

Formation of ladders from $R_4^4(8)$ and $R_6^6(12)$ rings in 8-hydroxyquinolinium chloride monohydrate: comparisons with the supramolecular arrangements in related salts

Janet M. S. Skakle,^{a*} James L. Wardell^b and Solange M. S. V. Wardell^c

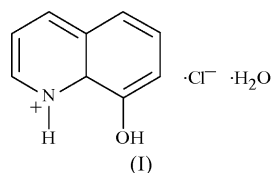
^aDepartment of Chemistry, College of Physical Sciences, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland, ^bDepartamento de Química Inorgânica, Instituto de Química, Universidade Federal do Rio de Janeiro, 21945-970 Rio de Janeiro, RJ, Brazil, and ^cFundação Oswaldo Cruz, Instituto de Tecnologia em Fármacos, Departamento de Síntese Orgânica, Manguinhos, CEP 21041250 Rio de Janeiro, RJ, Brazil
Correspondence e-mail: j.skakle@abdn.ac.uk

Received 3 April 2006
Accepted 13 April 2006
Online 16 May 2006

Molecules of the title compound, $C_9H_8NO^+ \cdot Cl^- \cdot H_2O$, are linked into two rings by strong hydrogen bonding *via* the free water molecules and the Cl^- anions. The two hydrogen-bonded rings are joined to give a corrugated chain along [001]. Comparisons with other 8-hydroxyquinoline-based salts are also presented, highlighting similar ring structures in a 1:1 salt with Kemp's triacid (*r*-1,*c*-3,*c*-5-trimethylcyclohexane-1,3,5-tricarboxylic acid) and in 8-hydroxy-1-methylquinolinium chloride monohydrate.

Comment

In a continuation of our interest in the supermolecular arrangements of organic molecules, we now report the crystal structure of hydrated 8-hydroxyquinolinium chloride, 8-HOQH⁺·Cl⁻. The title compound, (I), was isolated from a reaction mixture consisting of 2-chloronicotinoyl chloride and 8-hydroxyquinoline, 8-HOQ, in acetone, followed by recrystallization of the reaction residues from ethanol. Clearly, the water present in the solvent(s) had led to hydrolysis of the acyl chloride with formation of hydrogen chloride, which then formed the salt with 8-hydroxyquinoline.



Compound (I) crystallizes in the space group $P\bar{1}$ and, for convenience, the reference positions of the free Cl atoms and water molecules were chosen to give the most direct

hydrogen-bonding scheme (Fig. 1 and Table 1). The hydrogen bonding was analysed with the aid of *PLATON* (Spek, 2003).

The 8-HOQ molecule is protonated at the N atom (8-HOQH⁺) and is very nearly planar; the angle between the fused rings is $0.32(6)^\circ$ and the Cremer & Pople (1975) total puckering amplitude, Q , is $0.0247(17) \text{ \AA}$.

The intramolecular N⁺—H···O hydrogen bond in 8-HOQH⁺ has been observed in other 8-hydroxyquinolinium and related cations. In 7-iodo-8-hydroxyquinoline-5-sulfonic acid (Balasubramanian & Muthiah, 1996) and in an 8-hydroxyquinolinium salicylate–salicylic acid complex, 8-HOQH⁺·C₇H₅O₃⁻·C₇H₆O₃ (Jebamony & Thomas Muthiah, 1998), this hydrogen bond was observed to result in an enhancement of the internal angle at the nitrogen centre. This interaction has also been highlighted in the crystal structures of 8-hydroxyquinoline-5-sulfonic acid dihydrate (Banerjee *et al.*, 1984), 8-hydroxy-7-nitroquinoline-5-sulfonic acid monohydrate (Balasubramanian & Thomas Muthiah, 1996) and 8-hydroxyquinolinium 3-carboxy-4-hydroxybenzenesulfonate monohydrate, 8-HOQH⁺·C₇H₅O₆S⁻·H₂O (Smith *et al.*, 2004).

The solvent water molecules and free chloride ions lead to a number of intra- and intermolecular hydrogen bonds (Table 1).

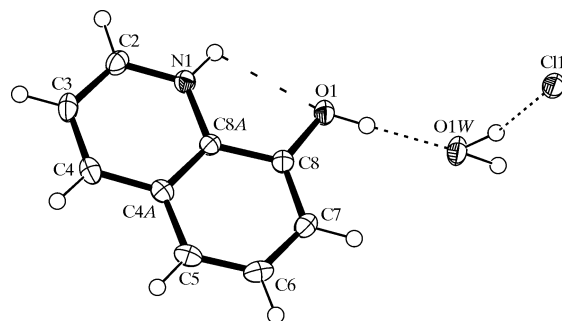


Figure 1
The molecule of the title compound, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as circles of arbitrary radii and hydrogen bonds are shown as broken lines.

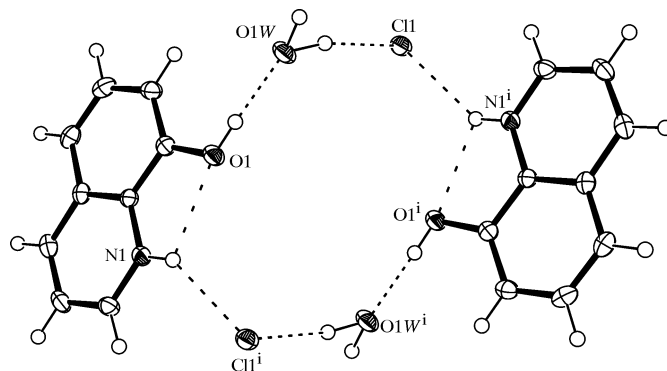


Figure 2
Part of the crystal structure of the title compound, showing the formation of an $R_6^6(12)$ ring. Displacement ellipsoids are shown at the 50% probability level, H atoms are shown as circles of arbitrary radii and dashed lines indicate hydrogen bonds. [Symmetry code: (i) $-x + 1, -y, -z$.]

Taking these entities alone first, the water molecule at (x, y, z) participates in $O1W-H1WA \cdots Cl1$ and $O1W-H1WB \cdots Cl1^{ii}$ hydrogen bonds [symmetry code: (ii) $-x + 1, -y, -z - 1$], forming small $R_4^4(8)$ rings (Bernstein *et al.*, 1995). This type of interaction is identical to that observed in 8-hydroxy-1-methylquinolinium chloride monohydrate (Rømming & Uggerud, 1983) and the isostructural iodide (Barczyński *et al.*, 2006), both of which also crystallize in $P\bar{1}$. In these latter structures, however, the methyl substitution at the N atom hinders further strong hydrogen-bonding interactions, and thus this centrosymmetric $R_4^4(8)$ dimer is the only motif observed.

In (I), another ring forms from a combination of hydrogen bonds [$O1-H1A \cdots O1W$, $O1W-H1WA \cdots Cl1$, $N1-H1 \cdots Cl1^i$ and $N1-H1 \cdots O1$; symmetry code: (i) $-x + 1, -y, -z$].

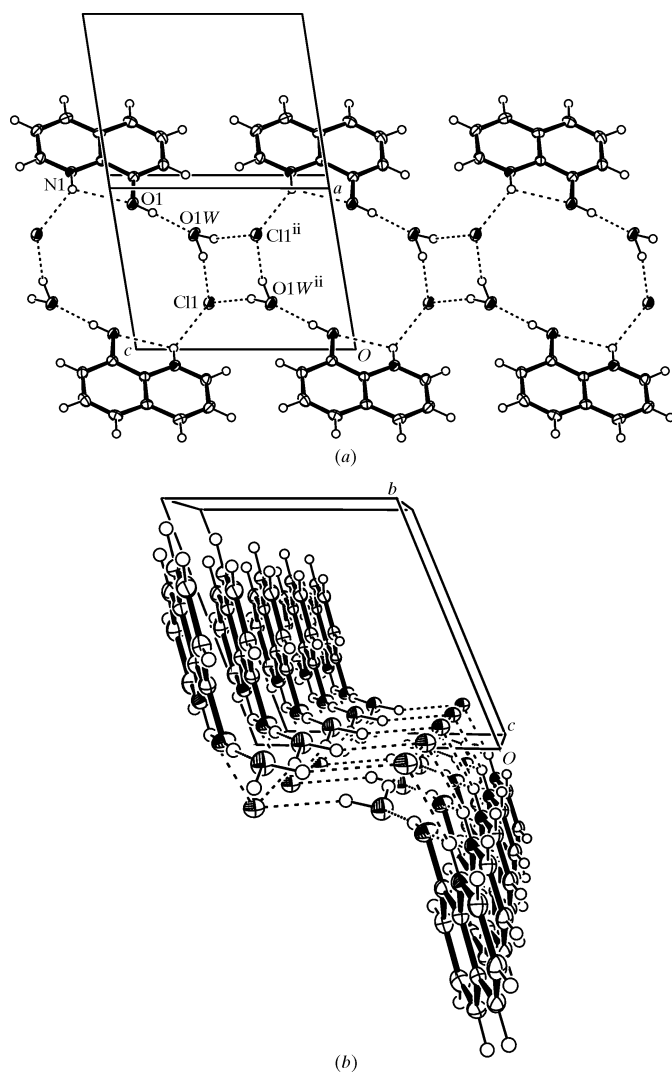


Figure 3 Part of the crystal structure of the title compound, showing (a) the formation of 'ladders' and (b) the relative conformation of the molecules in the 'ladder' formed from the two hydrogen-bonded rings. Displacement ellipsoids are shown at the 50% probability level, H atoms are shown as circles of arbitrary radii and dashed lines indicate hydrogen bonds. [Symmetry code: (ii) $-x + 1, -y, -z - 1$.]

Together, these form an $R_6^6(12)$ dimeric ring centred at $(\frac{1}{2}, 0, 0)$ (Fig. 2).

The two rings join to form a polymeric ladder along [001] (Fig. 3a); viewed in the orientation shown in Fig. 3(a), the ladder appears flat, but viewed along the direction of the ladder, it can be seen that the molecules hydrogen bond in a chair-like configuration (Fig. 3b). The interactions forming this ladder are similar to those observed in the structure of $8-HOQH^+ \cdot KTA^-$ (KTA is Kemp's triacid, *r*-1,*c*-3,*c*-5-trimethylcyclohexane-1,3,5-tricarboxylic acid), in which a polymeric chain forms *via* the carboxylate groups of KTA and the hydroxy and N^+H groups of $8-HOQH^+$, leading to similar dimeric $R_6^6(12)$ rings which then form chains *via* the symmetric KTA molecule (Smith *et al.*, 2000). The presence of the intramolecular $N^+-H \cdots O$ hydrogen bond in $8-HOQH^+$ was not shown in the cited work, but the effect of this intramolecular bond is to provide a 'short-cut' in the ring by providing an extra hydrogen bond, shortening the ring from $R_4^4(18)$ to $R_6^6(12)$.

There is also similarity with $8-HOQH^+ \cdot C_7H_5O_6S^- \cdot H_2O$ (Smith *et al.*, 2004), in that the hydroxy group of the $8-HOQH^+$ ion acts as a donor to the free water molecule. In this case, the water molecule then goes on to act as a donor to O atoms from the sulfonate group, as does the carboxylate group, forming a three-dimensional network.

The hydrogen-bonding scheme in $8-HOQH^+$ salicylate-salicylic acid, $8-HOQH^+ \cdot C_7H_5O_3^- \cdot C_7H_6O_3$, was described in terms of the interactions present but not in terms of the symmetry of these interactions (Jebamony & Thomas Muthiah, 1998). Two of the hydrogen bonds described are between molecules in the same asymmetric unit and do not lead to any continuity of the structure. The other three intermolecular interactions described occur between molecules at (x, y, z) and $(-x + 1, -y + 1, -z + 1)$, forming an isolated dimer. Thus, no chain or network structure is formed in this compound.

The crystal structure of $8-HOQ$ 2,4,5-trichlorophenol (Singh *et al.*, 2001) shows an interesting phenomenon. The asymmetric unit consists of two molecules of 2,4,5-trichlorophenol and two of $8-HOQ$. In one of these latter molecules, the H atom is located at the hetero-N atom, whereas in the other it is at the hydroxy group; thus, neither molecule is protonated as in the present study. The intramolecular $N-H \cdots O$ bond in the $8-HOQ$ molecule is still observed; hydrogen-bonded chains are supported by a number of intramolecular hydrogen bonds involving both forms of the $8-HOQ$ molecule, with the unprotonated N and O atoms acting as acceptors.

Experimental

A solution of equimolar (2.0 mmol) 2-chloronicotinoyl chloride and 8-hydroxyquinoline in acetone (30 ml) was refluxed for 20 min; all volatiles were removed under vacuum and the residue was taken up in EtOH. Crystals of the title compound were deposited slowly. IR: 3500–2200 (KBr, with spike at 3327), 1631, 1602, 1552, 1500, 1472, 1398, 1300, 1268, 1220, 1205, 1098, 1059, 999, 661, 821, 756, 711, 523, 578, 540, 488, 412 cm^{-1} .

Crystal data

$C_9H_8NO^+ \cdot Cl^- \cdot H_2O$
 $M_r = 199.63$
 Triclinic, $P\bar{1}$
 $a = 7.2865$ (3) Å
 $b = 8.2885$ (4) Å
 $c = 8.4596$ (3) Å
 $\alpha = 78.328$ (2)°
 $\beta = 86.105$ (2)°
 $\gamma = 66.388$ (2)°
 $V = 458.41$ (3) Å³
 $Z = 2$
 $D_x = 1.446$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.38$ mm⁻¹
 $T = 120$ (2) K
 Shard, light orange
 $0.36 \times 0.20 \times 0.14$ mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2003)
 $T_{min} = 0.802$, $T_{max} = 0.928$
 9570 measured reflections
 2098 independent reflections
 1835 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.031$
 $\theta_{max} = 27.5^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.033$
 $wR(F^2) = 0.085$
 $S = 1.14$
 2098 reflections
 131 parameters
 H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 0.18P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} < 0.001$
 $\Delta\rho_{max} = 0.32$ e Å⁻³
 $\Delta\rho_{min} = -0.28$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
O1—H1A...O1W	0.84	1.80	2.6329 (15)	174
N1—H1...O1	0.89 (2)	2.35 (2)	2.7050 (16)	103.7 (15)
N1—H1...Cl1 ⁱ	0.89 (2)	2.37 (2)	3.1048 (13)	140.2 (17)
O1W—H1WA...Cl1 ⁱⁱ	0.82 (2)	2.30 (3)	3.1245 (13)	176 (2)
O1W—H1WB...Cl1	0.79 (2)	2.36 (3)	3.1550 (14)	175 (2)

Symmetry codes: (i) $-x + 1, -y, -z$; (ii) $-x + 1, -y, -z - 1$.

The space groups $P1$ and $P\bar{1}$ were possible; $P\bar{1}$ was selected and confirmed by the structure analysis. All H atoms were located from difference maps, and the parameters of water and NH H atoms were refined freely. All other H atoms were treated as riding, with C—H distances of 0.95 Å, O—H distances of 0.84 Å and $U_{iso}(H)$ values of $1.2U_{eq}(C)$ or $1.5U_{eq}(O)$.

Data collection: COLLECT (Hooft, 1998); cell refinement: DENZO (Otwinowski & Minor, 1997) and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure:

OSCAIL (McArdle, 2003) and SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: OSCAIL and SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

We are indebted to the EPSRC for the use of both the Chemical Database Service at Daresbury, primarily for access to the Cambridge Structural Database (Fletcher *et al.*, 1996), and the X-ray service at the University of Southampton for data collection. We thank CNPq, Brazil, for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3016). Services for accessing these data are described at the back of the journal.

References

Balasubramanian, T. & Muthiah, P. T. (1996). *Acta Cryst.* **C52**, 2072–2073.
 Balasubramanian, T. & Thomas Muthiah, P. (1996). *Acta Cryst.* **C52**, 1017–1019.
 Banerjee, T., Basak, A. K., Mazumdar, S. K. & Chaudhuri, S. (1984). *Acta Cryst.* **C40**, 507–509.
 Barczyński, P., Komasa, A., Ratajczak-Sitarz, M., Katrusiak, A. & Brzezinski, B. (2006). *J. Mol. Struct.* In the press.
 Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
 Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.
 Hooft, R. W. W. (1998). COLLECT. Nonius BV, Delft, The Netherlands.
 Jebamony, J. R. & Thomas Muthiah, P. (1998). *Acta Cryst.* **C54**, 539–540.
 McArdle, P. (2003). OSCAIL for Windows. Version 10. Crystallography Centre, Chemistry Department, NUI Galway, Ireland.
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
 Rømming, C. & Uggerud, E. (1983). *Acta Chem. Scand. Ser. B*, **37**, 791–795.
 Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
 Sheldrick, G. M. (2003). SADABS. Version 2.10. University of Göttingen, Germany.
 Singh, N. B., Srivastava, A. & Fröhlich, R. (2001). *J. Chem. Soc. Perkin Trans. 2*, pp. 838–842.
 Smith, G., Wermuth, U. D. & White, J. M. (2000). *Chem. Commun.* pp. 2349–2350.
 Smith, G., Wermuth, U. D. & White, J. M. (2004). *Acta Cryst.* **C60**, o575–o581.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.