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A supramolecular ladder in diaqua(μ-8-hydroxy-7-iodoquinoline-5-sulfonato-κ^4N,O,O',O'')cadmium(II) dihydrate

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Key indicators

Single-crystal X-ray study
T = 93 K
Mean σ(C–C) = 0.010 Å
H-atom completeness 92%
R factor = 0.055
wR factor = 0.161
Data-to-parameter ratio = 17.8

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

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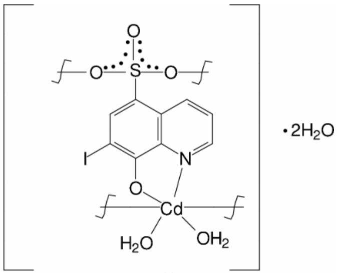
In the title complex, $\{[Cd(C_9H_4INO_4S)(H_2O)_2]\cdot 2H_2O\}_n$, the Cd^{2+} ion has a distorted octahedral geometry, surrounded by two O atoms of sulfonate groups, N and O atoms of the oxine ring (bidentate chelation) and two water molecules. Inversion-related ligands, stacked over one another, form the rungs of the ladder whereas the O—Cd—O(sulfonate) bonds form the rails of the ladder. These supramolecular ladders are further cross-linked by O—H···O hydrogen bonds involving the water molecules and the sulfonate O atoms.

Comment

The crystal structures of metal phosphonates have been more extensively studied than those of metal sulfonates. The multiple coordination modes of the phosphonate group lead to rigid and layered structures (Poojary *et al.*, 1996; Mao *et al.*, 2002). The various coordination modes of metal sulfonates/sulfoxinates are of current interest (Husgen *et al.*, 1998). Recently, we have reported the crystal structures of many metal complexes of 8-hydroxy-7-iodoquinoline-5-sulfonate (ferron). In these crystal structures, two types of networks have been observed. In type I, neighbouring supramolecular ladders are interconnected through hydrogen bonding only. This is observed in the crystal structures of nickel (Raj *et al.*, 2003), zinc (Francis *et al.*, 2003*a*), copper (Francis *et al.*, 2003*b*) and cobalt (Balasubramanian, 1995) complexes of ferron, and of a nickel complex of 8-hydroxyquinoline-5-sulfonate (HQS; Raj *et al.*, 2001). In type II, ladders are bridged by both hydrogen bonding and coordination of the sulfonate O atoms. This type of network is observed in calcium (Francis *et al.*, 2003) and barium (Muthiah *et al.*, 2003) complexes of ferron, and also in sodium (Raj *et al.*, 2002) and potassium (Francis *et al.*, 2003*c*) complexes of HQS. The mode of coordination in the crystal structure of the title compound, (I), resembles that present in the copper complex of ferron (type I) (Francis *et al.*, 2003*b*) and the structure differs only in the number of uncoordinated water molecules.



(I)

In the title crystal structure, the asymmetric unit contains a Cd^{2+} ion, an 8-hydroxy-7-iodoquinoline-5-sulfonate anion,

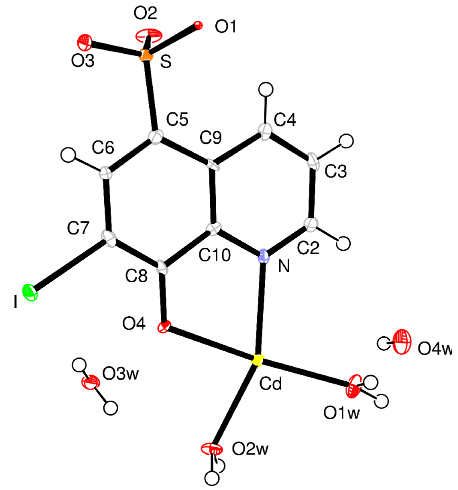


Figure 1
The asymmetric unit of (I), showing 50% probability displacement ellipsoids.

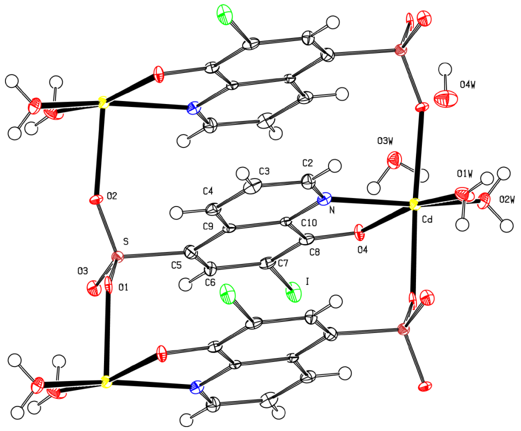


Figure 2
The supramolecular ladder in (I), showing 50% probability displacement ellipsoids.

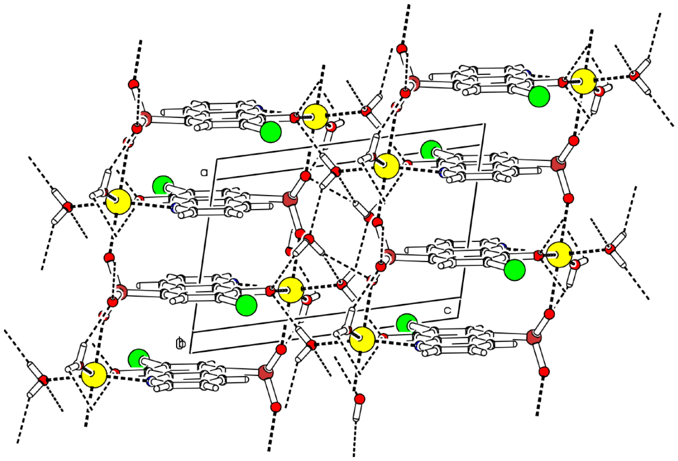


Figure 3
The overall packing arrangement of (I).

two coordinated water molecules and two uncoordinated water molecules (Fig. 1). The coordination geometry of the Cd^{2+} ion is a distorted octahedron, formed by N and O (O4) atoms of the oxine ring (bidentate chelation), two O atoms ($O1^{i}$ and $O2^{ii}$; symmetry codes as in Table 1) of the sulfonate groups and two water molecules. Atoms O1*W* and O2*W* of the coordinated water molecules and N and O (O4) atoms of the oxine ring occupy the equatorial positions, while two sulfonate O atoms ($O1^{i}$ and $O2^{ii}$) occupy the axial positions. The bond distances and angles are listed in Table 1. The Cd—O(sulfonate) bond distances in (I) agree with those reported in other cadmium–sulfonate complexes (Cai *et al.*, 2001; Zhou *et al.*, 2003; Harvey *et al.*, 2003). However, these values are slightly longer than those in the cadmium phosphonate complex (Mao *et al.*, 2002).

Inversion-related ligands, stacked over one another, form the rungs of a ladder, while the O—Cd—O(sulfonate) bonds form the rails of the ladder (Fig. 2). These supramolecular ladders are further cross-linked by O—H$\cdots$O hydrogen bonds involving water molecules (type I) and the sulfonate O atoms (Table 2). The mode of coordination in this crystal structure resembles that observed in the copper complex of ferron (Francis *et al.*, 2003*b*). Regarding π–π stacking, the pyridine and benzene rings are stacked alternately, with centroid-to-centroid distances of 3.451 (6) and 3.520 (6) Å, respectively, and the corresponding slip angles (the angle between the plane normal and line joining the centroids) are 17.6 and 10.1°, respectively. The overall supramolecular architecture present in the crystal structure is shown in Fig. 3.

In this crystal structure, an intermolecular I$\cdots$O interaction is also observed [$I\cdots O3(2 - x, -y - 1, 2 - z) = 3.304$ (5) Å]. Similar types of halogen–oxygen interactions have also been observed in related crystal structures (Raj *et al.*, 2003; Balasubramanian & Muthiah, 1996).

Experimental

Hot aqueous solutions of 8-hydroxy-7-iodoquinoline-5-sulfonic acid (ferron) (84 mg, Riedel de–Haen) and trimethoprim (73 mg, Shilpa Antibiotics Ltd) were mixed in 1:1 molar ratio. After warming for one hour over a water bath, a hot aqueous solution of $CdBr_2\cdot 4H_2O$ (85 mg, Sarabhai M. Chemical Ltd) was added. The colour of the solution changed from orange to yellow. The solution was again warmed for three hours and filtered. After a few days, needle-shaped yellow crystals separated from the filtrate.

Crystal data

$[Cd(C_9H_4INO_4S)(H_2O)_2]\cdot 2H_2O$
$M_r = 533.57$
Triclinic, $P\overline{1}$
$a = 6.9220$ (8) Å
$b = 10.1310$ (12) Å
$c = 10.9630$ (13) Å
$\alpha = 76.013$ (2)°
$\beta = 74.869$ (2)°
$\gamma = 85.318$ (2)°
$V = 720.00$ (15) Å^3

$Z = 2$
$D_x = 2.457$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2610 reflections
$\theta = 2.0$–28.3°
$\mu = 3.84$ mm^{-1}
$T = 93$ (2) K
Needle, yellow
0.24 × 0.04 × 0.04 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.714$, $T_{max} = 0.858$
5418 measured reflections

3385 independent reflections
2753 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 28.3°$
$h = -9 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.161$
$S = 1.04$
3385 reflections
190 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.122P)^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 5.21$ e Å^{-3}
$\Delta\rho_{\min} = -1.20$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cd—O1*W*	2.232 (5)	Cd—N	2.296 (6)
Cd—O2*W*	2.257 (5)	Cd—O1^{i}	2.380 (5)
Cd—O4	2.266 (5)	Cd—O2^{ii}	2.321 (5)
O1*W*—Cd—O2*W*	101.0 (2)	O2^{ii}—Cd—O2*W*	82.8 (2)
O1*W*—Cd—O4	167.6 (2)	O4—Cd—N	73.8 (2)
O1*W*—Cd—N	102.1 (2)	O1^{i}—Cd—O4	83.90 (18)
O1^{i}—Cd—O1*W*	84.15 (19)	O2^{ii}—Cd—O4	107.3 (2)
O1*W*—Cd—O2^{ii}	84.4 (2)	O1^{i}—Cd—N	87.05 (18)
O2*W*—Cd—O4	85.1 (2)	O2^{ii}—Cd—N	91.66 (19)
O2*W*—Cd—N	155.6 (2)	O1^{i}—Cd—O2^{ii}	167.9 (2)
O1^{i}—Cd—O2*W*	103.12 (18)		

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*W*···O3^{i}	0.81	2.07	2.845 (8)	160
O1*W*—H2*W*···O4*W*	0.82	2.30	2.677 (8)	109
O2*W*—H3*W*···O3*W*^{v}	0.81	2.18	2.910 (8)	150
O2*W*—H4*W*···O4^{iii}	0.82	2.03	2.837 (8)	168
O3*W*—H5*W*···O4	0.83	2.46	2.885 (8)	113
O3*W*—H6*W*···O1^{iv}	0.82	2.43	3.027 (7)	130
O3*W*—H6*W*···O2*W*	0.82	2.55	3.293 (8)	151
O4*W*—H7*W*···O3^{ii}	0.81	2.16	2.905 (8)	153

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

The H atoms of the aromatic groups were positioned geometrically and those of water molecules were obtained from a difference Fourier map. All the H atoms were treated as riding atoms, with C—H and O—H distances of 0.93 and 0.81–0.82 Å, respectively, and with isotropic displacement parameters of $1.2U_{\rm eq}$ of the parent atom. One of the H atoms of the water molecule O4*W* was not located. The highest peak in the difference map was found at a distance of 0.90 Å from O1 and the deepest hole is at 1.40 Å from iodine. The maximum residual electron density is larger than that normally expected. An analysis of the reflections having poorest agreement showed that F_o^2 are greater than F_c^2, a possible sign of twinning, but no suitable twin law was identified.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2001); 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* (Spek, 1997); software used to prepare material for publication: *SHELXL*97.

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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. (1995). PhD thesis, Department of Chemistry, Bharathidasan University, Tiruchirappalli, India.

Balasubramanian, T. & Muthiah, P. T. (1996). *Acta Cryst.* C**52**, 2072–2073.

Bruker (2001). *SMART*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cai, J., Chen, C.-H., Feng, X.-L., Liao, C.-Z. & Chen, X.-M. (2001). *J. Chem. Soc. Dalton Trans.* pp. 2370–2375.

Francis, S., Muthiah, P. T., Bocelli, G. & Cantoni, A. (2003*a*). *Acta Cryst.* E**59**, m87–m90.

Francis, S., Muthiah, P. T., Bocelli, G. & Cantoni, A. (2003*b*). *Acta Cryst.* E**59**, m1157–m1159.

Francis, S., Muthiah, P. T., Bocelli, G. & Cantoni, A. (2003*c*). *Acta Cryst.* E**59**, m1154–m1156.

Francis, S., Muthiah, P. T., Rychlewska, U. & Warzajtis, B. (2003). *Acta Cryst.* E**59**, m1160–m1163.

Harvey, M., Baggio, S., Russi, S. & Baggio, R. (2003). *Acta Cryst.* C**59**, m171–m174.

Husgen, N. S., Luinstra, G. A., Schaper, F. & Schmidt, K. (1998). *Inorg. Chem.* **37**, 3471–3474.

Mao, J.-G., Wang, Z. & Clearfield, A. (2002). *Inorg. Chem.* **41**, 3713–3720.

Muthiah, P. T., Francis, S., Bocelli, G. & Cantoni, A. (2003). *Acta Cryst.* E**59**, m1164–m1167.

Poojary, D. M., Zhang, B., Bellinghausen, P. & Clearfield, A. (1996). *Inorg. Chem.* **35**, 4942–4949.

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). *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (1997). *PLATON*. Utrecht University, The Netherlands.

Zhou, J.-S., Cai, J.-W. & Ng, S. W. (2003). *Acta Cryst.* E**59**, o1185–o1186.

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