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Bis(μ-8-hydroxy-7-iodoquinoline-5-sulfonato-$\kappa^3N,O:O'$)bis[triaquazinc(II)] tetrahydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.028
wR factor = 0.061
Data-to-parameter ratio = 17.0

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

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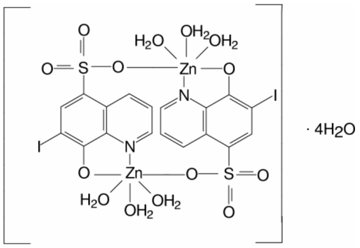
In the title compound, $[Zn_2(C_9H_4INO_4S)_2(H_2O)_6]\cdot 4H_2O$, the coordination geometry around the Zn^{II} atom is a distorted octahedron, formed by three water molecules, the N and deprotonated O atoms of the quinolinol ring and one of the O atoms of the sulfonate group. In the centrosymmetric binuclear complex, there is a π–π-stacking interaction between the quinolinol rings. The water molecules of crystallization play an important role in the hydrogen-bonding patterns of the three-dimensional network.

Comment

Oxine [8-hydroxyquinoline (HQ)] derivatives are well known analytical reagents and are also known for their anti-amoebic, antibacterial and antifungal activities, which could be correlated to their ability for bidentate chelation to metals. Many metal complexes of HQ have been reported (Palenik, 1964). The crystal structures of 8-hydroxy-7-nitroquinoline-5-sulfonic acid monohydrate (Balasubramanian & Muthiah, 1996) and 2-methyl-8-hydroxyquinoline-5-sulfonic acid monohydrate (Merrit & Duffin, 1970) have also been reported. As groups with coordination abilities are present on both sides, the sulfoxine ligand is capable of forming dimers. The iodo substitution at the 7-position in the sulfoxine ligand [7-iodo-8-hydroxyquinoline-5-sulfonic acid (ferron)] tends to result predominantly in isomorphous crystal structures with metal ions. Owing to its stability, a cage-like dimeric structure is formed rather than a polymeric network. Both types of crystal structure have already been reported (Petit, Coquerel & Perez, 1993; Petit, Ammor *et al.*, 1993) for the copper complex of sulfoxine [8-hydroxyquinoline-5-sulfonic acid (HQS)]. The structures of the cobalt complex of ferron (Balasubramanian, 1995), the nickel complex of ferron (Baskar Raj, Muthiah *et al.*, 2003), the lithium complex of HQS (Murugesan & Muthiah, 1997), the sodium complex of HQS (Baskar Raj *et al.*, 2002) and the nickel complex of HQS (Baskar Raj *et al.*, 2001) have been reported by our laboratory. The present study concerns the structure of the title zinc compound, (I).



(I)

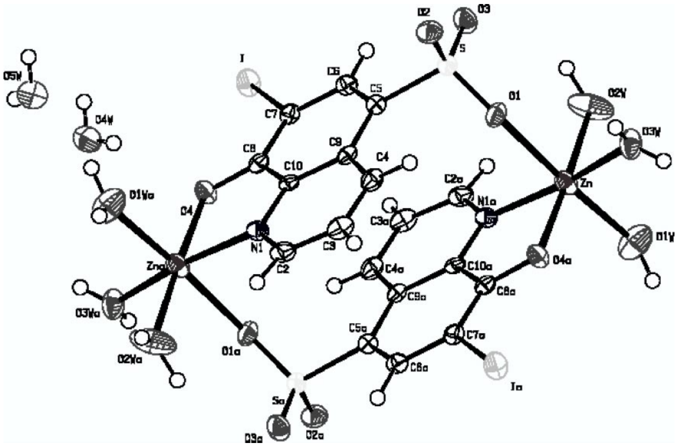


Figure 1
A view of the dimeric complex of (I), showing 50% probability displacement ellipsoids for non-H atoms.

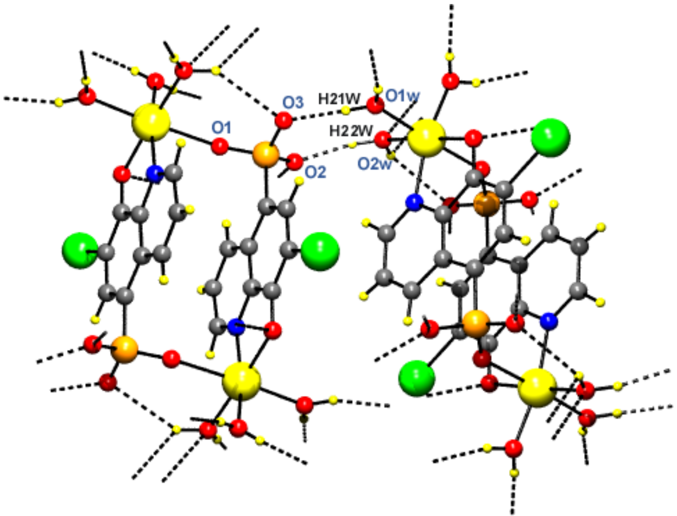


Figure 3
A view of the fork-like hydrogen-bonding interaction in (I).

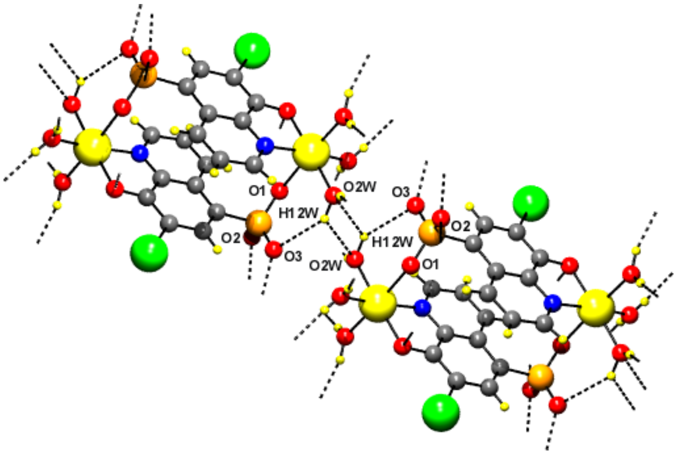


Figure 2
The tandem-type of hydrogen-bonding pattern in (I).

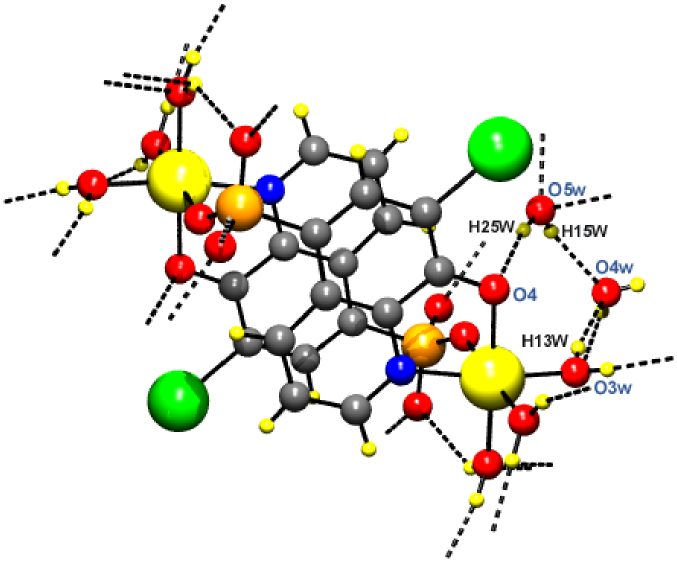


Figure 4
Hydrogen-bonding patterns involving water molecules of crystallization in (I).

The asymmetric unit of (I) contains one monomeric unit of [Zn(ferron)(H_2O)$_3$] and two uncoordinated water molecules. Two inversion-related ligands and two Zn atoms form a cage-like dimer (Fig. 1 and Table 1). The coordination of Zn is a distorted octahedron, the metal atom being surrounded by three water molecules, one of the O atoms of the sulfonate group (O1) and the N and O atoms of the oxine ring. In the octahedral geometry, two O atoms of coordinated water molecules (O2*W* and O3*W*) and N1, O4 of the oxine moiety occupy equatorial positions, and the sulfonate O atom and one O atom of a water molecule (O1*W*) are in axial positions. The Zn—N1, Zn—O and S—O bond distances and the N1—Zn—O4 bite angle [80.56 (9)°] are very close to those found in the nickel complex of ferron (Baskar Raj, Muthiah *et al.*, 2003). In (I), π–π-stacking is observed between quinolinol rings within the dimer. The interplanar and centroid-to-centroid distances are 3.464 and 3.520 Å, respectively, and the slip angle (angle between the centroid vector and normal to the plane) is 9.45°.

The water molecules and the hetero O atoms play an important role in the formation of hydrogen-bonding patterns (Table 2) and in the formation of supramolecular motifs. The non-coordinated O atom (O3) of the sulfonate group acts as an acceptor to the coordinated water molecule (O2*W*), forming a six-membered ring within the dimer. The tandem hydrogen bonding between each of the two coordinated water molecules of the adjacent dimeric units forms an $R_2^2(4)$ ring motif (Fig. 2). Atom O3 also acts as an acceptor to the coordinated water molecule (O1*W*) of the neighbouring unit. Another O atom of the SO_3 group (O2) is also involved in hydrogen bonds, one with an uncoordinated water molecule (O4*W*) and another with a neighbouring coordinated water molecule (O2*W*). Two coordinated water molecules (O1*W* and O2*W*) of one dimer donate H atoms to two of the O atoms (O2 and O3) of the sulfonate group of a neighbouring unit, reminiscent of the fork-like interactions (Fig. 3) observed in trimethoprim–sulfonate complexes (Baskar Raj, Sethuraman

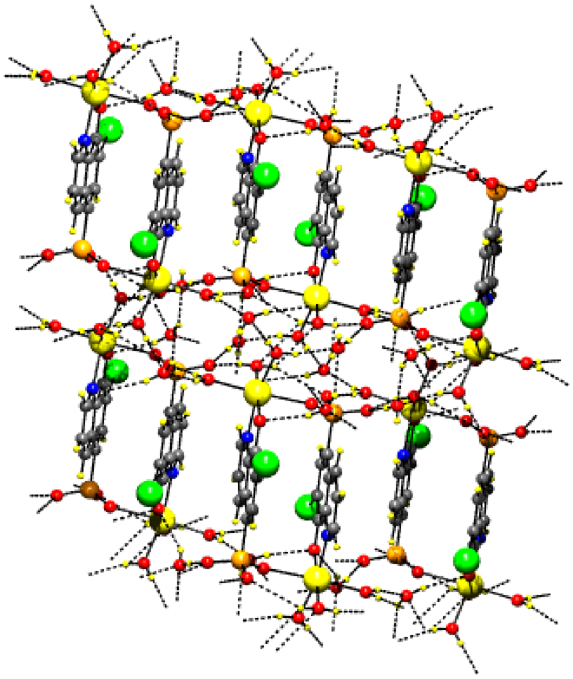


Figure 5
The supramolecular architecture in (I).

et al., 2003). The quinolinol O atom (O4) acts as a hydrogen-bonding acceptor to two uncoordinated water molecules, O4*W* and O5*W*, resulting in two types of hydrogen-bonding pattern. One (O4···H25*W*—O5*W*—H15*W*···O4*W*···H13*W*—O3*W*—Zn) makes an eight-membered ring (Fig. 4) and the other (O4···H24*W*—O4*W*—H14*W*···O2) is intermolecular in nature, bridges neighbouring moieties through the hydrogen-bonded chain. The overall supramolecular architecture consists of parallel supramolecular chains, made up of a metal atom and O atoms (of sulfonate and water molecules), linked by the aromatic part of the oxine moieties acting as ladders (Fig. 5).

Experimental

Hot aqueous solutions of trimethoprim (obtained as a gift from Shilpa Antibiotics Ltd, 0.072 g) and ferron (Riedel-de-Haen, 0.085 g) were mixed in a 1:1 molar ratio. Then a hot aqueous solution of $ZnSO_4 \cdot 7H_2O$ (S. D. Fine Chemicals Ltd, 0.072 g) was added to the above solution and warmed over a water bath for 8 h. After a few days of slow evaporation, needle-shaped yellow crystals of (I) separated out from the mother liquor.

Crystal data

$[Zn_2(C_9H_4INO_4S)_2(H_2O)_6] \cdot 4H_2O$
$M_r = 1009.14$
Monoclinic, $C2/c$
$a = 22.278\ (4)$ Å
$b = 10.076\ (3)$ Å
$c = 13.496\ (2)$ Å
$\beta = 102.29\ (3)°$
$V = 2960.1\ (12)$ Å^3
$Z = 4$

$D_x = 2.264$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 3.1$–$30.1°$
$\mu = 3.93$ mm^{-1}
$T = 293\ (2)$ K
Thin plate, yellow
0.31 × 0.26 × 0.23 mm

Data collection

Philips PW1100 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.303$, $T_{max} = 0.405$
4484 measured reflections
4326 independent reflections
2975 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$

$\theta_{max} = 30.0°$
$h = -31 \rightarrow 30$
$k = 0 \rightarrow 14$
$l = 0 \rightarrow 18$
1 standard reflection every 100 reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.061$
$S = 0.90$
4326 reflections
255 parameters

All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0239P)^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.91$ e Å^{-3}
$\Delta\rho_{min} = -1.00$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

I—C7	2.093 (3)	S—O1	1.461 (2)
Zn—O1	2.311 (2)	S—O2	1.466 (2)
Zn—O1*W*	2.132 (3)	S—O3	1.457 (2)
Zn—O2*W*	2.101 (3)	S—C5	1.771 (3)
Zn—O3*W*	2.017 (3)	O4—C8	1.311 (4)
Zn—O4^{i}	2.085 (2)	N1—C10	1.370 (4)
Zn—N1^{i}	2.073 (3)	N1—C2	1.325 (4)
O1—Zn—O1*W*	176.67 (11)	O2—S—O3	112.54 (14)
O1—Zn—O2*W*	89.46 (12)	O2—S—C5	105.36 (13)
O1—Zn—O3*W*	82.17 (10)	O3—S—C5	106.37 (14)
O1—Zn—O4^{i}	88.14 (9)	Zn—O1—S	140.92 (13)
O1—Zn—N1^{i}	87.41 (10)	Zn^{i}—O4—C8	111.74 (18)
O1*W*—Zn—O2*W*	89.19 (14)	Zn^{i}—N1—C2	128.6 (2)
O1*W*—Zn—O3*W*	94.70 (12)	C2—N1—C10	118.9 (3)
O1*W*—Zn—O4^{i}	93.25 (11)	Zn^{i}—N1—C10	112.23 (18)
O1*W*—Zn—N1^{i}	95.80 (12)	N1—C2—C3	122.8 (3)
O2*W*—Zn—O3*W*	85.97 (13)	S—C5—C6	119.4 (2)
O2*W*—Zn—O4^{i}	177.50 (13)	S—C5—C9	121.2 (2)
O2*W*—Zn—N1^{i}	98.63 (11)	I—C7—C6	119.6 (2)
O3*W*—Zn—O4^{i}	94.40 (11)	I—C7—C8	117.6 (2)
O3*W*—Zn—N1^{i}	168.59 (11)	O4—C8—C7	124.5 (3)
O4^{i}—Zn—N1^{i}	80.56 (9)	O4—C8—C10	119.9 (3)
O1—S—O2	110.85 (13)	N1—C10—C9	122.0 (3)
O1—S—O3	113.43 (14)	N1—C10—C8	115.4 (3)
O1—S—C5	107.74 (14)		

Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H11*W*···O5*W*^{i}	0.91 (3)	1.97 (3)	2.855 (4)	163 (4)
O2*W*—H12*W*···O3	0.94 (5)	2.56 (5)	3.333 (5)	140 (5)
O2*W*—H12*W*···O2*W*^{ii}	0.94 (5)	2.58 (5)	3.156 (5)	120 (5)
O3*W*—H13*W*···O4*W*^{iii}	0.83 (5)	1.97 (5)	2.777 (4)	165 (4)
O4*W*—H14*W*···O2^{iv}	0.79 (4)	2.04 (4)	2.813 (4)	168 (4)
O5*W*—H15*W*···O4*W*^{v}	0.79 (5)	2.05 (5)	2.771 (4)	151 (5)
O1*W*—H21*W*···O3^{vi}	0.92 (3)	1.91 (3)	2.834 (4)	177 (4)
O2*W*—H22*W*···O2^{vi}	0.93 (3)	1.83 (3)	2.753 (4)	170 (4)
O3*W*—H23*W*···O5*W*^{vii}	0.80 (4)	1.96 (4)	2.761 (4)	176 (4)
O4*W*—H24*W*···O4	0.72 (5)	2.29 (5)	2.947 (4)	152 (5)
O5*W*—H25*W*···O4^{viii}	0.84 (5)	2.16 (5)	2.988 (4)	168 (5)
C6—H6···O3	0.96 (4)	2.42 (4)	2.867 (4)	108 (3)

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

H atoms were located from difference Fourier maps and their coordinates and isotropic displacement parameters were refined. The

Acta Cryst. (2003). E**59**, m87–m90 Savarimuthu Francis *et al.* • $[Zn_2(C_9H_4INO_4S)_2(H_2O)_6] \cdot 4H_2O$ **m89**

C—H and O—H bond lengths are 0.90 (3)–0.96 (4) and 0.72 (5)–0.94 Å, respectively.

Data collection: *FEBO* (Belletti, 1996); cell refinement: *MolEN* (Fair, 1990); data reduction: *MolEN*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*97 (Spek, 1997); software used to prepare material for publication: *PLATON*97.

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