

# The Crystal Structures of 7-Nitroso-8-hydroxyquinoline-5-sulfonic Acid [ $\rightleftharpoons$ 7-(Hydroxyimine)-8-oxo-quinoline-5-sulfonic Acid] and Its Disodium Salt Monohydrate

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Crystals of  $H_2L$  [ $L=7$ -nitroso-8-oxidoquinoline-5-sulfonate,  $(C_9H_4O_5N_2S)^{2-}$ ] are monoclinic,  $a=8.342(4)$ ,  $b=8.568(3)$ ,  $c=13.428(5)$  Å,  $\beta=90.15(4)^\circ$ ,  $Z=4$ , space group  $P2_1/n$ . Crystals of  $Na_2L \cdot H_2O$  are triclinic,  $a=8.046(4)$ ,  $b=8.528(4)$ ,  $c=9.669(5)$  Å,  $\alpha=86.23(4)$ ,  $\beta=67.63(4)$ ,  $\gamma=71.74(4)^\circ$ ,  $Z=2$ , space group  $P\bar{1}$ . The structures were solved by direct methods with the MULTAN program and refined by least-squares methods to the  $R$  values 0.061 ( $H_2L$ ) and 0.041 ( $Na_2L \cdot H_2O$ ) for 1382 and 1916 observed reflections, respectively.

The C7–N [1.299(7) Å], N–O [1.368(6) Å] bond lengths, the C–N–O bond angle [112.2(4)°] and the C8–O bond distance [1.229(6) Å] together indicate that  $H_2L$  exists in a tautomeric oxime form in which the oxime group and the carbonyl oxygen are in the *anti* configuration. The acid has a zwitterion structure, the sulfonic acid proton being attached to the quinoline nitrogen atom.

The organic anion in  $Na_2L \cdot H_2O$  has an oximate-like structure with bond lengths C7–N, 1.351(3); N–O 1.281(4) and C8–O, 1.253(4) Å and bond angle C7–N–O, 116.3(3)°. One of the sodium ions is in a strongly distorted octahedral environment, while the other is surrounded by only five atoms. Two hydrogen bonds are present in both structures.

Our preceding communications have shown that sulfonic acid derivatives of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol exist in their tautomeric quinone oxime forms in the solid state and that the quinonoid character of the ligands is retained in their metal complexes.<sup>1,2</sup> Our study on free and metal-coordinated nitrosophenol  $\rightleftharpoons$  quinone oxime compounds has now been extended with solid 7-nitroso-8-hydroxyquinoline-5-sulfonic acid, which

is very similar in structure to the 2-nitroso-1-naphthol sulfonates studied earlier. The present compound is particularly interesting as a metal-chelating ligand because it has two coordination sites: one like that of 2-nitroso-1-naphthol and one like 8-hydroxyquinoline, the hydroxyl group being functional at both sites. This acid and its disodium salt have been specially selected for X-ray investigation to facilitate our prospective research on the metal chelates of the ligand.

## EXPERIMENTAL

The preparation and crystallization of 7-nitroso-8-hydroxyquinoline-5-sulfonic acid ( $=H_2L$ ) and its disodium salt monohydrate ( $=Na_2L \cdot H_2O$ ) have been described earlier.<sup>3</sup>

Crystal data for  $H_2L$  are:

$a=8.342(4)$ ,  $b=8.568(3)$ ,  $c=13.428(5)$  Å,  
 $\beta=90.15(4)^\circ$ ,  $Z=4$ , Space group  $P2_1/n$ ,  
 $D_x=1.759$  g cm<sup>-3</sup>,  $D_m=1.78$  g cm<sup>-3</sup> (by flotation)  
 $V=959.8$  Å<sup>3</sup>,  $\mu=31.1$  cm<sup>-1</sup> (CuK $\alpha$ )

Cell dimensions for  $H_2L$  were determined from Weissenberg photographs and refined using the data obtained from a powder photograph taken with a Hägg-Guinier camera with CuK $\alpha$  radiation and calcium fluoride as an internal standard. The space group, from systematic absences, is  $P2_1/n$ .

The crystal selected for the data collection had dimensions ca. 0.2  $\times$  0.2  $\times$  0.2 mm. Intensity data from levels  $0kl-7kl$  were collected with a Stoe-Güttinger diffractometer using Ni-filtered Cu radiation (CuK $\alpha$ ,  $\lambda=1.5418$  Å). Of the 1694 recorded reflections, 1382 with  $I > 3\sigma(I)$  were used for the structure analysis. The data were corrected for Lorentz and polarization effects.

Crystal data for Na<sub>2</sub>L.H<sub>2</sub>O are:

$$a = 8.046(4), b = 8.528(4), c = 9.669(5) \text{ \AA},$$

$$\alpha = 86.23(4), \beta = 67.63(4), \gamma = 71.74(4)^\circ,$$

$$Z = 2, \text{ Space group } P\bar{1}, D_x = 1.805 \text{ g cm}^{-3},$$

$$D_m = 1.82 \text{ g cm}^{-3} \text{ (by flotation)}, V = 581.6 \text{ \AA}^3,$$

$$\mu = 3.9 \text{ cm}^{-1} \text{ (MoK}\alpha\text{)}$$

Preliminary Weissenberg photographs showed the crystals of Na<sub>2</sub>L.H<sub>2</sub>O to be triclinic. Unit cell dimensions and intensity data were measured on a Syntex P2<sub>1</sub> diffractometer with graphite-monochromatized Mo radiation (MoK $\alpha$ ,  $\lambda = 0.7107 \text{ \AA}$ ). The cell parameters given above are the results of a least-squares refinement of automatically centered reflections.

The intensity data of a single crystal (0.2  $\times$  0.3  $\times$  0.3 mm) were collected by the  $\theta$ -2 $\theta$  scan mode ( $5^\circ < 2\theta < 60^\circ$ ). The intensity of a test reflection remeasured after every 40 reflections showed no significant change during the data collection. The absorption correction was made from  $\phi$ -scan data and corrections for Lorentz and polarization effects were then applied.<sup>4</sup> Of the 3105 recorded reflections, 1916 with  $F_o > 9\sigma(F_o)$  were used in the calculations.

*Determination and refinement of the structures.* The structures were both solved by direct methods

with the MULTAN program.<sup>5</sup> The non-hydrogen atoms were localized in *E* maps. The positional and isotropic temperature parameters for the non-hydrogen atoms were refined by block-diagonal least-squares technique (X-RAY system).<sup>6</sup> All hydrogen atoms were located on the respective difference Fourier maps. Finally, the parameters for the non-hydrogen atoms in the structures were refined anisotropically; those for the hydrogen atoms of Na<sub>2</sub>L.H<sub>2</sub>O were refined isotropically, and a fixed temperature factor  $U = 0.04 \text{ \AA}^2$  was used for the hydrogen atoms in H<sub>2</sub>L. The atomic scattering factors for the non-hydrogen atoms were taken from Ref. 7 and those for the hydrogen atoms from Ref. 8. The weighting scheme used in the calculations was  $w = 1/(A + |F_o| + B|F_o|^2)$  with  $A = 40.0$  and  $20.0$ , and  $B = 0.015$  and  $0.020$  for H<sub>2</sub>L and Na<sub>2</sub>L.H<sub>2</sub>O, respectively. The final *R* value was 0.061 for H<sub>2</sub>L and 0.041 for Na<sub>2</sub>L.H<sub>2</sub>O.

The atomic coordinates with standard deviations for the non-hydrogen atoms in H<sub>2</sub>L and in Na<sub>2</sub>L.H<sub>2</sub>O are given in Tables 1 and 2, respectively; the atomic parameters and bond lengths for the hydrogen atoms in Tables 3 and 4. Lists of the observed and calculated structure factors and the anisotropic thermal parameters for the non-

Table 1. Fractional atomic coordinates ( $\times 10^4$ ) for the non-hydrogen atoms in H<sub>2</sub>L.

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
C2	3504(7)	2635(7)	466(4)	N1	2009(6)	2930(5)	147(3)
C3	4794(7)	2873(7)	-162(4)	N2	-1799(6)	4857(5)	-2171(3)
C4	4522(7)	3399(7)	-1120(4)	O1	-1050(5)	3570(5)	-362(3)
C5	2515(7)	4225(6)	-2461(4)	O2	-1986(5)	5500(5)	-3097(3)
C6	986(7)	4568(6)	-2708(4)	S	4004(2)	4481(1)	-3396(1)
C7	-331(6)	4427(6)	-2003(4)	O3	4910(5)	5850(4)	-3048(3)
C8	-21(6)	3780(6)	-1002(4)	O4	4985(5)	3069(4)	-3371(3)
C9	1700(6)	3460(6)	-775(4)	O5	3151(5)	4740(5)	-4311(3)
C10	2949(6)	3699(6)	-1448(4)				

Table 2. Fractional atomic coordinates ( $\times 10^4$ ) for the non-hydrogen atoms in Na<sub>2</sub>L.H<sub>2</sub>O.

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
C2	601(5)	6794(4)	347(4)	N2	7239(4)	689(3)	-1897(4)
C3	220(5)	6760(4)	1885(4)	O1	4464(4)	2988(3)	-2584(2)
C4	1318(5)	5462(4)	2408(3)	O2	8494(4)	-347(3)	-1498(3)
C5	4125(4)	2834(4)	1790(3)	S	3892(1)	2587(1)	3689(1)
C6	5565(5)	1705(4)	743(3)	O3	5452(4)	1120(3)	3670(3)
C7	5785(4)	1752(4)	-805(3)	O4	2075(4)	2332(3)	4512(3)
C8	4450(4)	2986(4)	-1284(3)	O5	4027(4)	4082(3)	4232(3)
C9	3013(4)	4315(4)	-136(3)	O6	8915(3)	2100(3)	4016(3)
C10	2805(4)	4202(4)	1382(3)	Na1	7051(2)	4574(2)	3403(1)
N1	1943(4)	5600(3)	-646(3)	Na2	6667(2)	860(2)	5615(1)

Table 3. Fractional atomic coordinates and bond distances (Å) for the hydrogen atoms in H<sub>2</sub>L.

Atom	X/a	Y/b	Z/c	Bond length
H(C2)	0.361(7)	0.222(7)	0.117(4)	1.02(6)
H(C3)	0.606(7)	0.265(7)	0.014(4)	1.14(6)
H(C4)	0.546(7)	0.355(7)	-0.165(4)	1.06(6)
H(C6)	0.082(7)	0.500(7)	-0.345(4)	1.07(6)
H(N1)	0.093(7)	0.260(7)	0.063(4)	1.15(6)
H(O2)	-0.342(7)	0.576(7)	-0.315(4)	1.22(6)

hydrogen atoms are obtainable from the authors on request.

## DESCRIPTION AND DISCUSSION OF THE STRUCTURES

The molecular dimensions of H<sub>2</sub>L can be seen in Fig. 1. They show that the acid has a quinone oxime structure rather than a nitroso-hydroxy-quinoline structure. This is revealed in the C7–N2 [1.299(7) Å], N2–O2 [1.368(6) Å] bond lengths and in the C7–N2–O2 bond angle [112.2(4)°] which are all typical values for an oxime group,<sup>1,9</sup> and in the C8–O1 distance [1.229(6) Å] which is almost equal to the C=O double bond length found in naphthoquinone compounds (average 1.22 Å)<sup>10</sup> and thus markedly shorter than the C–O(H) single bond [1.330(5) Å] reported for 2-methyl-8-hydroxyquinoline-5-sulfonic acid.<sup>11</sup> The quinonoid nature of the hexagonal C5–C10 carbon ring is further indicated by the considerable shortening of the C5–C6 bond as compared with the other C–C bonds in the ring. Such localization cannot

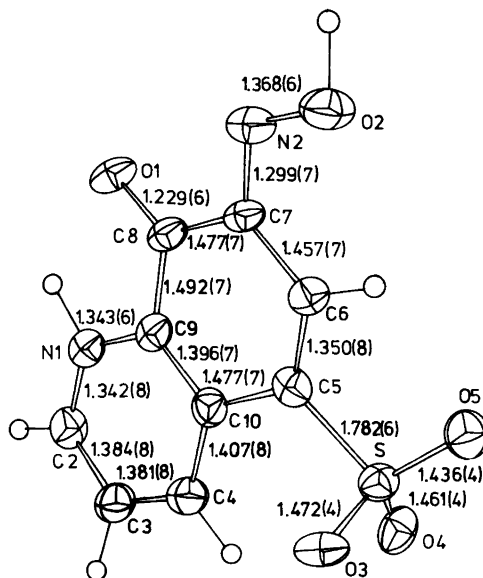


Fig. 1. ORTEP drawing of H<sub>2</sub>L showing bond lengths (Å). The non-hydrogen atoms are represented by their thermal ellipsoids with 50% probability.

be found in 2-methyl-8-hydroxyquinoline-5-sulfonic acid where both of the rings in the quinoline nucleus are clearly aromatic. As a whole the structure of the H<sub>2</sub>L molecule closely resembles the known structures of 1,2-naphthoquinone-2-oxime-sulfonic acids; in all these compounds the oxime group is in the *anti* configuration with respect to the quinone oxygen atom.

The acid H<sub>2</sub>L is a zwitter-ion compound, the proton being transferred from the sulfonic acid group to the quinoline nitrogen. Since the acidity

Table 4. Fractional atomic coordinates, isotropic thermal parameters and bond distances (Å) for the hydrogen atoms in Na<sub>2</sub>L.H<sub>2</sub>O.

Atom	X/a	Y/b	Z/c	U	Bond length
H(C2)	-0.010(6)	0.770(6)	-0.003(5)	0.046(13)	0.95(5)
H(C3)	-0.086(6)	0.759(5)	0.261(5)	0.034(11)	0.98(3)
H(C4)	0.108(6)	0.548(6)	0.344(5)	0.047(13)	0.94(5)
H(C6)	0.652(6)	0.087(5)	0.096(5)	0.032(11)	0.95(4)
H1(O6)	0.962(6)	0.151(6)	0.319(5)	0.050(14)	0.86(4)
H2(O6)	0.977(7)	0.227(7)	0.424(6)	0.070(17)	0.85(7)

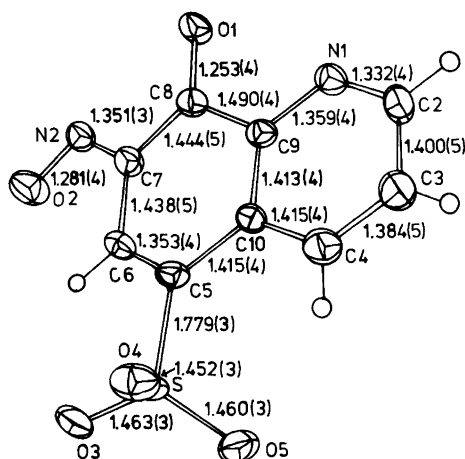


Fig. 2. ORTEP drawing of the organic anion in  $\text{Na}_2\text{L}\cdot\text{H}_2\text{O}$  showing bond lengths (Å).

of the sulfonic acid is distinctly greater than that of the  $-\text{NH}^+$  group, this transfer could well be anticipated, and it has been observed in several related compounds, *e.g.* in 2-methyl-8-hydroxyquinoline-5-sulfonic acid.<sup>11</sup>

The bond lengths of the organic anion in  $\text{Na}_2\text{L}\cdot\text{H}_2\text{O}$  are presented in Fig. 2, and the bond angles in both of the present compounds are collected in Table 5. It can be seen that removal of the protons brings about some changes in the bond lengths of the quinoline ring, the shortening of the C5–C10 distance being most prominent. However, the differences between the degree of the

localization of the ring structures in these two compounds are not very marked, and the most significant changes are rather associated with the oxime group: the C7–N2 bond is lengthened to 1.351(3) Å, the N2–O2 is shortened to 1.281(4) Å, and the C7–N2–O2 angle is opened to the value 116.3(3)°. Another observation, although not very significant, is that the C8–O1 bond is lengthened to 1.253(4) Å. It is interesting to note that all these changes are very similar to those found as a result of coordination of transition metal ions ( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$  or  $\text{Zn}^{2+}$ ) to naphthoquinone oximate ligands, in which cases the chelation occurs through oxime nitrogen and quinone oxygen atoms.<sup>1,2</sup>

The coordinations about the two sodium cations in the structure of  $\text{Na}_2\text{L}\cdot\text{H}_2\text{O}$  are distinctly different. One of the sodium ions (Na2) is in a strongly distorted octahedral environment, being surrounded by one nitrogen atom and five oxygen atoms. The nitrogen atom is the oxime nitrogen, one of the oxygen atoms is the quinone oxygen of the same molecule, three other oxygens are derived from two separate sulfonate groups, and the sixth is the water oxygen. The water oxygen also takes part in the coordination environment of Na1, which consists additionally of two sulfonate oxygens, the quinoline nitrogen and the quinone oxygen, the last two from the same molecule. Thus there are only five bond contacts, the distance from Na1 to the next nearest atom (which is another Na1 in the structure) being 3.464(2) Å. The spatial arrangement of the atoms is such that the coordination geometry of Na1 may be best described as trigonal bipyramidal, with the quinone oxygen ( $1-x, 1-y, -z$ ) and the water

Table 5. Bond angles (°) related to Figs. 1 and 2.

	$\text{H}_2\text{L}$	$\text{Na}_2\text{L}\cdot\text{H}_2\text{O}$		$\text{H}_2\text{L}$	$\text{Na}_2\text{L}\cdot\text{H}_2\text{O}$
C2–N1–C9	122.2(5)	118.1(3)	C6–C7–N2	125.2(5)	123.3(3)
N1–C2–C3	120.1(5)	123.0(3)	C8–C7–N2	115.3(5)	115.9(3)
C2–C3–C4	119.3(5)	119.1(3)	C7–C8–O1	124.8(5)	123.6(2)
C3–C4–C10	120.1(5)	119.6(3)	C9–C8–O1	120.3(4)	120.2(3)
C4–C10–C5	124.8(5)	124.4(3)	C7–N2–O2	112.2(4)	116.3(3)
C4–C10–C9	117.9(4)	116.7(3)	C10–C5–S	121.1(4)	121.1(2)
C5–C10–C9	117.3(5)	118.9(2)	C6–C5–S	117.4(4)	117.6(3)
C10–C5–C6	121.5(5)	121.4(3)	C5–S–O3	103.4(2)	105.9(1)
C5–C6–C7	122.4(5)	121.2(3)	C5–S–O4	105.9(2)	107.5(2)
C6–C7–C8	119.5(5)	120.8(2)	C5–S–O5	106.1(3)	107.4(2)
C7–C8–C9	114.9(4)	116.3(3)	O3–S–O4	111.5(2)	111.1(2)
C8–C9–N1	115.6(4)	115.9(3)	O3–S–O5	113.7(2)	112.1(2)
C8–C9–C10	124.1(4)	120.7(3)	O4–S–O5	115.1(2)	112.4(2)
N1–C9–C10	120.3(5)	123.4(2)			

Table 6. Interatomic angles (°) related to Fig. 3; the coordination spheres of sodium ions.

The coordination sphere of sodium ion Na1			
O5–Na1–O6	101.1(1)	O6–Na1–O1 <sup>II</sup>	173.5(1)
O5–Na1–O5 <sup>I</sup>	86.8(1)	O6–Na1–N1 <sup>II</sup>	106.2(1)
O5–Na1–O1 <sup>III</sup>	84.6(1)	O5 <sup>I</sup> –Na1–O1 <sup>II</sup>	89.1(1)
O5–Na1–N1 <sup>II</sup>	102.1(1)	O5 <sup>I</sup> –Na1–N1 <sup>II</sup>	155.4(1)
O6–Na1–O5 <sup>I</sup>	94.3(1)	O1 <sup>II</sup> –Na1–N1 <sup>II</sup>	69.2(1)
The coordination sphere of sodium ion Na2			
O3–Na2–O6	86.9(1)	O6–Na2–O4 <sup>IV</sup>	113.8(1)
O3–Na2–O1 <sup>III</sup>	104.4(1)	O1 <sup>III</sup> –Na2–N2 <sup>III</sup>	66.8(1)
O3–Na2–N2 <sup>III</sup>	167.8(1)	O1 <sup>III</sup> –Na2–O3 <sup>IV</sup>	95.3(1)
O3–Na2–O3 <sup>IV</sup>	75.7(1)	O1 <sup>III</sup> –Na2–O4 <sup>IV</sup>	136.9(1)
O3–Na2–O4 <sup>IV</sup>	97.5(1)	N2 <sup>III</sup> –Na2–O3 <sup>IV</sup>	96.3(1)
O6–Na2–O1 <sup>III</sup>	104.1(1)	N2 <sup>III</sup> –Na2–O4 <sup>IV</sup>	84.8(1)
O6–Na2–N2 <sup>III</sup>	103.1(1)	O3 <sup>IV</sup> –Na2–O4 <sup>IV</sup>	54.8(1)
O6–Na2–O3 <sup>IV</sup>	156.7(1)		

Symmetry relations for atoms in Fig. 3 and in Table 6: <sup>I</sup> 1–x, 1–y, 1–z    <sup>II</sup> 1–x, 1–y, –z    <sup>III</sup> x, y, 1+z  
<sup>IV</sup> 1–x, –y, 1–z

Table 7. Hydrogen bonding details.

X–H···Y	Position of acceptor atom	X···Y (Å)	X–H (Å)	H···Y (Å)	X–H···Y (°)
<b>H<sub>2</sub>L:</b>					
N1–H···O4	$-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$	2.749(5)	1.15(6)	1.66(6)	157(5)
O2–H···O3	$-1 + x, y, z$	2.608(6)	1.22(6)	1.40(6)	169(5)
<b>Na<sub>2</sub>L.H<sub>2</sub>O:</b>					
O6–H1···O2	$2 - x, -y, -z$	2.677(3)	0.86(4)	1.83(4)	169(6)
O6–H2···O4	$1 + x, y, z$	2.827(5)	0.85(7)	1.98(7)	170(5)

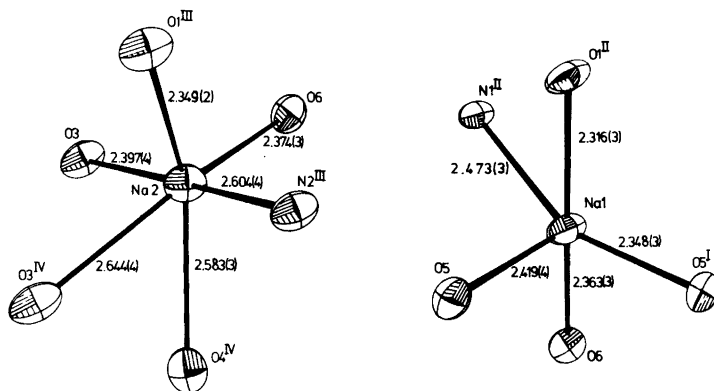


Fig. 3. ORTEP drawing of the coordination environments of the sodium ions showing bond lengths (Å).

oxygen in the apical positions. The bond contacts around the sodium ions Na1 and Na2 shown in Fig. 3 are normal, ranging from 2.316 to 2.644 Å. The respective angles are presented in Table 6.

There are two hydrogen bonds in Na<sub>2</sub>L.H<sub>2</sub>O both of which are associated with the water molecule. One of these bonds is a relatively weak interaction with a sulfonate oxygen atom: O···O 2.827(5) Å, O—H···O angle 170(5)°; the other is formed with the oxime oxygen atom: O···O separation 2.677(3) Å and O—H···O angle 169(6)°.

In the structure of H<sub>2</sub>L there are layers made up of infinite parallel chains running along the *a*-axis. Successive molecules within each chain are connected by a hydrogen bond of 2.608(6) Å, with O—H···O angle of 169(5)° from the oxime oxygen to a sulfonate oxygen atom. Between the chains of separate layers there is also hydrogen-bond interaction of 2.749(6) Å involving the N—H···O angle of 157(5)°, formed *via* the quinoline nitrogen and a neighbouring sulfonate oxygen. Details of the hydrogen bonding in the structures are given in Table 7.

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