Bisquinolinium tetrachlorocuprate dihydrate

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Key indicators

The asymmetric unit of the title compound, $2C_9H_8N^+ \cdot CuCl_4^{2-} \cdot 2H_2O$, comprises one quinolinium cation, one water molecule and one-half of the $CuCl_4^{2-}$ anion with the other half generated by crystallographic twofold symmetry. The water molecules are linked to the anions through O—H$\cdots$Cl hydrogen bonds to form two-dimensional molecular networks parallel to (110). The cations are arranged between two networks in parallel stacks. The N—H$\cdots$O, C—H$\cdots$O and C—H$\cdots$Cl intermolecular hydrogen bonds link the cations and the anion networks to form a three-dimensional network.

Comment

Crystals of the title compound, (I), were obtained after several days from the cooled reaction solution following the heating of $CuCl_2$ and *E*-2-acetylbenzene-8-quinonylhydrazone in dilute HCl. We are currently studying the derivatives of both quinonylhydrazones (Lynch & McClenaghan, 2001*a*) and pyrrolo[3,2-*h*]quinolines (Lynch & McClenaghan, 2001*b*), and it was our intention to prepare the copper(II) complex of *E*-2-acetylbenzene-8-quinonylhydrazone before proceeding with the Cu complex of the corresponding pyrrolo[3,2-*h*]quinoline. However, the acidic conditions used to solublize the hydrazone were also sufficient to hydrolyse this compound back to the quinonylhydrazine, and then the presence of Cu^{2+} and air oxidized the hydrazine to quinoline itself; the latter process was reported by Timmons (1970).

(I)
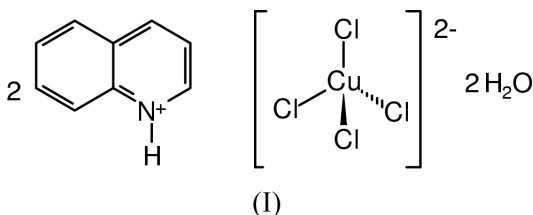
The asymmetric unit of (I) consists of one quinolinium cation, one water molecule and one half of the $CuCl_4^{2-}$ anion (the other half is generated by crystallographic twofold symmetry). The Cu atom in the distorted tetrahedral anion (Table 1) lies on a twofold axis and the two independent Cl atoms are both disordered over two sites with main site occupancies of 80%. The anions and the water molecules form two-dimensional hydrogen-bonding networks parallel to (110), in which one of the water H atoms, H1W, is involved in three-centered hydrogen bonds with Cl1 and Cl2 atoms (Table 2). The cations are arranged between two anion-water networks in parallel stacks with their centroids alternately
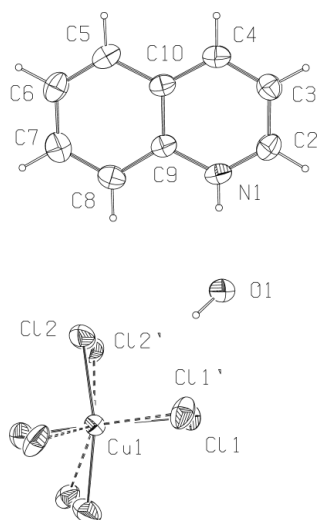
Figure 1
Molecular configuration and atom-numbering scheme for the title compound, showing 50% probability ellipsoids. One of the two H atoms attached to the water O atom is hidden.

separated by 3.685 (3) and 4.057 (3) Å (Fig. 2). The cations are linked to the anion–water networks through N—H⋯O, C—H⋯O and C—H⋯Cl intermolecular hydrogen bonds (Table 2), to form a three-dimensional molecular network. A previously reported structure, similar to (I), is bis[cinchonium tetrachlorocuprate(II)] trihydrate (Dyrek *et al.*, 1987).

Experimental

The title compound was obtained from Key Organics Ltd and crystals were grown from dilute HCl solution.

Crystal data

$2C_9H_8N^+ \cdot Cl_4Cu^{2-} \cdot 2H_2O$	$D_x = 1.595$ Mg m^{-3}
$M_r = 501.70$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 5373
$a = 11.815$ (2) Å	reflections
$b = 9.837$ (2) Å	$\theta = 2.9$–$27.5°$
$c = 18.311$ (4) Å	$\mu = 1.57$ mm^{-1}
$\beta = 101.05$ (3)$°$	$T = 150$ (2) K
$V = 2088.7$ (7) Å^3	Plate, yellow
$Z = 4$	$0.38 \times 0.36 \times 0.04$ mm

Data collection

Bruker–Nonius KappaCCD area-detector diffractometer	2330 independent reflections
	2001 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.044$
Absorption correction: multi-scan	$\theta_{max} = 27.5°$
(*SORTAV*; Blessing, 1995)	$h = -14 \rightarrow 15$
$T_{min} = 0.586$, $T_{max} = 0.940$	$k = -11 \rightarrow 12$
7197 measured reflections	$l = -23 \rightarrow 23$

Refinement

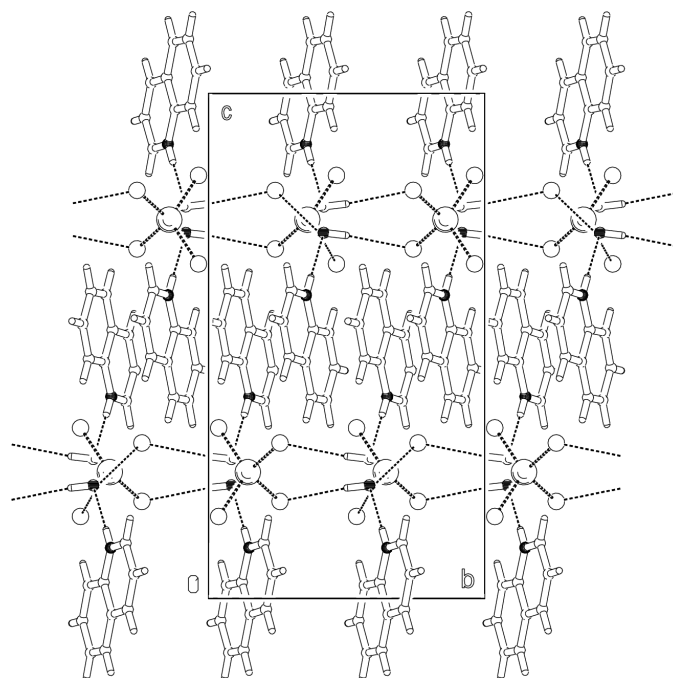|	
Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0588P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.037$	$+ 1.3968P]$
$wR(F^2) = 0.100$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} < 0.001$
2330 reflections	$\Delta\rho_{max} = 0.47$ e Å^{-3}
153 parameters	$\Delta\rho_{min} = -0.62$ e Å^{-3}
H atoms treated by a mixture of independent and constrained refinement	

Figure 2
Packing diagram viewed down the *a* axis. H-bonding interactions and Cu—Cl bonds are shown as dotted lines.

Table 1
Selected geometric parameters (Å).

Cl1—Cu1—Cl2	100.45 (6)	Cl2—Cu1—Cl2^i	124.11 (7)
Cl2—Cu1—Cl1^i	107.12 (5)	Cl1—Cu1—Cl1^i	118.98 (8)

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

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1⋯O1W	0.79 (3)	1.94 (3)	2.727 (3)	179 (3)
O1W—H1W⋯Cl1	0.86 (4)	2.77 (4)	3.474 (3)	140 (3)
O1W—H2W⋯Cl1^i	0.80 (5)	2.43 (5)	3.234 (5)	175 (4)
O1W—H1W⋯Cl2	0.86 (4)	2.60 (4)	3.311 (2)	141 (3)
C2—H2⋯O1W^{ii}	0.95	2.51	3.274 (3)	137
C4—H4⋯Cl1^{iii}	0.95	2.79	3.730 (3)	169
C7—H7⋯Cl2^{iv}	0.95	2.81	3.578 (3)	138
C8—H8⋯Cl2	0.95	2.76	3.660 (3)	158

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

The C-bound H atoms were included in the refinement at calculated positions, as riding models with C—H set to 0.95 Å. All other H atoms involved in the H-bonding network were located from a difference map and both positional and isotropic displacement parameters were refined. The Cu—Cl bond lengths for the two minor Cl atom sites were restrained to be the same as for their corresponding major sites.

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Hooft, 1998); cell refinement: *DENZO* and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLUTON*94 (Spek, 1994) and *PLATON*97 (Spek, 1997); software used to prepare material for publication: *SHELXL*97.

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