Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Metal-binding modes in sulfoxines: supramolecular network in (8-hydroxyquinoline-5-sulfonato-N^1,O^8)sodium(I)

Savarimuthu Baskar Raj,[a] Packianathan Thomas Muthiah,[a]* Gabriele Bocelli[b] and Rita Olla[b]

[a]Department of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, Tamilnadu, India, and [b]IMEM-CNR, Palazzo Chimico-Campus, Parco Area delle Scienze 17/a, I-43100 Parma, Italy

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

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.031
wR factor = 0.091
Data-to-parameter ratio = 15.8

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

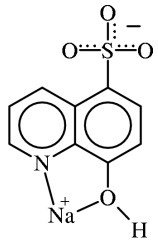
Received 19 August 2002
Accepted 21 August 2002
Online 13 September 2002

In the title compound, [Na($C_9H_6NO_4S$)], the sodium ion is coordinated by the N and O atoms of the quinolinol moiety (usual bidentate chelation) and three O atoms from three different sulfonate groups. The quinolinol O atom and one of the sulfonate O atoms are in the axial positions and the ring N atom and two O atoms from two different sulfonate groups lie in the equatorial positions of the trigonal bipyramid around sodium. Unlike other metal sulfoxinates, the quinolinol O atom is not deprotonated, but is involved in hydrogen bonding. Moreover, all three sulfonate O atoms are involved in coordination, leading to a supramolecular three-dimensional network structure.

Comment

Oxine and its derivatives are well known analytical reagents and antiamoebic agents (Bambury, 1979). Oxine is a bidentate chelator forming complexes with many metal ions through the quinoline N and deprotonated quinolinol O atoms. Metal chelation has been implicated in the biological activity of oxine derivatives (Martel & Calvin, 1959). The incorporation of sulfonic acid in the oxine moiety provides additional metal-binding and potential hydrogen-bonding acceptor sites/modes. This type of ligand is called sulfoxine (sulfonic acid + oxine). In metal sulfoxinates, in addition to the usual bidentate chelation of the oxine moiety through the N and O atoms, sulfonic O atoms also coordinate to the metal. Hydrogen-bonding patterns and metal-binding modes of sulfoxinates are of current interest (Cai, Chen, Liao, Feng & Chen, 2001; Cai, Chen, Liao, Yao *et al.*, 2001; Cai, Chen, Feng *et al.*, 2001). It has recently been demonstrated that the combination of coordination and the sulfonate group can result in the formation of strong supramolecular aggregates through hydrogen bonding and this represents a new strategy for the design of SHG (second harmonic generation) materials (Xie *et al.*, 2002). Information on the structural chemistry of metal sulfoxinates is relatively rare, due to the poor coordinating ability of sulfoxinates compared with that of phosphonates. Various remarkable structural features of metal sulfoxinates have prompted us to investigate systematically the structural chemistry of these compounds. The crystal structures of 7-iodo-8-hydroxyquinoline-5-sulfonic acid (ferron; Balasubramanian & Muthiah, 1996*a*), 7-nitro-8-hydroxyquinoline-5-sulfonic acid monohydrate (Balasubramanian & Muthiah, 1996*b*), the cobalt complex of ferron (Balasubramanian, 1995), the nickel complex of 8-hydroxyquinoline-5-sulfonic acid (HQS; Baskar Raj *et al.*, 2001), the nickel complex of ferron (Baskar Raj *et al.*, 2002) and the lithium complex of HQS (Murugesan & Muthiah, 1997) have also been reported from our laboratory.

In metal sulfoxinates, the sulfonate motifs can be linked in two ways. In one type, in addition to the usual bidentate chelation of the oxine motif, two centrosymmetrically related monomers are bridged by one of the sulfonate O atoms involved in the coordination, forming a cage-like dimer, as observed in the copper–sulfoxinate complexes (Petit, Coquerel *et al.*, 1993; Petit, Ammor *et al.*, 1993), the cobalt complex of ferron (Balasubramanian, 1995), the nickel complex of ferron (Baskar Raj *et al.*, 2002) and the lithium complex of HQS (Murugesan & Muthiah, 1997). In another type, in addition to the usual bidentate chelation, a sulfonic acid O atom of one molecule is coordinated to the metal atom of another molecule, leading to a one-dimensional polymeric arrangement, as observed in the copper–sulfoxinate complex (Petit, Coquerel *et al.*, 1993).



(I)

In the sodium complex of HQS, (I), the coordination geometry around the sodium ion is distorted trigonal bipyramidal. In addition to the usual bidentate chelation involving the N and O atoms of the oxine moiety, three sulfonate O atoms from three different sulfonate groups are coordinated

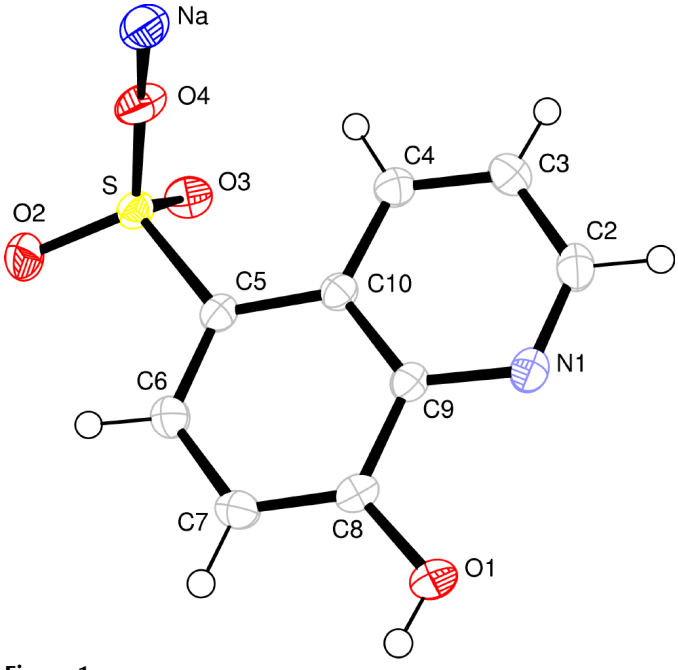


Figure 1
View of (I), with the atom-labelling scheme and 50% probability displacement ellipsoids.

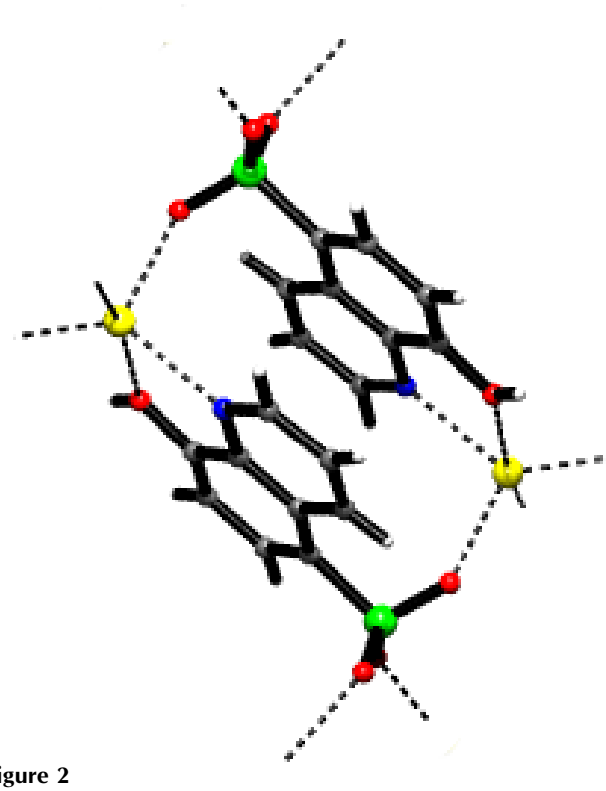


Figure 2
The cage-like dimeric arrangement of (I), made up of two inversion-related monomers.

to the sodium ion. The O atom of the quinolinol moiety and one of the O atoms (O3) from the sulfonate group bind to the Na^+ ion at the axial positions and two O atoms (O2 and O4) from two different sulfonate groups and the ring N atom lie in the equatorial positions. A view of the complex unit of (I), with the atom-labelling scheme, is shown in Fig. 1. One of the sulfonate O atoms bridges the two inversion-related monomers, leading to a cage-like dimeric unit (Fig. 2). The distance between two neighbouring Na atoms is 5.4718 (15) Å. A view of the packing is shown in Fig. 3. The present sodium complex is quite different from other metal sulfoxinates reported in the literature (Balasubramanian, 1995; Murugesan & Muthiah, 1997; Petit, Coquerel *et al.*, 1993; Petit, Ammor *et al.*, 1993; Baskar Raj *et al.*, 2001, 2002) in the sense that all three sulfonate O atoms are involved in the coordination, leading to a supramolecular network structure. The smaller N—Na—O bite angle in (I) may be the result of longer coordination bonds than those in the Co and Ni complexes. The Na—O(quinolinol) and Na—N(ring) bond distances are not significantly different from one another. The Na—N(ring) distance [2.4418 (15) Å] in (I) agrees with the range of values [2.459 (7)–2.539 (6) Å] reported in the literature (Papadimitriou *et al.*, 1998). Also, the Na—O(quinolinol) distance [2.4892 (14) Å] in (I) agrees with the corresponding distance [2.42 (9) Å] in small molecules (Harding, 2002) reported in the Cambridge Structural Database (Allen & Kennard, 1993). The Na—O(sulfonate) distances agree with the corresponding distance reported in the literature (Cai, Chen, Liao, Feng & Chen, 2001; Cai, Chen, Liao, Yao *et al.*, 2001; Cai, Chen, Feng

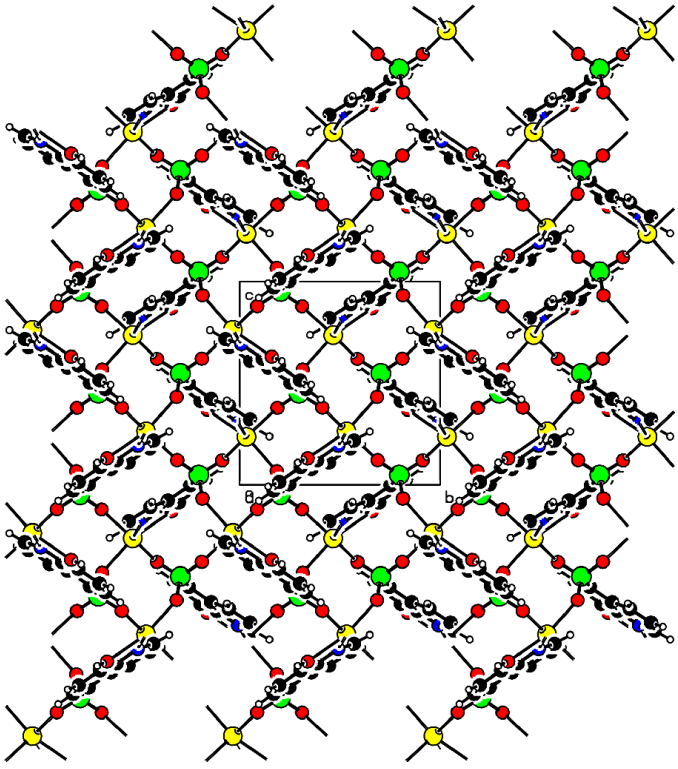


Figure 3
View of the packing diagram of (I), showing the dimeric arrangement in the *bc* plane.

et al., 2001) and are significantly shorter than the Na—O(quinolinol) distance (Table 1).

Unlike other sulfoxinates, the quinolinol O atom is not deprotonated, but is involved in a hydrogen bond with a symmetry-related O atom of the sulfonic acid group [O1—H1···O3^{i}; symmetry code: (i) 1 + *x*, *y*, *z*]. Atoms C4 and C6 are also involved in intramolecular hydrogen bonding with atoms O4 and O2 of the sulfonate group (Table 2), forming five-membered rings on both sides of the S—C bond. Intramolecular hydrogen bonding involving atom C6 with one of the sulfonate O atoms has also been observed in both 7-nitro-8-hydroxyquinoline-5-sulfonic acid monohydrate (Balasubramanian & Muthiah, 1996*b*) and ferron (Balasubramanian & Muthiah, 1996*a*). There is also a glide-related C—H···π interaction [H···*Cg* 2.6341 (6) Å and C2—H2···*Cg* 134.02 (5)°; atom C2 is in the pyridine ring and *Cg* is the phenyl-ring centroid]. Stacking interactions between the pyridine and phenyl rings in adjacent complex units are observed. The centroid-to-centroid and interplanar distances are 3.499 (9) and 3.303 (4) Å, respectively. The slip angle (angle between the centroid vector and the normal to the plane) is 20.73 (3)°.

Experimental

An aqueous solution of sodium diethyldithiocarbamate (0.113 g) and an aqueous solution of 8-hydroxyquinoline-5-sulfonic acid monohydrate were mixed and warmed over a water bath for 30 min. The product was then recrystallized from acetonitrile.

Crystal data

[Na(C$_9$H$_6$NO$_4$S)]
M_r = 247.21
Monoclinic, $P2_1/c$
a = 8.284 (2) Å
b = 10.488 (2) Å
c = 10.916 (2) Å
β = 103.25 (2)°
V = 923.2 (3) Å^3
Z = 4
D_x = 1.779 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 50 reflections
θ = 3.0–29.6°
μ = 0.39 mm^{-1}
T = 293 (2) K
Cuboid, colourless
0.34 × 0.26 × 0.17 mm

Data collection

Bruker AXS SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SHELXTL-NT*; Bruker, 1997)
T_{min} = 0.787, T_{max} = 0.936
132 007 measured reflections
2662 independent reflections
2119 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 30.6°
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.091
S = 1.01
2662 reflections
169 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0587P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.35 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S—O2	1.4482 (12)	Na—O3^{ii}	2.4175 (13)
S—O3	1.4731 (12)	Na—O1^{iii}	2.4892 (14)
S—O4	1.4563 (12)	Na—N1^{iii}	2.4418 (15)
S—C5	1.7740 (15)	O1—C8	1.3551 (18)
Na—O2	2.2979 (14)	N1—C2	1.3213 (19)
Na—O4^{i}	2.3357 (13)	N1—C9	1.3735 (18)
O2—S—O3	112.20 (7)	O1^{iii}—Na—N1^{iii}	64.86 (4)
O2—S—O4	114.35 (7)	Na^{iv}—O1—C8	121.03 (9)
O2—S—C5	106.31 (7)	S—O2—Na	133.30 (7)
O3—S—O4	110.92 (7)	S—O3—Na^{ii}	139.97 (7)
O3—S—C5	105.53 (7)	S—O4—Na^{v}	140.35 (7)
O4—S—C5	106.88 (7)	Na^{iv}—N1—C2	121.33 (10)
O2—Na—O4^{i}	122.27 (5)	C2—N1—C9	117.40 (12)
O2—Na—O3^{ii}	91.71 (5)	Na^{iv}—N1—C9	121.24 (9)
O1^{iii}—Na—O2	85.61 (5)	N1—C2—C3	123.97 (13)
O2—Na—N1^{iii}	131.41 (5)	S—C5—C10	120.01 (10)
O3^{ii}—Na—O4^{i}	93.20 (5)	S—C5—C6	119.61 (10)
O1^{iii}—Na—O4^{i}	103.57 (5)	O1—C8—C9	115.68 (12)
O4^{i}—Na—N1^{iii}	102.47 (5)	O1—C8—C7	124.04 (13)
O1^{iii}—Na—O3^{ii}	161.68 (5)	N1—C9—C10	122.93 (12)
O3^{ii}—Na—N1^{iii}	104.65 (5)	N1—C9—C8	117.16 (12)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O3^{i}	0.805 (18)	1.902 (18)	2.7029 (17)	173.4 (17)
C4—H4···O4	0.936 (17)	2.584 (18)	3.1235 (19)	117.1 (13)
C6—H6···O2	0.972 (18)	2.381 (17)	2.8657 (19)	110.2 (12)

Symmetry code: (i) $1+x, y, z$.

The H atoms were located in difference Fourier maps and refined with isotropic displacement parameters. The C—H and O—H bond lengths are 0.883 (18)-0.98 (3) and 0.805 (18) Å, respectively.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); 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: *PLATON*.

SBR thanks the Council of Scientific and Industrial Research, New Delhi, India, for the award of a Senior Research Fellowship [reference No. 9/475(103)2002 EMR-I].

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Balasubramanian, T. & Muthiah, P. T. (1996*a*). *Acta Cryst.* C**52**, 2072–2073.
Balasubramanian, T. & Muthiah, P. T. (1996*b*). *Acta Cryst.* C**52**, 1017–1019.
Balasubramanian, T. (1995). PhD thesis, Department of Chemistry, Bharathidasan University, Tiruchirappalli, India.
Bambury, R. E. (1979). *Burger's Medicinal Chemistry*, edited by M. E. Wolff, pp. 41–48. New York: John Wiley.
Baskar Raj, S., Muthiah, P. T., Bocelli, G. & Righi, L. (2001). *Acta Cryst.* E**57**, m591–m594.
Baskar Raj. S., Muthiah, P. T., Rychlewska, U., Warżajtis. B., Bocelli, G. & Olla, R. (2002). *Acta Cryst.* C**58**. Submitted.
Bruker (1997). *SAINT, SMART* and *SHELXTL-NT*. 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.
Cai, J., Chen, C.-H., Liao, C.-Z., Feng, X.-L. & Chen, X.-M. (2001). *Acta Cryst.* B**57**, 520–530.
Cai, J., Chen, C.-H., Liao, C.-Z., Yao, J.-H., Hu, X.-P. & Chen, X.-M. (2001). *J. Chem. Soc. Dalton Trans.* pp. 1137–1142.
Harding, M. M. (2002). *Acta Cryst.* D**58**, 872–874.
Martel, A. E. & Calvin, M. (1959). *Chemistry of Metal Chelate Compounds*. Englewood Cliffs: Prentice Hall.
Murugesan, S. & Muthiah, P. T. (1997). XXVIIIth National Seminar on Crystallography, Kottayam, India, September 24–26. (Deposited at CCDC, No. CCDC 166283.)
Papadimitriou, C., Veltsistas, P., Marek, J., Novosad, J., Slawin, A. M. Z. & Woollins, J. D. (1998). *Inorg. Chem. Commun.* **1**, 418–420.
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., Louer, D. & Lover, M. (1993). *New. J. Chem.* **17**, 187–192.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (1997). *PLATON.* Utrecht University, The Netherlands.
Xie, Y.-R., Xiong, R.-G., Xue, X., Chen, X.-T., Xue, Z. & You, X.-Z. (2002). *Inorg. Chem.* **41**, 3323–3326.