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Guanidinium 8-hydroxy-7-iodoquinoline-5-sulfonate monohydrate

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Key indicators

Single-crystal X-ray study

T = 295 K

Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$

R factor = 0.034

wR factor = 0.095

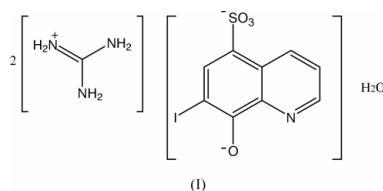
Data-to-parameter ratio = 14.8

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

The crystal structure of guanidinium 8-hydroxy-7-iodoquinoline-5-sulfonate monohydrate, $[(\text{CH}_6\text{N}_3^+)_2(\text{C}_9\text{H}_4\text{INO}_4\text{S}^{2-}) \cdot \text{H}_2\text{O}]$, shows a three-dimensional hydrogen-bonded polymer structure, in which the two guanidinium cations and the water molecule are involved in extensive hydrogen bonding, linking together rows of the dianions. The dianions result from deprotonation of both the sulfonic acid and the phenolic hydroxy groups of the substituted quinoline molecule.

Comment

The compound 8-hydroxy-7-iodoquinoline-5-sulfonic acid is a bidentate complexing agent similar to 8-hydroxyquinoline (Oxine) but with greater selectivity due to the steric requirements of the 7-iodo substituent, and it has analytical applications as a selective colour reagent (Ferron) for the detection of iron(III) but not iron(II) (Vogel, 1964). Furthermore, because of the presence of the sulfonic acid group it has the advantage of imparting water solubility to the complex species, allowing its use as a colorimetric reagent for quantitative analysis (IUPAC, 1963). The crystal structure of Ferron (Merritt & Duffin, 1970) was later redetermined (Balasubramanian & Muthiah, 1996), showing it to be zwitterionic. Guanidine is a strong base ($\text{p}K_a = 13.5$) and readily reacts with all types of organic acids to give salts with good crystallinity, largely because of the presence of six potential donor sites for hydrogen-bonding interactions. Extension of basic hydrogen-bonding rules (Etter, 1990) suggested that sulfonate salts of guanidine should assemble into ordered two-dimensional networks, because of equal numbers of donor and acceptor sites on both species, together with their threefold symmetry. Both alkyl and aryl guanidinium sulfonates have been investigated in this respect with the aim of creating materials with useful non-linear optical properties (Russell *et al.*, 1994a,b).



With the polycyclic aryl sulfonate Ferron, both the sulfonic acid group and the 8-substituted phenol group are sufficiently acidic ($\text{p}K_{a1} 2.25$; $\text{p}K_{a2} 7.25$) to protonate guanidine, so that our reaction between the two was expected to give the dianionic Ferron²⁻ species. The crystal structure determination has confirmed this and has found the product to be a hydrate, the title compound $[(\text{CH}_6\text{N}_3^+)_2(\text{C}_9\text{H}_4\text{INO}_4\text{S}^{2-}) \cdot \text{H}_2\text{O}]$

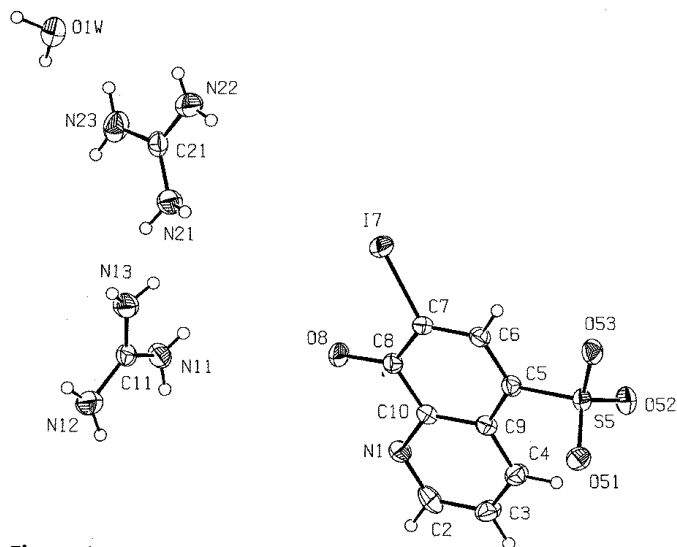


Figure 1
Molecular configuration and atom-naming scheme for the individual cation, anion and water species in (I), with non-hydrogen atoms shown as 40% probability ellipsoids

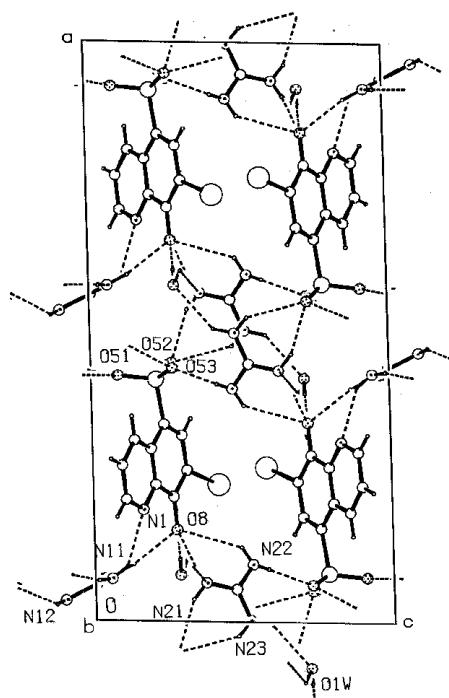


Figure 2
Perspective view of the packing in the unit cell, viewed down the *b* axis, showing hydrogen-bonding associations as broken lines.

(I) (Fig. 1). All H atoms on the two guanidinium cations are involved in a total of 12 hydrogen-bonding associations with both of the Ferron acceptors (N1, O8 and the sulfonate O atoms, O51–O53) as well as the water molecule (O1W) (Table 1). The result is the formation of rows of Ferron anions which extend along the *c* cell direction, linked *via* the sulfonate, phenolate and quinoline acceptors across the *a* and *b* cell directions by the rows of guanidinium cations and the water molecule (Fig. 2). This gives a three-dimensional network structure.

Experimental

The synthesis of the title compound 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 guanidine carbonate in 50 ml of 50% ethanol/water. After concentration to *ca.* 40 ml, partial room temperature evaporation of the hot-filtered solution gave large pale brown prismatic crystals, m. p. 441–445 K. Infrared (KBr): 3624, 3358, 3189, 1670, 1571, 1531, 1485, 1440, 1396, 1344, 1219, 1198, 1168, 1100, 1039, 839, 716, 677, 607, 543, 512, 471 cm^{-1} .

Crystal data

$2\text{CH}_6\text{N}_3^+ \cdot \text{C}_9\text{H}_4\text{INO}_4\text{S}^{2-} \cdot \text{H}_2\text{O}$
 $M_r = 487.28$
 Monoclinic, $P2_1/a$
 $a = 22.329(2) \text{ \AA}$
 $b = 6.9918(19) \text{ \AA}$
 $c = 11.3456(8) \text{ \AA}$
 $\beta = 92.646(7)^\circ$
 $V = 1769.4(5) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.829 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 25 reflections
 $\theta = 12.5\text{--}16.1^\circ$
 $\mu = 1.97 \text{ mm}^{-1}$
 $T = 295(2) \text{ K}$
 Plate, pale brown
 $0.50 \times 0.50 \times 0.20 \text{ mm}$

Data collection

Rigaku AFC-7R diffractometer
 ω - 2θ scans
 Absorption correction: ψ scan
 (TeXsan for Windows; Molecular Structure Corporation, 1999)
 $T_{\min} = 0.398$, $T_{\max} = 0.674$
 4344 measured reflections
 4057 independent reflections
 3559 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -10 \rightarrow 28$
 $k = 0 \rightarrow 9$
 $l = -14 \rightarrow 14$
 3 standard reflections
 every 150 reflections
 intensity decay: 18.9%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.095$
 $S = 1.02$
 4057 reflections
 275 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0541P)^2 + 2.4019P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.018$
 $\Delta\rho_{\text{max}} = 1.32 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.19 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97 (Sheldrick, 1997)
 Extinction coefficient: 0.0012(3)

Table 1
Hydrogen-bonding geometry (\AA , $^\circ$).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O1W–H1A...O8 ⁱ	0.95 (6)	1.92 (6)	2.865 (4)	175 (6)
N11–H11A...N1	0.74 (5)	2.25 (4)	2.883 (4)	144 (4)
N11–H11B...O51 ⁱⁱ	0.84 (4)	2.06 (4)	2.894 (4)	169 (4)
N12–H12A...O53 ⁱⁱ	0.72 (4)	2.48 (4)	3.121 (5)	148 (4)
N12–H12B...O52 ⁱⁱⁱ	0.78 (5)	2.41 (5)	3.036 (5)	139 (4)
N13–H13A...O8	0.86 (4)	2.09 (4)	2.943 (4)	170 (4)
N13–H13B...O51 ⁱⁱⁱ	0.71 (5)	2.22 (5)	2.925 (4)	171 (5)
N21–H21A...O8	0.80 (6)	1.98 (6)	2.754 (4)	165 (6)
N21–H21B...O53 ^{iv}	0.85 (6)	2.16 (7)	2.958 (4)	156 (6)
N22–H22A...O52 ^v	0.77 (5)	2.10 (5)	2.858 (5)	172 (5)
N22–H22B...O8	0.80 (6)	2.54 (6)	3.186 (5)	139 (6)
N23–H23A...O1W ^{vi}	0.90 (6)	2.26 (5)	2.979 (6)	137 (4)
N23–H23B...O53 ^{iv}	0.87 (7)	2.46 (7)	3.209 (5)	144 (6)
C4–H4...O52	0.95	2.58	3.180 (4)	122
C6–H6...O53	0.95	2.41	2.841 (4)	107

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

H atoms involved in hydrogen-bonding interactions, the guanidinium and the water H atoms, were located in difference maps and their positional and isotropic displacement parameters were refined. Others were included in the refinement as riding models. For refined

hydrogen atoms the N–H range is 0.71 (5)–0.90 (6) Å. Significant crystal decay during data collection (18.9%) was allowed for, using a linear correction. The highest peak and deepest hole were located adjacent to the iodine.

Data collection: *MSC/AFD Diffractometer Control Software* (Molecular Structure Corporation, 1999); cell refinement: *MSC/AFD Diffractometer Control Software*; data reduction: *TeXsan for Windows* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *PLATON for Windows*.

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