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

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Key indicators

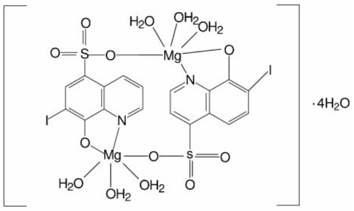
Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
R factor = 0.024
wR factor = 0.057
Data-to-parameter ratio = 14.7

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

In the title crystal structure, $[Mg_2(C_9H_4INO_4S)_2(H_2O)_6]\cdot 4H_2O$, the Mg^{2+} ion has a distorted octahedral coordination geometry, surrounded by N and O atoms of the oxine ring (bidentate chelation), one of the O atoms of a sulfonate group and three water molecules. The inversion-related ligands, water molecules and Mg^{2+} ions form a cage-like dimer. These dimers are further cross-linked by O—H···O hydrogen bonds. The title compound is isomorphous with earlier reported ferron complexes of Co, Ni and Zn.

Comment

Metal–sulfonate interactions are of current interest. In the crystal structure of tetraaquabis(hydroxymethanesulfonato)magnesium(II), the sulfonate group and water molecules are involved in coordination (Cameron *et al.*, 1990), whereas in the three other crystal structures, namely hexaaquamagnesiumbis(8-anilino-1-naphthalenesulfonate) hexahydrate (Cody & Hazel, 1977), hexaaqua(1,5-napthalenedisulfonato)magnesium (Cai *et al.*, 2001) and the magnesium salt of 7-hydroxy-8-(phenylazo)-1,3-naphthalenedisulfonic acid (Ojala *et al.*, 1994), the sulfonate groups are not involved in coordination and the metal atoms are surrounded only by water molecules. Recently, many crystal structures of metal–sulfoxinate complexes have been reported. In one type, the organic ligands are stacked over one another, each pair of adjacent members of the stack being inversion related. They also serve as the rungs of a ladder, whereas the O—M—O(sulfonate) bonds form the rails of a ladder. This arrangement has been observed in the ferron complexes of copper (Francis *et al.*, 2003*a*), cadmium (Francis *et al.*, 2004), barium (Muthiah *et al.*, 2003) and calcium (Francis *et al.*, 2003). In another type, two inversion-related ligands, metal ions and water molecules form a cage-like dimer. These discrete dimeric units are further cross-linked through O—H···O hydrogen bonds. This has been observed in the ferron complexes of nickel (Raj *et al.*, 2003), cobalt (Balasubramanian, 1995) and zinc (Francis *et al.*, 2003*b*), and in the title compound, (I).



(I)

In the title crystal structure, the asymmetric unit contains half of the dimeric unit and two uncoordinated water mol-

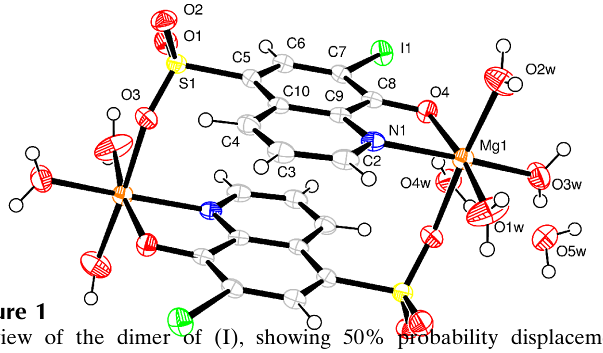


Figure 1
A view of the dimer of (I), showing 50% probability displacement ellipsoids.

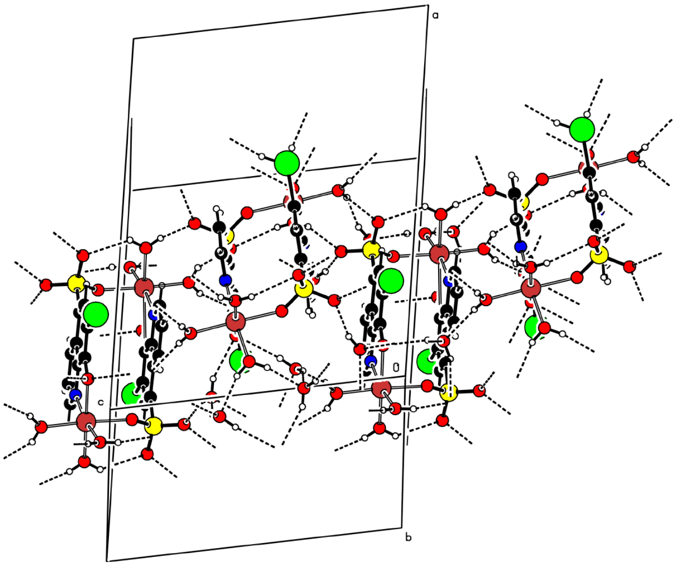


Figure 2
The supramolecular ladder in (I), made up of Mg—O(sulfonate) bonds and O—H···O hydrogen bonds.

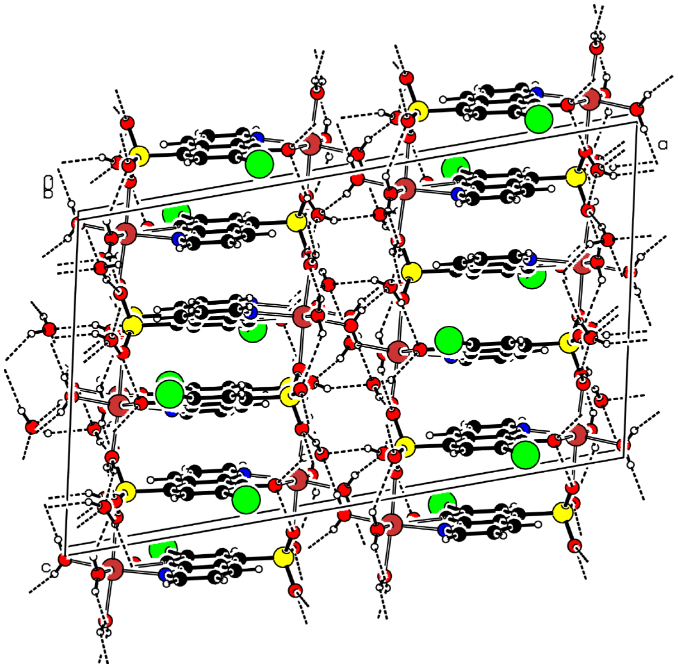


Figure 3
A view of the molecular network in (I).

ecules. The coordination of the Mg^{2+} ion is distorted octahedral, consisting of N (N1) and O (O4) atoms of the oxine ring, one of the O ($O3^{i}$) (symmetry code as in Table 1) atoms of a sulfonate group and three water molecules (Fig. 1). The bond distances and angles (Table 1) in this complex agree with those in related sulfonate complexes (Cai *et al.*, 2001; Cameron *et al.*, 1990; Francis *et al.*, 2003*b*). The two inversion-related ligands, two Mg^{2+} ions and coordinated water molecules form a cage-like dimer. Neighbouring dimers are cross-linked through O—H···O hydrogen bonds, leading to supramolecular ladders involving water molecules and O atoms (O1 and O2) of the sulfonate group (Fig. 2). This is represented as ($-\mathrm{Mg1}-\mathrm{O1}W-\mathrm{H2}W\cdots\mathrm{O2^{ii}}-\mathrm{S1^{ii}}-\mathrm{O3^{ii}}-\mathrm{Mg1^{ii}}$) and ($-\mathrm{Mg1}-\mathrm{O2}W-\mathrm{H3}W\cdots\mathrm{O1^{ii}}-\mathrm{S1^{ii}}-\mathrm{O3^{ii}}-\mathrm{Mg1^{ii}}$) (symmetry code as in Table 2). These ladders are interconnected by O—H···O hydrogen bonds, leading to a three-dimensional network (Fig. 3).

One of the uncoordinated O atoms (O1) of the sulfonate group accepts an H atom from the coordinated water molecule (O1*W*) to form a six-membered hydrogen-bonded ring. The coordinated water molecules (O1*W* and O2*W*) donate H atoms to the sulfonate O atoms (O1 and O2) of the neighbouring dimer to form a fork-like interaction. The neighbouring dimers are bridged by an uncoordinated water molecule (O5*W*), schematically represented as $\mathrm{O4^{iv}}\cdots\mathrm{H10}W-\mathrm{O5}W-\mathrm{H9}W\cdots\mathrm{O2^{v}}-\mathrm{S^{v}}-\mathrm{O3^{v}}-\mathrm{Mg1^{v}}$. The water molecules (O3*W*, O4*W* and O5*W*) interact with quinolinol oxygen (O4) to generate a hydrogen-bonded ring motif ($\mathrm{O4^{iv}}\cdots\mathrm{H10}W-\mathrm{O5}W\cdots\mathrm{H5}W-\mathrm{O3}W-\mathrm{H6}W\cdots\mathrm{O4}W^{\mathrm{iv}}-\mathrm{H8}W^{\mathrm{iv}}\cdots\mathrm{O4^{iv}}$). Two such motifs are further bridged by a pair of O4*W*—H7*W*···O5*W* hydrogen bonds (Table 2). The hydrogen-bonded network and coordination geometry of the title compound resemble those observed in the ferron complexes of zinc (Francis *et al.*, 2003*b*), cobalt (Balasubramanian, 1995) and nickel (Raj *et al.*, 2003), with which it is isomorphous. Within the dimer, the benzene and pyridine rings are stacked over one another. The interplanar and centroid-to-centroid distances are 3.448 and 3.487 (2) Å, respectively, and the angle between the plane normal and the line joining the centroids (slip angle) is 7.6°.

Experimental

A hot aqueous solution of ferron (85 mg, Riedel de-Haen) was added to a suspension of MgO (10 mg, LOBA) in 15 ml of acetone. The solution was warmed over a water bath for 5 h. The solution was filtered hot. After a few days of slow evaporation, plate-shaped yellow crystals were obtained.

Crystal data

$[Mg_2(C_9H_4INO_4S)_2(H_2O)_6]\cdot 4H_2O$
M_r = 926.98
Monoclinic, $C2/c$
a = 22.584 (5) Å
b = 10.026 (2) Å
c = 13.401 (3) Å
β = 102.26 (3)°
V = 2965.1 (12) Å^3
Z = 4

D_x = 2.077 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 13536 reflections
θ = 4.2–26.1°
μ = 2.39 mm^{-1}
T = 293 (2) K
Plate, yellow
0.40 × 0.30 × 0.10 mm

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Data collection

Kuma KM-4 CCD diffractometer
ω scans
Absorption correction: multi-scan (*XEMP*; Siemens, 1990)
$T_{\min} = 0.566$, $T_{\max} = 0.788$
16426 measured reflections
2924 independent reflections
2605 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\max} = 26.1°$
$h = -27 \rightarrow 27$
$k = -10 \rightarrow 12$
$l = -15 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.057$
$S = 1.05$
2924 reflections
199 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0313P)^2 + 3.8372P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.55$ e Å^{-3}
$\Delta\rho_{\min} = -0.72$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Mg1—O1*W*	2.077 (2)	Mg1—O4	2.0707 (19)
Mg1—O2*W*	2.089 (2)	Mg1—N1	2.174 (2)
Mg1—O3*W*	2.023 (2)	Mg1—O3$^{\rm i}$	2.124 (2)
O1*W*—Mg1—O2*W*	90.39 (9)	O2*W*—Mg1—O3$^{\rm i}$	176.34 (10)
O1*W*—Mg1—O3*W*	93.60 (10)	O3*W*—Mg1—O4	95.28 (9)
O1*W*—Mg1—O4	170.63 (10)	O3*W*—Mg1—N1	171.71 (9)
O1*W*—Mg1—N1	92.67 (10)	O3$^{\rm i}$—Mg1—O3*W*	85.65 (9)
O1*W*—Mg1—O3$^{\rm i}$	87.29 (9)	O4—Mg1—N1	78.21 (8)
O2*W*—Mg1—O3*W*	91.68 (10)	O3$^{\rm i}$—Mg1—O4	90.39 (8)
O2*W*—Mg1—O4	92.35 (9)	O3$^{\rm i}$—Mg1—N1	89.23 (9)
O2*W*—Mg1—N1	93.69 (10)		

Symmetry code: (i) $\frac{1}{2} - x, \frac{3}{2} - y, 1 - z$.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O1$^{\rm i}$	0.83	2.41	3.070 (3)	138
O1*W*—H2*W*···O2$^{\rm ii}$	0.82	2.01	2.779 (3)	157
O2*W*—H3*W*···O1$^{\rm ii}$	0.85	2.03	2.819 (3)	153
O2*W*—H4*W*···O4*W*$^{\rm iii}$	0.85	2.09	2.911 (3)	162
O3*W*—H5*W*···O5*W*	0.85	1.92	2.751 (3)	165
O3*W*—H6*W*···O4*W*$^{\rm iv}$	0.85	1.97	2.790 (3)	162
O4*W*—H7*W*···O5*W*	0.85	2.04	2.828 (3)	154
O4*W*—H8*W*···O4	0.85	2.25	3.086 (3)	169
O5*W*—H9*W*···O2$^{\rm v}$	0.85	2.03	2.848 (3)	163
O5*W*—H10*W*···O4$^{\rm iv}$	0.85	2.20	2.973 (3)	151
C4—H4···O3	0.96	2.56	3.142 (3)	119
C6—H6···O1	0.96	2.45	2.869 (3)	106

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

H atoms of the aromatic C atoms were positioned geometrically and all other H atoms were located in a difference Fourier map. All H atoms were treated as riding atoms, with C—H and O—H distances of 0.93–0.96 and 0.82–0.85 Å, respectively [$U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(C or O)].

Data collection: *KM*-4 *CCD Software* (Kuma, 1999); cell refinement: *KM*-4 *CCD Software*; data reduction: *KM*-4 *CCD Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON*97 (Spek, 1997); software used to prepare material for publication: *SHELXL*97.

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