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catena-Poly[[[1-benzoyl-2-(2-hydroxyethyl)-3-(2-pyridyl)guanidine]chloridocopper(II)] chloride 0.61-hydrate]

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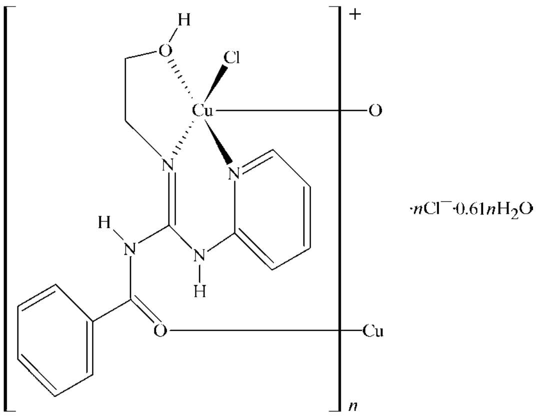
The title copper(II) complex, $\{[CuCl(C_{15}H_{16}N_4O_2)]Cl\cdot 0.61H_2O\}_n$, is a one-dimensional zigzag coordination polymer structure extending along the (010) direction. The Cu^{II} atom has a square-pyramidal geometry, where the basal plane is formed by two *cis* N atoms and one O atom from the ligand, and by a Cl atom. The apical position is occupied by a carbonyl O atom from a symmetry-related molecule. In the crystal structure, there are O—H···Cl and N—H···Cl hydrogen bonds, which link parallel polymer chains along the *c* direction, so building a two-dimensional structure *via* the interstitial Cl atoms.

Comment

Guanidine chemistry has been extensively studied, as much for its biological activity as for its occurrence in natural products (Bahekar *et al.*, 2007; Berlinck *et al.*, 2005). Guanidines are well established as versatile and flexible ligand systems for a variety of transition metals. Among the important features of these molecules are the donor ability of the nitrogen centers and the potential to explore both the steric and the electronic effects induced by varying organic substituents on the ligand framework (Place *et al.*, 1998). In addition, the 1,2,3-substituted groups allow the design of metal–guanidine fragments with the potential to form coordination polymers. These are of great interest as functional materials with physical properties, such as photoluminescence (Janiak, 2003), nonlinear optical (Lin *et al.*, 2000) and magnetomolecular (Wang *et al.*, 2005). One-dimensional chains are basic building blocks in coordination polymers, and intermolecular interactions play an important role in the structural organization of these complexes (Chen *et al.*, 2006). Recently, a ligand system based on triaminoguanidine with copper(II) has been employed to build a three-dimensional coordination polymer containing two interpenetrating networks of (10,3)-*a* topology (Zharkouskaya *et al.*, 2005). We report here a new zigzag one-dimensional coordination polymer, (I), obtained by the self-assembly of the cationic fragment $[CuCl(BHPG)]^+$ on reaction of the guanidine derivative 1-benzoyl-2-(2-hydroxyethyl)-3-(2-pyridyl)guanidine (BHPG) with copper(II) chloride.



(I)

The molecular structure of (I) is illustrated in Fig. 1, and selected geometric parameters are given in Table 1. Complex (I) is a one-dimensional zigzag coordination polymer, with parallel chains extending along the *b* axis. Each repeating unit is built up of roto-translated complex $[CuCl(BHPG)]^+$ cations. The copper(II) ion lies on a general position, connecting neighboring complex units *via* the apical carbonyl $O1^i$ atom [symmetry code: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$], which is weakly bonded at a distance of 2.417 (2) Å. The coordination polyhedron around copper(II) is square pyramidal, as indicated by the angular structure parameter $\tau = (\beta - \alpha)/60 = 0.051$ [Addison *et al.*, 1984; α and β are the angles N1—Cu1—Cl1 =

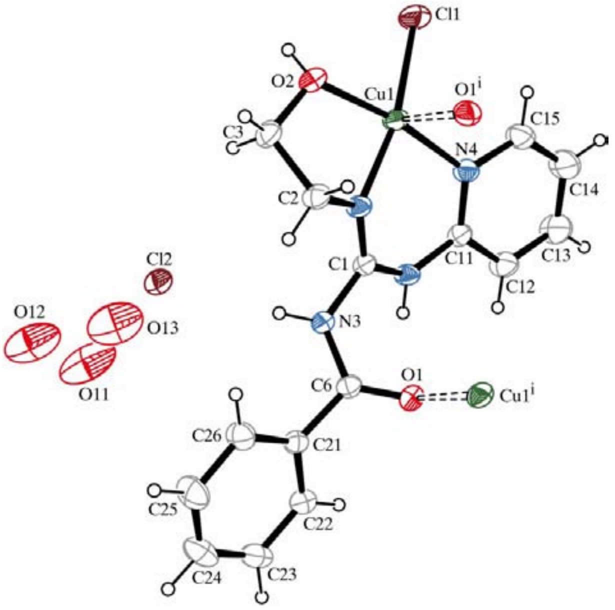


Figure 1
The asymmetric unit of (I), showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level. H atoms are shown as small spheres of arbitrary radii. The symmetry code is as in Table 1.

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168.15 (7)° and N4—Cu1—O2 = 171.16 (9)°, respectively]. Looking down the polymer chain, it can be seen that the arrangement of the copper(II) polyhedra is antiparallel, with copper(II) ions separated by a minimum distance of 6.092 Å. The basal plane of the coordination environment is formed by two *cis* N atoms from the imine and the pyridine groups [Cu1—N1 = 1.940 (2) Å and Cu1—N4 = 1.997 (2) Å], a Cl atom and an O atom from the hydroxyl group [Cu1—Cl1 = 2.2162 (8) Å and Cu1—O2 = 2.037 (2) Å]. It is interesting to note that the symmetrically substituted guanidine (Zharkouskaya *et al.*, 2005) led to the formation of a three-dimensional polymer with $(Cu_3L)^+$ stoichiometry and two distinct metal environments. One has a square-pyramidal coordination environment, with a bridging O atom at the apical position at a distance of 2.270 (6) Å, and the other contains a basal plane similar to that of (I), except that the Cu—Cl distance is slightly longer [2.291 (7) Å].

The BHPG ligand acts as a bidentate chelate, leading to the formation of a five-membered ring (Cu1/O2/C3/C2/N1, showing an *E* form with C2 as the flap atom) and a six-membered ring (Cu1/N1/C1/N2/C11/N4, showing a boat conformation with atoms Cu and N2 lying out of the plane of the other atoms). The formation of the six-membered ring and the planarity of the basal plane are indications of the stability of the complex. The least-squares plane through atoms N4, N1, O2 and Cl1 in the basal plane has an r.m.s. deviation of 0.03 Å and the Cu^{II} ion is displaced 0.097 (1) Å above this plane towards the apical $O1^i$ atom. The bond angles centered at the Cu^{II} ion sum to 360°.

The cationic complex is counterbalanced by a chloride anion, which is at the interstitial position between the parallel polymer chains, allowing the formation of a two-dimensional arrangement extending in the *c* direction. Thus, the crystal packing (Fig. 2) stabilization is mediated by strong N—H···Cl and O—H···Cl hydrogen bonds (see Table 2 and Fig. 2 for details). The benzene ring is rotated to allow compact packing, so the N3—C6—C21—C26 torsion angle becomes −54.4 (4)° and the C6—C21 bond distance [1.490 (3) Å] is elongated by 0.03 Å from the expected formal single-bond value as a result of the lack of π–π overlap. In the unit cell, a hydrophobic cavity of volume 476.5 Å^3, in the vicinity of the inversion center at (0, $\frac{1}{2}$, 0), was found to contain a number of very disordered and uncoordinated water molecules. These water molecules are shown in Fig. 2 as three disordered O atoms.

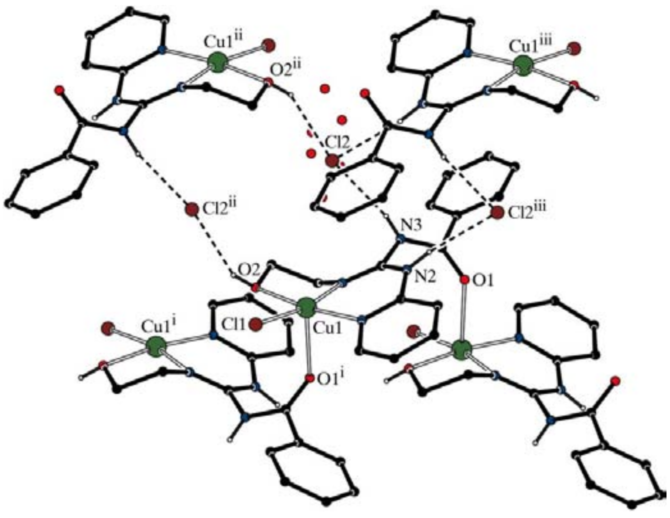

Figure 2
Partial crystal packing diagram of (I), viewed approximately parallel to the (101) plane; the *b* axis points to the left. Intermolecular hydrogen bonds are shown as dashed lines (only the H atoms involved in hydrogen bonding are shown). The symmetry codes are as in Tables 1 and 2.

Experimental

The BHPG ligand was synthesized as described by Cunha *et al.* (2001). A solution containing BHPG (56.8 mg, 0.2 mmol) dissolved in chloroform (5 ml) was added dropwise to a solution containing copper(II) chloride dihydrate (34.1 mg, 0.2 mmol) dissolved in methanol (5 ml). The resulting green mixture was stirred for 2 h at room temperature and evaporated under vacuum (yield 80.8 mg, 96%; m.p. 443–446 K). Analysis calculated for $C_{15}H_{18}Cl_2CuN_4O_2$: C 42.82, H 4.31, N 13.3%; found: C 43.13, H 4.21, N 12.81%. IR (KBr): ν(C=N) 1556 (*vs*) and 1622 (*s*); ν(C=O) 1681 (*s*); ν(CH_3) 2936 (*m*) and 3046 (*m*) cm^{-1}. Blue single crystals suitable for X-ray crystallographic analysis were grown in a methanol/ethyl acetate–ether interface by diffusion.

Crystal data

$[CuCl(C_{15}H_{16}N_4O_2)]Cl\cdot 0.61H_2O$
$M_r = 429.75$
Monoclinic, $C2/c$
$a = 27.022$ (3) Å
$b = 9.114$ (1) Å
$c = 17.005$ (3) Å
$\beta = 118.116$ (10)°
$V = 3693.8$ (9) Å^3
$Z = 8$
Cu $K\alpha$ radiation
$\mu = 4.50$ mm^{-1}
$T = 297$ (2) K
0.15 × 0.12 × 0.10 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: Gaussian (*PLATON*; Spek, 2003)
$T_{min} = 0.594$, $T_{max} = 0.72$
7066 measured reflections
3318 independent reflections
2952 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
2 standard reflections
frequency: 120 min
intensity decay: 6%

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$
$wR(F^2) = 0.138$
$S = 1.07$
3318 reflections
246 parameters
18 restraints
H-atom parameters constrained
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ e Å^{-3}

Atoms H2, H3 and H2*C* were located in difference Fourier maps. However, all H atoms were included in calculated positions and treated as riding atoms [O—H = 0.82 Å, N—H = 0.86 Å and C—H = 0.93–0.97 Å, with $U_{iso}(H) = 1.5U_{eq}(O)$ and $1.2U_{eq}(C,N)$]. The solvent O atoms were refined with an isotropically restrained displacement tensor (ISOR) and their occupancies were adjusted for a U_{eq} value of *ca* 0.11 Å^2; the solvent site occupation decreased from 1.0 to 0.61. It is worth noting that the solvent site refinement with occupation 1.0 led to a 1% improvement in fitted residuals, suggesting that one or alternatively two water molecules fill the cavity.

Data collection: *CAD-4-PC* (Enraf–Nonius, 1993); cell refinement: *CAD-4-PC*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997);

Table 1
Selected geometric parameters (Å, °).

Cu1—N1	1.940 (2)	O1—C6	1.220 (3)
Cu1—N4	1.997 (2)	N1—C1	1.278 (3)
Cu1—O2	2.037 (2)	N2—C1	1.352 (3)
Cu1—Cl1	2.2162 (8)	N3—C1	1.410 (3)
Cu1—O1^{i}	2.417 (2)	C14—C15	1.358 (5)
N1—Cu1—N4	90.38 (9)	O2—Cu1—Cl1	88.92 (7)
N1—Cu1—O2	81.39 (8)	N1—Cu1—O1^{i}	86.55 (8)
N4—Cu1—O2	171.16 (9)	N4—Cu1—O1^{i}	93.70 (9)
N1—Cu1—Cl1	168.15 (7)	O2—Cu1—O1^{i}	89.03 (8)
N4—Cu1—Cl1	98.85 (7)	Cl1—Cu1—O1^{i}	100.17 (5)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*C*···Cl2^{ii}	0.82	2.42	3.173 (2)	153
N2—H2···Cl2^{iii}	0.86	2.35	3.204 (2)	172
N3—H3···Cl2	0.86	2.43	3.275 (2)	169

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

molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SU3009). Services for accessing these data are described at the back of the journal.

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