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The 1/1/1 adduct hydrate of 8-hydroxy-7-iodoquinoline-5-sulfonic acid (ferron) with urea

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Key indicators

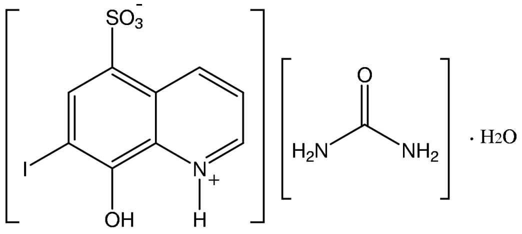
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.005 Å
R factor = 0.027
wR factor = 0.087
Data-to-parameter ratio = 12.1

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

The crystal structure of 8-hydroxy-7-iodoquinoline-5-sulfonic acid–urea–water, $C_9H_6INO_4S\cdot CH_4N_2O\cdot H_2O$, shows the zwitterionic (quinoline–sulfonate group) ferron molecule lying in a crystallographic mirror plane which related two of the sulfonate O atoms. Both the urea and the water molecule lie across the same plane and are inter-associated with the ferron molecules both within and between the planes by extensive hydrogen bonding, involving most available donor and acceptor sites on all three molecules. This includes a cyclic $R_2^2(8)$ sulfonate–urea association. The result is a three-dimensional layered structure.

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. Because of the acidity of the sulfonic acid group, ferron is capable of protonating most Lewis bases, but the crystal structures of only a small number of such proton-transfer compounds have been reported. With 4,4′-bipyridine (Hemamalini *et al.*, 2004) a monoprotonated 1:1 dihydrate is formed, whereas with guanidine (gu) carbonate, the base is sufficiently strong to give the dianionic ferron species in the monohydrate compound $[2(\mathrm{gu}^+)(\mathrm{ferron}^{2-})\cdot H_2O]_n$ (Smith *et al.*, 2003). We have been interested in the urea adducts of carboxylic acids and have determined a number of structures of such compounds, particularly with the stronger nitro-substituted aromatic acids (Smith *et al.*, 1997). However, there is a paucity of structural data on similar adducts with the sulfonic acids in the crystallographic literature. The large crystals of the title compound, the adduct $C_9H_6INO_4S\cdot CH_4N_2O\cdot H_2O$, (I), obtained from the combination of ferron with urea in 1:1 ethanol/water were, therefore, atypical among the attempted cocrystallizations of a number of aromatic sulfonic acid–urea adducts.



(I)

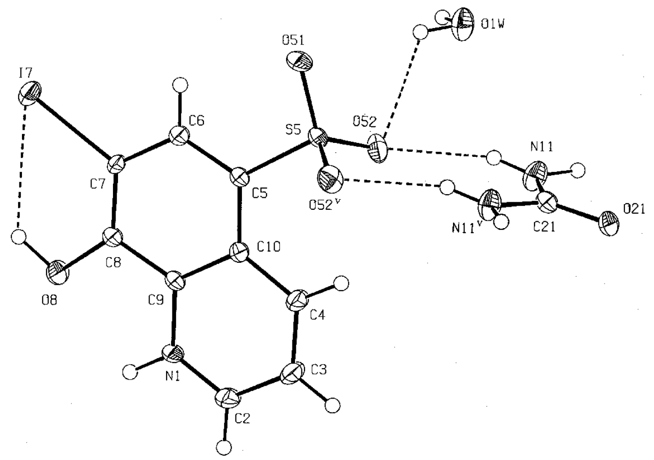


Figure 1
The molecular configuration and atom-labelling scheme for the individual ferron, urea and water species in (I), with non-H atoms shown as 40% probability ellipsoids. Symmetry code (v) as in Table 1.

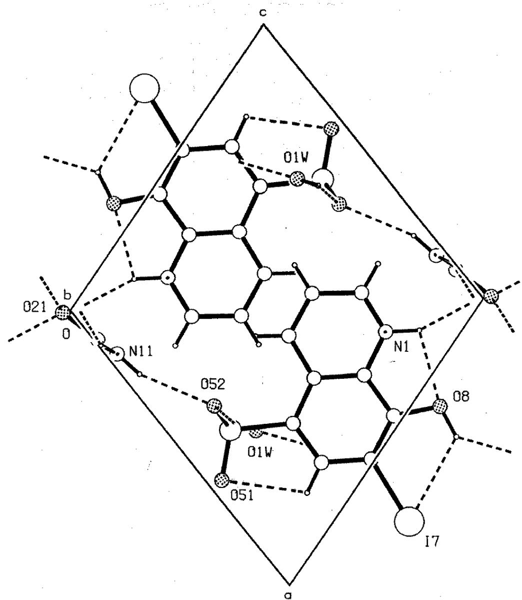


Figure 2
The packing of (I) in the unit cell, viewed down *b*, showing hydrogen-bonding associations as broken lines.

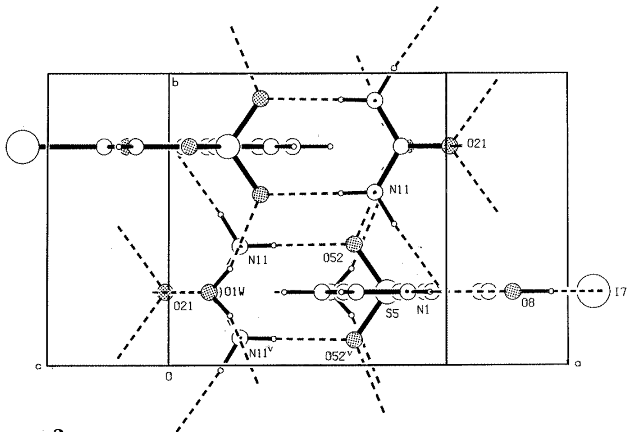


Figure 3
Perspective view of the packing in the unit cell, viewed perpendicular to *b*.

The crystal structure determination of (I) has confirmed the presence of zwitterionic ferron molecules which lie in the crystallographic mirror planes at $y = \frac{1}{4}, \frac{3}{4}$, with two O atoms of the non-planar sulfonate group [O52 and O52^{v}; symmetry code: (v) $x, \frac{1}{2} - y, z$] above and below the plane (Fig. 1). The sulfonate–quinoline group zwitterion is similar to that found in the structure of the parent ferron molecule (Merritt & Duffin, 1970; Balasubramanian & Muthiah, 1996). Other common intramolecular structural features of the ferron molecule [present also in the proton-transfer compound with 8-hydroxyquinoline (Smith *et al.*, 2004)] are also seen in (I): the N1—H1$\cdots$O8 hydrogen bond [2.628 (5) Å]; the C6—H6$\cdots$O51 hydrogen bond [2.865 (4) Å]; and the O8—H8$\cdots$I7 association [3.382 (3) Å]. The urea and water molecules both lie across the mirror planes and are interlinked by hydrogen bonds to the ferron molecule, both within and between the planes, through most available donor and acceptor atoms (Table 1, and Figs. 2 and 3). The zwitterionic N$^+$—H group of ferron forms strong symmetrical hydrogen bonds to urea O-atom acceptors [N1—H1$\cdots$O21^{i}/O21^{ii} = 2.684 (4) Å], while the 8-hydroxy group is linked to two mirror-related water molecules [O8—H8$\cdots$O1W^{iv}/O1W^{vii} = 2.565 Å; symmetry codes: (iv) $1 + x, y, z$; (vii) $1 + x, \frac{1}{2} - y, z$].

The urea molecule also forms cyclic $R_2^2(8)$ hydrogen-bonding associations with two sulfonate O atoms [N11—H11$A\cdots$O52 and N11^{v}—H11$A^{v}\cdots$O52^{v}; N$\cdots$O = 3.124 (3) Å], a feature common among urea–carboxylic acid adducts (Smith *et al.*, 1997). The result is a three-dimensional layered structure.

Experimental

The synthesis of the title compound, (I), was carried out by heating under reflux for 10 min a solution containing 1 mmol of 8-hydroxy-7-iodoquinoline-5-sulfonic acid (ferron) and 1 mmol of urea in 50 ml of 50% ethanol/water. After concentration to *ca* 40 ml, partial room-temperature evaporation of the hot filtered solution gave large yellow flat prisms (m.p. 502.1–503.3 K). The crystal used in data collection was a cleaved portion of the flat prism.

Crystal data

$C_9H_6INO_4S\cdot CH_4N_2O\cdot H_2O$
$M_r = 429.19$
Monoclinic, $P2_1/m$
$a = 10.025$ (3) Å
$b = 7.335$ (3) Å
$c = 9.845$ (3) Å
$\beta = 108.05$ (2)°
$V = 688.3$ (4) Å^3
$Z = 2$

$D_x = 2.071$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 12.5$–16.9°
$\mu = 2.51$ mm^{-1}
$T = 298$ (2) K
Block, yellow
0.30 × 0.30 × 0.25 mm

Data collection

Rigaku AFC-7*R* rotating-anode diffractometer
ω–2θ scans
Absorption correction: ψ scan (*TEXSAN for Windows*; Molecular Structure Corporation, 1999)
$T_{min} = 0.485$, $T_{max} = 0.534$
1898 measured reflections
1698 independent reflections

1637 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 27.5°$
$h = -5 \rightarrow 13$
$k = 0 \rightarrow 9$
$l = -12 \rightarrow 12$
3 standard reflections every 150 reflections
intensity decay: 1.4%

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.087$
$S = 0.89$
1698 reflections
140 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1P)^2 + 0.4367P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.012$
$\Delta\rho_{\rm max} = 1.16$ e Å^{-3}
$\Delta\rho_{\rm min} = -1.34$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.115 (6)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O8	0.95 (3)	2.25 (3)	2.628 (5)	103 (2)
N1—H1···O21$^{\rm i}$	0.95 (3)	1.79 (3)	2.684 (4)	155 (4)
N1—H1···O21$^{\rm ii}$	0.95 (3)	1.79 (3)	2.684 (4)	155 (4)
O1W—H1W···O52$^{\rm iii}$	0.86 (4)	2.03 (4)	2.823 (3)	153 (4)
O8—H8···I7	0.98 (7)	2.74 (6)	3.382 (3)	124 (4)
O8—H8···O1$W^{\rm iv}$	0.98 (7)	1.79 (7)	2.565 (5)	133 (5)
O8—H8···O1$W^{\rm vii}$	0.98 (7)	1.79 (7)	2.565 (5)	133 (5)
N11—H11A···O52	0.86 (3)	2.30 (3)	3.124 (3)	161 (3)
C2—H2···O51$^{\rm vi}$	0.95	2.28	3.231 (5)	178
C4—H4···O52	0.95	2.60	3.145 (4)	117
C4—H4···O52$^{\rm v}$	0.95	2.60	3.145 (4)	117
C2—H2···O51$^{\rm viii}$	0.95	2.28	3.231 (5)	178
C3—H3···O1W	0.95	2.46	3.304 (5)	147
C6—H6···O51	0.95	2.44	2.865 (4)	107

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

H atoms involved in hydrogen-bonding interactions (H1, H8, H11*A*, H11*B* and H1*W*) were located by difference methods and their positional and isotropic displacement parameters were refined. Others were included in the refinement as riding atoms [C—H = 0.95 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$]. A large difference electron-density peak (1.16 e Å^{-3}) was adjacent to the iodine substituent of ferron (I7).

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: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *PLATON for Windows*.

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