catena-Poly[[(2,2′-biimidazole-$\kappa^2 N,N'$)chlorocopper(II)]-μ-chloro]

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In the polymeric title compound, $[CuCl_2(C_6H_6N_4)]_n$, each Cu^{II} ion is five-coordinated by four basal atoms (two N atoms from a 2,2′-biimidazole molecule and two Cl^- anions) and one axial Cl^- anion, in a distorted square-pyramidal coordination geometry. Cl^- anions bridge the $\{Cu(C_6H_6N_4)Cl\}$ units into one-dimensional linear chains, which are reinforced by π–π interactions. Adjacent linear chains are linked by N—H···Cl hydrogen bonds, resulting in a grid layer. The hydrogen-bonding pattern can be described in graph-set notation as $C_2^2(9)R_2^2(9)R_2^2(14)$. This study extends our knowledge of the multifunctional properties of the 2,2′-biimidazole ligand and of the coordination stereochemistry of copper(II).

Comment

2,2′-Biimidazole is a multifunctional ligand that can be coordinated to a transition metal in non-deprotonated (neutral, H_2biim), mono-deprotonated (monoanion, $Hbiim^-$) and di-deprotonated (dianion, $biim^{2-}$) forms (Cancela et al., 2001). The metal-binding ability of its three forms has been well documented since the same 3d metal complexes with either neutral or deprotonated forms were first reported by Holmes et al. (1961). In the neutral state, H_2biim can bind metals as either a bidentate chelate, seen, for example, with Cu^{II} (Liu & Su, 1996), V^{IV} (Sang et al., 2002), and Co^{II} and Ni^{II} (Atencio et al., 2004), or as a bridging ligand between two metal centres (Kirchner & Krebs, 1987), and can act as a donor in hydrogen-bonding interactions. Coordinated H_2biim usually forms hydrogen bonds with counter-anions and solvent molecules (Ye et al., 1999). On account of the bridging and counter-anion properties of the Cl^- anion, as well as the flexibility of the coordination stereochemistry of the Cu^{II} cation, we are interested in copper complexes with the Cl^- anion and H_2biim. In addition, copper(II) chloride yields adducts with H_2biim in which the bi-heterocyclic ligand binds in the typical chelating mode, and one such complex, $[Cu(H_2biim)_2]Cl_2$, has been reported previously (Atencio et al., 2005). The present study uses a similar method for synthesizing a new adduct with copper(II) chloride and H_2biim by adjusting the molar ratio of copper(II) chloride and H_2biim, which yielded the title compound, $[Cu(C_6H_6N_4)Cl_2]_n$, (I).

(I)
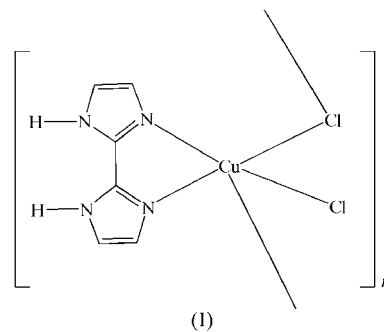
In (I), each Cu^{II} ion is five-coordinated with a distorted square-pyramidal geometry (Fig. 1 and Table 1). The basal plane is formed by atoms N1 and N4 from one H_2biim ligand in chelating mode, along with anions Cl1 and Cl2, with an r.m.s. deviation of 0.018 Å. The apical site is occupied by a Cl^- anion, $Cl2^i$ [symmetry code: (i) $x - 1$, y, z], with a Cu—Cl bond distance of 2.892 (2) Å, which is longer than the average equatorial Cu—Cl bond distance of 2.271 (2) Å. The Cu—N bond distances and the chelating mode of the H_2biim ligand are similar to those observed in $[CuCl(C_6H_6N_4)(H_2O)]$-$[Cu(C_4H_5NO_4)Cl]\cdot H_2O$ (Gao et al., 2005). Atom Cu1 is located 0.1623 (8) Å out of the basal plane towards atom $Cl2^i$.
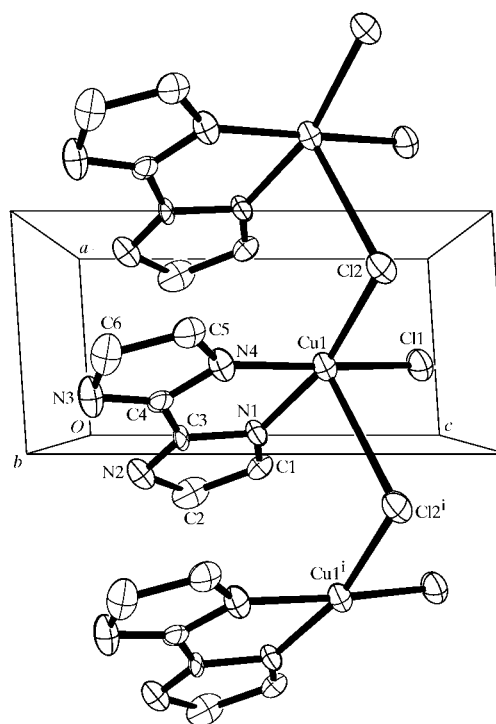
Figure 1
A view along [010], showing the one-dimensional chain of (I) which propagates along the a axis. The atom numbering and displacement ellipsoids at the 50% probability level are also shown. H atoms have been omitted to improve clarity. [Symmetry code: (i) $x - 1$, y, z.]

metal-organic compounds

Five-coordinate copper(II) complexes have geometries ranging from trigonal–bipyramidal to square-pyramidal. Energetically, the limiting trigonal–bipyramidal and square-pyramidal forms are often almost equally favourable, with a low activation barrier to interconversion. In the present instance, the observed geometry is very nearly square-pyramidal, as determined by the observed distortion value τ (van Albada *et al.*, 1999; Addison *et al.*, 1984) of 0.05, which is very near the ideal value of $\tau = 0$; for perfect trigonal–bipyramidal geometry, $\tau = 1$.

The bond distances and angles of the complexed H$_2$biim ligand are unexceptional and compare well with those of the free ligand (Cromer *et al.*, 1987). Of note is the dihedral angle between the two imidazole rings. The free ligand is found to crystallize in a *trans* conformation, with a dihedral angle of 4.6°, but in (I), the H$_2$biim ligand takes on a *cis* conformation, with a dihedral angle of 2.3 (4)°. This angle is smaller than that observed in [Ag(NO$_3$)(C$_6$H$_6$N$_4$)]$_n$ [23.2 (2)°; Hester *et al.*, 1997], in which H$_2$biim functions as a bridging ligand to link the Ag atoms, forming a right-hand helical chain. In (I), the Cl2^i anion connects adjacent [Cu(C$_6$H$_6$N$_4$)Cl$_2$] units to produce a linear chain along the crystallographic *a* axis, with a Cu1$\cdots$Cu1^i separation of 3.8671 (12) Å (Fig. 1). In the chain, the heterocyclic rings are either parallel or nearly parallel to each other.

The above *cis* conformation and parallel disposition of H$_2$biim preserve favourable π–π interactions between the two sets of parallel symmetry-related rings of the H$_2$biim moieties [at (x, y, z) and ($x - 1, y, z$) or ($x + 1, y, z$)]. Ring centroids are separated by 3.867 (2) Å in both cases, and the perpendicular separations between the two sets of planes are 3.377 (3) and 3.351 (3) Å. These π–π interactions reinforce the linear chains. Adjacent linear chains are linked by N2—H2$A\cdots$Cl1^{ii} and N3—H3$A\cdots$Cl2^{ii} [symmetry code: (ii) $x - 1$, y, $z - 1$] hydrogen bonds along the [101] direction, resulting in a grid layer parallel to (010) (Fig. 2 and Table 2). The hydrogen-bonding pattern, as shown in Fig. 2, can be described in graph-set notation (Etter, 1990; Grell *et al.*, 2000) as $C_2^2(9)R_2^2(9)R_2^2(14)$.
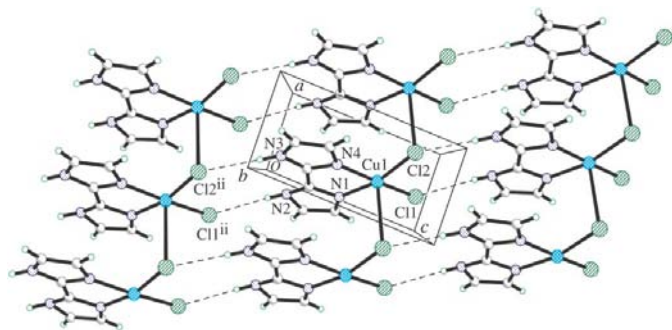

Figure 2
A view along [010] of the two-dimensional layer in (I), formed by N—H$\cdots$Cl hydrogen-bond interactions (dashed lines). [Symmetry code: (ii) $x - 1$, y, $z - 1$.]

Experimental

CuCl$_2$·2H$_2$O (1 mmol, 0.17 g) and 2,2′-biimidazole (1 mmol, 0.14 g) were suspended in water (30 ml). To the resulting mixture, concentrated aqueous HCl was added until the suspension became clear. The resulting solution was filtered and the filtrate allowed to evaporate slowly at room temperature. After three weeks, blue crystals of (I) appeared.

Crystal data

[CuCl$_2$(C$_6$H$_6$N$_4$)]	Mo $K\alpha$ radiation
$M_r = 268.59$	Cell parameters from 1408
Monoclinic, $P2_1$	reflections
$a = 3.8671$ (4) Å	$\theta = 2.7$–24.2°
$b = 14.8937$ (17) Å	$\mu = 3.05$ mm^{-1}
$c = 7.6363$ (9) Å	$T = 298$ (2) K
$\beta = 93.742$ (2)°	Needle, blue
$V = 438.88$ (9) Å^3	$0.34 \times 0.06 \times 0.05$ mm
$Z = 2$	
$D_x = 2.032$ Mg m^{-3}	

Data collection

Bruker APEX area-detector diffractometer	1522 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.038$
φ and ω scans	$\theta_{max} = 25.2°$
Absorption correction: multi-scan	$h = -4 \rightarrow 4$
(*SADABS*; Bruker, 2002)	$k = -17 \rightarrow 17$
$T_{min} = 0.424$, $T_{max} = 0.863$	$l = -9 \rightarrow 9$
4178 measured reflections	
1590 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.053$	$+ 0.9884P]$
$wR(F^2) = 0.103$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.19$	$(\Delta/\sigma)_{max} < 0.001$
1590 reflections	$\Delta\rho_{max} = 0.70$ e Å^{-3}
118 parameters	$\Delta\rho_{min} = -0.76$ e Å^{-3}
H-atom parameters constrained	Absolute structure: Flack (1983), with 761 Friedel pairs
	Flack parameter: 0.07 (3)

Table 1
Selected geometric parameters (Å, °).

Cu1—N4	2.009 (6)	Cu1—Cl2	2.280 (2)
Cu1—N1	2.011 (6)	Cu1—Cl2^i	2.892 (2)
Cu1—Cl1	2.262 (2)	Cu1—Cu1^i	3.8671 (12)
N4—Cu1—N1	80.8 (2)	Cl1—Cu1—Cl2	96.27 (7)
N4—Cu1—Cl1	169.71 (19)	N4—Cu1—Cl2^i	95.03 (19)
N1—Cu1—Cl1	91.79 (18)	N1—Cu1—Cl2^i	93.80 (17)
N4—Cu1—Cl2	89.83 (19)	Cl1—Cu1—Cl2^i	92.58 (7)
N1—Cu1—Cl2	166.96 (18)	Cl2—Cu1—Cl2^i	96.07 (7)

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3$A\cdots$Cl2^{ii}	0.86	2.44	3.221 (7)	152
N2—H2$A\cdots$Cl1^{ii}	0.86	2.49	3.227 (7)	145

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

All H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of C—H = 0.93 Å or N—H = 0.86 Å, with U_{iso}(H) = 1.2U_{eq}(parent atom).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: RB1010). Services for accessing these data are described at the back of the journal.

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