

Triaqua(μ -7-iodo-8-oxidoquinoline-5-sulfonato- κ^2 N, O^8)dioxidouranium(VI) dihydrate

Pandian Sasikumar and Packianathan Thomas Muthiah*

School of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, Tamilnadu, India

Correspondence e-mail: tomtrichy@yahoo.co.in

Received 17 September 2009

Accepted 15 December 2009

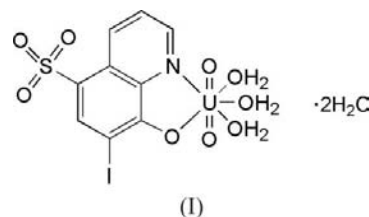
Online 22 January 2010

In the title compound, $[U(C_9H_4INO_4S)O_2(H_2O)_3] \cdot 2H_2O$, the asymmetric unit contains a UO_2^{2+} ion coordinated by the N and O atoms of a 7-iodo-8-oxidoquinoline-5-sulfonate dianion (ferron anion) and three coordinated water molecules, and two uncoordinated water molecules. The UO_2^{2+} ion exhibits a seven-coordinate pentagonal bipyramidal geometry. The usual sulfonate oxygen coordination is absent but the sulfonate O atoms, along with the coordinated and lattice water molecules, play a vital role in assembling the three-dimensional structure via an extensive network of intermolecular O—H...O hydrogen bonds and π – π stacking interactions.

Comment

The most common uranium compounds are those containing the linear symmetrical UO_2^{2+} ion [uranyl(2+) ion]. The number of known complexes of UO_2^{2+} is enormous and virtually every kind of oxygen-donor ligand, as well as many nitrogen donors, and even sulfur donors, have been found in such complexes (Cotton *et al.*, 1999). Derivatives of 8-hydroxyquinoline (oxine) are known for their anti-amoebic, antibacterial and antifungal activities, which are correlated with their metal-chelating ability (Banerjee & Saha, 1986). Oxine and its derivatives have long been extensively used in analytical chemistry (Hollingshead, 1954–1956), and oxine derivatives are fluorogenic ligands for many metal ions (Launay *et al.*, 2001). 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. We have reported the crystal structures of 8-hydroxy-7-iodoquinoline-5-sulfonic acid (Balasubramanian & Muthiah, 1996), the sodium, copper, strontium, zinc and nickel complexes of ferron (Raj *et al.*, 2003; Francis *et al.*, 2003a; Balasubramani *et al.*, 2004; Francis *et al.*, 2003c; Raj *et al.*, 2001, respectively), and potassium complexes of HQS

(Francis *et al.*, 2003b). The crystal structures of uranyl complexes of 4,4'-bipyridine (Thuéry, 2007), uranyl *n*-pentane-1,5-dicarboxylate (Borkowski *et al.*, 2005) and uranyl pyridazine-3-carboxylate dihydrate (Leciejewicz *et al.*, 2009) have also been reported. The crystal structure of the title complex, triaqua(μ -7-iodo-8-oxidoquinoline-5-sulfonato)dioxidouranium(VI) dihydrate, (I), is presented here.



In the crystal structure of (I), the asymmetric unit contains a UO_2^{2+} ion, a 7-iodo-8-oxidoquinoline-5-sulfonate (ferron) dianion, three coordinated water molecules and two uncoordinated water molecules (Fig. 1). The uranium ion adopts seven-coordinate pentagonal bipyramidal geometry. Two short uranyl U—O bonds are observed in axial positions, with distances (Table 1) close to the average reported value of 1.758 (3) Å (Burns *et al.*, 1997). The O5—U1—O6 angle is close to 180°. The N and O atoms of the oxine system (bidentate chelation) and the three water molecules (O1W, O2W and O3W) are coordinated to the metal atom in equatorial positions (Table 1). In the chelate, the U1—O4 bond distance is significantly shorter than the U1—N1 bond distance. This trend has also been observed in various metal complexes of ferron and related ligands (Francis *et al.*, 2003a,b, 2004; Raj *et al.*, 2001; Thuéry, 2007; Leciejewicz *et al.*, 2009). Hydrogen-bonding patterns involving the sulfonate oxygen in biological systems and metal complexes are of current interest (Onoda *et al.*, 2001). The sulfonate O atoms are not involved in the coordination but make an extensive network of O—H...O hydrogen bonds with all of the coordinated and uncoordinated water molecules (Table 2). The sulfonate O atoms (O1 and O2) interact with the coordinated and uncoordinated water molecules to form a chain of $R_3^3(10)$ rings (Etter, 1990; Bernstein *et al.*, 1995) running parallel to [100].

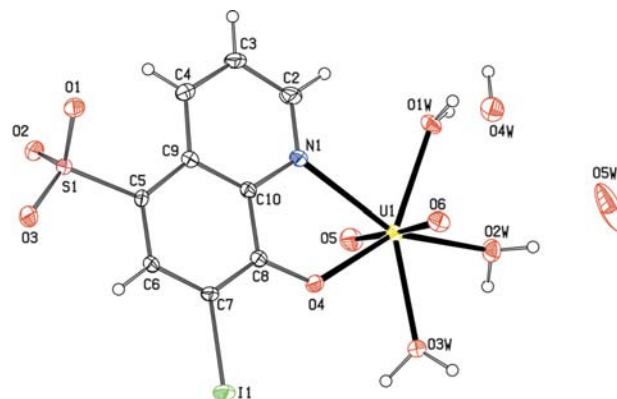
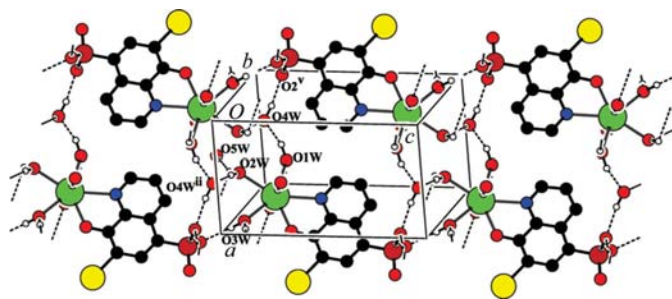
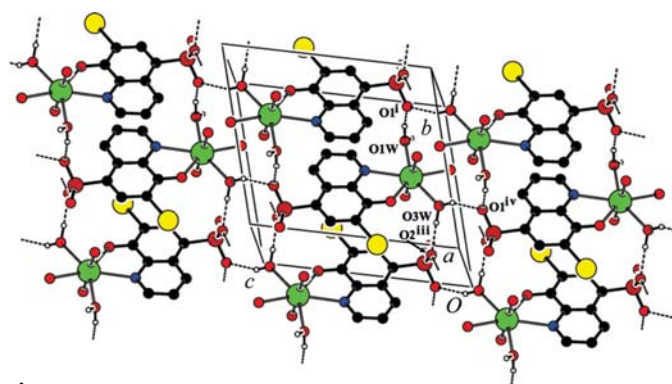


Figure 1
The asymmetric unit of (I), shown with 50% probability displacement ellipsoids.


Figure 2

The hydrogen-bonded network in (I). Dashed lines indicate hydrogen bonds and H atoms not involved in hydrogen bonding have been omitted. [Symmetry codes: (ii) $-x + 1, -y + 1, -z$; (v) $-x + 1, -y + 1, -z + 1$; (v) $x - 1, y + 1, z - 1$.]


Figure 3

The supramolecular three-dimensional network and stacking in (I). Dashed lines indicate hydrogen bonds and H atoms not involved in hydrogen bonding have been omitted. [Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (iii) $-x + 2, -y, -z + 1$; (iv) $x, y, z - 1$.]

These chains are interlinked by the coordinated water molecule, O1W, acting as a donor, one uncoordinated water molecule (O4W) acting as both donor and acceptor and a sulfonate O atom (O2) as an acceptor, *via* further O—H...O hydrogen bonds (Table 2), to form a supramolecular sheet which lies parallel to (110) (Fig. 2). The organic ligands are stacked over one another. Each pair of adjacent ligands stack in an inversion-related manner, and are linked to one another *via* O—H...O hydrogen bonds involving two of the coordinated water molecules (O1W and O3W) and sulfonate O atoms to form a ladders. These supramolecular ladder are crosslinked *via* O—H...O hydrogen bonds to form the three-dimensional network (Fig. 3). π - π stacking interactions between oxine rings, with a perpendicular separation of 3.6009 (17) Å, a centroid-centroid distance of 3.634 (2) Å and a slip angle (the angle between the centroid vector and the normal to the plane) of 7.77°, further stabilize the crystal structure.

Experimental

A hot aqueous solution of ferron (176 mg, Riedel de-Hean) and $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (125 mg, LOBA Chemie) were mixed in a 1:2 molar ratio and warmed in a water bath for 3 h, forming a red solution. After a few days of slow evaporation, red crystals of (I) were

obtained. In the IR spectrum, a stretching band at 916 cm^{-1} (Malutan *et al.*, 2008), characteristic of the UO_2^{2+} group, was observed. Stretching bands at 1707.50, 1191.13 and 1045 cm^{-1} (Gonzalez-Baro *et al.*, 2001) correspond to $\nu_{(\text{CN})}$, $\nu_{(\text{CO})}$ and $\nu_{(\text{SO})}$, respectively.

Crystal data

$[\text{U}(\text{C}_9\text{H}_4\text{INO}_4\text{S})\text{O}_2(\text{H}_2\text{O})_3] \cdot 2\text{H}_2\text{O}$	$\gamma = 66.701 (1)^\circ$
$M_r = 707.20$	$V = 878.04 (3)\text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.3742 (2)\text{ \AA}$	Mo $K\alpha$ radiation
$b = 10.1785 (2)\text{ \AA}$	$\mu = 11.17\text{ mm}^{-1}$
$c = 11.6146 (2)\text{ \AA}$	$T = 293\text{ K}$
$\alpha = 74.958 (1)^\circ$	$0.15 \times 0.13 \times 0.12\text{ mm}$
$\beta = 84.717 (1)^\circ$	

Data collection

Bruker SMART APEXII CCD	21488 measured reflections
area-detector diffractometer	6209 independent reflections
Absorption correction: multi-scan	5581 reflections with $I > 2\sigma(I)$
(SADABS; Bruker, 2008)	$R_{\text{int}} = 0.031$
$T_{\text{min}} = 0.286, T_{\text{max}} = 0.348$	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$	218 parameters
$wR(F^2) = 0.059$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\text{max}} = 1.70\text{ e \AA}^{-3}$
6209 reflections	$\Delta\rho_{\text{min}} = -1.16\text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

U1—O1W	2.417 (3)	U1—O5	1.763 (3)
U1—O2W	2.427 (2)	U1—O6	1.759 (3)
U1—O3W	2.426 (3)	U1—N1	2.605 (3)
U1—O4	2.281 (3)		
O1W—U1—O2W	75.84 (9)	O3W—U1—O5	93.23 (13)
O1W—U1—O3W	148.59 (8)	O3W—U1—O6	89.79 (12)
O1W—U1—O4	139.84 (9)	O3W—U1—N1	135.24 (9)
O1W—U1—O5	91.87 (12)	O4—U1—O5	93.45 (13)
O1W—U1—O6	84.63 (11)	O4—U1—O6	89.22 (11)
O1W—U1—N1	76.08 (9)	O4—U1—N1	64.80 (9)
O2W—U1—O3W	73.66 (9)	O5—U1—O6	176.50 (13)
O2W—U1—O4	144.25 (9)	O5—U1—N1	85.08 (13)
O2W—U1—O5	85.84 (13)	O6—U1—N1	94.03 (11)
O2W—U1—O6	93.32 (10)	O1—S1—O2	110.55 (18)
O2W—U1—N1	150.13 (10)	O1—S1—O3	112.96 (18)
O3W—U1—O4	70.69 (9)	O2—S1—O3	112.50 (16)

The H atoms of the aromatic groups were positioned geometrically. The water H atoms were located using difference Fourier synthesis and their positional parameters were initially refined with O—H distance restraints of 0.97 (2) Å and H...H restraints of 1.54 (2) Å. Subsequently, all H atoms were treated as riding atoms, with C—H and O—H distances of 0.93 and 0.88–0.95 Å, respectively, and with isotropic displacement parameters of $1.2U_{\text{eq}}$ of the parent atom. H atoms could not be located reliably on O5W nor the second H atom on O4W and these atoms were not included in the model.

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2009); software used to prepare material for publication: PLATON.

Table 2

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1 <i>W</i> —H1 <i>A</i> ...O4 <i>W</i>	0.95	1.72	2.644 (4)	163
O1 <i>W</i> —H1 <i>B</i> ...O1 ⁱ	0.95	1.77	2.671 (4)	157
O2 <i>W</i> —H2 <i>A</i> ...O5 <i>W</i>	0.91	1.78	2.616 (6)	153
O2 <i>W</i> —H2 <i>B</i> ...O4 <i>W</i> ⁱⁱ	0.88	2.10	2.975 (4)	175
O3 <i>W</i> —H3 <i>A</i> ...O2 ⁱⁱⁱ	0.95	1.81	2.752 (4)	170
O3 <i>W</i> —H3 <i>B</i> ...O1 ^{iv}	0.95	1.93	2.829 (4)	156
O4 <i>W</i> —H4 <i>B</i> ...O2 ^v	0.94	1.87	2.798 (4)	172

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

The authors thank the DST India (FIST programme) for use of the Bruker APEXII diffractometer at the School of Chemistry, Bharathidasan University.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM3028). Services for accessing these data are described at the back of the journal.

References

- Balasubramani, K., Francis, S., Muthiah, P. T., Bocelli, G. & Cantoni, A. (2004). *Acta Cryst.* **E60**, m1576–m1579.
- Balasubramanian, T. & Muthiah, P. T. (1996). *Acta Cryst.* **C52**, 2072–2073.
- Banerjee, T. & Saha, N. N. (1986). *Acta Cryst.* **C42**, 1408–1411.
- Bernstein, J., Davis, R. E., Shimon, L. & Chang, N. L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
- Borkowski, L. A. & Cahill, C. L. (2005). *Acta Cryst.* **E61**, m816–m817.
- Bruker (2008). *APEX2, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Burns, P. C., Ewing, R. C. & Hawthorne, F. C. (1997). *Can. Mineral.* **35**, 1551–1570.
- Cotton, F. A., Wilkinson, G., Murillo, C. A. & Bochmann, M. (1999). *Advanced Inorganic Chemistry*, 6th ed. New York: John Wiley & Sons Inc.
- Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
- Francis, S., Muthiah, P. T., Bocelli, G. & Cantoni, A. (2003a). *Acta Cryst.* **E59**, m1157–m1159.
- 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**, m87–m90.
- Francis, S., Muthiah, P. T. & Butcher, R. J. (2004). *Acta Cryst.* **E60**, m62–m64.
- Gonzalez-Baro, A. C. & Baran, E. J. (2001). *J. Braz. Chem. Soc.* **12**, 208–214.
- Hollingshead, R. G. W. (1954–1956). *Oxine and its Derivatives*, Vols. I–IV. London: Butterworth.
- Launay, F., Alain, V., Destandau, E., Ramos, N., Bardez, E. & Pierre, J. L. (2001). *New J. Chem.* **25**, 1269–1280.
- Leciejewicz, J. & Starosta, W. (2009). *Acta Cryst.* **E65**, m94.
- Malutan, T., Pui, A., Malutan, C., Tataru, L. & Humelnicu, D. (2008). *J. Fluoresc.* **18**, 707–713.
- 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. & Righi, L. (2001). *Acta Cryst.* **E57**, m591–m594.
- Raj, S. B., Muthiah, P. T., Rychlewska, U., Warzajtis, B., Bocelli, G. & O'lla, R. (2003). *Acta Cryst.* **E59**, m46–m49.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Thuéry, P. (2007). *Acta Cryst.* **C63**, m54–m56.