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Accepted version (Final draft)

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Puttreddy, R., von Essen, C., & Rissanen, K. (2018). Halogen Bonds in Square Planar 2,5-Dihalopyridine-Copper(II) Bromide Complexes. European Journal of Inorganic Chemistry, 2018 (20-21), 2393-2398. doi:10.1002/ejic.201800144
Title: Halogen Bonds in Square Planar 2,5-Dihalopyridine-Copper(II) Bromide Complexes

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To be cited as: Eur. J. Inorg. Chem. 10.1002/ejic.201800144

Link to VoR: http://dx.doi.org/10.1002/ejic.201800144
Halogen Bonds in Square Planar 2,5-Dihalopyridine-Copper(II) Bromide Complexes

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Dedication (optional)

Abstract: Halogen bonding in self-complementary 1:2 metal-ligand complexes obtained from copper(II) bromide (CuBr₂) and seven 2,5-dihalopyridines are analyzed using single-crystal X-ray diffraction. All presented discrete complexes form 1-D polymeric chains connected with C-X···Br-Cu halogen bonds (XB). In (2-chloro-5-X-pyridine):CuBr₂ (X = Cl, Br and I), only the C5-halogen, and in (2-bromo-5-X-pyridine):CuBr₂ (X = Cl, Br and I) both, C2- and C5-halogen, form C-X···Br-Cu halogen bonds with the X acting as the XB donor and copper-coordinated bromide as the XB acceptor. The electron withdrawing C2-chloride in 2-chloro-5-X-pyridine-CuBr₂ complexes has only a minor effect on the C5-X5···Br-Cu XB, and the X5···Br distances follow expected order, I5 < Br5 < Cl5 in the Rₓ values of 0.91, 0.94 and 0.99, respectively. In 2-bromo-5-X-pyridine-CuBr₂ complexes, due to the polarization of both halogens, the C2–X2···Br–Cu and C5–X5···Br–Cu the Rₓ values are very similar [0.92–0.99] due to competition of C2- and C5-halogen for XB formation. In addition to the classical halogen bonds the square planar Cu(II) complexes exhibit C2–X2···Cu (X = Cl and Br) contacts perpendicular to the Br–Cu–Br plane with shorter C2–Cu···Cu than C2–C2···Cu contacts. These interactions induce a pseudo-octahedral geometry for Cu(II) ions. Notably, C2–X2···Br–Cu halogen bonds and the additional C2–X2···Cu contacts are slightly enhanced by the C5-halogen electronegativity.

Introduction

The importance of hydrogen bonds[11] (HB) in organic, organometallic and inorganic compounds has led to significant interest to other non-covalent interactions, most recently to the utilization of halogen bonding. The halogen bonds (XB)[2,3] are predominantly studied in organic molecules and in the solid-state, as strong, specific and highly directional non-covalent interactions equivalent to HBs resulting in a rapidly developing area within supramolecular chemistry.[4] Over the past decade, C–X···A···C[5] (C = carbon, X = halogen as XB donor, A = XB acceptor, often halide anion), halogen bonding interactions have been of growing interest as valuable crystal engineering tool.[6] The halogen bond has recently been defined[7] by IUPAC and has recently been extensively studied[8,9] also for complex halide anions[10] using solid-state X-ray crystallography and computational methods.[11,12] In transition metal complexes, the importance and the role of two descriptors are well studied, viz., (a) primary coordination sphere or metal-ligand interactions, and (b) secondary coordination sphere or non-covalent interactions.[13] Structure and reactivity of metal complexes depend on metal-ligand interactions, while most chemical and physical properties are influenced by non-covalent interactions, e.g., HB and XB. In the solid-state X-ray crystal structures, the functional groups attached to the ligands in the coordination complexes gives rise to rich chemical environments allowing for variety of intra- and intermolecular non-covalent interactions from the substituents. To investigate XBs in metal complexes, halopyridines coordinated to metal ions makes it possible to study both C–X···A···C and C–X···A···M (X = halogen substituent, M = metal ion, A = XB acceptor) interactions. A few research groups, mainly, Brammer et al.[14] have crystallographically studied complexes of the type M(LX)₂A [LX = 2-, 3- and 4-halopyridines, M = metal and A = metal bound halide], where A acts as XB acceptor and X as XB donor. Furthermore, Brammer et al. explored the cooperative and competitive nature of HBs and XB of [LH]⁺ species as acceptors to tetrahedral MA₄ anions.[15] To complement this, we have previously studied neutral pincer type viz., (2,6-bis[(di-t-butyolphosphino)-methyl]phenyl)PdY (Y = Cl, Br and I) and (terpyridine)M₆P₄ complexes where the metal bound halogen acts as the XB acceptor.[16]

![Figure 1. Representation of 2,5-dihalopyridine core numbering, and chemical structures of 2,5-dichloropyridine (1), 5-bromo-2-chloropyridine (2), 2-chloro-5-iodopyridine (3), 2-bromo-5-fluoropyridine (4), 2-bromo-5-chloropyridine (5), 2,5-dibromopyridine (6) and 2-bromo-5-iodopyridine (7).](source)

In the present study, we analyze the halogen bonds in coordination complexes formed from 2,5-dihalopyridines and copper(II) bromide (CuBr₂). We utilize a series of seven 2,5-dihalopyridines, three based on 2-chloropyridine (1–3) and four based on 2-bromopyridine (5–7), with a different halogen substituent at the 5-position of the pyridine ring [X5, Fig. 1]. We anticipated that, upon complexation with CuBr₂, the X5

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The complexes were synthesized by mixing a 2:1 molar ratio of 2,5-dihalo.pyridine and CuBr in acetonitrile at room temperature. If necessary, the reaction mixtures were sonicated to dissolve all the components. Slow evaporation of the resulting solution provides single crystals suitable for X-ray crystallography (See Experimental Section for more details). Attempts to obtain crystals with 2-chloro-5-fluoropyridine were unsuccessful. In all complexes, the Cu(II) ion binds to two 2,5-dihalo.pyridine ligands and has centrosymmetric N2Br coordination sphere. In complexes (1):CuCl2 and (2):CuBr2, Cu(II) is square planar, while (3):CuBr2 has see-saw geometry with an θ value of 0.47°. In contrast to the reported square planar structure, (2-CF3Py):CuBr2 (CCDC code PAMLEW),[11a] the C2-chlorides in (1):CuCl2 and (2):CuBr2 are in anti-arrangement. However, the anti-arrangement of X5 substituent in (1):CuBr2 and (2):CuBr2 is similar to 2-CF3Py:CuBr2 (CCDC code PAMLEW) and (3):BrPy:CuBr2 (CCDC code YENXUL).[11b] The small energy difference between syn- and anti-arrangements of the C2 substituents are reported,[11a] the C2-C2···Cu contacts, particularly in anti-positions play a crucial role to stabilize square planar rather than distorted four coordinate Cu(II) geometries. The trans-C2-C2···Cu contacts of 3.0 Å around Cu(II) ion in (1):CuBr2 and (2):CuBr2 are remarkably short, ca. 3.04 Å, while the distance of ca. 3.12 Å around see-saw geometry Cu(II) ion in (3):CuBr2 is similar to reported (2CF3Py):CuBr2.[11a]

### Results and Discussion

Complexes (1):CuBr2 and (2):CuBr2 are isomorphous and isostructural, and (3):CuBr2 is remarkably different in both crystallographic cell parameters as well as from structural perspective. The discrete metal complexes are extended to 1-D polymers via C5—X5···Br—X (X = Cl, Br and I) halogen bonds, as shown in Fig. 3 and Table 1. The C2-chlorides in (1):CuCl2 and (2):CuBr2 are not showing halogen bonding. The C5—C35···Br—C5 and C5—Br5···Br—C5 halogen bonds in (1):CuBr2 [R(x) = 0.99] and (2):CuBr2 [R(x) = 0.94] are stronger when compared to C3—X3···Br—Cu distances observed in (3):CF3Py:CuBr2 [R(x) = 1.02] and (3):BrPy:CuBr2 [R(x) = 0.98], respectively. This suggests that the electron withdrawing Cl2-substituent para to X5 increase the electrophilic character of X5 resulting in shorter C5—X5···Br—Cu contacts. Despite the CIE being XB passive in (1):CuBr2 and (2):CuBr2, the 1-D chains are connected via weak C2—C2···H—C3 HB interactions to form a 3-D crystal lattice [See ESI, Fig. S1a].

### Table 1: Solid-state X-ray crystallography bond parameters* for complexes (1):CuBr2 - (7):CuBr2.

| Complex | d(X2···X) | d(C2—X) | θ | d(X5···X) | θ |
|---------|-----------|---------|---|-----------|---|
| (1):CuBr2 | Cu—Br 1 | C—Br 2 | C—Br 3 | C—Br 4 | C—Br 5 |
| (2):CuBr2 | C—Br 1 | C—Br 2 | C—Br 3 | C—Br 4 | C—Br 5 |
| (3):CuBr2 | C—Br 1 | C—Br 2 | C—Br 3 | C—Br 4 | C—Br 5 |

*The values in parentheses are C2 and C3-halogen based XB bond parameters in mono-substituted halopyridine-CuBr complexes extracted from CSD database. The normalized interaction ratio, R(x), is defined as (R(x) = d(x)/d(x)Ref), where d(x)Ref is the distance between the donor atom (X) and the acceptor atoms (Br) and divided by the sum of vdw radii [Å] of X and Br. The van der Waals radii determined by Bondi were used to calculate R(x) values. The values are only for reference purpose and no C2—C2···H—C3 HBs were observed. Part of current study, see supporting information Fig S1b for X-ray crystal structure. For comparison, crystal structure not available for (3-fluoropyridine):CuBr2.

Figure 2. X-ray crystal structure of (a) (1):CuBr2, (b) (2):CuBr2, (c) and (3):CuBr2 with the previously reported[11a] structure of (d) (2CF3Py):CuBr2. The electrostatic potential surfaces of X5 in free ligands (e) for 1 (Cl), (f) for 2 (Br) and (g) for 3 (I).
In (3)·CuBr₂, the distorted Cu(II) geometry and the relative syn-positions of bromides bound to Cu(II) ion and 5 of 3 favour 1-D polymeric zig-zag structure [Fig. 3c] through C5–I5·Br–Cu halogen bonds [R = 0.91]. A closer inspection of crystal packing in (3)·CuBr₂, reveals also weak C2–C2···Br–Cu contacts between adjacent 1-D chains [See ESI, Fig. S1b]. Thus, the order of XB strength increases in the order: (1)·CuBr₂ < (2)·CuBr₂ < (3)·CuBr₂ according to the electrophilic character of the halogens[6b] i.e., Cl5<Br5<15 [Fig. 2e-g].

The 2BrPy in the previously published (2-BrPy): CuCl₂ complex can be regarded as chelating rather than mono-dentate ligand, and Cu(II) ion as octahedral rather than square planar.[16] The report[16] reasoned that, the unusually short C2–Br2–Cu distance between the ortho-bromide and square planar Cu(II) ion results in a pseudo-octahedral N₃Cl₂Br₂ coordination sphere. In fact, the role of C2–X···Cu type interactions were overlooked in solid-state chemistry, although they are important to stabilize both metals and coordination polymers. The X-ray crystal structures of (4)·CuBr₂, (5)·CuBr₂, (6)·CuBr₂ and (7)·CuBr₂ all contain square planar Cu(II) ions, and exhibit C2–Br2–Cu interactions as shown in Fig. 4. The increase in size of the X2, Cl to Br, increases the possibility to X2···Cu interactions, and makes it a significant synthet of interest. Such systems have been studied using computational methods and X-ray crystal structures by Awwadi et al.[17] The electrostatic negative potential around X2 interacts with the electrophile i.e., Cu(II) ion. Halogens F, Cl, Br and I positioned para to the Br2 have an influence to the C2–Br2–Cu interaction, as shown in Fig. 4. Our results show that the higher the electronegativity of the X5 is, the shorter the shorter the C2–Br2–Cu interaction distances. The C2–Br2–Cu contacts of 3.074 Å in (4)·CuBr₂ is similar to distances observed in (2BrPy):CuBr₂ [3.071 Å].[16]

**Figure 3.** Section of crystal packing to display the 1-D halogen bonded polymeric structures in (a) 1·CuBr₂, (b) 2·CuBr₂ and (c) 3·CuBr₂. The halogen bonds are shown in black dotted lines.

**Figure 4.** X-ray Crystal structures of (a) 4·CuBr₂, (b) 5·CuBr₂, (c) 6·CuBr₂ and (d) 7·CuBr₂, to display pseudo-octahedral Cu(II) ion with N₃Br₂ coordination sphere. The electrostatic potential surfaces of the X5 of the free ligands are shown in (e) for 4, (f) for 5 (Cl), (g) for 6 (Br) and (h) for 7 (I).

Complexes (4)·CuBr₂, (5)·CuBr₂ and (6)·CuBr₂ crystallize in the triclinic space group P-1, are isomorphous and isostructural, while (7)·CuBr₂ crystallizes in monoclinic space group P2₁/n and packs with a herringbone pattern. The structure of (6)·CuBr₂ is similar to previously reported (CCDC code XIBSAE).[17] The formation of 1-D polymers in (4)·(5)/6(7)·CuBr₂ is due to interactions between the Br2 and Br–Cu instead of X5 as observed in (1)·(2)/3·CuBr₂ structures. The C2–Br2–Br–Cu XBs in (4)/(5)/6(7)·CuBr₂ have R = 0.94, 0.96, 0.96 and 0.95, respectively. The C5–X5·Br–Cu (X = Cl, Br and I) halogen bonded 1-D polymers in (5)/(6)/(7)·CuBr₂ are interconnected with secondary weak XBs between the Br2 and the adjacent polymer Br–Cu, extending the polymers into 2-D network as shown in Fig. 5a-c. The X5···Br halogen bond distances with R = 3.09, 0.95 and 0.92 are longer than the corresponding values observed in (1)/(2)/(3)·CuBr₂ complexes. The C5–F5·Br–Cu distances in (4)/(5)/(6)/(7)·CuBr₂ are above the sum of the vdW radii [3.32 Å] and cannot be regarded as halogen bonds. However, their relative positioning in the crystal lattice is caused due to favourable electrostatic interactions. To rationalize C–X···Br–Cu contacts, X-ray crystal structure coordinates of 1:2 metal-ligand complexes were used to calculate electrostatic potential surfaces for the X2- and X5 substituents [see ESI].[18] The X2 and X5 substituents, notably chlorides, in modelled free ligands [Fig. 2 and 4] show more pronounced positive potential compared to Cu(II) complexes [see ESI, Fig. S3-S9].

Non-covalent electrostatic interactions can either be strong or act at long range, and are overlooked due to difficulty in visualizing clear surface potentials. The isoostructural packing in (4)·CuBr₂, (5)·CuBr₂ and (6)·CuBr₂ can be used to view ligand alignments for short and long range contacts. In (4)·CuBr₂, the formally negatively charged bromide of Cu–Br and aromatic C5-carbon of C5-F5 exhibit Cu–Br···C–(n) contacts with R = 0.98 [3.485 Å]. The halogen···C(n) interaction in (4)·CuBr₂, and similarly short contacts observed in other...
structures were analysed using Hirshfeld surfaces. The red-hot spots as an indication of short contacts between halogens and carbons were depicted in Fig. S10. The C2–X2···Br–Cu and C5–X5···Br–Cu XB distances are dependent on electronegativity of X2 and X5 substituents. For example, the more electronegative CI2 in (1)·CuBr2 and (3)·CuBr2 causes shortening of C5–X5···Br–Cu distances by electron-withdrawing effect. Similar behaviour can be observed in (4)·CuBr2, i.e., the more electronegative F5 shortens C2–X2···Br–Cu contacts. The C2–X2···Br–Cu and C5–X5···Br–Cu XB distances in (5)·CuBr2, (6)·CuBr2 and (7)·CuBr2 are similar, due to relatively similar electronegativity of X2 and X5 substituents and simultaneous competition for halogen bonds. This further explains the longer C2–Br2···Br–Cu distances in (5)·CuBr2 [<Rab = 0.96] compared to (2-BrPy)·CuBr2 [<Rab = 0.94] despite the more electronegative Cl2. In contrast, the more electronegative Cl2 has a significant influence on C5–Br5···Br–Cu XB distances in (4)·CuBr2.

Conclusions

The modulation of the C–X···Br–Cu halogen bonds and C–X···Cu interactions using a series of 2,5-dihalopyridine–copper(II) bromide complexes. Compared to previously published mono-substituted halopyridines, the di-substituted halopyridines have been proven to act as better synths for understanding the electronic donor-acceptor properties in solid-state. The discrete 1:2 metal-ligand complexes form 1-D polymer chains through halogen bonds between the halogen X2 or X5 substituent (donor) and copper-bound bromide anion (acceptor). In (2-chloro-5-halopyridine)·CuBr2 complexes, only X5 forms halogen bonds. However, in (2-bromo-5-halopyridine)·CuBr2 both X2 and X5 substituents form C–X···Br–Cu halogen bonds. The more electronegative F5 in (2-bromo-5-fluoropyridine)·CuBr2 is XB passive but polarizes the Br2 to form Br2···Br–Cu halogen bonds. The C5–X5···Br–Cu halogen bond angles for the (2,5-dihalopyridine)·CuBr2 complexes are closer to 180° when compared to the previously reported C3–X3···Br–Cu in [3-halopyridine]·CuBr2 complexes. The C2–X2···Br–Cu and C5–X5···Br–Cu halogen bonds are of similar strength in (2-bromo-5-halopyridine)·CuBr2 complexes due to competition of both X2 and X5 for halogen bonds. All complexes exhibit pseudo-octahedral C2–X···Cu contacts, with stronger interactions for bromide than for chloride.

Experimental Section

General information: All solvents used for crystal growth were reagent grade and are used as received without further purification. The ligands, 2,5-dichloropyridine (1), 5-bromo-2-chloropyridine (2), 2-chloro-5-iodopyridine (3), 2-bromo-5-fluoropyridine (4), 2-bromo-5-chloropyridine (5), 2,5-dibromopyridine (6), 2-bromo-5-iodopyridine (7) and 3-iodopyridine (3IPy) were purchased from TCI Chemicals Europe, and copper(II) bromide from Sigma Aldrich. Infrared spectra were recorded using Bruker Tensor 27 FTIR spectrometer in attenuated total reflection (ATR) mode. See Supporting Information Figs. S11 – S18 for IR spectra.
General crystallization procedure: To a solution of CuBr₂ (0.067 mmol) in acetonitrile (1.0 ml), was added respective 2,5-dihalopyridine (0.134 mmol) dissolved in acetonitrile (0.5 ml) at room temperature. In case of precipitation, the samples were sonicated to clear solutions. The solutions were left in dark at room temperature, and subjected to slow evaporation to give single crystals suitable for X-ray diffraction analysis.

Crystal structure determination: The X-ray single crystal data and experimental details for data collections are given in Supporting Information Table S1 and S2. Single-crystal X-ray data for (1): CuBr₂, (2): CuBr₂, (3): CuBr₂, (4): CuBr₂, (5): CuBr₂, (6): CuBr₂ and (7): CuBr₂ were measured on a Bruker-Nonius Kappa CCD diffractometer equipped with an Apex-II CCD detector using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation. The data for (3)P₂Y₄:CuBr₂ was measured at 120.0 K using a Rigaku SuperNova dual-source X-ray diffractometer equipped with an Atlas detector using mirror-monochromated Cu-Kα (λ = 1.5418 Å) radiation. The data collection and reduction for (3)P₂Y₄:CuBr₂ were performed using the program CrysAlisPro.²² For the data obtained from Bruker Nonius Kappa diffractometer were performed using the program COLLECT²¹ and HKL DENZO AND SCALEPACK.²² The gaussian face index absorption correction method²² was used for (3)P₂Y₄:CuBr₂. The intensities for data collected using Bruker Nonius Kappa diffractometer were corrected for absorption using SADAB²³ with multi-scan absorption correction type method. All structures were solved with direct methods (SHELXS²⁴ and refined by full-matrix least squares on F² using the OLEX2 software²⁵, which utilizes the SHELXL-2013 module.²⁶

Acknowledgements

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

Keywords: halogen bond • halopyridine • copper(II) complexes • X-ray crystallography • intermolecular interactions

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Table of contents text: 2,5-Dihalopyridine-copper(II) bromide complexes were investigated aiming to understand the mutual polarization of X2 on X5 and vice versa, and their effect on C–X2/X5···Br–Cu halogen bond distances in solid-state X-ray crystal structures. In this approach, the change in C–X2/X5···Br–Cu halogen bond distances due to X2/X5-substituent effects are evaluated by comparing with C–X2/X3···Br–Cu halogen bonds in (2-X-pyridine)₂CuBr₂ (X = Cl and Br) and (3-X-pyridine)₂CuBr₂ (X = Cl, Br and I) complexes, respectively. Our results reveal, in (2-chloro-5-X-pyridine)₂CuBr₂ (X = Cl, Br and I), only the X5, and in (2-bromo-5-X-pyridine)₂CuBr₂ (X = Cl, Br and I) both, X2- and X5, form C–X···Br–Cu halogen bonds. Several other interesting results such as predominant square planar Cu(II) centers and unique C–X···Cu interactions are reported as a part of our structure-property study that utilizes C–X···Br–Cu halogen bonds.