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catena-Poly[[[diaquabis(5-chloropyridinium-2-olato-κO)copper(II)]-μ-pyrazine-κ^2N:N'] diperchlorate]

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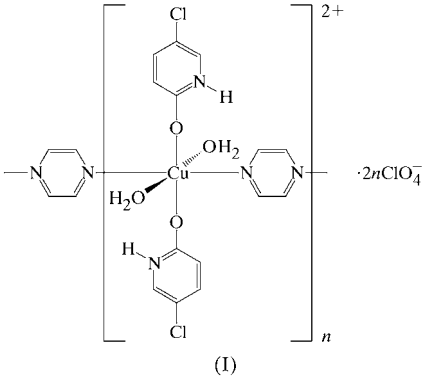
In the title compound, $[Cu(C_5H_4ClNO)_2(C_4H_4N_2)(H_2O)_2](ClO_4)_2$, the Cu atom, which lies on an inversion centre, has an octahedral environment. The pyrazine ligand also lies about an inversion centre and links adjacent Cu atoms into a chain running along the *b* axis; perchlorate anions occupy the space between the chains, and the chains use the coordinated water molecules to link to the anions, resulting in a hydrogen-bonded ribbon structure. The donor 5-chloro-2-hydroxypyridine ligand exists in the zwitterionic form, *i.e.* 5-chloropyridinium-2-olate.

Comment

The synthesis of one-, two- and three-dimensional supramolecular architectures is currently an active field of research owing to the diversity of motifs and also to their potential use as microporous solids in molecular adsorption, ion exchange and heterogeneous catalysis (Aakeroy, 1997; Moulton & Zaworotko, 2001; Yaghi *et al.*, 1998). The title compound, (I), represents a contribution to this field.



(I)

The crystal structure of (I) comprises one-dimensional cationic polymeric $[Cu(ClpyOH)_2(pyz)(H_2O)_2]_n^{2n+}$ chains and counter-ions (pyz is pyrazine). As shown in Fig. 1, the Cu^{II} atom, located on an inversion centre, has an elongated octahedral CuN_2O_4 coordination, with two O atoms from two 5-chloropyridinium-2-olate zwitterions and two pyz N atoms in the equatorial positions [Cu—O 1.967 (2) Å and Cu—N 2.053 (2) Å] and two aqua ligands at the apical positions [Cu—O1*W* 2.387 (2) Å]. The $Cu—N_{pyz}$ bond distance is similar to those [2.036 (3)–2.037 (3) Å] found in related Cu^{II} complexes with pyrazine as spacer (Kondo *et al.*, 1999; Tong *et al.*, 1998). The spacer pyrazine molecules also lie about inversion centres and link adjacent Cu atoms into a chain parallel to the *b* axis; the Cu···Cu separation is the length of the *b* axis. The zwitterionic ligand uses the pyridinium H atom to form an intramolecular hydrogen bond to the water molecule [N···O = 2.826 (3) Å]. The counter-ions are located between the chains (Fig. 2) and each forms two acceptor hydrogen bonds with two adjacent aqua ligands; each aqua ligand forms one acceptor hydrogen bond with the pyridyl group from the intra-chain ClpyOH ligand, as well as two donor hydrogen bonds with the adjacent ClO_4^- anions (Table 2). As each water molecule interacts with two anions, a hydrogen-bonded layer structure results (Fig. 3).

It should be noted that the non-classical C—H···O hydrogen-bonding interaction plays a role in consolidating the solid-state structure of (I), in addition to the above-mentioned classical strong hydrogen bonding. It is interesting that there is an uncommon short C···O distance between the pyz and ClpyOH ligands of different polymeric chains. The C7···O1^{ii} distance and C7—H7*A*···O1^{ii} angle are 3.016 (3) Å and 110°,

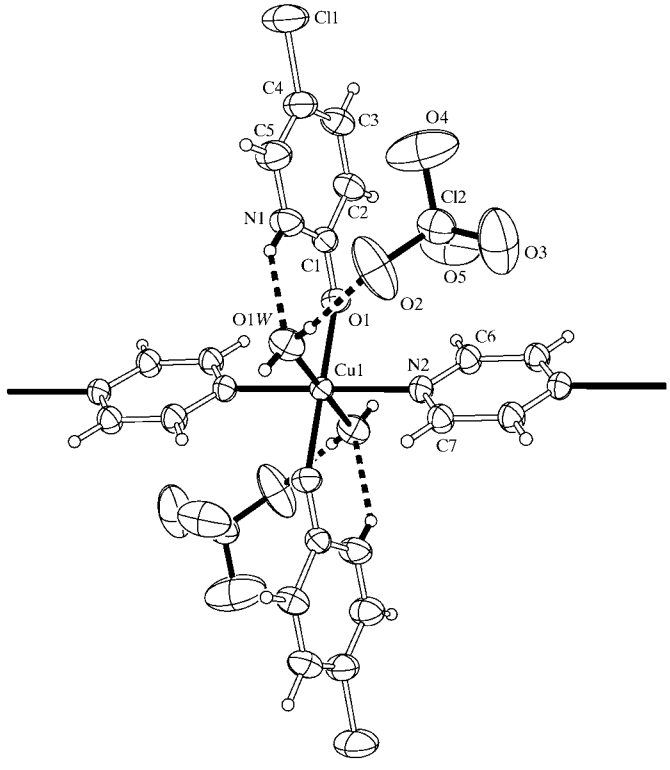


Figure 1
*ORTEP*II (Johnson, 1976) plot (ellipsoids at the 50% probability level) illustrating the coordination environment of the Cu^{II} atom.

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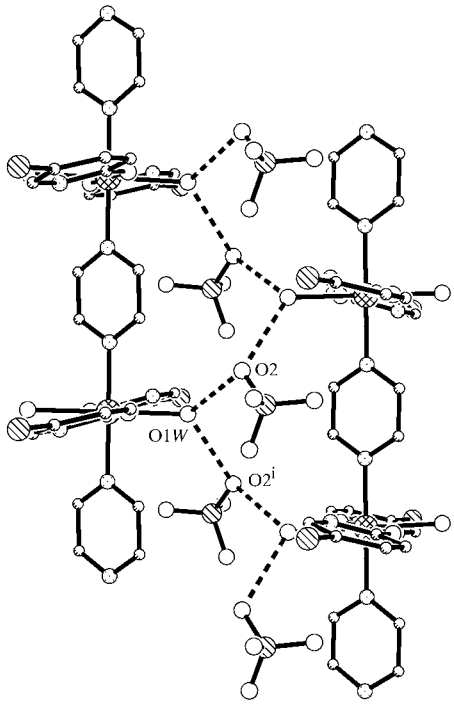

Figure 2
Perspective view of the interchain hydrogen bonding in (I). [Symmetry code: (i) $\frac{1}{2}-x, y+\frac{1}{2}, \frac{1}{2}-z$.]

respectively [symmetry code: (ii) $x-1, -y, z-\frac{1}{2}$], which are comparable to a recently reported distance in related species [C···O = 3.075 (5) Å; Steiner, 2001] and very close to the smallest bent angle (110°) proposed by Desiraju (1996). There is also a hydrogen-bonding interaction between the perchlorate counter-ions and the adjacent ClpyOH ligands [C···O = 3.438 (4)–3.466 (5) Å and C—H···O = 154–167°], which is comparable to that reported in a related compound (Tong *et al.*, 1999).

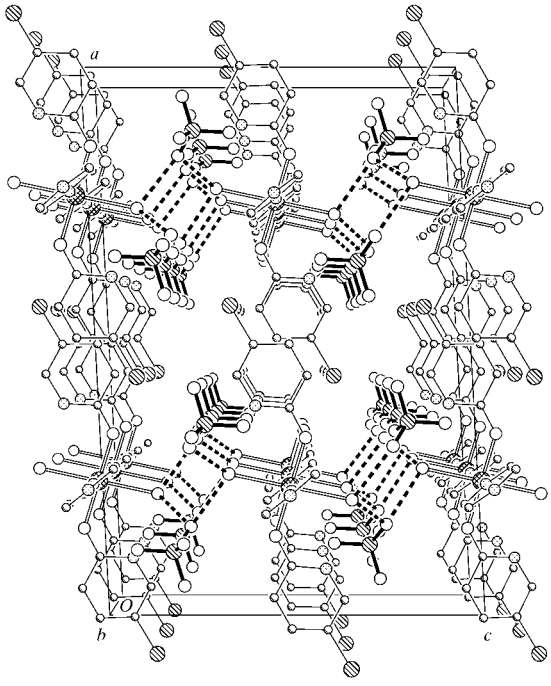

Figure 3
Perspective view of the molecular packing of (I) viewed along the *b* axis.

Experimental

To a solution of copper perchlorate in a 1:1 (*v*/*v*) aqueous methanol mixture was added an appropriate stoichiometric amount of 5-chloro-2-hydroxypyridine, also dissolved in methanol. The mixture was stirred to dissolve the reagents and then a methanol solution of pyrazine was added. Large deep-blue crystals separated from the solution after it was set aside for several days to crystallize, and the product was isolated in 90% yield.

Crystal data

$[Cu(C_5H_4ClNO)_2(C_4H_4N_2)(H_2O)_2](ClO_4)_2$
$M_r = 637.65$
Monoclinic, $C2/c$
$a = 22.247$ (8) Å
$b = 6.888$ (2) Å
$c = 15.211$ (4) Å
$\beta = 93.07$ (1)°
$V = 2328$ (1) Å^3
$Z = 4$
$D_x = 1.820$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 7$–15°
$\mu = 1.47$ mm^{-1}
$T = 298$ (2) K
Block, blue
0.46 × 0.42 × 0.36 mm

Data collection

Siemens *R*3*m* four-circle diffractometer
ω scans
Absorption correction: empirical *via* ψ scan (North *et al.*, 1968)
$T_{min} = 0.515$, $T_{max} = 0.590$
3006 measured reflections
2941 independent reflections
2251 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 29.0°$
$h = 0 \rightarrow 27$
$k = 0 \rightarrow 9$
$l = -20 \rightarrow 20$
2 standard reflections
every 150 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.122$
$S = 1.02$
2941 reflections
172 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2 + 3.7085P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.76$ e Å^{-3}

Table 1
Selected interatomic distances (Å).

Cu1—O1	1.967 (2)	Cu1—O1*W*	2.387 (2)
Cu1—N2	2.053 (2)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*1···O2	0.85 (3)	1.97 (3)	2.816 (4)	172 (3)
O1*W*—H1*W*2···O2^{i}	0.84 (3)	2.06 (3)	2.895 (4)	172 (4)
N1—H1N1···O1*W*	0.85 (1)	2.10 (3)	2.826 (3)	144 (4)

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

The water and pyridinium H atoms were located and refined subject to O—H/N—H distance restraints of 0.85±0.01 Å. The remaining H atoms were refined as riding (C—H = 0.93 Å).

Data collection: *R*3*m Software* (Siemens, 1990); cell refinement: *R*3*m Software*; data reduction: *R*3*m Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1367). Services for accessing these data are described at the back of the journal.

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