

Proton-transfer compounds of 8-hydroxy-7-iodoquinoline-5-sulfonic acid (ferron) with 4-chloroaniline and 4-bromoaniline

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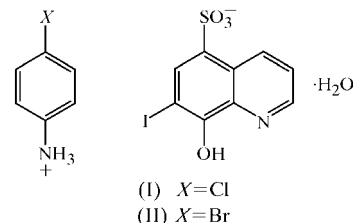
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The crystal structures of the proton-transfer compounds of ferron (8-hydroxy-7-iodoquinoline-5-sulfonic acid) with 4-chloroaniline and 4-bromoaniline, namely 4-chloroanilinium 8-hydroxy-7-iodoquinoline-5-sulfonate monohydrate, $C_6H_7ClN^+ \cdot C_9H_5INO_4S^- \cdot H_2O$, and 4-bromoanilinium 8-hydroxy-7-iodoquinoline-5-sulfonate monohydrate, $C_6H_7BrN^+ \cdot C_9H_5INO_4S^- \cdot H_2O$, have been determined. The compounds are isomorphous and comprise sheets of hydrogen-bonded cations, anions and water molecules which are extended into a three-dimensional framework structure through centrosymmetric $R_2^2(10)$ O—H...N hydrogen-bonded ferron dimer interactions.

Comment

Ferron (8-hydroxy-7-iodoquinoline-5-sulfonic acid) is a bidentate complexing agent which has analytical applications as a selective colour reagent for the detection of iron(III) but not iron(II) (Vogel, 1964). The crystal structure of ferron (Merritt & Duffin, 1970; Balasubramanian & Muthiah, 1996) has shown the molecule to exist as a sulfonate–quinolinium zwitterion. This is also the case in the structure of the 1:1:1 adduct hydrate of ferron with urea (Smith *et al.*, 2004*b*). As a sulfonic acid, ferron is potentially capable of protonating most Lewis bases, but the crystal structures of only a small number of such salts have been reported to date. With 8-hydroxyquinoline a 1:1 sesquihydrate is formed (Smith *et al.*, 2004*a*), while with bifunctional 4,4'-bipyridine a monoprotated 1:1 dihydrate is found (Hemamalini *et al.*, 2004). However, with guanidine carbonate, a dianionic ferron species is found in the hydrated compound $[(gu^+)_2(ferron)^{2-}] \cdot H_2O$ (Smith *et al.*, 2003). Since no compounds of ferron with aniline-type Lewis bases have been reported so far, and considering that anilines are particularly effective in giving stable crystalline salts with aromatic sulfonic acids, *e.g.* the 1:1 compounds of 5-sulfosalicylic acid with aniline (Bakasova *et al.*, 1991) and the 4-*X*-

substituted anilines ($X = F, Cl$ or Br) (Smith *et al.*, 2005), we attempted the preparation of compounds of the same Lewis base set with ferron in 50% ethanol–water solvent. The chemically stable 1:1 monohydrated crystalline title compounds 4-chloroanilinium 8-hydroxy-7-iodoquinoline-5-sulfonate monohydrate, (I), and 4-bromoanilinium 8-hydroxy-7-iodoquinoline-5-sulfonate, (II), were obtained using 4-chloroaniline and 4-bromoaniline, and their crystal structures are reported here. The reaction with 4-fluoroaniline resulted in the previously observed deiodination reaction of ferron, giving 8-hydroxyquinoline-5-sulfonic acid.



The crystal structure determinations of (I) and (II) show the presence of three-dimensional hydrogen-bonded framework structures and confirm that these two compounds are isomorphous, which is consistent with previous observations (Dey & Desiraju, 2004) that, within the structures of both the 4-*X*-substituted anilines and 4-(4-*X*-phenoxy)-substituted anilines ($X = Cl, Br, I$ and ethynyl), with only one exception (4-iodoaniline), all series members are isomorphous. Although the 4-chloro- and 4-bromoanilinium compounds with 5-sulfosalicylic acid are not isomorphous, they are found to be similar structurally (Smith *et al.*, 2005).

In (I) and (II), the anilinium group of the cation and the sulfonate O-atom acceptors of the anion interact head-to-tail and, together with the water molecule, give a cyclic hydrogen-bonded $R_3^3(8)$ (Bernstein *et al.*, 1995) association (the asymmetric unit) (Figs. 1 and 2). Further aminium...sulfonate and water...sulfonate interactions (Tables 1 and 2) form sheets which extend across the *bc* planes in the cell. These sheets are linked across the *a*-cell direction through centrosymmetric $R_2^2(10)$ cyclic hydrogen-bonded ferron...ferron dimer interactions between the 8-hydroxy donor and hetero-N-atom acceptor groups (Figs. 3 and 4). This represents the first

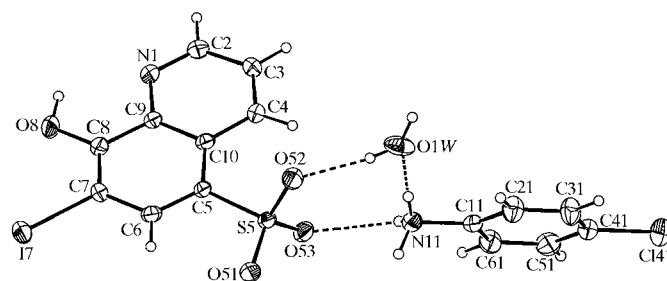


Figure 1

The molecular conformation and atom-numbering scheme for the individual cation, anion and water species in (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Inter-species hydrogen bonding is shown as dashed lines.

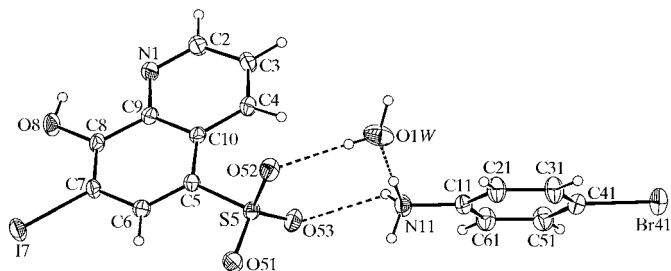


Figure 2
The molecular conformation and atom-numbering scheme for the individual cation, anion and water species in the isomorphous compound (II). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Inter-species hydrogen bonding is shown as dashed lines.

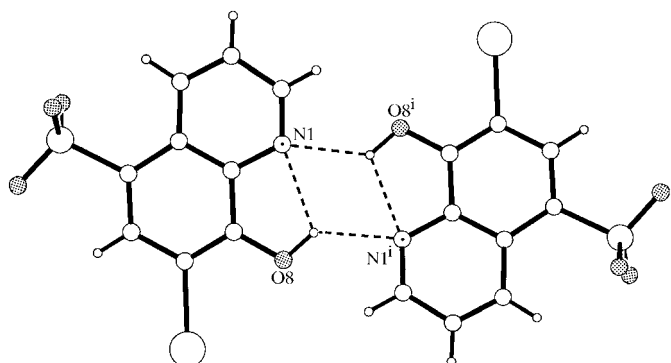


Figure 3
The centrosymmetric hydrogen-bonded (dashed lines) $R_2^2(10)$ ferron dimer found in (I) and (II). [Symmetry code: (i) $-x, -y + 1, -z + 1$].

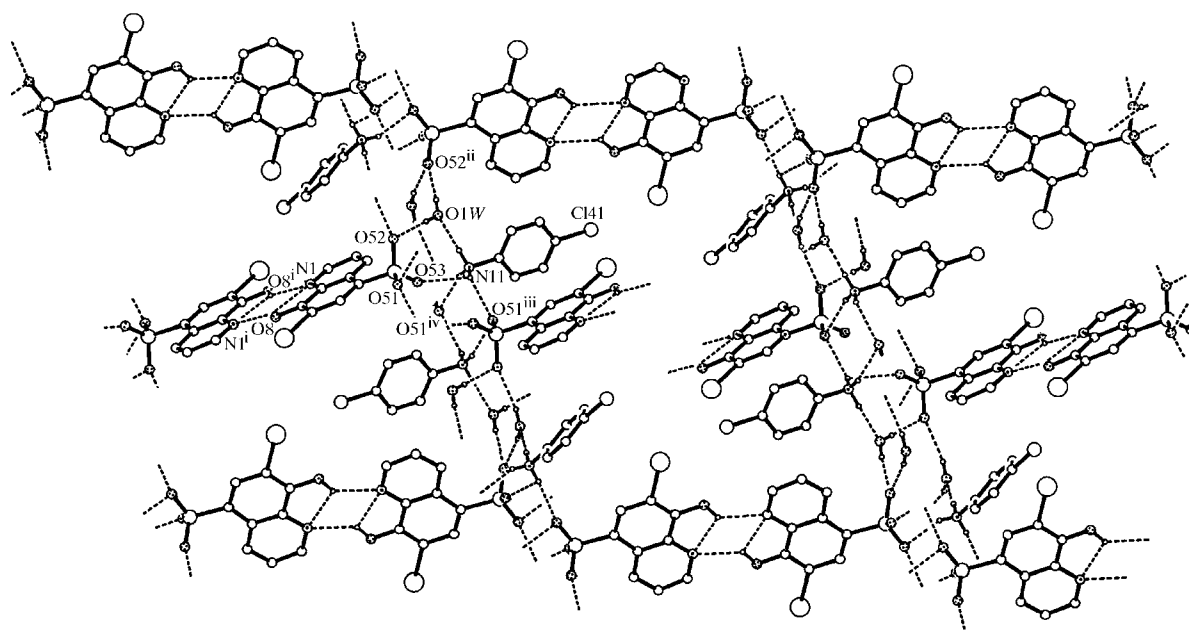


Figure 4
A perspective view of the packing of (I) in the unit cell, viewed down the approximate b -cell direction, showing hydrogen-bonding associations as dashed lines. This packing also represents that found in (II). See Table 1 for symmetry codes.

observed occurrence of this type of association in ferron structures, although a similar type of interaction is known in some of the adduct structures of the parent 8-hydroxyquinoline (oxine) (Hughes & Truter, 1979). It is usually precluded in ferron and its neutral adducts because of the presence of the sulfonate–quinolinium group zwitterion. In (I) and (II), three-dimensional framework structures are formed. Also found in the peripheral structure extension in (I) are $\text{Cl} \cdots \text{Cl}$ contacts [$\text{Cl}41 \cdots \text{Cl}41^v = 3.538(5) \text{ \AA}$; symmetry code: (v) $-x + 1, y, -z + \frac{3}{2}$]. In the isomorphous structure of (II), similar short $\text{Br} \cdots \text{Br}$ contacts [$\text{Br}41 \cdots \text{Br}41^v = 3.612(3) \text{ \AA}$] are also found. Interionic aromatic ferron $\text{C}2\text{--H} \cdots \text{O}8^i$ interactions are also present [$2.977(7) \text{ \AA}$ in (I) and $2.998(6) \text{ \AA}$ in (II); symmetry code: (i) $-x, -y + 1, -z + 1$].

With the ferron anion, the intra-ionic $\text{O}8\text{--H}8 \cdots \text{N}1$ hydrogen bond which is present in other nonzwitterionic compounds of ferron (Hemamalini *et al.*, 2004; Smith *et al.*, 2004b) is also found in both (I) and (II) [$2.714(6)$ and $2.707(5) \text{ \AA}$ in (I) and (II), respectively]. Also, the common aromatic ring $\text{C}6\text{--H}6 \cdots \text{O}51$ (sulfonate) association [$2.857(6) \text{ \AA}$ in (I) and $2.859(5) \text{ \AA}$ in (II)] maintains the $\text{S}5\text{--O}51$ bond close to the plane of the aromatic ring [torsion angle $\text{C}6\text{--C}5\text{--S}5\text{--O}51 = 3.8(4)^\circ$ in (I) and $3.1(3)^\circ$ in (II)].

Experimental

The title compounds were synthesized by heating solutions containing 8-hydroxy-7-iodoquinoline-5-sulfonic acid (ferron) (1 mmol) and, respectively, 4-chloroaniline (1 mmol) or 4-bromoaniline (1 mmol) in 50% ethanol–water (50 ml) for 10 min under reflux. After concentration to *ca* 40 ml, partial room-temperature evaporation of the hot-filtered solutions gave pale-brown flat prisms of (I) (m.p. 460.6–462.3 K) and large brown flat plates of (II) (m.p. 512.4–513.3 K).

Compound (I)

Crystal data

$C_6H_7ClN^+ \cdot C_9H_5INO_4S^- \cdot H_2O$	$V = 3581 (4) \text{ \AA}^3$
$M_r = 496.70$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 33.403 (10) \text{ \AA}$	$\mu = 2.08 \text{ mm}^{-1}$
$b = 5.902 (5) \text{ \AA}$	$T = 297 (2) \text{ K}$
$c = 19.970 (7) \text{ \AA}$	$0.40 \times 0.25 \times 0.20 \text{ mm}$
$\beta = 114.56 (2)^\circ$	

Data collection

Rigaku AFC-7R diffractometer	4108 independent reflections
Absorption correction: ψ scan (<i>TEXSAN for Windows</i> ; Molecular Structure Corporation, 1999)	3356 reflections with $I > 2\sigma(I)$ $R_{int} = 0.047$
$T_{min} = 0.541$, $T_{max} = 0.660$	25 standard reflections frequency: 150 min intensity decay: 0.7%
4800 measured reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.163$	$\Delta\rho_{max} = 1.20 \text{ e \AA}^{-3}$
$S = 1.10$	$\Delta\rho_{min} = -1.09 \text{ e \AA}^{-3}$
4108 reflections	
250 parameters	

Table 1

Hydrogen-bond geometry (\AA , $^\circ$) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O8—H8···N1	1.00 (8)	2.19 (8)	2.714 (6)	111 (6)
O8—H8···N1 ⁱ	1.00 (8)	2.10 (8)	2.853 (6)	131 (7)
O1W—H1W···O52 ⁱⁱ	0.75 (6)	2.06 (6)	2.796 (5)	167 (6)
O1W—H2W···O52	0.85 (7)	1.99 (7)	2.822 (6)	168 (7)
N11—H11A···O53	0.87 (5)	2.42 (6)	2.781 (6)	106 (4)
N11—H11A···O51 ⁱⁱⁱ	0.87 (5)	2.18 (5)	2.822 (6)	130 (5)
N11—H11B···O51 ^{iv}	0.85 (7)	2.10 (7)	2.902 (6)	157 (7)
N11—H11C···O1W	0.91 (6)	1.87 (6)	2.775 (7)	180 (9)
C2—H2···O8 ⁱ	0.95	2.43	2.977 (7)	116
C4—H4···O53	0.95	2.55	3.090 (6)	117
C6—H6···O51	0.95	2.43	2.857 (6)	107

Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iv) $x, y + 1, z$.

Compound (II)

Crystal data

$C_6H_7BrN^+ \cdot C_9H_5INO_4S^- \cdot H_2O$	$V = 3612 (3) \text{ \AA}^3$
$M_r = 541.15$	$Z = 8$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 33.494 (9) \text{ \AA}$	$\mu = 4.13 \text{ mm}^{-1}$
$b = 5.927 (4) \text{ \AA}$	$T = 297 (2) \text{ K}$
$c = 19.963 (7) \text{ \AA}$	$0.25 \times 0.20 \times 0.20 \text{ mm}$
$\beta = 114.29 (2)^\circ$	

Data collection

Rigaku AFC-7R diffractometer	4153 independent reflections
Absorption correction: ψ scan (<i>TEXSAN for Windows</i> ; Molecular Structure Corporation, 1999)	3149 reflections with $I > 2\sigma(I)$ $R_{int} = 0.015$
$T_{min} = 0.368$, $T_{max} = 0.436$	3 standard reflections frequency: 150 min intensity decay: 3.1%
4852 measured reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.110$	$\Delta\rho_{max} = 0.60 \text{ e \AA}^{-3}$
$S = 0.81$	$\Delta\rho_{min} = -0.63 \text{ e \AA}^{-3}$
4153 reflections	
250 parameters	

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O8—H8···N1	0.84 (6)	2.19 (6)	2.707 (5)	120 (6)
O8—H8···N1 ⁱ	0.84 (6)	2.28 (7)	2.880 (5)	129 (6)
O1W—H1W···O52 ⁱⁱ	0.90 (6)	1.91 (6)	2.799 (5)	170 (6)
O1W—H2W···O52	0.80 (5)	2.04 (6)	2.833 (6)	170 (6)
N11—H11A···O53	0.86 (4)	2.47 (5)	2.778 (5)	102 (3)
N11—H11A···O51 ⁱⁱⁱ	0.86 (4)	2.20 (4)	2.844 (5)	132 (4)
N11—H11B···O51 ^{iv}	0.81 (6)	2.12 (6)	2.889 (5)	160 (6)
N11—H11C···O1W	0.91 (5)	1.86 (5)	2.768 (6)	176 (5)
C2—H2···O8 ⁱ	0.95	2.44	2.998 (6)	117
C4—H4···O53	0.95	2.56	3.097 (5)	116
C6—H6···O51	0.95	2.44	2.859 (5)	107

Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iv) $x, y + 1, z$.

H atoms involved in hydrogen-bonding interactions (H8, H11A, H11B, H11C, H1W and H2W) were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were included in the refinements in calculated positions, with $C-H = 0.95 \text{ \AA}$, and were treated as riding atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. In the case of (I), large residual difference electron-density peaks (maximum 1.20 e \AA^{-3}) were located adjacent to the iodo substituent of the ferron anion.

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3040). Services for accessing these data are described at the back of the journal.

References

- Altomare, A., Cascarano, G., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Bakasova, Z. B., Abdybaliev, D. A., Sharipov, Kh. T., Akbaev, A. A., Ibragimov, B. T., Talipov, S. A. & Ismankulov, A. I. (1991). *Uzb. Khim. Zh.* pp. 22–25.
- Balasubramanian, T. & Muthiah, P. T. (1996). *Acta Cryst.* **C52**, 2072–2073.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Dey, A. & Desiraju, G. R. (2004). *CrystEngComm*, **6**, 642–646.
- Hemamalini, M., Muthiah, P. T., Bocelli, G. & Cantoni, A. (2004). *Acta Cryst.* **C60**, o284–o286.
- Hughes, D. L. & Truter, M. R. (1979). *J. Chem. Soc. Dalton Trans.* pp. 520–527.
- Merritt, L. L. Jr & Duffin, B. (1970). *Acta Cryst.* **B26**, 734–744.
- Molecular Structure Corporation (1999). *MSC/AFC Diffractometer Control Software and TEXSAN*. Versions 1.06. MSC, The Woodlands, Texas, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Smith, G., Wermuth, U. D. & Healy, P. C. (2003). *Acta Cryst.* **E59**, o1455–o1457.
- Smith, G., Wermuth, U. D. & Healy, P. C. (2004a). *Acta Cryst.* **C60**, o600–o603.
- Smith, G., Wermuth, U. D. & Healy, P. C. (2004b). *Acta Cryst.* **E60**, o1040–o1042.
- Smith, G., Wermuth, U. D. & White, J. M. (2005). *Acta Cryst.* **C61**, o105–o109.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Vogel, A. I. (1964). *Textbook of Macro and Semi-Micro Qualitative Inorganic Analysis*, 4th ed., p. 266. London: Longmans.