catena-Poly[[chloro(1,10-phenanthroline-κ²N,N′)copper(II)]-μ-imidazolato-κ²N:N′]

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In the polymeric title compound, $[Cu(im)Cl(phen)]_n$, where im is the imidazolate anion $(C_3H_3N_2)$ and phen is 1,10-phenanthroline $(C_{12}H_8N_2)$, each Cu^{II} ion is five-coordinated by four basal N atoms (two from two different im anions and two from one phen ligand) and one axial Cl atom, in a distorted square-pyramidal coordination geometry. Moreover, each im anion bridges two identical $\{CuCl(phen)\}^+$ cations through its two N atoms, resulting in a one-dimensional zigzag chain along the crystallographic a axis. In addition, pairs of adjacent chains are staggered by π–π interactions, generating a two-dimensional layer, and neighbouring layers are further linked by two different kinds of C—H⋯Cl interactions, producing a three-dimensional network.

Comment

Imidazole plays an important role in biological systems, since the imidazole moiety of the histidyl residues in a large number of metalloproteins constitutes all or part of the binding sites of various transition metal ions (Messerschmidt, 1993). For example, studies of bovine erythrocyte superoxide dismutase reveal the presence of an imidazolate-bridged Cu^{II}–Zn^{II} centre at the active site, and it can catalyze some biological reactions (Bertini et al., 1990; Kolks & Lippard, 1977). Furthermore, it is of interest that polydentate ligands incorporating an imidazole moiety can be used to synthesize metal complexes that are capable of undergoing reversible interconversions between a monomer and a self-assembled oligomer by alteration of the external conditions, specifically a change in pH (Matsumoto et al., 1999). By controlling the pH, it is then possible to interconvert a protonated monomer to an imidazolate-bridged deprotonated oligomer and vice versa, thus affording new functional materials with potential switching ability. In view of all this, studies aimed at characterizing the bonding between imidazole and transition metal ions are of considerable interest. There are numerous examples of syntheses, crystal structure determinations and char-

acterizations of imidazolate-bridged complexes (Mao et al., 1995; Koch et al., 1989; Colacio et al., 1998, and references therein). We have selected the Cu–im–phen system to extend this research and we present here the crystal structure of the title compound, $[Cu(im)Cl(phen)]_n$, (I).
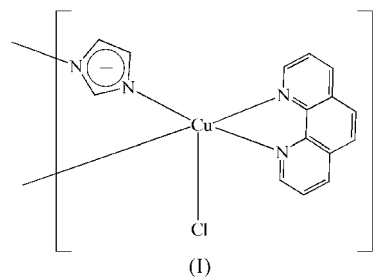
In the molecule of (I), each Cu^{II} ion is five-coordinated, with a distorted square-pyramidal geometry (Fig. 1 and Table 1). The basal plane is formed by atoms N1 and N2 from one phen ligand, along with atoms N3 and N4^i from two im anions, with a mean deviation of 0.1785 Å [symmetry code: (i) $x - \frac{1}{2}, y, \frac{1}{2} - z$]. A Cl⁻ ion, Cl1, occupies the apical position. The Cu—N_{im} bond lengths are similar to those observed in imidazolate-bridged dicopper(II) complexes (Drew et al., 1980; Salata et al., 1991) and are shorter than the average basal Cu—N bond length (2.037 Å) around Cu1 in (I). Atom Cu1 is not in the basal plane, but is located 0.335 (1) Å out of the mean basal plane towards atom Cl1.

According to the valence-bond theory, if a Cu (d^9) ion is five-coordinated, there will be two probable coordination geometries around the metal ion, viz. trigonal–bipyramidal and square pyramidal. In the former, the Cu ion adopts dsp^3 or sp^3d hybridization, and in the latter d^2sp^2 or sp^2d^2. These two configurations of a d^9 ion possess approximately equal energy and they can interconvert. If the coordination polyhedron is a regular square pyramid, the distortion value is 0, and if it is a regular trigonal bipyramid, the distortion value is 1. The
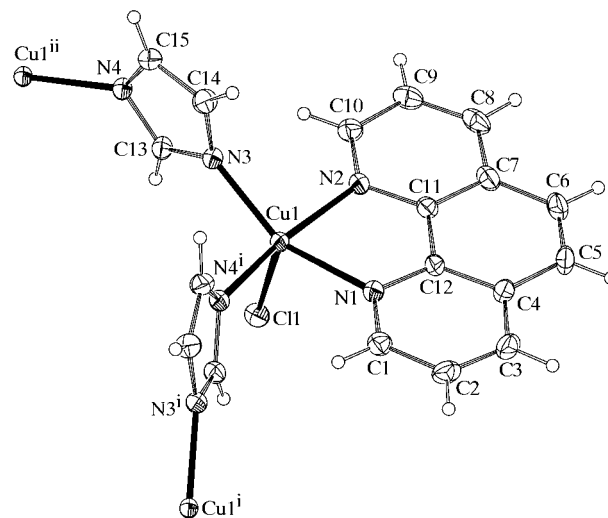
Figure 1
The coordination environment of the Cu^{II} ion in (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii. [Symmetry codes: (i) $x - \frac{1}{2}, y, \frac{1}{2} - z$ (ii) $\frac{1}{2} + x, y, \frac{1}{2} - z$.]
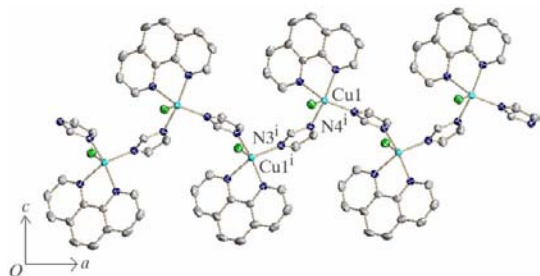
metal-organic compounds

Figure 2
A view of the one-dimensional zigzag chain of (I) along the a axis. [Symmetry code: (i) $x - \frac{1}{2}, y, \frac{1}{2} - z$.]
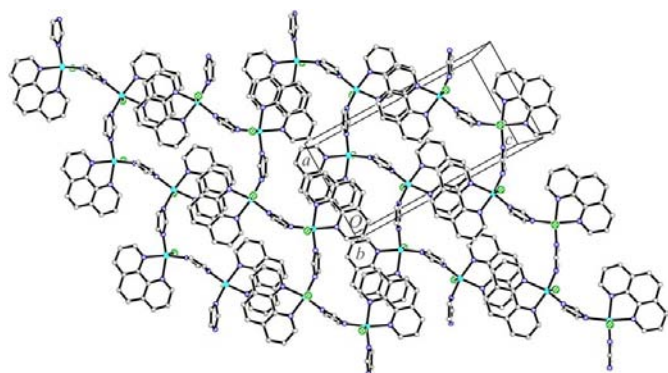

Figure 3
A perspective view of the two-dimensional network in (I) along the b axis.

distortion value of the coordination polyhedron for the Cu^{II} ion in (I) has been calculated according to the method reported by van Albada and Addison (van Albada *et al.*, 1999; Addison *et al.*, 1984). The distortion value of 0.283 obtained for atom Cu1 indicates that the coordination geometry around each Cu^{II} ion in (I) is a distorted square pyramid and that the Cu (d^9) ions probably adopt sp^2d^2 hybrid orbitals to accept electrons from the ligands, which may be favourable to the paramagnetism and stability of (I).

Each im anion in (I) acts as a bidentate ligand, connecting two Cu^{II} ions through its two N atoms, resulting in a one-dimensional zigzag chain along the crystallographic a axis with a Cu1$\cdots$Cu1^i separation of 5.8693 (4) Å (Fig. 2). In order to minimize steric effects, the dihedral angle between the im ring and the heterocyclic ring of phen in each subunit is 89.44 (8)°, and within the chain all heterocyclic rings are approximately parallel to each other. Interestingly, the im plane is approximately perpendicular to the basal plane [88.80 (9)°], while the dihedral angle between the heterocyclic rings and the basal plane is only 10.65 (4)°.

In the crystal structure of (I), there are π–π interactions between inversion-related rings of the phen moieties [at (x, y, z) and ($-x$, $2 - y$, $1 - z$)], with the ring centroids separated by 3.489 Å. These π–π interactions link chains into extended layers approximately parallel to (010) (Fig. 3). The layers are linked into a three-dimensional network by insertion of the apical Cl$^-$ ions of one layer into an adjacent layer and their stabilization there *via* C—H$\cdots$Cl interactions (Table 2).

Experimental

The title compound was synthesized by a hydrothermal method from a mixture of imidazole (2 mmol, 0.14 g), CuCl$_2$·2H$_2$O (1 mmol, 0.17 g) and 1,10-phenanthroline (3 mmol, 0.54 g) in water (20 ml) in a 30 ml Teflon-lined stainless steel reactor. The solution was heated to 425 K for 5 d, after which the reaction system was cooled slowly to room temperature. Green block-shaped crystals of (I) were collected and washed with distilled water.

Crystal data

[Cu(C$_3$H$_3$N$_2$)Cl(C$_{12}$H$_8$N$_2$)]	Mo $K\alpha$ radiation
$M_r = 346.27$	Cell parameters from 4117
Orthorhombic, $Pbca$	reflections
$a = 9.5540$ (5) Å	$\theta = 2.6$–$25.0°$
$b = 15.4561$ (11) Å	$\mu = 1.80$ mm^{-1}
$c = 18.4412$ (9) Å	$T = 298$ (2) K
$V = 2723.2$ (3) Å^3	Block, green
$Z = 8$	$0.17 \times 0.15 \times 0.14$ mm
$D_x = 1.689$ Mg m^{-3}	

Data collection

Bruker APEX CCD area-detector diffractometer	2443 independent reflections
	2096 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.031$
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)	$\theta_{max} = 25.2°$
	$h = -10 \rightarrow 11$
$T_{min} = 0.750$, $T_{max} = 0.787$	$k = -18 \rightarrow 16$
13 486 measured reflections	$l = -22 \rightarrow 14$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.030$	$+ 1.7259P]$
$wR(F^2) = 0.074$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
2443 reflections	$\Delta\rho_{max} = 0.38$ e Å^{-3}
190 parameters	$\Delta\rho_{min} = -0.22$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cu1—N4^i	1.978 (2)	Cu1—N1	2.128 (2)
Cu1—N3	1.996 (2)	Cu1—Cl1	2.4603 (7)
Cu1—N2	2.047 (2)	Cu1—Cu1^i	5.8693 (4)
N4^i—Cu1—N3	96.20 (8)	N2—Cu1—N1	78.85 (8)
N4^i—Cu1—N2	166.95 (8)	N4^i—Cu1—Cl1	95.82 (6)
N3—Cu1—N2	90.74 (8)	N3—Cu1—Cl1	106.21 (6)
N4^i—Cu1—N1	89.72 (8)	N2—Cu1—Cl1	92.82 (6)
N3—Cu1—N1	149.95 (8)	N1—Cu1—Cl1	102.43 (6)

Symmetry code: (i) $x - \frac{1}{2}, y, \frac{1}{2} - z$.

Table 2
Geometry of C—H$\cdots$Cl interactions (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C6—H6$\cdots$Cl1^i	0.93	2.82	3.741 (3)	170
C5—H5$\cdots$Cl1^{ii}	0.93	2.76	3.485 (3)	136

Symmetry codes: (i) $x, \frac{3}{2} - y, \frac{1}{2} + z$; (ii) $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$.

The H atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H distances of 0.93 Å and with U_{iso}(H) = $1.2U_{eq}$(C).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve

structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Bruker, 2002); software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1475). Services for accessing these data are described at the back of the journal.

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