Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Interplay of hydrogen bonding and coordination modes in diaquabis(8-hydroxy-7-iodoquinoline-5-sulfonato)calcium(II) monohydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
R factor = 0.066
wR factor = 0.103
Data-to-parameter ratio = 14.7

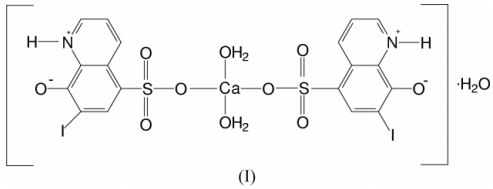
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 7 October 2003
Accepted 20 October 2003
Online 22 November 2003

In the crystal structure of the title compound, $[Ca(C_9H_5INO_4S)_2(H_2O)_2]\cdot H_2O$, the asymmetric unit consists of one calcium ion, two organic ligands, two coordinated water molecules and one uncoordinated water molecule. The calcium ion has a pentagonal-bipyramidal geometry, formed by O atoms of three different sulfonate groups, deprotonated O atoms of two different oxine rings and two water molecules. In the ligands of type I, two O atoms of the sulfonate group are involved in coordination, whereas in type II ligands, only one O atom is involved. Ligands of type I are stacked over one another, each pair of adjacent members of the stack being related by an inversion centre. Ligands of type II are also stacked in a similar manner. Both of these molecular stacks are cross-linked by Ca—O(sulfonate) and Ca—O(quinolinol) bonds, leading to a three-dimensional network. This network is further stabilized by a number of O—H···O and N—H···O hydrogen bonds.

Comment

Calcium is essential for physiological functions. Studies of metal complexes of drugs will contribute towards the understanding of metal–drug interactions at the molecular level (Guo & Sadler, 2000). The coordination chemistry of the metal–sulfonate system has not been extensively explored and rationalized compared to the well studied metal–phosphonates; this is due to the weak coordination strength of sulfonates with respect to metal ions. Various coordination modes of the sulfonate group in the crystal structures of metal–aryl sulfonates have been reported (Cai, Chen, Feng *et al.*, 2001; Cote *et al.*, 2002). The crystal structures of the calcium complex of 1,5-naphthalenedisulfonate dihydrate (Cai, Chen, Liao *et al.*, 2001), two calcium salts of *o*-toluidine-6,6′-disulfonate (Gunderman & Squattrito, 1996) and heptaaquacalcium 1,2-benzenedisulfonimide (Moers *et al.*, 1997) have been reported.



(I)

8-Hydroxyquinoline (oxine) and its derivatives are well known for their antifungal, antibacterial and antiamoebic activities (Bambury, 1979). The biological activities of oxine derivatives have been correlated with their capacity for metal chelation. Crystal structures have been reported for the

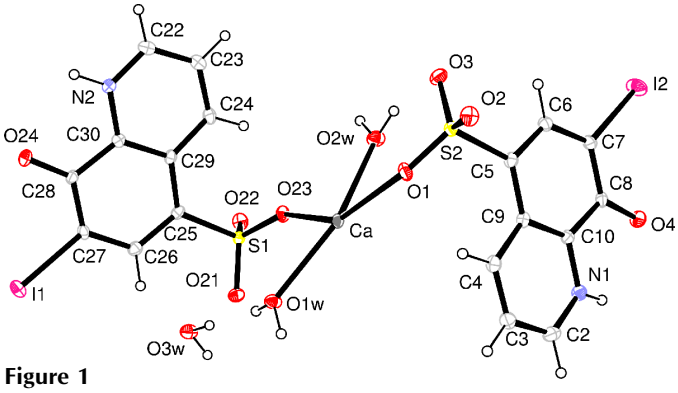


Figure 1
A view of the asymmetric unit of (I), showing 30% probability displacement ellipsoids.

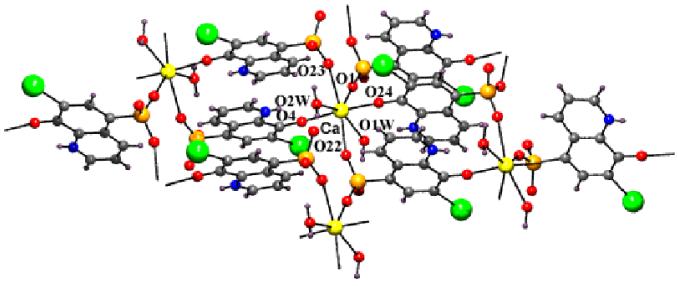


Figure 2
The coordination geometry of Ca in (I).

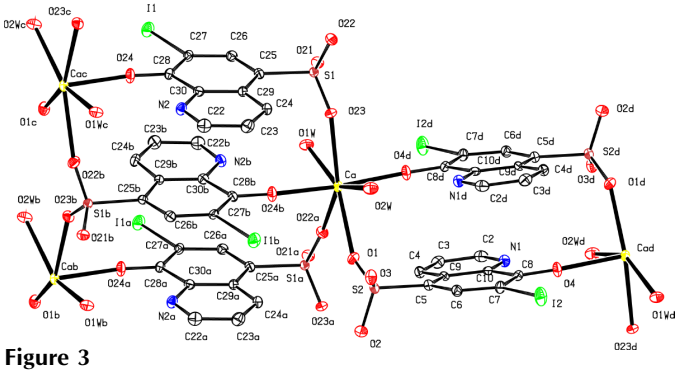


Figure 3
The polymeric network of (I). Suffixes *a*, *b* and d correspond to the symmetry codes (i), (ii) and (iii), respectively, given in Table 1.

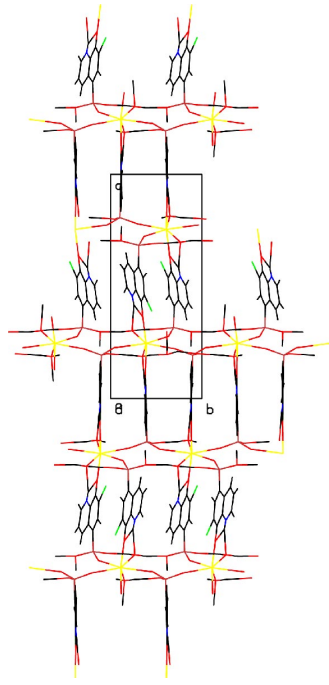


Figure 4
The supramolecular architecture of (I).

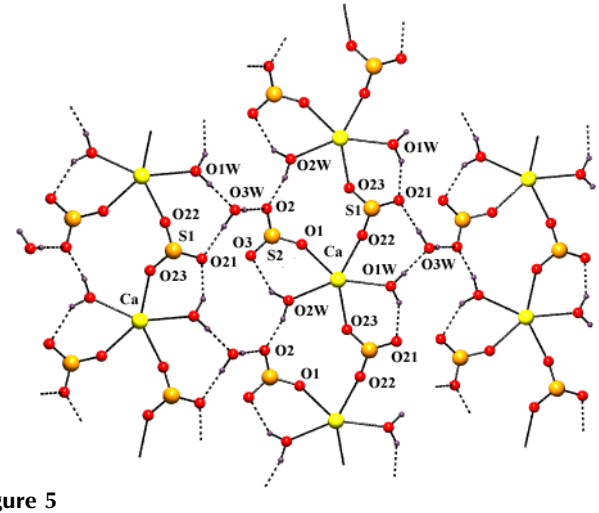


Figure 5
The hydrogen-bonded network in the complex (I).

copper complex of 8-hydroxyquinoline-5-sulfonic acid (HQS) (Petit, Ammor *et al.*, 1993; Petit, Coquerel *et al.*, 1993), the nickel complex of HQS (Raj *et al.*, 2001), the lithium complex of HQS (Murugesan & Muthiah, 1997), the sodium complex of HQS (Raj *et al.*, 2002), the nickel complex of 8-hydroxy-7-iodoquinoline-5-sulfonic acid (ferron) (Raj *et al.*, 2003), the cobalt complex of ferron (Balasubramanian, 1995) and the zinc complex of ferron (Francis *et al.*, 2003).

In the present crystal structure, (I), the asymmetric unit contains a Ca^{2+} ion, two 8-hydroxy-7-iodoquinoline-5-sulfonate (ferron) anions and three water molecules. The metal–ligand ratio is 1:2. A view of the asymmetric unit is shown in Fig. 1. In this complex, the coordination geometry around calcium is that of a seven-coordinate pentagonal bipyramid, formed by O atoms (O4 and O24) of the oxine ring, O atoms (O1, O22 and O23) of three different sulfonate groups of the ferron anions and two water molecules (Fig. 2). The Ca—O distances (Table 1) agree with those in related calcium sulfonate crystal structures (Cai, Chen, Liao *et al.*, 2001; Onoda *et al.*, 2001).

In the ligands of type I, two O atoms of the sulfonate group are involved in coordination, whereas in type II ligands, only one O atom is involved. Ligands of type I (atom labels N2 and C22–C30) are stacked over one another, each pair of adjacent members of the stack being related by an inversion centre. Ligands of type II (atom labels N1 and C2–C10) are also stacked in a similar manner. Both of these molecular stacks are cross-linked by Ca—O(sulfonate) and Ca—O(quinolinol) bonds, leading to a three-dimensional network (Fig. 3). In the overall three-dimensional network, the planes of the oxine rings in adjacent layers are slightly twisted, by 16.4 (1)°, with respect to each other (Fig. 4).

The O atoms (O1*W* and O2*W*) of the coordinated water molecules donate H atoms to the sulfonate O atoms (O21 and O3) of two sulfonate groups to form six-membered hydrogen-bonded rings on either side of the Ca atom. Another H atom of the coordinated water molecule (O2*W*) acts as a donor to one of the sulfonate O atoms, O2, generating a ten-membered hydrogen-bonded ring. The non-coordinated water molecule donates H atoms to the O atoms (O2 and O21) of the sulfonate groups to form a 16-membered ring. It also acts as an acceptor with one of the coordinated water molecules (O1*W*), to produce an eight-membered ring and bridges the two complex moieties, through hydrogen bonding, as shown in Fig. 5. In both type I and type II ligands, the protonated N atom of the oxine ring forms an unsymmetrical bifurcated hydrogen bond with the O atom of the same ring and the coordinated water molecule (Fig. 6).

In this crystal structure, π–π stacking interactions are also observed between the oxine rings. For the type I ligand, the interplanar and centroid-to-centroid distances are 3.463 and 3.628 (3) Å, respectively, and the slip angle (defined as the angle between the plane normal and the line joining the centroids) is 17.69°. The corresponding values for the type II ligand are 3.318 and 3.509 (3) Å and 21.09°, respectively. Similar stacking has also been observed in the crystal structures of the nickel complex of ferron (Raj *et al.*, 2003), and the zinc complex of ferron (Francis *et al.*, 2003). In the title complex, two I···O interactions are observed, *viz*. I2···O2 [3.470 (4) Å; symmetry code: $\frac{1}{2}-x,\ y+\frac{1}{2},\ 1-z$] and I2···O3*W* [3.592 (4) Å; symmetry code: $1-x,\ 1-y,\ 1-z$]. This type of oxygen–halogen interaction has also been observed in the crystal structures of ferron (Balasubramanian & Muthiah, 1996) and its nickel complex (Raj *et al.*, 2003), among others.

Experimental

Hot aqueous solutions of ferron (88 mg, Riedel de-Haen) and salicylic acid (35 mg, Merck) were mixed in a 1:1 molar ratio. The resultant solution was added to $CaCO_3$ (25 mg, LOBA) in a 1:1:1 molar ratio and warmed over a water bath for 90 min. The red solution was filtered and allowed to evaporate slowly. After a few days, red plate-shaped crystals separated from the solution.

Crystal data

$[Ca(C_9H_5INO_4S)_2(H_2O)_2]H_2O$
M_r = 794.35
Monoclinic, $P2_1/c$
a = 20.326 (4) Å
b = 6.958 (1) Å
c = 19.219 (4) Å
β = 117.19 (3)°
V = 2417.7 (4) Å^3
Z = 4
D_x = 2.182 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10575 reflections
θ = 3.1–26.1°
μ = 3.05 mm^{-1}
T = 293 (2) K
Plate, red
0.40 × 0.15 × 0.05 mm

Data collection

Kuma KM-4 CCD diffractometer
ω scans
Absorption correction: multi-scan (*XEMP*; Siemens, 1990)
T_{min} = 0.593, T_{max} = 0.859
26674 measured reflections
4771 independent reflections
4526 reflections with $I > 2\sigma(I)$
R_{int} = 0.053
θ_{max} = 26.1°
$h = -24 \rightarrow 25$
$k = -8 \rightarrow 5$
$l = -23 \rightarrow 23$

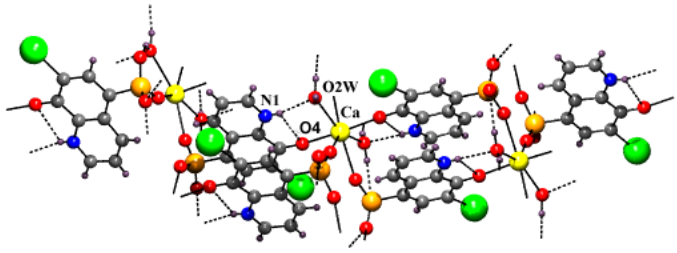


Figure 6
Bifurcated hydrogen-bonding in (I).

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.066
$wR(F^2)$ = 0.103
S = 1.36
4771 reflections
325 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 1.7598P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 1.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.88 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ca—O1	2.411 (4)	Ca—O22^{i}	2.460 (4)
Ca—O1*W*	2.460 (4)	Ca—O24^{ii}	2.237 (5)
Ca—O2*W*	2.519 (4)	Ca—O4^{iii}	2.256 (5)
Ca—O23	2.489 (4)		
O1—Ca—O1*W*	140.85 (15)	O2*W*—Ca—O23	75.59 (13)
O1—Ca—O2*W*	70.54 (14)	O2*W*—Ca—O22^{i}	141.34 (14)
O1—Ca—O23	145.11 (14)	O2*W*—Ca—O24^{ii}	95.04 (15)
O1—Ca—O22^{i}	71.10 (13)	O2*W*—Ca—O4^{iii}	78.56 (14)
O1—Ca—O24^{ii}	90.38 (15)	O22^{i}—Ca—O23	143.06 (13)
O1—Ca—O4^{iii}	92.54 (15)	O23—Ca—O24^{ii}	84.37 (16)
O1*W*—Ca—O2*W*	148.57 (15)	O4^{iii}—Ca—O23	88.76 (16)
O1*W*—Ca—O23	73.14 (13)	O22^{i}—Ca—O24^{ii}	89.84 (16)
O1*W*—Ca—O22^{i}	70.02 (14)	O4^{iii}—Ca—O22^{i}	98.54 (16)
O1*W*—Ca—O24^{ii}	85.09 (15)	O4^{iii}—Ca—O24^{ii}	171.62 (16)
O1*W*—Ca—O4^{iii}	97.53 (15)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H1···O24	0.90	2.33	2.671 (6)	103
N2—H1···O1*W*^{iv}	0.90	1.99	2.863 (8)	162
O1*W*—H1W···O3*W*^{i}	0.85	1.87	2.706 (6)	169
O1*W*—H2*W*···O21	0.85	2.03	2.793 (6)	149
O2*W*—H3*W*···O3	0.85	2.16	2.882 (6)	143
O2*W*—H4*W*···O2^{v}	0.85	1.88	2.714 (6)	166
O3*W*—H5*W*···O21	0.85	2.00	2.815 (6)	159
N1—H6···O4	0.90	2.27	2.681 (6)	107
N1—H6···O2*W*^{iii}	0.90	2.06	2.892 (8)	153
O3*W*—H6*W*···O2^{vi}	0.85	2.05	2.878 (7)	165
C23—H3···O3*W*^{vii}	0.96	2.36	3.314 (8)	174
C24—H4···O23	0.96	2.44	3.034 (8)	120
C26—H5···O21	0.96	2.44	2.857 (8)	106
C4—H9···O1	0.96	2.35	2.945 (8)	120
C4—H9···O23^{i}	0.96	2.60	3.457 (7)	149
C6—H10···O3	0.96	2.47	2.868 (8)	104

Symmetry codes: (i) $x, y-1, z$; (iii) $2-x, 1-y, 2-z$; (iv) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (v) $x, 1+y, z$; (vi) $x, \frac{3}{2}-y, z-\frac{1}{2}$; (vii) $x, \frac{5}{2}-y, \frac{1}{2}+z$.

H atoms were located in a difference map and were treated as riding atoms, with C—H, O—H and N—H distances of 0.96, 0.85 and 0.90 Å, respectively; U_{iso} values were set at 1.2U_{eq} of the carrier atom.

The highest residual electron-density peak is located 0.941 Å from atom I2.

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* (Spek, 1997); software used to prepare material for publication: *SHELXL*97.

SF thanks the Council of Scientific and Industrial Research (CSIR), New Delhi, India, for the award of a Senior Research Fellowship [reference No. 9/475(109)2002 EMR–I].

References

Balasubramanian, T. P. (1995). PhD thesis, Department of Chemistry, Bharathidasan University, Tiruchirappalli, India.
Balasubramanian, T. & Muthiah, P. T. (1996). *Acta Cryst.* C**52**, 2072–2073.
Bambury, R. E. (1979). Burger's Medicinal Chemistry, Part II, edited by M. E. Wolff, pp. 41–81. New York: John Wiley.
Cai, J., Chen, C.-H., Feng, X.-L., Liao, C.-Z. & Chen, X.-M. (2001). *J. Chem. Soc. Dalton Trans.* pp. 2370–2375.
Cai, J., Chen, C.-H., Liao, C.-Z., Feng, X.-L. & Chen, X.-M. (2001). *Acta Cryst.* B**57**, 520–530.
Cote, A. P., Ferguson, M. J., Khen, K. A., Enright, G. D., Kulynych, A. D., Dalrymple, S. A. & Shimizu, G. K. H. (2002). *Inorg. Chem.* **41**, 287–292.
Francis, S., Muthiah, P. T., Bocelli, G. & Cantoni, A. (2003). *Acta Cryst.* E**59**, m87–m90.
Gunderman, B. J. & Squattrito, P. J. (1996). *Acta Cryst.* C**52**, 1896–1901.
Guo, Z. & Sadler, P. J. (2000). *Adv. Inorg. Chem.* **49**, 183–306.
Kuma (1999). *KM*-4 *CCD Software*. Version 163. Kuma Diffraction, Wrocław, Poland.
Moers, O., Blaschette, A. & Jones, P. G. (1997). *Acta Cryst.* C**53**, 845–848.
Murugesan, S. & Muthiah, P. T. (1997). XXVIIIth National Seminar on Crystallography, Kottayam, India, September 24–26. (Deposited at the Cambridge Structural Database, deposition number 166283. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.)
Onoda, A., Yamada, Y., Doi, M., Okamura, T. & Ueyama, N. (2001). *Inorg. Chem.* **40**, 516–521.
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.* E**58**, m513–m516.
Raj, S. B., Muthiah, P. T., Bocelli, G. & Righi, L. (2001). *Acta Cryst.* E**57**, m591–m594.
Raj, S. B., Muthiah, P. T., Rychlewska, U., Warzajtis, B., Bocelli, G. & Olla, R. (2003). *Acta Cryst.* E**59**, m46–m49.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Siemens (1990). *XEMP*. Version 4.2. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Spek, A. L. (1997). *PLATON*97. Utrecht University, The Netherlands.