metal-organic papers

Hydrogen-bonded supramolecular motifs in aqua(8-hydroxyquinoline-5-sulfonato-$\kappa^2 N,O$)potassium(I)

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In the title compound, [K(C$_9$H$_6$NO$_4$S)(H$_2$O)], (I), the K$^+$ ion, surrounded by the N and O atoms of the quinolinol moiety (bidentate chelation), three O atoms from the sulfonate groups and a water molecule, has a distorted octahedral geometry. The multiple coordination mode of the sulfonate group, the bidentate chelation of the oxine moiety and the hydrogen-bonded network lead to a supramolecular architecture in the crystal structure of (I).

Comment

8-Hydroxyquinoline (oxine) and its derivatives are useful for tracing metal ions (analytical reagent). They are also well known antibacterial and antiamoebic agents. Many bidentate chelate complexes of oxine with metal ions have been reported (Okabe & Saishu, 2001; Okabe *et al.*, 2002; Hughes & Truter, 1978). The sulfoxine (oxine + sulfonic acid) ligand has additional hydrogen-bonding/metal-binding sites and modes. Hence the sulfoxine system has been extensively used to design supramolecular architectures. The crystal structures of the sodium complex of 8-hydroxyquinoine-5-sulfonic acid (HQS) (Raj *et al.*, 2002), the lithium complex of HQS (Murugesan & Muthiah, 1997), the nickel complex of HQS (Raj *et al.*, 2001), the cobalt complex of ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid) (Balasubramanian, 1995), the nickel complex of ferron (Raj *et al.*, 2003) and the zinc complex of ferron (Francis *et al.*, 2003) have been reported from our laboratory. Various coordination modes of the sulfonate group in the crystal structures of metal–aryl sulfonates have been reported (Cai, Chen, Liao *et al.*, 2001; Cai, Chen, Feng *et al.*, 2001; Husgen *et al.*, 1998). Two types of coordination modes have been reported in copper–sulfoxinate complexes (Petit, Coquerel *et al.*, 1993; Petit, Ammor *et al.*, 1993). In one mode, two centrosymmetrically related monomers are bridged by the coordination of one of the sulfonate O atoms. This bridging, along with bidentate chelation of the oxine moiety, forms a cage-like dimer. This mode has also been reported in the metal complexes of ferron (Balasubramanian, 1995; Raj *et al.*, 2003; Francis *et al.*, 2003). In the other mode, in addition to the bidentate chelation of the oxine moiety, one of the sulfonate O atoms is coordinated to the metal atom of another unit, forming a (linear) polymeric arrangement.
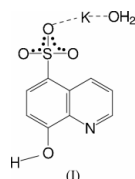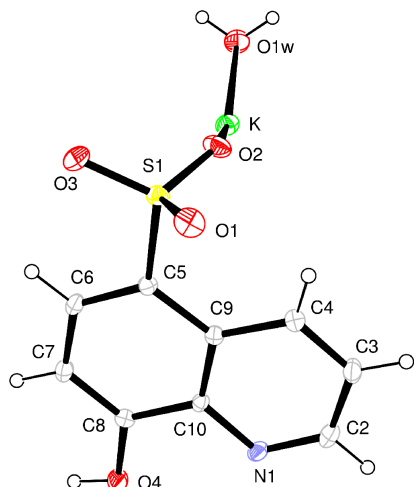
Figure 1
A view of the asymmetric unit of (I), showing 30% probability displacement ellipsoids.

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

Figure 3
The overall supramolecular architecture of (I).
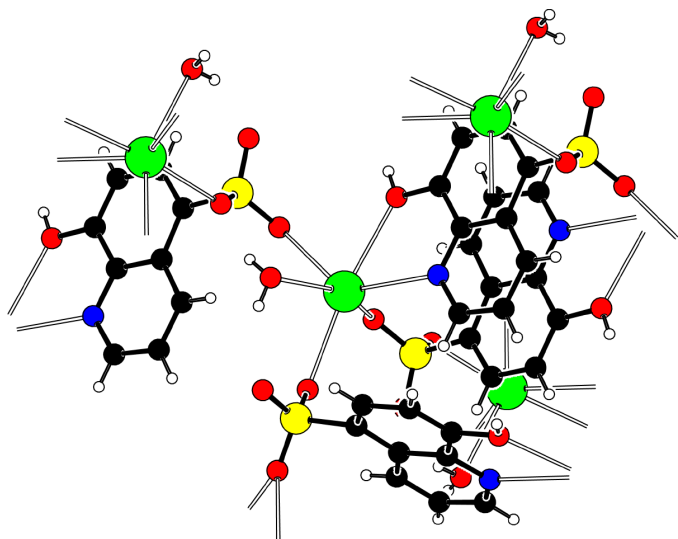
In the title crystal structure, (I), the asymmetric unit contains a K^+ ion, an 8-hydroxyquinoline-5-sulfonate anion (HQS) and a water molecule (Fig. 1). The coordination geometry around the K^+ ion is that of a distorted octahedron. It is surrounded by three O atoms (O2, O2^{ii} and O1^{iii}; symmetry code as in Table 1) from three different SO_3 groups, atoms N and O4 (bidentate chelation of the oxine moiety), and a water molecule (Fig. 2). Atoms O1, O2 and O2^i of the SO_3 group and atom O4 of the oxine moiety occupy the equatorial positions, and atom O1W of the water molecule and atom N1 of the oxine moiety lie in the axial positions. The bond lengths and angles (Table 1) agree with the reported data for potassium complexes (Cai, Chen, Liao *et al.*, 2001; Hughes & Truter, 1978). The hydroxy group of the quinolinol moiety is not deprotonated and is involved in the hydrogen bonding. The closest distance between two K^+ ions, 4.038 (1) Å, is longer than those in the potassium complex of 8-hydroxyquinoline (Hughes & Truter, 1978).
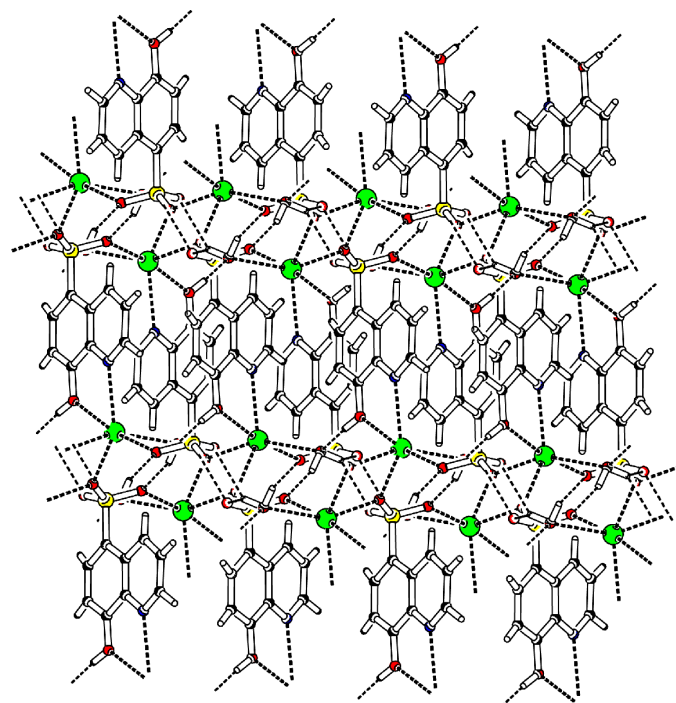
All three O atoms of the SO_3 group act differently. The first (O1) is involved in both hydrogen bonding and coordination, whereas the second (O2) bridges two different K^+ ions through bidentate coordination to make a four-membered ring. The third O atom (O3) is involved only in hydrogen bonding. The SO_3 group bridges three K^+ ions. A pleated sheet consisting of 16-membered rings is constructed by four K—O—S—O units. This is further extended to form a chain along the c axis. The non-coordinated O atom (O3) of the SO_3 group is involved in hydrogen bonding with a neighbouring water molecule (Table 2). The water molecule bridges two sulfonate groups *via* O—H···O hydrogen bonds (Table 2). This hydrogen-bonded interaction extends along the c axis, forming a chain. The overall supramolecular architecture is shown in Fig. 3.

Experimental

Crystal data

[K(C9H6NO4S)(H2O)]	$D_x = 1.696$ Mg m^{-3}
$M_r = 281.33$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25
$a = 9.885$ (2) Å	reflections
$b = 10.083$ (2) Å	$\theta = 3.2$–30.0°
$c = 11.269$ (3) Å	$\mu = 0.68$ mm^{-1}
$\beta = 101.14$ (2)°	$T = 293$ (2) K
$V = 1102.0$ (4) Å^3	Plate, colourless
$Z = 4$	$0.37 \times 0.29 \times 0.21$ mm

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Data collection

Philips PW1100 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$\quad T_{min} = 0.787, T_{max} = 0.870$
3023 measured reflections
2802 independent reflections
2038 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$

$\theta_{max} = 30.0°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 14$
$l = -15 \rightarrow 15$
1 standard reflection
$\quad$ every 100 reflections
$\quad$ frequency: 60 min
$\quad$ intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.157$
$S = 1.13$
2802 reflections
154 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0924P)^2]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.65$ e Å^{-3}
$\Delta\rho_{min} = -0.68$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

K—O1W	2.878 (2)	K—N1^i	2.809 (3)
K—O2	2.719 (2)	K—O2^{ii}	2.697 (2)
K—O4^i	2.783 (2)	K—O1^{iii}	2.718 (2)
O1W—K—O2	154.26 (7)	O1^{iii}—K—O2	87.06 (7)
O1W—K—O4^i	103.08 (7)	O4^i—K—N1^i	57.18 (6)
O1W—K—N1^i	101.16 (7)	O2^{ii}—K—O4^i	75.89 (7)
O1W—K—O2^{ii}	82.60 (7)	O1^{iii}—K—O4^i	170.06 (7)
O1^{iii}—K—O1W	78.92 (7)	O2^{ii}—K—N1^i	132.70 (7)
O2—K—O4^i	94.46 (7)	O1^{iii}—K—N1^i	112.92 (7)
O2—K—N1^i	104.17 (7)	O1^{iii}—K—O2^{ii}	114.05 (7)
O2—K—O2^{ii}	83.61 (7)		

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

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1W—H1W$\cdots$O3^i	0.81	2.18	2.924 (3)	153
O1W—H2W$\cdots$O1^{ii}	0.83	2.03	2.826 (3)	161
O4—H5$\cdots$O1W^{iii}	0.85	1.82	2.675 (3)	174

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

H atoms were treated as riding atoms, with C—H distances of 0.93 Å and O—H distances of 0.81–0.85 Å, and with isotropic displacement parameters of 1.2 times U_{eq} of the parent atom.

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