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Key indicators

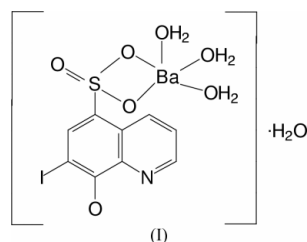
Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.012\text{ \AA}$
H-atom completeness 34%
 R factor = 0.077
 wR factor = 0.236
Data-to-parameter ratio = 17.5For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Supramolecular organization via varied
coordination modes in triqua(μ -8-hydroxy-
7-iodoquinoline-5-sulfonato)barium(II)
monohydrate

In the crystal structure of $[\text{Ba}(\text{C}_9\text{H}_4\text{INO}_4\text{S})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$, the asymmetric unit contains a Ba^{2+} ion, an 8-hydroxy-7-iodoquinoline-5-sulfonate anion, three coordinated water molecules and an uncoordinated water molecule. The Ba^{2+} ion has a nine-coordinate monocapped antiprismatic geometry, formed by four O atoms of three different sulfonate groups, the chelating N and O atoms of the oxine ring, and three water molecules. Each sulfonate group bridges three neighbouring Ba^{2+} ions. The organic ligands are stacked over one another, each pair of adjacent members of the stack being related by inversion symmetry. These stacks are crosslinked by Ba^{2+} ions, leading to a three-dimensional network, which is further stabilized by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds.

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Comment

8-Hydroxyquinoline and its derivatives are analytical reagents and also well known antibacterial, antiamoebic and antifungal agents. Many bidentate metal complexes of oxine and their crystal structures have been reported (*e.g.* Palenik, 1964; Hughes & Truter, 1977). The incorporation of a sulfonic acid group in the oxine molecule offers additional metal binding and hydrogen-bonding sites. Various coordination modes of 8-hydroxyquinoline-5-sulfonic acid (HQS) and 8-hydroxy-7-iodoquinoline-5-sulfonic acid (ferron) have been reported.



The crystal structures of copper complexes of HQS (Petit, Coquerel & Perez, 1993; Petit, Ammor *et al.*, 1993) have also been investigated. From our laboratory, the crystal structures of an Li complex of HQS (Murugesan & Muthiah, 1997), an Na complex of HQS (Raj *et al.*, 2002), an Ni complex of HQS (Raj *et al.*, 2001), a K complex of HQS (Francis, Muthiah, Bocelli & Cantoni, 2003*b*), a Cu complex of ferron (Francis, Muthiah, Bocelli & Cantoni, 2003*c*), a Ca complex of ferron (Francis, Muthiah, Rychlewska & Warzajtis, 2003), and the isomorphous cage-like dimeric structures of Ni (Raj *et al.*, 2003), Co (Balasubramanian, 1995) and Zn complexes (Francis, Muthiah, Bocelli & Cantoni, 2003*a*) of ferron have been reported. Metal sulfonate complexes are of current interest. The crystal structures of barium 2-*O*-sulfonato-L-

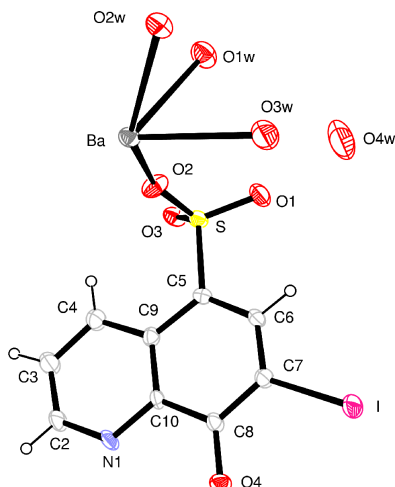


Figure 1
The asymmetric unit of (I), shown with 30% probability displacement ellipsoids.

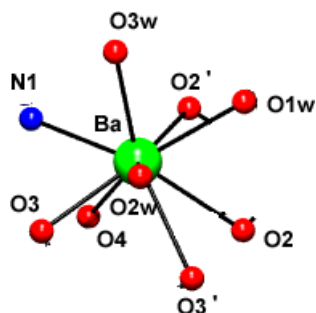


Figure 2
The coordination of barium in (I)

ascorbate dihydrate (McClelland, 1974), a Ba complex of 1,3,5-tris(sulfomethyl)benzene (Dalrymple & Shimizu, 2002), and a Ba–1,5-naphthalenedisulfonate complex (Cai *et al.*, 2001), among others, have also been reported. In the present crystal structure, (I), the coordination mode of the ligand is different from those in earlier structures.

In the crystal structure of $[\text{Ba}(\text{C}_9\text{H}_4\text{NO}_4\text{IS})(\text{H}_2\text{O})_3]\cdot\text{H}_2\text{O}$, (I), the asymmetric unit contains a Ba^{2+} ion, an 8-hydroxy-7-iodoquinoline-5-sulfonate (ferron) anion, three coordinated water molecules and one uncoordinated water molecule (Fig. 1). The Ba^{2+} ion has a nine-coordinate monocapped antiprismatic geometry, formed by four O atoms (O2, O2ⁱⁱⁱ, O3 and O3ⁱ; symmetry codes as in Table 1) of three different sulfonate groups, the N and O atoms of an oxine ring, and three water molecules (Fig. 2). Bond distances and angles are given in Table 1. The distance between two adjacent Ba^{2+} ions is 4.6102 (17) Å. These values are similar to those in the related crystal structures of barium sulfonates (McClelland, 1974; Cai *et al.*, 2001). The O4–Ba–N1 bite angle is 58.4 (2)°, compared with 57.0° in the K complex of oxine (Hughes & Truter, 1977).

In this structure, two O atoms (O3 and O2) of the same sulfonate group are involved in bidentate chelation and these O atoms also bridge the neighbouring Ba^{2+} ions on each side,

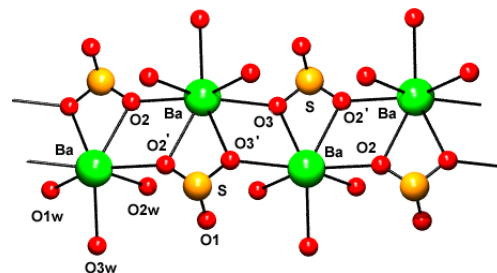


Figure 3
The supramolecular chain of (I).

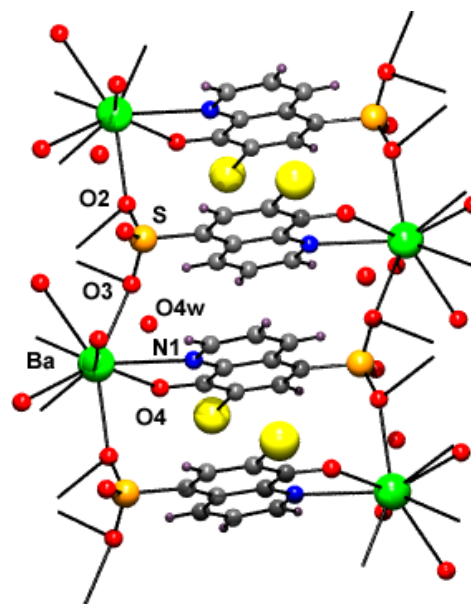


Figure 4
The polymeric network of (I).

leading to two four-membered rings. Hence, the sulfonate group connects three neighbouring Ba^{2+} ions. These bridges are repeated to form a supramolecular chain along the *a* axis. This supramolecular motif, made up of $\text{Ba}\cdots\text{O}_{\text{sulfonate}}$ interactions, is shown in Fig. 3 (the bidentate chelating oxine component has been omitted for clarity). The organic ligands are stacked over one another. Each pair of adjacent ligands in the stack is inversion related. These stacks are crosslinked by metal-sulfonate interactions, leading to a three-dimensional network (Fig. 4), which is further stabilized by $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. Similar types of molecular self-assembly have also been observed in the crystal structures of Cu (Francis, Muthiah, Bocelli & Cantoni, 2003c) and Ca complexes (Francis, Muthiah, Rychlewska & Warzajtis, 2003) of ferron. An overall view of the supramolecular architecture is shown in Fig. 5.

In this crystal structure, a $\pi-\pi$ stacking interaction is observed. The interplanar and centroid-to-centroid distances are 3.729 and 3.7992 Å, respectively, and the slip angle (defined as the angle between the plane normal and the line joining the centroids) is 10.2°. Three intermolecular $\text{I}\cdots\text{O}$ interactions $[\text{I}\cdots\text{O1W}(x, y+1, z)] = 3.630$ Å,

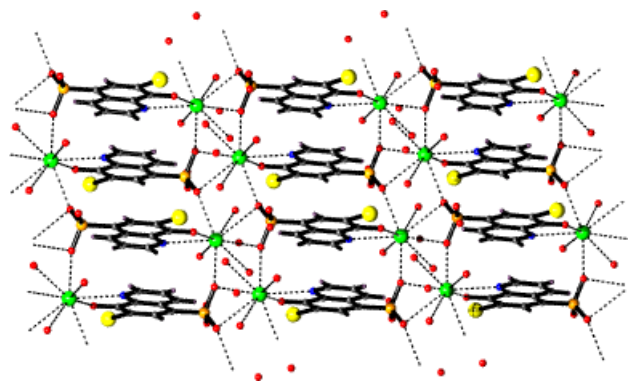


Figure 5
An overall view of the supramolecular architecture of (I).

$I \cdots O2W(x-1, y+1, z) = 3.719 \text{ \AA}$ and $I \cdots O3W(2-x, 1-y, 2-z) = 3.558 \text{ \AA}$] are also found. Such interactions have been observed in the crystal structures of ferron (Balasubramanian & Muthiah, 1996), and in its Ni (Raj *et al.*, 2003), Cu (Francis, Muthiah, Bocelli & Cantoni, 2003c) and Ca complexes (Francis, Muthiah, Rychlewska & Warzajtis, 2003). The crystal structure is further stabilized by $O-H \cdots O$ hydrogen bonds involving water molecules (Table 2). Even though these H atoms have not been located in difference maps, the hydrogen bonds are inferred from the donor-acceptor ($O \cdots O$) distances.

Experimental

A hot aqueous solution of ferron (85 mg, Riedel de Haen) was added to $BaCO_3$ (50 mg, LOBA) in a 1:1 molar ratio and warmed in a water bath for 5 h. 10 ml of acetone was added to the mixture and the solution was filtered. Yellowish plate crystals were obtained by slow evaporation of the solvent.

Crystal data

$[Ba(C_9H_4INO_4S)(H_2O)_3] \cdot H_2O$	$Z = 2$
$M_r = 558.43$	$D_x = 2.422 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 7.600 (3) \text{ \AA}$	Cell parameters from 8112 reflections
$b = 10.089 (2) \text{ \AA}$	$\theta = 2.0\text{--}28.3^\circ$
$c = 10.261 (3) \text{ \AA}$	$\mu = 4.78 \text{ mm}^{-1}$
$\alpha = 89.60 (3)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 77.52 (2)^\circ$	Plate, yellow
$\gamma = 85.63 (3)^\circ$	$0.39 \times 0.33 \times 0.24 \text{ mm}$
$V = 765.9 (4) \text{ \AA}^3$	

Data collection

Bruker SMART CCD diffractometer	3329 independent reflections
ω scans	2911 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2001)	$R_{int} = 0.043$
$T_{min} = 0.208, T_{max} = 0.318$	$\theta_{max} = 28.3^\circ$
8112 measured reflections	$h = -10 \rightarrow 9$
	$k = -12 \rightarrow 13$
	$l = -13 \rightarrow 13$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.077$	$w = 1/[\sigma^2(F_o^2) + (0.1968P)^2]$
$wR(F^2) = 0.236$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.06$	$\Delta\rho_{max} = 7.08 \text{ e \AA}^{-3}$
3329 reflections	$\Delta\rho_{min} = -1.59 \text{ e \AA}^{-3}$
190 parameters	

Table 1
Selected geometric parameters ($\text{\AA}, ^\circ$).

Ba—O1W	2.782 (9)	Ba—O4 ⁱⁱ	2.721 (7)
Ba—O2	2.734 (8)	Ba—N1 ⁱⁱ	2.853 (8)
Ba—O2W	2.896 (8)	Ba—O2 ⁱⁱⁱ	2.926 (8)
Ba—O3W	2.813 (9)	Ba—O3 ⁱⁱⁱ	2.995 (7)
Ba—O3 ⁱ	2.766 (7)		
O1W—Ba—O2	68.3 (2)	O2 ⁱⁱⁱ —Ba—O2W	101.7 (2)
O1W—Ba—O2W	77.4 (2)	O2W—Ba—O3 ⁱⁱⁱ	64.5 (2)
O1W—Ba—O3W	67.4 (3)	O3 ⁱ —Ba—O3W	100.0 (3)
O1W—Ba—O3 ⁱ	144.9 (2)	O3W—Ba—O4 ⁱⁱ	135.0 (2)
O1W—Ba—O4 ⁱⁱ	140.0 (2)	O3W—Ba—N1 ⁱⁱ	76.9 (2)
O1W—Ba—N1 ⁱⁱ	131.0 (2)	O2 ⁱⁱⁱ —Ba—O3W	136.4 (3)
O1W—Ba—O2 ⁱⁱⁱ	69.0 (2)	O3 ⁱⁱⁱ —Ba—O3W	129.5 (2)
O1W—Ba—O3 ⁱⁱⁱ	89.2 (2)	O3 ⁱ —Ba—O4 ⁱⁱ	72.4 (2)
O2—Ba—O2W	145.4 (2)	O3 ⁱ —Ba—N1 ⁱⁱ	71.8 (2)
O2—Ba—O3W	94.7 (3)	O2 ⁱⁱⁱ —Ba—O3 ⁱ	114.6 (2)
O2—Ba—O3 ⁱ	146.8 (2)	O3 ⁱ —Ba—O3 ⁱⁱⁱ	73.64 (19)
O2—Ba—O4 ⁱⁱ	76.2 (2)	O4 ⁱⁱ —Ba—N1 ⁱⁱ	58.4 (2)
O2—Ba—N1 ⁱⁱ	82.9 (2)	O2 ⁱⁱⁱ —Ba—O4 ⁱⁱ	82.7 (2)
O2—Ba—O2 ⁱⁱⁱ	70.9 (2)	O3 ⁱⁱⁱ —Ba—O4 ⁱⁱ	91.79 (19)
O2—Ba—O3 ⁱⁱⁱ	118.2 (2)	O2 ⁱⁱⁱ —Ba—N1 ⁱⁱ	137.5 (2)
O2W—Ba—O3W	66.9 (3)	O3 ⁱⁱⁱ —Ba—N1 ⁱⁱ	139.8 (2)
O2W—Ba—O3 ⁱ	67.6 (2)	O2 ⁱⁱⁱ —Ba—O3 ⁱⁱⁱ	47.3 (2)
O2W—Ba—O4 ⁱⁱ	137.7 (2)	Ba—O2—Ba ⁱⁱⁱ	109.1 (2)
O2W—Ba—N1 ⁱⁱ	118.2 (2)	Ba ^{iv} —O3—Ba ⁱⁱⁱ	106.4 (2)

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

Table 2
Hydrogen-bonding geometry ($\text{\AA}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C2—H2 \cdots O3W ⁱⁱ	0.93	2.57	3.323 (13)	139
C4—H4 \cdots O3	0.93	2.48	3.097 (12)	124
C6—H6 \cdots O1	0.93	2.43	2.855 (12)	108
O2W \cdots O1 ^{iv}			2.849 (12)	
O2W \cdots O3 ^{iv}			3.151 (11)	
O1W \cdots O4 ^v			2.788 (12)	
O2W \cdots O4 ^{vi}			2.793 (11)	
O4W \cdots O2W ^{vii}			2.834 (13)	
O4W \cdots O3W ^{vii}			2.918 (17)	
O2W \cdots O4W ^{vii}			2.834 (13)	
O4W \cdots O1			2.792 (16)	
O4W \cdots O3W			2.699 (17)	
O1W \cdots O3W			3.104 (13)	
O2W \cdots O3W			3.147 (12)	
O1W \cdots O2			3.097 (11)	

Symmetry codes: (ii) $-x, 1-y, 1-z$; (iv) $1+x, y, z$; (v) $x, y-1, z$; (vi) $1+x, y-1, z$; (vii) $2-x, -y, 2-z$.

H atoms bonded to C were treated as riding atoms, with C—H distances of 0.93 \AA and $U_{iso}(H) = 1.2U_{eq}(C)$. Those of the water molecules were not located. The largest difference peak and hole lie close to Ba.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2001); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1997); software used to prepare material for publication: *SHELXL97*.

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References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Balasubramanian, T. P. (1995). PhD thesis, Department of Chemistry, Bharathidasan University, Tiruchirappalli, India.
- Balasubramanian, T. & Muthiah, P. T. (1996). *Acta Cryst.* **C52**, 2072–2073.
- Bruker (2001). *SMART, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cai, J., Chen, C.-H., Liao, C.-Z., Feng, X.-L. & Chen, X.-M. (2001). *Acta Cryst.* **B57**, 520–530.
- Dalrymple, S. A. & Shimizu, G. K. H. (2002). *Chem. Eur. J.* **13**, 3010–3015.
- Francis, S., Muthiah, P. T., Bocelli, G. & Cantoni, A. (2003a). *Acta Cryst.* **E59**, m87–m90.
- Francis, S., Muthiah, P. T., Bocelli, G. & Cantoni, A. (2003b). *Acta Cryst.* **E59**, m1154–m1156.
- Francis, S., Muthiah, P. T., Bocelli, G. & Cantoni, A. (2003c). *Acta Cryst.* **E59**, m1157–m1159.
- Francis, S., Muthiah, P. T., Rychlewska, U. & Warzajtis, B. (2003). *Acta Cryst.* **E59**, m1160–m1163.
- Hughes, D. L. & Truter, M. R. (1977). *J. Chem. Soc. Dalton Trans.* pp. 520–527.
- McClelland, B. W. (1974). *Acta Cryst.* **B30**, 178–186.
- Murugesan, S. & Muthiah, P. T. (1997). XXVIII National Seminar on Crystallography, Kottayam, India, September 24–26, 1997.
- Palenik, G. J. (1964). *Acta Cryst.* **17**, 696–700.
- Petit, S., Ammor, S., Coquerel, G., Mayer, C. & Perez, G. (1993). *Eur. J. Solid State Inorg. Chem.* **30**, 497–507.
- Petit, S., Coquerel, G. & Perez, G. (1993). *New J. Chem.* **17**, 187–192.
- Raj, S. B., Muthiah, P. T., Bocelli, G. & Olla, R. (2002). *Acta Cryst.* **E58**, m513–m516.
- Raj, S. B., Muthiah, P. T., Bocelli, G. & Righi, L. (2001). *Acta Cryst.* **E57**, m591–m594.
- Raj, S. B., Muthiah, P. T., Rychlewska, U., Warzajtis, B., Bocelli, G. & Olla, R. (2003). *Acta Cryst.* **E59**, m46–m49.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (1997). *PLATON*. Utrecht University, The Netherlands.