catena-Poly[bis[(η²-1-allyl-3-aminopyridinium)copper(I)]-di-μ-chlorocopper(I)-di-μ-chlorocopper(I)-di-μ-chloro]

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Crystals of the title π-complex, $[Cu_4Cl_6(C_8H_{11}N_2)_2]_n$, were obtained by means of alternating-current electrochemical synthesis. The structure consists of infinite copper–chlorine chains to which 1-allyl-3-aminopyridinium moieties are attached *via* a η^2 Cu—(C═C) interaction. The two independent Cu atoms have distinct coordination environments. One is three-coordinate, surrounded by two chloro ligands and the olefinic bond, whereas the second copper center is surrounded by a tetrahedral arrangement of four Cl atoms. The lower basicity of 3-aminopyridine as compared with 2- and 4-aminopyridine lowers the capacity of the organic ligand for donating to N—H···Cl hydrogen bonds and results in the formation of a large inorganic fragment.

Comment

π-Complexes involving heterocyclic ligands have been investigated poorly. There have been only a few publications referring to copper(I) π-complexation with pyridine derivatives (for example, see Munakata *et al.*, 1987). The importance of metal complexes with heterocyclic ligands as compounds with potential biological activity (Ghiladi *et al.*, 2001; Rhames *et al.*, 2001) has led us to pursue a structural investigation of copper(I) π-complexes with 1-allyl-4-aminopyridinium (Goreshnik *et al.*, 2003a) and 1-allyl-2-aminopyridinium (Goreshnik *et al.*, 2003b) cations. To complete the comparison of structural peculiarities of complexes with isomeric *N*-allylaminopyridinium cations, the title copper(I) chloride π-complex, (I), with the 1-allyl-3-aminopyridinium cation has been prepared and structurally investigated.

The Cu and Cl atoms in (I) form infinite chains, propagating along [110]. These chains are composed of four- and eight-membered rings, each of which lies about an inversion center

with a common apex at atom Cu2 (Fig. 1). Both of the rings are centrosymmetric; the four-membered ring is essentially planar, while the eight-membered ring has a chair-like conformation. All Cl atoms act as bridges; atoms Cl1 and Cl2 connect pairs of Cu1 and Cu2 atoms in the eight-membered rings, whereas atom Cl3 bridges two Cu2 atoms in the four-membered ring. Atom Cu2 is tetrahedrally surrounded by four Cl atoms, whereas the trigonal-planar arrangement about atom Cu1 includes two Cl atoms and the olefinic bond of the allyl group of the 1-allyl-3-aminopyridinium ligand (Table 1). Because the coordination number is lower for atom Cu1 than for atom Cu2, the Cu1—Cl distances [2.2478 (14) and 2.2568 (14) Å] are noticeably shorter than the Cu2—Cl distances [2.3477 (15)–2.4167 (15) Å].

(I)
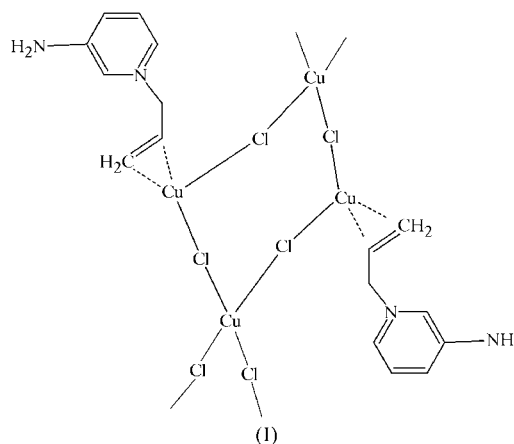
For a numerical characterization of the effectiveness of the copper(I)–olefin interaction, the C—Cu—C angle provides the most suitable parameter, being dependent on both the C═C bond elongation and the Cu—(C═C) distance shortening. The Cu^I—(C═C) bond consists of two components. The Cu^I←L σ donor–acceptor component – which is relatively insensitive to the olefinic bond orientation – is formed by the overlap of the occupied olefinic $p\pi$ orbital and the unoccupied $4s^0$ orbital of the Cu^I atom, and produces a shortening of the Cu—m distance (m is the mid-point of the C═C bond). The Cu^I→L π-dative component, based on electron transfer from the Cu^I $3d^{10}$ orbitals to the unoccupied antibonding orbital of the C═C group, which is strongly dependent on a proper olefinic group orientation in the metal coordination sphere, causes a lengthening of the C═C bond. Therefore, both components increase the value of the C—Cu—C angle. Thus, shortening of the Cu—m distance and lengthening of the C═C bond, as well as an increase in the C—Cu—C angle, are the most informative values for estimating the effectiveness of the Cu—(C═C) interaction. An effective Cu—(C═C) interaction leads to a transformation of the copper coordination polyhedron from tetrahedral to trigonal-pyramidal, with the olefinic group in the basal plane and with concomitant lengthening of the central atom–axial ligand distance; this lengthening can proceed as far as the removal of the axial ligand from the metal coordination sphere, with the formation, as in the present structure, of a trigonal-planar copper environment.

The coordinated olefinic group, with a C=C distance of 1.344 (7) Å, is only slightly elongated compared with the length of an uncoordinated C=C bond. This value, together with the C—Cu—C angle of 38.2 (2)° and a noteworthy 0.21 Å deviation of the olefinic C atoms from the Cl1/Cl2/m plane (corresponding to an 18° inclination of the C=C bond from the equatorial plane), reveal the low efficiency of the π interaction – that is, despite a rather effective σ-component [short Cu—m distance of 1.943 (6) Å], the π-dative component of the Cu—(C=C) interaction is less pronounced. Comparison of these values with the analogues in the structure of the copper(I) chloride π-complex with 1-allyl-4-amino-pyridinium, where the Cu atom also possesses a trigonal-planar 2Cl + C=C environment [C—Cu—C = 38.0 (2)°, Cu—m = 1.950 (6) Å and C=C = 1.343 (6) Å], shows a similarly modest π interaction in both cases. The Cu—m distances are rather short for copper(I) π-complexes in general because of the absence of steric hindrance in the trigonal-planar metal environment, which includes two Cl atoms in addition to the C=C bond. The Cu1—C10(terminal) distance is, as usual, slightly shorter than the Cu1—C9 distance. All pyridine rings are strictly parallel to each other, but the shortest ring–ring distance (4.5 Å) indicates an absence of any aromatic π–π stacking. Infinite chains, formed by the CuLCl2 and CuCl4 subunits, are interconnected into a three-dimensional structure by weak N—H···Cl hydrogen bonds (Table 2 and Fig. 2). The H···Cl distances (2.75 and 2.83 Å) differ significantly from the values of 2.39–2.57 Å observed for the copper(I) chloride π-complex with 1-allyl-4-aminopyridinium and 2.47–2.50 Å for the 1-allyl-2-aminopyridinium derivative. These π-complexes with N-allyl derivatives of aminopyridines, viz. (2-H2N–C5H4NC3H5)2[Cu2Cl4] and (4-H2N–C5H4NC3H5)-
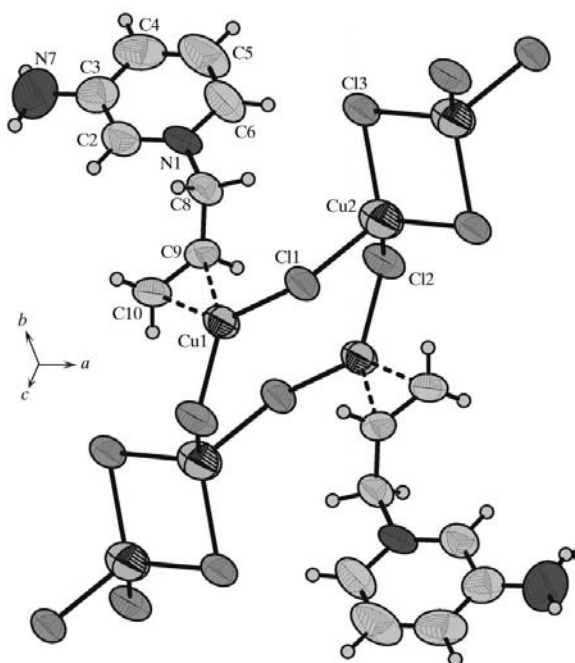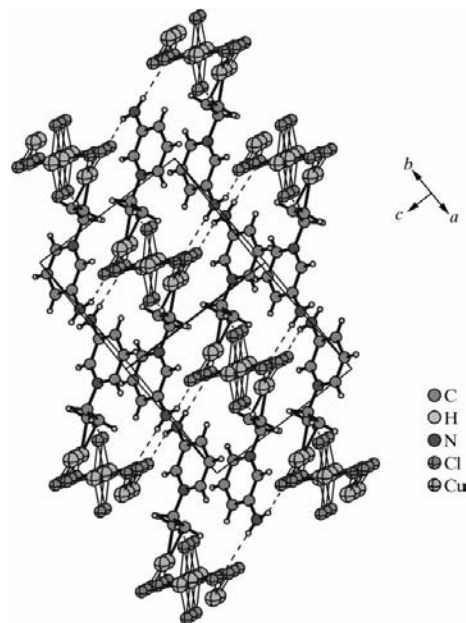

Figure 2
Hydrogen bonding in the structure of (I).

[CuCl2], possess structures with small inorganic fragments, Cu_2Cl_4 and $CuCl_2$, respectively, and rather strong N—H···Cl hydrogen bonds. We note that the progression from the simplest metal-containing fragment, $CuCl_2^-$, in the complex with 1-allyl-4-aminopyridinium, through $Cu_2Cl_4^{2-}$ in the complex with 1-allyl-2-aminopyridinium, to the complicated fragment $(Cu_4Cl_6)_n$ in (I) with 1-allyl-3-aminopyridinium corresponds to decreasing order of pK_a(base) values of the initial aminopyridines (9.25, 6.86 and 6.07, respectively). Thus, in (I), the electron-donor ability of the N atom of the NH2 group is weaker, which may be responsible for the elongated N—H···Cl contacts here as compared with the 2-amino- and 4-aminopyridinium analogues. Moreover, a 'chelating' ligand arrangement [a 1-allyl-2-aminopyridinium cation bonded to the same $Cu_2Cl_4^{2-}$ dimer via a Cu—(C=C) interaction and by N—H···Cl contacts] or a 'bridging' organization (a 1-allyl-4-aminopyridinium moiety connected to one of the Cu atoms through the C=C bond and to a chloro ligand of an adjacent metal atom through N—H···Cl hydrogen bonds) also promotes the formation of effective hydrogen bonds. In such cases, the H atom effectively completes the coordination about the Cl atom, hindering a bridging function for the halogen and thus effectively impeding the further association of small inorganic fragments into larger ones. In the case of (I), the weakly hydrogen-bonding amine H atoms cannot compete with the Cu atoms for a place in the chlorine environment, which in turn enables the formation of the infinite copper–chlorine chains.

Figure 1
Copper–chlorine chains and ligands in the structure of (I).

Experimental

1-Allyl-3-aminopyridinium chloride was prepared from 3-amino-pyridine (Aldrich) by a procedure similar to that used for obtaining 1-allyl-4-aminopyridinium chloride (Goreshnik *et al.*, 2003*a*). Good

quality crystals of the title compound were obtained using the alternating-current electrochemical technique (Mykhalichko & Mys'kiv, 1998) starting from 1-allyl-3-aminopyridinium chloride and copper(II) chloride. To an ethanol solution (2 ml) of $CuCl_2 \cdot 2H_2O$ (1 mmol) was added an ethanol solution (2 ml) of 1-allyl-3-amino-pyridinium chloride (1.2 mmol). The solution was placed in a small test tube and copper-wire electrodes in cork were inserted. After applying a 0.30 V alternating current (frequency 50 Hz) for some days, colorless crystals of the title compound appeared on the copper electrodes.

Crystal data

$[Cu_4Cl_6(C_8H_{11}N_2)_2]$	$D_m = 2.000$ Mg m^{-3}
$M_r = 737.24$	D_m measured by flotation in
Triclinic, $P\bar{1}$	chloroform–bromofrom
$a = 8.4148\ (12)$ Å	Cu $K\alpha$ radiation
$b = 8.7310\ (16)$ Å	Cell parameters from 25 reflections
$c = 9.8916\ (16)$ Å	$\theta = 35$–$45°$
$\alpha = 102.177\ (16)°$	$\mu = 10.14$ mm^{-1}
$\beta = 104.587\ (12)°$	$T = 295\ (2)$ K
$\gamma = 113.166\ (13)°$	Plate, colorless
$V = 606.1\ (2)$ Å^3	$0.24 \times 0.20 \times 0.04$ mm
$Z = 1$	
$D_x = 2.020$ Mg m^{-3}	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.106$
$\theta/2\omega$ scans	$\theta_{max} = 73.4°$
Absorption correction: numerical (de Meulenaer & Tompa, 1965)	$h = -10 \rightarrow 0$
	$k = -9 \rightarrow 9$
$T_{min} = 0.190$, $T_{max} = 0.696$	$l = -11 \rightarrow 12$
2615 measured reflections	3 standard reflections
2443 independent reflections	frequency: 60 min
2004 reflections with $I > 2\sigma(I)$	intensity decay: 5%

Table 1
Selected geometric parameters (Å, °).

Cu1—C10	2.048 (5)	Cu2—Cl3^{ii}	2.3922 (16)
Cu1—C9	2.064 (4)	Cu2—Cl1	2.4167 (15)
Cu1—Cl1	2.2478 (14)	N1—C8	1.492 (5)
Cu1—Cl2^i	2.2568 (14)	C8—C9	1.501 (6)
Cu2—Cl3	2.3477 (15)	C9—C10	1.344 (7)
Cu2—Cl2	2.3841 (18)		
C10—Cu1—C9	38.15 (19)	Cl2—Cu2—Cl1	103.51 (5)
Cl1—Cu1—Cl2^i	108.12 (5)	Cl3^{ii}—Cu2—Cl1	104.32 (5)
Cl3—Cu2—Cl2	110.82 (6)	C2—N1—C8	118.4 (4)
Cl3—Cu2—Cl3^{ii}	103.01 (5)	C6—N1—C8	119.6 (4)
Cl2—Cu2—Cl3^{ii}	119.73 (6)	N1—C8—C9	109.9 (4)
Cl3—Cu2—Cl1	115.89 (6)	C10—C9—C8	122.8 (4)
C2—N1—C8—C9	71.2 (6)	Cl1—Cu1—C9—C10	−160.6 (3)
C6—N1—C8—C9	−107.3 (5)	Cl2^i—Cu1—C9—C10	21.4 (4)
N1—C8—C9—C10	−93.3 (5)		

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N7—H7A$\cdots$Cl1^{iii}	0.83	2.83	3.618 (5)	158
N7—H7B$\cdots$Cl2^{iv}	0.93	2.75	3.629 (6)	160

Symmetry codes: (iii) $x - 1, y, z - 1$; (iv) $x - 1, y, z$.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1252P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.060$	$+ 0.1886P]$
$wR(F^2) = 0.175$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} < 0.001$
2443 reflections	$\Delta\rho_{max} = 1.28$ e Å^{-3}
136 parameters	$\Delta\rho_{min} = -0.95$ e Å^{-3}
H-atom parameters constrained	

The highest difference peak is located 0.92 Å from atom Cu1. All H atoms were allowed to ride on their parent atoms [C—H = 0.93 and 0.97 Å, and $U_{iso}(H) = 1.2U_{eq}(C,N)$].

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: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Bergerhoff, 1996); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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