, H. Adams, L. Brammer, *CrystEngComm* 2005, **7**, 350–354; (d) L. Brammer, G. Minguez Espallargas, H. Adams, *CrystEngComm* 2003, **5**, 343–345; (e) G. Minguez Espallargas, L. Brammer, P. Sherwood, *Angew. Chem. Int. Ed.* 2006, **45**, 435–440; (f) F. F. Awwadi, R. D. Willett, B. Twamley, *Cryst. Growth Des.* 2011, **11**, 5316–5323; (g) F. F. Awwadi, R. D. Willett, S. F. Haddad, B. Twamley, *Cryst. Growth Des.* 2006, **6**, 1833–1838; (h) G. Minguez Espallargas, L. Brammer, J. van de Streek, K. Shankland, A. J. Florence and H. Adams, *J. Am. Chem. Soc.*, 2006, **128**, 9584–9585; (i) F. F. Awwadi, R. D. Willett, B. Twamley, M. M. Turnbull, C. P. Landee, *Cryst. Growth Des.* 2015, **15**, 3746–3754; (j) F. F. Awwadi, S. F. Haddad, M. M. Turnbull, C. P. Landee, R. D. Willett, *CrystEngComm* 2013, **15**, 3111–3118; (k) F. F. Awwadi, R. D. Willett, K. A. Peterson, B. Twamley, *Chem. Eur. J.* 2006, **12**, 8952–896.
- (a) M. T. Johnson, Z. Džolić, M. Cetina, O. F. Wendt, L. Öhrström, K. Rissanen, *Cryst. Growth Des.* 2012, **12**, 362–368; (b) B. N. Ghosh, M. Lahtinen, E. Kalenius, P. Mal, K. Rissanen, *Cryst. Growth Des.* 2016, **16**, 2527–2534.
- R. Puttreddy, C. von Essen, K. Rissanen, *Eur. J. Inorg. Chem.* 2018 submitted
- (a) The Cambridge Structural database 2018 [updated December 2017], ConQuest version 1.19; (b) I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson, R. Taylor, *Acta Crystallogr. Sect. B* 2002, **58**, 389–397.
- L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* 2007, 955–964
- R. Puttreddy, O. Jurček, S. Bhowmik, T. Mäkelä, K. Rissanen, *Chem. Commun.* 2016, **52**, 2338–2341.
- A. Bondi, *J. Phys. Chem.* 1964, **68**, 441–451