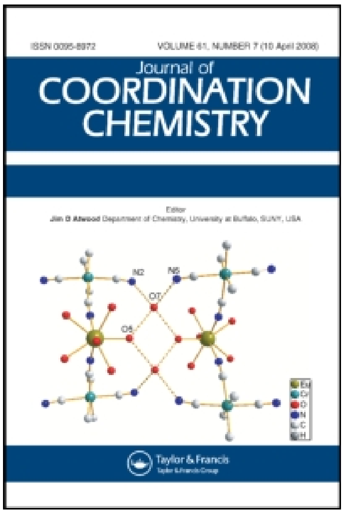

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis and crystal structure of lithium 8-hydroxyquinoline-5-sulfonate tetrahydrate

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To cite this Article Muthiah, P. Thomas and Murugesan, S.(2006) 'Synthesis and crystal structure of lithium 8-hydroxyquinoline-5-sulfonate tetrahydrate', Journal of Coordination Chemistry, 59: 10, 1167 — 1172
To link to this Article: DOI: 10.1080/00958970500410705
URL: http://dx.doi.org/10.1080/00958970500410705

Journal of Coordination Chemistry
Vol. 59, No. 10, 10 July 2006, 1167–1172

Synthesis and crystal structure of lithium 8-hydroxyquinoline-5-sulfonate tetrahydrate

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(*Received in final form 29 August 2005*)

A lithium salt of 8-hydroxyquinoline-5-sulfonic acid, $Li_2(C_9H_5NO_4S) \cdot 4H_2O$, has been synthesized and characterized by X-ray diffraction techniques. The salt is monoclinic, space group $P2_1/c$, with $a = 10.323(3)$, $b = 10.088(9)$, $c = 11.792(6)$ Å and $\beta = 92.21(3)°$. Li ions adopt two different distorted tetrahedral geometries. Li(1) is surrounded by a water molecule, N,O atoms of the oxine ring and one of the oxygen atoms of the sulphonate group. Li(2) is surrounded by three water molecules and an oxygen atom of the sulphonate group. The two lithium ions are bridged by a water molecule, leading to a polymeric network.

Keywords: Lithium; 8-Hydroxyquinoline-5-sulfonic acid; Crystal structure; Polymeric network

1. Introduction

8-Hydroxyquinoline and its derivatives are well known for their antifungal, antibacterial and antiamoebic activities [1] and biological activities have been correlated with their capacity to chelate metal ions [2]. Research on metal sulphonates is of contemporary interest [3], since the coordination chemistry of metal sulphonates is not well explored due to the weak coordinating ability of sulphonates compared to phosphonates [4–5]. The small radius of Li^+ gives versatile Li^+ coordination numbers and polyhedra [6–8]. Incorporation of a sulphonic acid group in an oxine (sulphoxine) gives, in addition to the usual bidentate chelation involving N and O atoms, the possibility of coordination of one or more of the sulphonate oxygen atoms; dimeric or polymeric structures may be generated. The crystal structure of 8-hydroxyquinoline-5-sulfonic acid (HQS) [9] and its copper [10–11], zinc [12], Na [13], Ni [14] and K complexes [15] have been reported. Here we report the preparation and structure of a lithium complex of 8-hydroxyquinoline-5-sulfonic acid, $Li_2(C_9H_5NO_4S) \cdot 4H_2O$.

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Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970500410705

2. Experimental

2.1. *Synthesis*

Aqueous solutions of 8-hydroxyquinoline-5-sulphonic acid and lithium carbonate were mixed in a 1 : 1 molar ratio. On warming this mixture on a water bath for 30 min, the light yellow solution became darker. The solution was kept at room temperature for crystallization and yellow thick plates shaped appeared within a few days.

2.2. *Crystal structure*

X-ray data were collected on a CAD4 Enraf Nonius diffractometer equipped with graphite monochromated Mo-Kα radiation by the ω–2θ scan method using a crystal of size $0.40 \times 0.25 \times 0.33\,\text{mm}^3$. The structure was solved by direct methods using SHELXS86 [16] and refined by the full-matrix least-squares methods on F^2 using SHELXL93 [17]. All hydrogen atoms including those of water molecules were located in difference Fourier maps and included in the refinement. Geometric calculations were done using PLATON97 [18]. Crystal data and refinement parameters are listed in table 1. Selected bond lengths and angles are given in table 2 and hydrogen bonding geometries in table 3.

3. Results and discussion

An ORTEP view of the asymmetric unit is shown in figure 1. The two lithium ions are bridged by a water molecule (O12). Both lithium ions have tetrahedral coordination geometry. To one lithium ion, the oxine moiety binds as the usual bidentate chelate involving quinoline nitrogen and the deprotonated oxygen atoms.

Table 1. Crystal data and refinement details for $Li_2(C_9H_5NO_4S) \cdot 4H_2O$.

Formula	$C_9H_{11}Li_2NO_7S$
Formula weight	291.14
Crystal system	Monoclinic
Space group	$P2_1/c$
a, b, c [Å]	10.323(2), 10.088(4), 11.792(6)
β [°]	92.21(3)
V [Å^3]	1227.1(8)
Z	4
D(Calcd) [g cm^{-3}]	1.576
μ(Mo-Kα) [mm^{-1}]	0.291
F(000)	600
Crystal size [mm^3]	$0.252 \times 0.30 \times 0.40$
Temperature (K)	293
Radiation [Å]	Mo-Kα 0.71073
θ (Min, Max) [°]	2.7, 25.0
Dataset	0 : 12; 0 : 11; −13 : 13
Total unique data R(int)	2270, 2146, 0.036
Observed data [$I > 2\sigma(I)$]	1976
Nref, Npar	2146, 226
R, wR_2, S	0.0273, 0.0773, 1.13
Maximum and average shift/error	0.00, 0.01
Min. and max. resd. dens. [e Å^{-3}]	−0.34, 0.32

Table 2. Bond distances and bond angles (Å, °) involving the non-hydrogen atoms of $Li_2(C_9H_5NO_4S)\cdot 4H_2O$.

S5–O1	1.472(1)	S5–O2	1.455(1)
S5–O3	1.448(2)	S5–C5	1.756(2)
O2–Li2	1.933(3)	O4–C8	1.316(2)
O11–Li2	1.963(3)	O12–Li1	1.988(3)
O12–Li2	1.989(3)	O13–Li2	1.901(3)
N1–C9	1.366(2)	N1–C2	1.320(2)
O1–S5–O2	109.8(8)	O1–S5–O3	110.9(8)
O1–S5–C5	107.1(7)	O2–S5–O3	113.8(8)
O2–S5–C5	107.6(8)	O3–S5–C5	107.4(8)
S5–O2–Li2	133.9(1)	Li1–O12–Li2	116.1(1)
C2–N1–C9	118.4(1)	N1–C2–C3	123.1(2)
S5–C5–C10	120.3(1)	S5–C5–C6	119.6(1)
O4–C8–C9	118.5(2)	O4–C8–C7	124.1(2)
N1–C9–C10	122.5(1)	N1–C9–C8	115.8(1)
O4^{i}–Li1–N1^{i}	84.89(1)	O1^{ii}–Li1–O4^{i}	118.2(1)
O1^{ii}–Li1–O12	106.3(2)	O4^{i}–Li1–O12	115.1(2)
O12–Li1–N1^{i}	116.1(1)	O1^{ii}–Li1–N1^{i}	115.7(2)
O12–Li2–O13	111.5(2)	O2–Li2–O11	104.4(2)
O2–Li2–O12	109.8(2)	O2–Li2–O13	112.6(1)
O11–Li2–O12	110.6(1)	O11–Li2–O13	107.5(2)

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

Table 3. Hydrogen bonding geometries (Å, °) for $Li_2(C_9H_5NO_4S)\cdot 4H_2O$.

D–H···A	D–H	H···A	D···A	D–H···A
O(11)–H(11A)···O(4)^{i}	0.82(3)	1.87(3)	2.676(2)	168(3)
O(11)–H(11B)···O(3)^{ii}	0.83(3)	2.05(3)	2.878(2)	171(3)
O(12)–H(12A)···O(1)^{iii}	0.85(2)	1.95(2)	2.789(2)	170(2)
O(12)–H(12B)···O(11)^{iii}	0.85(2)	1.91(2)	2.749(2)	171(2)
O(13)–H(13A)···O(4)^{iv}	0.86(3)	1.90(3)	2.763(3)	178(3)
O(13)–H(13B)···O(3)^{v}	0.82(3)	2.02(3)	2.816(3)	166(3)
Intra 1 C(4)–H(4)···O(1)	0.963(2)	2.599(2)	3.097(3)	112(1)
Intra 1 C(6)–H(6)···O(3)	0.922(2)	2.495(2)	2.877(3)	105(1)

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

Coordination geometry is completed by the bridging water molecule and one of the sulphonate oxygen atoms (O1) of a neighbouring ligand to form a dimer. The dimers are cross-linked by the second lithium ions, bridging water molecule and sulphonic oxygens to form an infinite polymeric network structure. The second lithium ion has a coordination geometry made up of four oxygen atoms, three coordinated water O atoms and a sulphonate oxygen atom (figure 2). The distance between the two lithium ions is 3.374(4) Å and the two lithium ions make an angle of 116.1(1)° with the bridging oxygen of the water molecule. Within the dimer the Li1···O1–S5 angle is 137.1(1)°. Average Li–O and S–O bond distances are 1.954(3) and 1.458(3) Å, respectively. These values are in agreement with related structures [4].

The crystal structure is stabilized by a network of O–H···O hydrogen bonds. One of the coordinated water molecules (O13) is hydrogen bonded to the non-coordinated oxygen atom (O3) of the sulphonate group. Two such inversion-related hydrogen bonds form a ring. The water molecule (O12) that bridges the two lithium ions is hydrogen bonded to one of the coordinated sulphonate O atoms (O1),

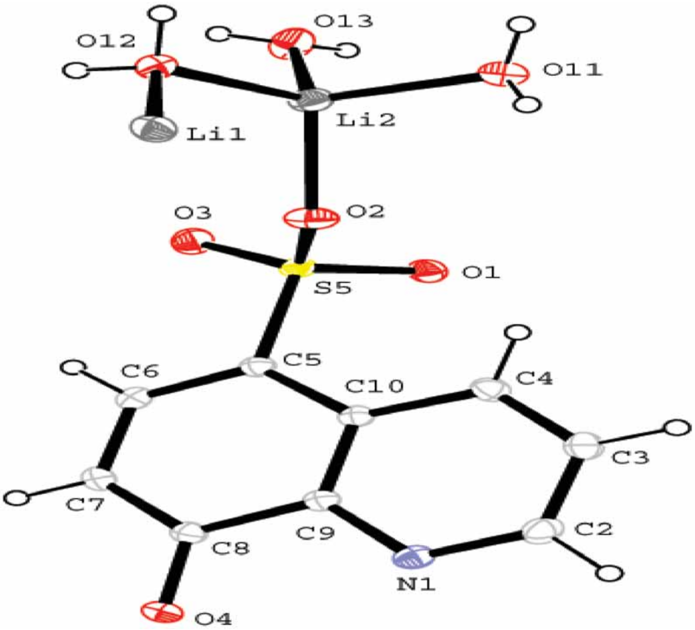

Figure 1. An ORTEP view of $Li_2(C_9H_5NO_4S) \cdot 4H_2O$ showing the atom numbering scheme.

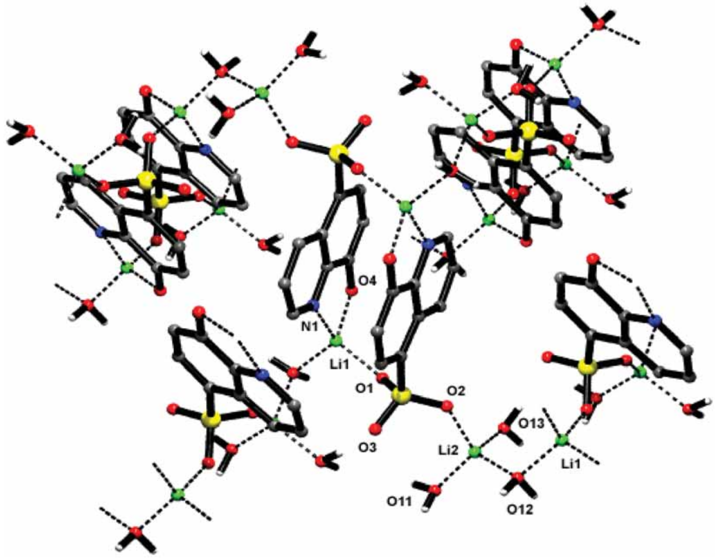

Figure 2. Coordination geometry around Li(1) and Li(2).

leading to a hydrogen-bonded ring of chair conformation and π–π interactions between the aromatic rings are observed (figure 3). Two neighbouring inversion-related pyridine rings (N1, –C6) of HQS overlap with a perpendicular separation of 3.872(2) Å, a centroid-to-centroid distance of 3.406 Å and a slip angle (between the centroid vector

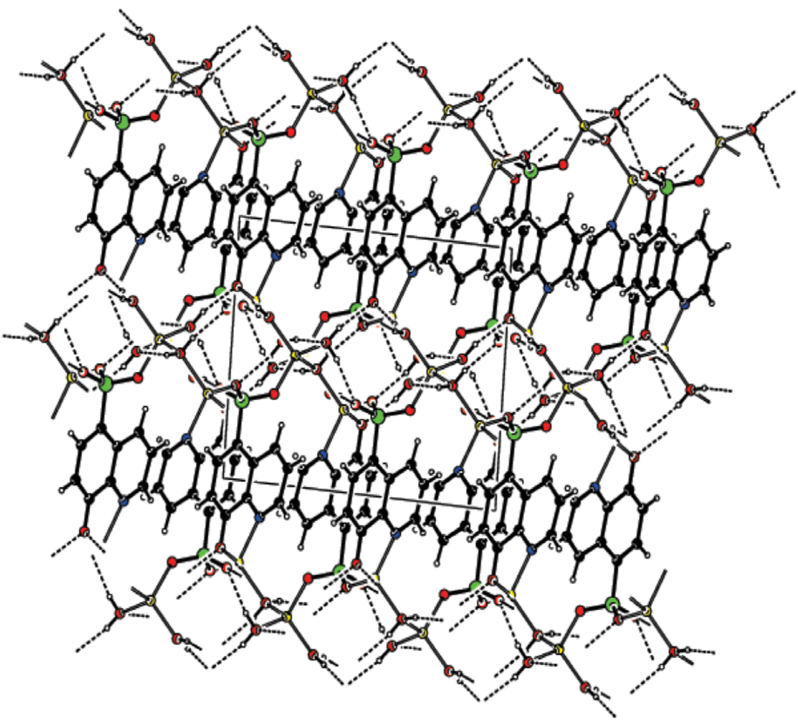

Figure 3. A view of the crystal packing in $Li_2(C_9H_5NO_4S) \cdot 4H_2O$.

and the normal to the plane) of 28.41°. The pyridine ring (N1, C2–C6) of HQS overlaps the phenyl ring (C5–C10) of HQS with perpendicular separation, centroid offset and the slip angle of 3.495(2), 3.491(2) Å and 12.58°, respectively.

Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 166283). Copies of this information can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, by emailing date_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, UK; fax: +44 1223 336033.

Acknowledgement

S.M. thanks U.G.C. (New Delhi) for the award of a Junior Research Fellowship.

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