Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Influence of Cl/Br substitution on the stereochemical peculiarities of copper(I) π-complexes with the 1-allyl-2-aminopyridinium cation

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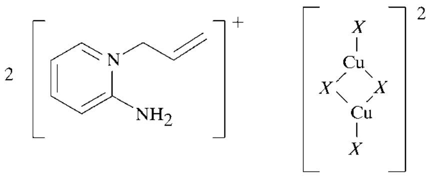
Received 18 August 2003
Accepted 2 October 2003
Online 22 October 2003

By using alternating-current electrochemical synthesis, crystals of the Cu$^{\rm I}$ π-complexes bis(1-allyl-2-aminopyridinium) di-μ-chloro-bis[chlorocopper(I)], $(C_8H_{11}N_2)_2[Cu_2Cl_4]$ or $[H_2NC_5H_4NC_3H_5][CuCl_2]$, and bis(1-allyl-2-aminopyridinium) di-μ-(chloro/bromo)-bis[(chloro/bromo)copper(I)], $(C_8H_{11}N_2)_2[Cu_2Br_{2.2}Cl_{1.8}]$ or $[H_2NC_5H_4NC_3H_5][CuBr_{1.10}Cl_{0.90}]$, have been obtained and structurally investigated. In each of the isostructural (isomorphous) compounds, the distorted tetrahedral Cu environment involves three halide atoms and the C=C bond of the ligand. Both compounds reside on inversion centres, and the dimeric $[Cu_2X_4{\cdot}2H_2NC_5H_4NC_3H_5]$ units are bonded into a three-dimensional structure by N—H$\cdots$*X* hydrogen bonds. The Br content in the terminal *X*1 position is much higher than that in the bridged *X*2 site.

Comment

Few investigations of Cu π-complexes with heterocyclic ligands have been reported; for example, only a few publications refer to Cu$^{\rm I}$ π-complexes with pyridine derivatives (*e.g.* Munakata *et al.*, 1987). Potential biological activity (Ghiladi *et al.*, 2001; Rhames *et al.*, 2001) in such compounds has led us to focus our scientific interests on structural investigations of Cu$^{\rm I}$ π-complexes with the allyl derivatives of heterocycles. The Cu$^{\rm I}$ halide π-complexes with the 1-allyl-4-aminopyridinium cation (Goreshnik *et al.*, 2003) have shown some interesting peculiarities in their stereochemistry, such as non-isomorphic chlorine/bromine replacement and the noticeable influence of Cl/Br substitution on the π interaction. This result has prompted our structural investigations of Cl– and Cl/Br–Cu$^{\rm I}$ π-complexes with the 1-allyl-2-aminopyridinium cation, *viz.* the title complexes, (I) and (II).

In the crystal structures of (I) and (II), the Cu and Cl atoms form centrosymmetric Cu_2X_4 dimers (Fig. 1). Similar inorganic fragments have been found in Cl– and Cl/Br–Cu$^{\rm I}$ π-complexes with the *N*-allylbenzothiazolium cation (Goreshnik & Mys'kiv, 1999). The distorted tetrahedral Cu-atom geometry includes a terminal halide atom (*X*1) and a pair of symmetrically generated bridging *X*2 atoms. The fourth site is occupied by the C=C bond of the allyl-containing cation. In (I), the distance from the Cu atom to the terminal Cl atom (Cl1) is the shortest Cu—Cl distance, whereas the distances to bridging atoms Cl2 and Cl2′ are longer and noticeably different from one another (Table 1). In (II), the short Cu—*X*1 distance is elongated compared with that in (I) (Table 3); this behaviour is consistent with a partial replacement of Cl atoms by Br atoms. The Cu–bridging halide distance in (II) is only slightly longer than that in (I).



(I) X = Cl
(II) X = Cl/Br

The C—Cu—C angle provides a suitable parameter for measuring the Cu–olefin interaction, being dependent on both the C=C bond elongation and the Cu—(C=C) distance contraction. The Cu—(C=C) bond consists of the (Cu$^{\rm I}$—*L*)σ donor–acceptor component, formed as a result of the overlapping of the occupied olefin π orbital and the unoccupied $4s^0$ orbital of the Cu$^{\rm I}$ atom, and the (Cu$^{\rm I}$—*L*)π dative component, based on electron-density draw-off from the $3d^{10}$ Cu$^{\rm I}$ orbitals to the unoccupied antibonding orbital of the C=C group (*L* is a C=C group). The σ component is less sensitive to the olefin bond orientation and causes a shortening of the Cu$\cdots$*Cg* (*Cg* is the centroid of the C=C bond) distance, whereas the π-dative component, being strongly dependent on a proper olefin group orientation in the metal coordination sphere, causes a lengthening of the C=C bond. Therefore, both components effect an increase of the C—Cu—C angle. Thus, a shortening of the Cu$\cdots$*Cg* distance and a lengthening of the C=C distance, together with an increase of the C—Cu—C angle, are useful data for an estimation of the effectiveness of the Cu—(C=C) interaction. An effective Cu—(C=C) interaction leads, in turn, to transformation of the Cu-atom coordination polyhedron from tetrahedral to trigonal pyramidal, with the olefin group located in the basal plane and a lengthening of the M—$L_{\rm axial}$ distance.

In (I), the Cu$\cdots$*Cg* distance [1.968 (1) Å], C=C distance [1.357 (5) Å] and C—Cu—C angle [38.1 (1)°] indicate an efficient Cu$^{\rm I}$—(C=C) bonding. On the other hand, the distorted tetrahedral shape of the Cu environment shows that the (Cu$^{\rm I}$—*L*)π dative component of the metal–olefin interaction is strongly suppressed, which could be explained by the presence of three halide atoms in the Cu coordination sphere. It is well known that a high bromine content in a Cu$^{\rm I}$

DOI: 10.1107/S0108270103021978

arrangement suppresses the π interaction, as observed in (II). The Cu$\cdots$*Cg* distance is slightly elongated compared with that in (I) [1.980 (4) Å]; this fact, together with the smaller C—Cu—C angle [37.4 (2)°] and the length of the C=C bond [1.341 (6) Å] in (II), confirms a marked suppression of the metal–olefin interaction in (II).

In the terminal *X*1 site, the Br content [0.793 (5)] is much greater than that in the bridging *X*2 site [0.308 (5)]. Possibly, the bridging function of the *X*2 atom and, consequently, its bonding with two Cu atoms causes the Cl content of the *X*2 site to be higher than that of the *X*1 site. As in the structure of $C_{10}H_{10}NS^+\cdot[CuCl_{1.08}Br_{0.92}]^-\cdot H_2O$ (Goreshnik & Mys'kiv, 1999), the Br content is much higher for a terminal halide position than for a bridging one [0.654 (7) and 0.429 (7), respectively]. Isolated $[Cu_2X_4\cdot 2H_2NC_5H_4NC_3H_5]$ units are joined into a three-dimensional structure *via* strong N—H$\cdots$*X* hydrogen bonds [2.47 and 2.50 Å in (I), and 2.52–2.64 Å in (II); Tables 2 and 4]. The pyridine rings are oriented in the (101) plane, and the shortest ring–ring distance [3.67 (1) Å] corresponds to stacking of the aromatic fragments.

Recently, we proposed (Goreshnik *et al.*, 2003) that the shortest Cl$\cdots$Cl distances (3.6 Å) could be a cause of non-isomorphic Cl/Br replacement. Contrary to this proposal and despite the rather high Br content of (II), compounds (I) and (II) are isomorphous. The shortest Cl$\cdots$Cl distance in (I) is 3.559 (1) Å and the shortest distance in (II) is only slightly longer [3.655 (6) Å]. Comparisons of (I) and (II) with $C_{10}H_{10}NS^+\cdot[CuCl_2]^-\cdot H_2O$ and $C_{10}H_{10}NS^+\cdot[CuCl_{1.08}Br_{0.92}]^-\cdot H_2O$ reveals that only these pairs demonstrate an isomorphic chlorine/bromine replacement up to a high bromine content. In our opinion, the cationic status of the ligand and the formation of strong hydrogen bonds [O—H$\cdots$*X* for *N*-allylbenzothiazolium complexes, and N—H$\cdots$*X* for (I) and (II)] stabilize the 3Cl + C=C copper environment. In turn, such an environment adapts easily to the atomic size of bromine and allows the possibility of Cl/Br isomorphic replacement.

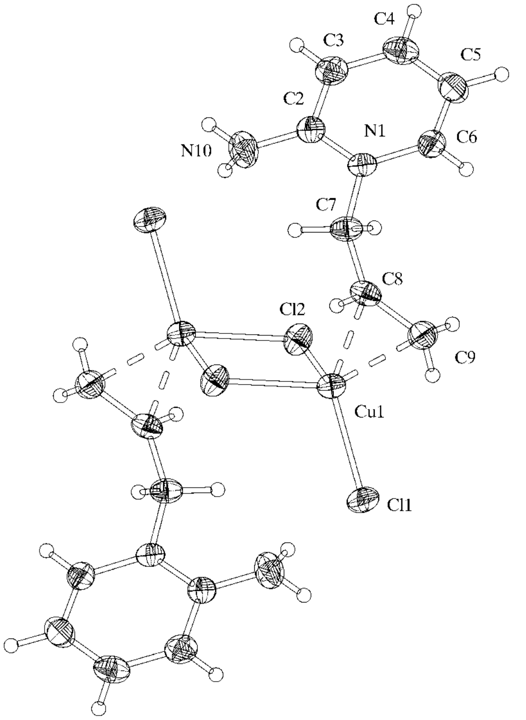


Figure 1
A view of (I), with the atom-labelling scheme. Displacement ellipsoids are shown at the 50% probability level. Compound (II) is isomorphous with (I).

The presence in inorganic–organic hybrid compounds of low-charged small organic cationic components promotes large inorganic fragment formation (Weitkamp & Puppe, 1999). However, in (I) and (II), and in the previously reported Cu^I π-complexes with the 1-allyl-4-aminopyridinium cation, only $[CuX_2]^-$ or $[Cu_2X_4]^{2-}$ inorganic anions are formed. The N—H$\cdots$*X* hydrogen bonds play an important role in such behaviour. Being strongly bonded to halide atoms, the H atoms compete with metal atoms for a place in a halide geometrical arrangement, preclude any bridging function of the halide atoms and, therefore, promote the formation of small inorganic fragments.

Experimental

1-Allyl-2-aminopyridinium chloride and 1-allyl-2-aminopyridinium bromide were obtained from 2-aminopyridine and allyl chloride or bromide, respectively, in $CHCl_3$ solution. All reagents were purchased commercially and used as received. Good quality crystals of (I) and (II) were obtained using the alternating-current electrochemical technique (Mykhalichko & Mys'kiv, 1989), starting from copper(II) chloride dihydrate and 1-allyl-2-aminopyridinium chloride or bromide, respectively. To an ethanol solution (2 ml) of $CuCl_2\cdot 2H_2O$ (1 mmol) was added an ethanol solution (2 ml) of 1-allyl-2-aminopyridinium chloride or 1-allyl-2-aminopyridinium bromide (1.2 mmol). The resulting solution was placed in a small test tube and Cu-wire electrodes in cork were inserted. After the application of a 0.30 V alternating current (frequency 50 Hz) for several days, colourless crystals of (I) and (II) appeared on the Cu electrodes. The density, measured by flotation in a $CHCl_3$/$CHBr_3$ mixture, was found to be 1.8 Mg m^{-3} for (I) and 2.0 Mg m^{-3} for (II).

Compound (I)

Crystal data

$(C_8H_{11}N_2)_2[Cu_2Cl_4]$
$M_r = 539.26$
Triclinic, $P\overline{1}$
$a = 6.8439 (6)$ Å
$b = 8.5266 (9)$ Å
$c = 9.4154 (8)$ Å
$\alpha = 78.634 (8)°$
$\beta = 74.531 (7)°$
$\gamma = 73.960 (9)°$
$V = 504.38 (9)$ Å^3
$Z = 1$
$D_x = 1.775$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 65–73°$
$\mu = 7.54$ mm^{-1}
$T = 193 (2)$ K
Block, colourless
0.78 × 0.18 × 0.16 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\omega$ scans
Absorption correction: numerical (de Meulenaer & Tompa, 1965)
$T_{min} = 0.090$, $T_{max} = 0.422$
2237 measured reflections
2056 independent reflections
2030 reflections with $I > 2\sigma(I)$
$R_{int} = 0.071$
$\theta_{max} = 73.8°$
$h = -8 \rightarrow 0$
$k = -10 \rightarrow 10$
$l = -11 \rightarrow 11$
3 standard reflections
frequency: 60 min
intensity decay: 4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.125$
$S = 1.14$
2056 reflections
126 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0743P)^2 + 0.5803P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.78$ e Å^{-3}
$\Delta\rho_{\min} = -0.98$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Cu1—Cl1	2.2672 (8)	C2—N10	1.324 (4)
Cu1—Cl2	2.3484 (8)	C2—C3	1.420 (4)
Cu1—Cl2^{i}	2.5260 (8)	C3—C4	1.357 (5)
Cu1—C8	2.090 (3)	C4—C5	1.400 (5)
Cu1—C9	2.073 (3)	C5—C6	1.360 (5)
N1—C2	1.352 (4)	C7—C8	1.505 (4)
N1—C6	1.363 (4)	C8—C9	1.357 (5)
N1—C7	1.489 (4)		
C8—Cu1—C9	38.05 (13)	C9—Cu1—Cl2^{i}	109.28 (11)
C8—Cu1—Cl1	142.81 (9)	C8—Cu1—Cl2^{i}	101.04 (8)
C9—Cu1—Cl1	106.46 (9)	Cl1—Cu1—Cl2^{i}	103.15 (3)
C8—Cu1—Cl2	95.41 (9)	Cl2—Cu1—Cl2^{i}	93.72 (3)
C9—Cu1—Cl2	130.00 (11)	Cu1—Cl2—Cu1^{i}	86.28 (3)
Cl1—Cu1—Cl2	110.65 (3)		

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N10—H10*A*···Cl1^{i}	0.92	2.50	3.408 (3)	168
N10—H10*B*···Cl2^{ii}	0.89	2.47	3.318 (3)	159

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, 2 - y, 1 - z$.

Compound (II)

Crystal data

$(C_8H_{11}N_2)_2[Cu_2Br_{2.2}Cl_{1.8}]$
$M_r = 637.07$
Triclinic, $P\overline{1}$
$a = 6.8847$ (5) Å
$b = 8.6835$ (12) Å
$c = 9.6042$ (14) Å
$\alpha = 78.096$ (12)°
$\beta = 74.172$ (9)°
$\gamma = 73.642$ (9)°
$V = 524.80$ (11) Å^3
$Z = 1$
$D_x = 2.016$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 65$–$74°$
$\mu = 9.58$ mm^{-1}
$T = 295$ (2) K
Block, colourless
0.31 × 0.19 × 0.12 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\omega$ scans
Absorption correction: numerical (de Meulenaer & Tompa, 1965)
$T_{\min} = 0.180$, $T_{\max} = 0.414$
2262 measured reflections
2129 independent reflections
2096 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\max} = 73.8°$
$h = -8 \rightarrow 8$
$k = -10 \rightarrow 10$
$l = -11 \rightarrow 0$
3 standard reflections
frequency: 60 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.097$
$S = 1.18$
2129 reflections
143 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 0.8022P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.72$ e Å^{-3}
$\Delta\rho_{\min} = -0.61$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0060 (6)

Table 3
Selected geometric parameters (Å, °) for (II).

Cu1—Br1	2.388 (3)	N1—C6	1.357 (5)
Cu1—Br2	2.385 (3)	N1—C7	1.490 (4)
Cu1—Br2^{i}	2.561 (4)	C2—N10	1.329 (5)
Cu1—Cl1	2.30 (3)	C2—C3	1.416 (5)
Cu1—Cl2	2.391 (5)	C3—C4	1.350 (6)
Cu1—Cl2^{i}	2.567 (4)	C4—C5	1.402 (6)
Cu1—C8	2.101 (3)	C5—C6	1.359 (5)
Cu1—C9	2.082 (4)	C7—C8	1.509 (5)
N1—C2	1.353 (5)	C8—C9	1.341 (6)
C8—Cu1—C9	37.40 (16)	C8—Cu1—Br2	96.23 (14)
C9—Cu1—Cl1	108.7 (6)	Cl1—Cu1—Br2	107.3 (6)
C8—Cu1—Cl1	143.6 (7)	C9—Cu1—Br1	104.60 (13)
C9—Cu1—Br2	130.33 (16)	C8—Cu1—Br1	140.07 (12)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N10—H10*A*···Cl2^{ii}	0.86	2.52	3.373 (6)	175
N10—H10*A*···Br2^{ii}	0.86	2.52	3.374 (5)	175
N10—H10*B*···Cl1^{i}	0.94	2.57	3.45 (3)	157
N10—H10*B*···Br1^{i}	0.94	2.64	3.516 (5)	155

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $1 - x, 2 - y, 1 - z$.

In both (I) and (II), H atoms were treated as riding, with variable displacement parameters [except for the H atoms attached to atom C7 in (I), for which $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$]. H atoms attached to atom N10 in (I) were refined isotropically.

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CORINC* (Dräger & Gattow, 1971); program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *enCIFer* (Cambridge Crystallographic Data Centre, 2003).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1181). Services for accessing these data are described at the back of the journal.

References

Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Bergerhoff, G. (1996). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.

Cambridge Crystallographic Data Centre (2003). *enCIFer*. URL: http://www.ccdc.cam.ac.uk/prods/encifer/.

Dräger, M. & Gattow, G. (1971). *Acta Chem. Scand.* **25**, 761–762. (Revised version of 1994 by L. Wiehl & D. Schollmeyer, University of Mainz, Germany.)

Enraf–Nonius (1989). *CAD*-4 *Software.* Version 5.0. Enraf–Nonius, Delft, The Netherlands.

Ghiladi, R. A., Hatwell, K. R., Karlin, K. D., Huang, H.-W., Moënne-Loccoz, P., Krebs, C., Marzilli, L. A., Cotter, R. J., Kaderli, S. & Zuberbühler, A. D. (2001). *J. Am. Chem. Soc.* **123**, 6183–6184.

Goreshnik, E. A. & Mys'kiv, M. G. (1999). *Pol. J. Chem.* **73**, 1245–1252.

Goreshnik, E. A., Schollmeyer, D. & Mys'kiv, M. G. (2003). *Z. Anorg. Allg. Chem.* **629**, 2040–2045.

Meulenaer, J. de & Tompa, H. (1965). *Acta Cryst.* **19**, 1014–1018.

Munakata, M., Kitagawa, S., Simono, H., Emory, T. & Masuda, H. (1987). *J. Chem. Soc. Chem. Commun.* pp. 1798–1799.

Mykhalichko, B. M. & Mys'kiv, M. G. (1998). Ukraine Patent UA 25450A, Bull. No. 6.

Rhames, F. C., Blackburn, N. J., Murthy, N. N. & Karlin, K. D. (2001). *J. Biol. Inorg. Chem.* **6**, 567–577.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Weitkamp, J. & Puppe, L. (1999). In *Catalysis and Zeolites.* Berlin: Springer Verlag.