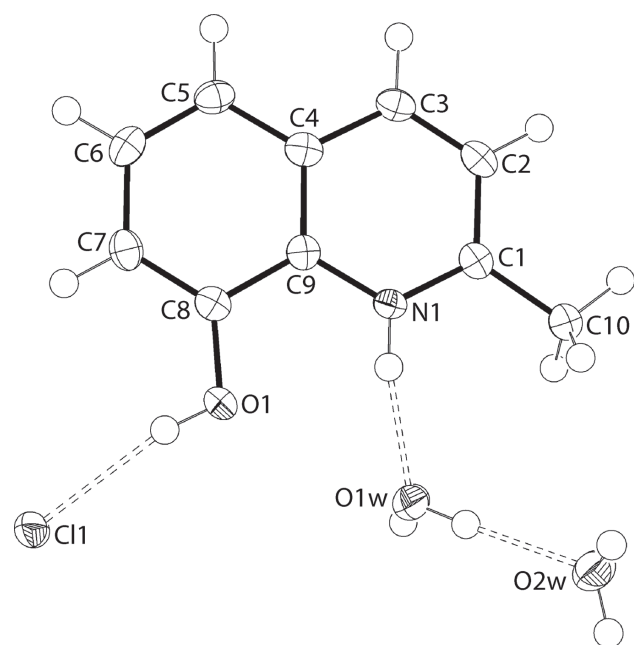


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Crystal structure of 8-hydroxy-2-methylquinolin-1-ium chloride dihydrate, $C_{10}H_{14}ClNO_3$



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Abstract

$C_{10}H_{14}ClNO_3$, monoclinic, $P2_1/c$ (no. 14), $a = 7.2706(2)$ Å, $b = 14.8440(5)$ Å, $c = 10.3910(3)$ Å, $\beta = 101.101(2)^\circ$, $V = 1100.46(6)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0268$, $wR_{ref}(F^2) = 0.0735$, $T = 100(2)$ K.

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The components of the asymmetric unit are shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

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Table 1: Data collection and handling.

Crystal:	Colourless block
Size:	0.09 × 0.08 × 0.05 mm
Wavelength:	Cu $K\alpha$ radiation (1.54184 Å)
μ :	2.99 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{max} , completeness:	67.0°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	13457, 1970, 0.034
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1815
$N(param)_{refined}$:	155
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U_{iso}^*/U_{eq}
Cl1	0.76794(4)	0.62873(2)	0.96240(3)	0.01854(12)
O1	0.46747(13)	0.62090(6)	0.71185(9)	0.0177(2)
H1O	0.5471(19)	0.6150(11)	0.7807(12)	0.027*
N1	0.25489(14)	0.62173(7)	0.47005(10)	0.0129(2)
H1N	0.3100(19)	0.6710(8)	0.5046(14)	0.015*
C1	0.14860(17)	0.62794(8)	0.35021(12)	0.0142(3)
C2	0.07143(17)	0.54896(9)	0.28740(12)	0.0161(3)
H2	-0.0061	0.5525	0.2028	0.019*
C3	0.10693(16)	0.46717(9)	0.34693(12)	0.0154(3)
H3	0.0559	0.4142	0.3025	0.018*
C4	0.21923(16)	0.46033(8)	0.47446(11)	0.0143(3)
C5	0.25945(17)	0.37800(9)	0.54184(12)	0.0165(3)
H5	0.2129	0.3230	0.5015	0.020*
C6	0.36630(17)	0.37799(9)	0.66600(12)	0.0173(3)
H6	0.3925	0.3226	0.7115	0.021*
C7	0.43780(17)	0.45876(9)	0.72709(12)	0.0165(3)
H7	0.5104	0.4571	0.8135	0.020*
C8	0.40398(16)	0.53999(9)	0.66349(11)	0.0141(3)
C9	0.29232(16)	0.54120(8)	0.53515(11)	0.0132(3)
C10	0.11424(18)	0.71830(9)	0.28760(12)	0.0191(3)
H10A	0.0477	0.7564	0.3406	0.029*
H10B	0.0381	0.7116	0.1994	0.029*
H10C	0.2343	0.7463	0.2816	0.029*
O1W	0.40536(13)	0.78536(6)	0.54775(9)	0.0195(2)
H1W	0.5107(15)	0.7959(11)	0.5272(16)	0.029*
H2W	0.3383(19)	0.8292(9)	0.5194(16)	0.029*
O2W	0.18351(13)	0.92449(7)	0.44925(10)	0.0237(2)
H3W	0.0733(16)	0.9126(12)	0.4609(17)	0.035*
H4W	0.206(2)	0.9782(7)	0.4747(17)	0.035*

Source of material

All chemicals and solvents were used as purchased without further purification. The melting point was determined using a Mel-temp II digital melting point apparatus and was uncorrected. The solid-state IR spectrum was obtained on a Bruker Vertex 70v FTIR Spectrometer from 4000 to 400 cm⁻¹.

Dibenzyltin dichloride was synthesized by the direct reaction of benzylchloride (Merck) and metallic tin powder (Merck) in toluene according to a literature procedure [5]. Dibenzyltin dichloride (0.37 g, 1 mmol) and 8-hydroxyquinoline (Sigma Aldrich, 0.16 g, 1 mmol) were dissolved in methanol (20 mL) and the mixture was refluxed for 2 h. The filtrate was evaporated until a white precipitate was obtained. The precipitate was washed with *n*-hexane and recrystallized from a methanol solution. The title compound was isolated as a side-product obtained from the slow evaporation of the solvent. Yield: 0.05 g (21.6%). *M*.pt: 494–495 K. IR (cm⁻¹): 1576 (*m*) ν(C–C), 1497 (*s*) ν(C–N), 1107 (*s*) ν(C–O).

Experimental details

The C-bound H atoms were geometrically placed (C–H = 0.95–0.98 Å) and refined as riding with $U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$. The O- and N-bound H-atoms were located in a difference Fourier map but were refined with distance restraints of O–H = 0.84 ± 0.01 Å and N–H = 0.88 ± 0.01 Å, respectively, and with $U_{\text{iso}}(\text{H})$ set to 1.5 $U_{\text{eq}}(\text{O})$ and 1.2 $U_{\text{eq}}(\text{N})$, respectively.

Comment

The crystal structure of water-free 8-hydroxy-2-methylquinolinium chloride has been determined previously [6] as have its dihydrogen phosphate salt, isolated as a monohydrate [7], and 2-chloro-5-nitro-benzoate salt, as a dihydrate [8]. Further, there are examples of the monocation being the counterion to metal complex anions [9]. During the course of studies on the synthesis of dibenzyltin Schiff base compounds [10], see Source of Material, crystals of 8-hydroxy-2-methylquinolinium chloride became available as a dihydrate, (I).

The crystallographic asymmetric unit of (I) comprises an 8-hydroxy-2-methylquinolinium cation, a chloride anion and two water molecules as shown in the figure (70% displacement ellipsoids). As expected, the 10 atoms comprising the fused-ring system are co-planar, exhibiting a r.m.s. deviation of 0.013 Å. The planarity extends to the hydroxyl-O1 and methyl-C10 atoms, which lie 0.008(1) Å above and below the plane, respectively.

Significant hydrogen bonding is found in the crystal of (I). As indicated in the figure, there are charge-assisted

hydroxy-O–H···Cl [O1–H1o···Cl1: H1o···Cl1 = 2.240(13) Å, O1o···Cl1 = 3.0617(10) Å with angle at H1o = 168.6(15)°] and pyridinium-N–H···O(water) [N1–H1n···O1w: H1n···O1w = 1.856(12) Å, N1···O1w = 2.7218(14) Å with angle at H1n = 169.1(13)°] hydrogen bonds as well as a water-O–H···O(water) [O1w–H2w···O2w: O1w–H2w···O2w = 1.866(14) Å, O1w–H2w···O2w = 2.6979(14) Å with angle at H2w = 177.5(17)°] hydrogen bonds providing direct links between the components of the asymmetric unit. The remaining water-O–H atoms form charge-assisted hydrogen bonds to the Cl1 atom [O1w–H1w···Cl1ⁱ: H1w···Cl1ⁱ = 2.385(13) Å, O1w···Cl1ⁱ = 3.2035(10) Å with angle at H1w = 162.3(15)°, O2w–H3w···Cl1ⁱⁱ: H3w···Cl1ⁱⁱ = 2.306(13) Å, O2w···Cl1ⁱⁱ = 3.1513(10) Å with angle at H3w = 171.7(17)° and O2w–H4w···Cl1ⁱⁱⁱ: H4w···Cl1ⁱⁱⁱ = 2.326(11) Å, O2w···Cl1ⁱⁱⁱ = 3.1677(11) Å with angle at H4w = 173.6(14)° for symmetry operations (i) $x, 3/2 - y, -1/2 + z$, (ii) $-1 + x, 3/2 - y, -1/2 + z$ and (iii) $1 - x, 1/2 + y, 3/2 - z$. This pattern of hydrogen bonding gives rise to a three-dimensional framework. Globally, the cations stack in columns parallel to the *a* axis with alternating pyridinium and C₆ rings being almost superimposable, enabling the formation of π···π stacking interactions [Cg(N1,C1–C4,C9)···Cg(C4–C9)]^{iv} = 3.7016(7) Å with angle of inclination = 1.08(6)° for (iv) $1 - x, 1 - y, 1 - z$ to further consolidate the packing.

A further analysis of the packing was made by calculating the Hirshfeld surfaces (including the full and delineated two-dimensional fingerprint plots) using Crystal Explorer 17 [11] and literature procedures [12]. The major contribution to the contacts of the overall asymmetric unit is from H···H, accounting for nearly half of all contacts, at 48.9%. Significant contacts also include Cl···H/H···Cl [18.9%], O···H/H···O [9.8%] C···H/H···C [9.0%] and C···C [8.6%], accounting for the bulk of the remaining contacts. An analysis was also performed for the individual water molecules as such calculations are useful in distinguishing between comparable molecules in a crystallographic asymmetric unit [13]. Indeed, significant differences are apparent in the percentage contributions to the individual surfaces of the water molecules reflecting the different hydrogen bonds formed by them. Thus, the major contributions to the Hirshfeld surface for the O1w-water molecule are H···H [50.3%], O···H/H···O [39.0%] and Cl···H/H···Cl [8.3%]. This compares with H···H [54.9%], O···H/H···O [28.4%] and Cl···H/H···Cl [14.0%] for the O2w-molecule. A comparison of the contacts formed by the two molecules shows decreased and increased contributions from O···H/H···O and Cl···H/H···Cl contacts, respectively, reflecting the formation of half the number of O–H···Cl hydrogen bonds for the O1w-water molecule compared with the O2w-water molecule.

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