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π–π Stacking in bis(quinolinium) tetrachlorozincate dihydrate

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The asymmetric unit of the title compound, $(C_9H_8N)_2[ZnCl_4]\cdot 2H_2O$, consists of one quinolinium cation, one-half of the $[ZnCl_4]^{2-}$ anion and one water molecule. The geometry around the Zn atom is approximately tetrahedral, with the Zn atom lying on a twofold axis. The water molecules hydrogen bond to the $[ZnCl_4]^{2-}$ anions and the quinolinium cations, forming a two-dimensional network with the cations protruding on both sides of the network and stacking through π–π interactions with adjacent networks.

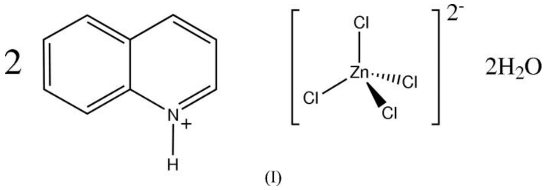
Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.004 Å
R factor = 0.049
wR factor = 0.087
Data-to-parameter ratio = 23.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

There is current interest in the supramolecular chemistry of halometallates (Angeloni *et al.*, 2004). Especially relevant are the results of Orpen (Orpen & Quayle, 2001), who have proved that the charge-assisted $N-H\cdots MX_2$ synthon observed in perhalometallate salts with organic cations is responsible for the recurring extended motifs observed, for example, with 4–4′-bipyridine.



(I)

During our studies of the predictability of π–π interactions in inorganic–organic hybrid materials using perhalometalates and nitrogen-containing aromatic organic salts, the title compound, (I), was obtained.

The asymmetric unit of (I) comprises one quinolinium cation, one water molecule and one-half of the $[ZnCl_4]^{2-}$ anion (Fig. 1). The geometry around the Zn atom is approximately tetrahedral (Table 1), with the Zn atom lying on a twofold axis. The water molecules hydrogen bond to the

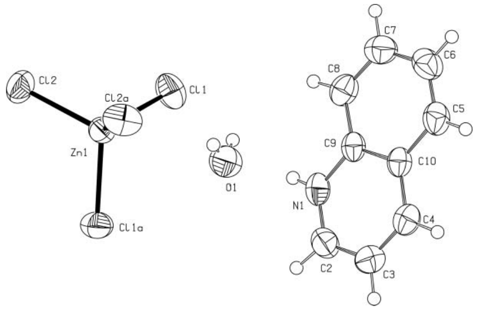


Figure 1
A drawing of the structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The suffix a corresponds to symmetry code (i) in Table 1.

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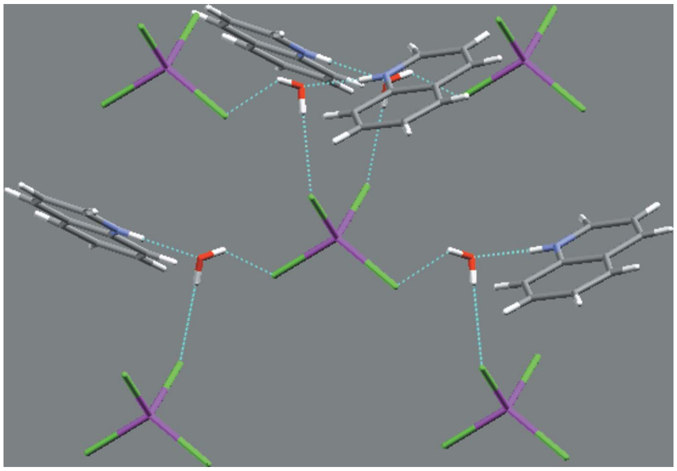

Figure 2
The hydrogen bonding (dashed lines) of water molecules, *viz*. N—H···O with quinolinium cations and O—H···Cl—Zn with $[ZnCl_4]^{2-}$ anions.

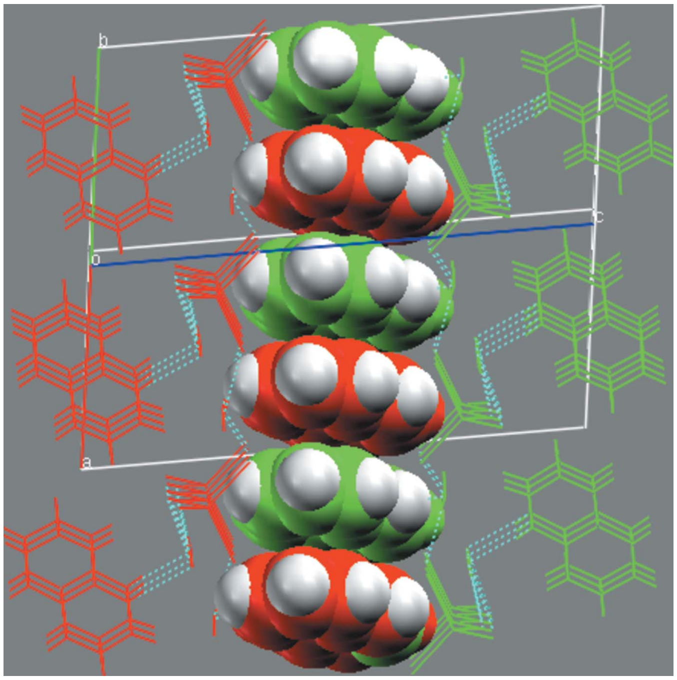

Figure 3
The molecular packing of (I), showing the π–π stacking between adjacent two-dimensional networks.

$[ZnCl_4]^{2-}$ anions and the quinolinium cations (Fig. 2 and Table 2). The $[ZnCl_4]^{2-}$ anions and the water molecules form a two-dimensional network, parallel to (001), with the hydrogen-bonded cations protruding on both sides of the network. Adjacent two-dimensional networks interpenetrate each other, and pack through π–π stacking interactions between the quinolinium cations (Fig. 3) (distance between centroids = 4.06 Å; perpendicular distance = 3.41 Å).

In contrast to what is observed in bisquinolinium tetrachlorocadmate(II) (Paulus & Gottlicher, 1969), in (I), as well as in bis(quinolinium) tetratrachlorocuprate (Lynch & McClenaghan, 2002), the charge-assisted $MX_2\cdots H—N$ interaction is not observed due to the interference of a water molecule. Nevertheless the expected π–π interactions are observed and act, in the three structures, as an important and predictable structural organizing tool.

Experimental

Commercially available starting materials were used without further purification. Quinoline (248 mg, 2.00 mmol) was dissolved in 10 ml of an EtOH/HCl solution (9:1 *v*/*v*) and added to a solution of $ZnCl_2$ (1.00 mmol, 136 mg) dissolved in 10 ml of the same EtOH/HCl solution. The mixture was heated under reflux and stirred for 15 min. The light-orange solution obtained was left undisturbed until colorless crystals formed (yield: 423 mg, 84%; decomposition 448 K).

Crystal data

$(C_9H_8N)_2[ZnCl_4]\cdot 2H_2O$
$M_r = 503.53$
Monoclinic, $C2/c$
$a = 11.7991\ (9)$ Å
$b = 10.0206\ (8)$ Å
$c = 18.423\ (1)$ Å
$\beta = 101.352\ (2)^\circ$
$V = 2135.6\ (3)$ Å^3
$Z = 4$
$D_x = 1.566$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4637 reflections
$\theta = 2.7$–30.8°
$\mu = 1.67$ mm^{-1}
$T = 294\ (2)$ K
Prism, colorless
0.20 × 0.19 × 0.17 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: analytical (*SHELXTL/PC*; Sheldrick, 1997)
$T_{min} = 0.664$, $T_{max} = 0.820$
14529 measured reflections
3867 independent reflections
2469 reflections with $I > 2\sigma(I)$
$R_{int} = 0.064$
$\theta_{max} = 32.6^\circ$
$h = -17 \rightarrow 17$
$k = -15 \rightarrow 14$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.087$
$S = 1.01$
3867 reflections
163 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0233P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.81$ e Å^{-3}
$\Delta\rho_{min} = -0.35$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zn1—Cl2	2.2425 (6)	Zn1—Cl1	2.2728 (6)
Cl2—Zn1—Cl2^i	112.34 (4)	Cl2—Zn1—Cl1	106.33 (2)
Cl2—Zn1—Cl1^i	111.08 (2)	Cl1^i—Zn1—Cl1	109.71 (4)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1	0.77 (2)	1.98 (2)	2.747 (3)	171 (2)
O1—H1B···Cl2^{ii}	0.78 (4)	2.65 (4)	3.288 (2)	140 (3)
O1—H1A···Cl1	0.72 (4)	2.46 (4)	3.181 (3)	178 (4)

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

H atoms were located in a difference map and refined freely [O—H = 0.72 (4)–0.78 (4) Å, N—H = 0.77 (2) Å and C—H 0.84 (2)–0.97 (2) Å].

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999; data reduction: *SAINT-Plus*; program(s) used to

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solve structure: *SHELXTL/PC* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL/PC*; molecular graphics: *MERCURY* (Bruno *et al.*, 2002) and *PLATON* (Spek, 2003); software used to prepare material for publication: *enCIFer* (Allen *et al.*, 2004).

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