

Structural Investigations of Sulfonated 1,2-Nitrosonaphthol (\rightleftharpoons 1,2-Naphthoquinone Oxime) Ligands. Part VI. The Crystal Structure of Potassium 1,2-Naphthoquinone-1-oxime-7-sulfonate Monohydrate: $\text{KC}_{10}\text{H}_6\text{NO}_5\text{S}\cdot\text{H}_2\text{O}$

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The crystal structure of the title compound has been determined from three-dimensional X-ray diffraction data and refined by least-squares methods. The space group is $P2_1/c$, $a = 7.195(4)$, $b = 21.278(10)$, $c = 7.973(5)$ Å, $\beta = 104.27(5)^\circ$, $Z = 4$. The final R value was 0.070 for 1304 observed reflections and the estimated standard deviation in the bond lengths for the non-hydrogen atoms was in the range 0.007–0.016 Å. The CN(1.31 Å), NO(1.39 Å), CO(1.22 Å), and C3–C4(1.31 Å) bond lengths indicate that the organic anion exists in its tautomeric oxime form. The oxime group and the quinone oxygen are in the *anti* configuration. The potassium ions are linked together by a bridging water molecule, which is hydrogen-bonded to two sulfonate oxygens. A third hydrogen bond is formed between the oxime nitrogen and sulfonate oxygen atoms. The results are compared with those obtained earlier for similar ligands in free and metal-coordinated state.

In previous papers we have described the structures of some complexes of copper(II) with 1,2-nitrosonaphthol ligands.^{1–3} The X-ray studies indicated that the coordinated ligand anions are consistent with significant contributions from the quinone oxime structure. In fact, the compounds in question have been classified according to their tautomeric oxime names. Apart from the metal chelates, we have also reported the crystal structures of several uncoordinated sulfonic acid derivatives of 2-nitroso-1-naphthol.^{4–8} All these ligands were found to be very similar in structure, having a tautomeric 1,2-naphthoquinone-2-oxime form

in which the oxime group is in the *anti* configuration with respect to the quinone oxygen. However, this decision cannot be confidently assumed for compounds derived from 1-nitroso-2-naphthol. Although the quinonoid character of all the 1,2-isomers can already be predicted, the orientation of the oxime group with respect to the quinone oxygen in 1-nitroso-2-naphthol compounds is still fully in doubt.

In order to clarify this particular relationship we have now determined the crystal structure of potassium 1,2-naphthoquinone-1-oxime-7-sulfonate monohydrate. Being the first representative of a free 1-nitroso-2-naphthol type of ligand investigated by X-rays, it also makes possible a more detailed discussion of the structures of such molecules in free and metal-coordinated state.

EXPERIMENTAL

Crystal preparation. Potassium 1,2-naphthoquinone-1-oxime-7-sulfonate was prepared from potassium 2-naphthol-7-sulfonate (Koch Light, pure, and Pfaltz & Bauer, Inc.) by nitrosation with potassium nitrite in acidic solution cooled to 0 °C.⁹ After it was recrystallized from water, microcrystalline yellow needles were obtained, which on further recrystallization from a water-acetone (3:1) mixture grew to thin lath-shaped prisms. The formula weight of the product based on potentiometric neutralization titration was found to be 307 ± 2 .

Crystal data. The space group, from systematic absences, and initial unit cell parameters were determined from Weissenberg photographs

Table 1. Fractional atomic coordinates ($\times 10^4$) and anisotropic thermal parameters a ($\times 10^3$) for non-hydrogen atoms. Estimated standard deviations are given in parentheses.

Atom	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	2889(13)	4403(4)	647(11)	35(6)	26(5)	22(4)	-6(4)	7(4)	-6(3)
C2	2645(14)	3995(4)	-959(11)	40(6)	24(5)	27(4)	-7(4)	7(4)	-3(4)
C3	2164(15)	4323(5)	-2625(13)	44(7)	43(6)	28(5)	-13(4)	9(4)	-13(4)
C4	1968(16)	4937(4)	-2699(12)	63(7)	32(5)	18(5)	-5(4)	0(4)	-1(4)
C5	1928(16)	5990(4)	-1460(13)	59(7)	28(5)	27(5)	8(4)	-1(5)	4(4)
C6	2180(13)	6390(4)	-52(11)	33(6)	33(5)	25(5)	0(4)	5(4)	4(4)
C7	2633(12)	6137(4)	1598(10)	31(6)	26(5)	19(4)	-2(3)	7(4)	-2(3)
C8	2824(13)	5502(4)	1885(10)	46(6)	16(4)	17(4)	-1(3)	8(4)	0(3)
C9	2650(14)	5080(4)	490(11)	52(6)	22(5)	20(4)	1(4)	6(4)	-4(3)
C10	2168(13)	5346(4)	-1224(10)	40(6)	25(4)	16(4)	-1(4)	9(4)	-1(3)
N	3406(12)	4049(3)	2030(9)	52(5)	25(4)	23(4)	1(3)	12(3)	-7(3)
O1	3680(11)	4375(3)	3577(8)	85(6)	24(4)	20(3)	4(3)	0(3)	1(2)
O2	2879(11)	3426(3)	-856(9)	87(6)	13(3)	44(4)	-2(3)	21(4)	-5(5)
S	2958(3)	6642(1)	3423(3)	39(1)	16(1)	21(1)	3(1)	3(1)	-1(1)
O3	2540(11)	7270(3)	2750(8)	72(5)	23(3)	33(4)	13(3)	-3(3)	-6(3)
O4	1714(11)	6408(3)	4440(8)	63(5)	37(4)	33(4)	-8(3)	19(3)	-10(3)
O5	4980(10)	6597(3)	4340(8)	54(5)	23(3)	28(3)	-8(3)	-6(3)	0(3)
K	3495(3)	2689(1)	2285(3)	58(2)	24(1)	31(1)	3(1)	12(1)	2(1)
O6	901(11)	2802(4)	4359(11)	33(5)	44(4)	62(5)	-1(3)	7(4)	-11(4)

^a The anisotropic thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + \dots)]$.

taken with $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation. More accurate cell constants were obtained by least-squares procedure from powder photographs taken with a Hagg-Guinier camera using calcium fluoride as internal standard ($a = 5.4630 \text{ \AA}$). The density was determined by the flotation technique. The crystal data for $\text{KC}_{10}\text{H}_8\text{NO}_5\text{S}\cdot\text{H}_2\text{O}$ are:

$a = 7.195(4) \text{ \AA}$ FW = 309.34
 $b = 21.278(10) \text{ \AA}$ $D_o = 1.72 \text{ g cm}^{-3}$
 $c = 7.973(5) \text{ \AA}$ $D_c = 1.736 \text{ g cm}^{-3}$
 $\beta = 104.27(5)^\circ$ $Z = 4$
 $V = 1182.97 \text{ \AA}^3$ Space group $P2_1/c$ (No. 14)

Intensity data. The crystal selected for data collection had approximate dimensions $0.25 \times 0.1 \times 0.1 \text{ mm}$. Ni-filtered Cu radiation ($\text{CuK}\alpha$, $\lambda = 1.5418 \text{ \AA}$) was used with a Stoe-Güttinger diffractometer. Of the 1758 recorded

independent reflections from the levels $0kl - 6kl$, 1304 had intensities greater than twice the standard deviations calculated from counting statistics. The data were corrected for Lorentz and polarization factors, but extinction and absorption corrections were not applied [$\mu(\text{CuK}\alpha) = 57.25 \text{ cm}^{-1}$].

Structure determination. The structure was solved by direct methods with the X-RAY 72 program system.¹⁰ All non-hydrogen atoms were located from an E map, computed by use of 278 reflections with $|E| \geq 1.40$. Refinement was carried out by full-matrix least-squares methods, using first isotropic and then anisotropic temperature factors. The function to be minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/(35.0 + |F_o| + 0.044|F_o|^2)$. The atomic scattering factors for non-hydrogen and hydrogen atoms were taken from Refs. 11 and 12, respectively. When the R value ($R = \sum ||F_o| -$

Table 2. Fractional atomic coordinates ($\times 10^3$) for hydrogen atoms.^a

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
H(C3)	184(14)	409(5)	-358(14)	H(C8)	310(14)	524(5)	306(13)
H(C4)	189(14)	511(5)	-371(14)	H(O1)	400(14)	406(5)	438(14)
H(C5)	149(14)	612(4)	-275(13)	H1(O6)	-37(15)	259(5)	377(13)
H(C6)	226(14)	693(5)	-17(13)	H2(O6)	3(17)	302(5)	471(14)

^a Isotropic temperature factors for hydrogen atoms were set at 3.2 \AA^2 .

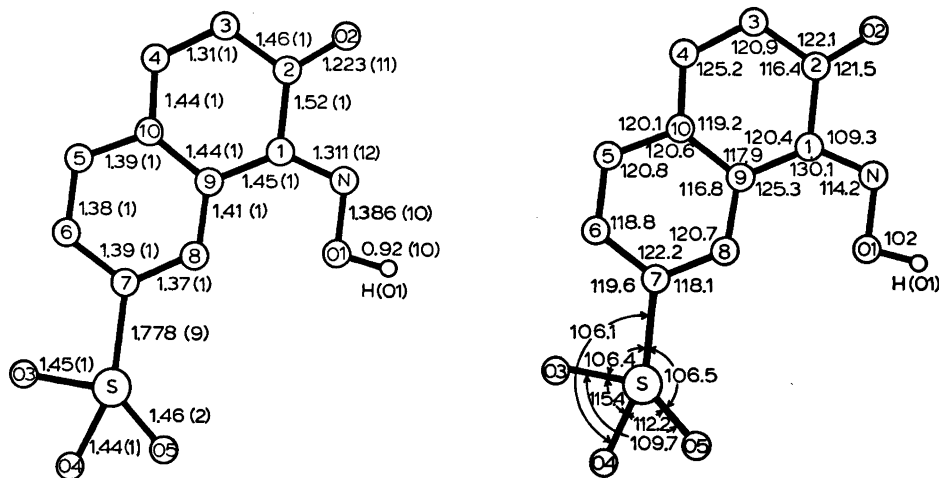


Fig. 1. Schematic representation of the anion showing bond lengths with their standard deviations (\AA) and bond angles ($^\circ$). The e.s.d.'s in angles are in the range $0.4 - 0.9^\circ$.

$|F_c|/|\sum|F_o||$ was reduced to 0.090, a difference Fourier map was computed and all hydrogen atoms were located. The positional parameters of the hydrogen atoms were allowed to vary in subsequent least-squares refinements but their temperature parameters were kept fixed at $B = 3.2 \text{ \AA}^2$. After the last cycle the average shift/e.s.d. value of variable parameters for the non-hydrogen atoms was 0.06 and for the hydrogen atoms 0.24. The final R value was 0.070 for 1304 observed reflections.

The atomic coordinates and thermal parameters for the non-hydrogen atoms are given in Table 1 and the atomic coordinates for hydrogen atoms in Table 2. A list of the observed and calculated structure factors is obtainable on request from the authors.

RESULTS AND DISCUSSION

The dimensions of the organic anion of the present compound which can be seen in Fig. 1 generally well accord with those of the 1,2-naphthoquinone-2-oximes studied previously.⁴⁻⁶ The characteristic CO, CN, NO, C1-C2, and C3-C4 bond distances, together with the CNO bond angle of all these compounds, are listed in Table 3. It is evident that the molecules exist in their tautomeric naphthoquinone oxime forms. Table 3 shows that the CN and NO distances remain fairly constant around 1.31 and 1.38 \AA , respectively. These values compare well with the average $\text{C}=\text{N}$ ($1.27 \pm$

0.02 \AA) and $\text{N}-\text{O}$ ($1.40 \pm 0.02 \text{ \AA}$) bond lengths collected by Chakravorty for several typical oximes.¹³ The average CNO bond angle in Table 3 (113°) is also consistent with the respective value 112° reported by Chakravorty. Additional evidence for the quinonoid character of these compounds is given by the average CO distance 1.21 \AA , which is closely equal to the $\text{C}=\text{O}$ bond lengths found in benzoquinone¹⁴ and naphthoquinone¹⁵ compounds, and the visibly long C1-C2 and short C3-C4 bond lengths (cf. Table 3). The quinonoid structure is not extended over the whole naphthalene carbon plane, however, as the C5-C10 carbon ring has maintained its aromatic character.

It is especially worthy of note that in the present compound the 1-oxime group and the quinone oxygen are in the *anti*-position, and are thus similar in their arrangement to the same groups in 1,2-naphthoquinone-2-oxime compounds. As we have pointed out earlier, both *anti* and *syn* configurations are found in benzoquinone oxime series.⁵

It is interesting to determine the magnitude of naphthalene *peri* effects on the orientation of the 1-oxime group. As can be seen from Fig. 1, the angle C9-C1-N (130°) is markedly larger than the angle C2-C1-N (109°), which together with the deviations of the N and O atoms from the naphthalene mean plane (Table 4) indicate a significant shift of the

Table 3. Characteristic bond distances (Å) and angles (°) of different 1,2-naphthoquinone oxime compounds.

Formula	qoH	CO	CN	NO	C3-C4	C1-C2	CNO	Ref.
Na(qoH).1½H ₂ O (mean)	I	1.20	1.31	1.35	1.34	1.52	111	4
H(qoH).H ₂ O	I	1.24	1.30	1.38	1.33	1.47	112	5
K(qoH).2H ₂ O	II	1.21	1.30	1.38	1.33	1.50	113	6
[Ni(H ₂ O) ₆](qoH) ₂ .4H ₂ O	III	1.21	1.31	1.37	1.33	1.49	113	7
KNa(qoH) ₂ .3H ₂ O (mean)	I	1.22	1.30	1.37	1.33	1.48	112	8
K(qoH).H ₂ O	IV	1.22	1.31	1.39	1.31	1.52	114	This work
[Cu(qo) ₂].2(CH ₃) ₂ CO	V	1.30	1.35	1.26	1.36	1.43	122	1
[Cu(qo) ₂].H ₂ O (mean)	VI	1.28	1.35	1.26	1.36	1.44	121	2
[Cu(qo)(H ₂ O) ₂].3H ₂ O	III	1.26	1.35	1.25	1.34	1.43	121	3

qoH = 2-nitroso-1-naphthol-5-sulfonate (I), 2-nitroso-1-naphthol-8-sulfonate (II), 2-nitroso-1-naphthol-4-sulfonate (III), 1-nitroso-2-naphthol-7-sulfonate (IV), 1-nitroso-2-naphthol (V), and 2-nitroso-1-naphthol (VI).

group away from the hydrogen on the 8-carbon atom.

The geometry of the sulfonate group attached to the 7-position of the naphthalene nucleus is as expected: the values of the C-S bond length (1.78 Å), the S-O distances (1.44–1.46 Å), the O-S-O angles (110–115°), and the C-S-O angles (106–107°) are all normal values frequently reported for several different sulfonate compounds.

The environment of the potassium ion is heteroatomic, being composed of six oxygen atoms and one nitrogen atom (Fig. 2). Two of these oxygen atoms are sulfonate oxygens, two are quinone oxygens, and the remaining two are water oxygens. In this way the same water molecule is connected with two adjacent

Table 4. The least-squares plane defined by the naphthalene carbon ring. Deviations (Å) of different atoms from the plane are given. X', Y', and Z' are orthogonal axes related to X, Y, and Z by $X' = X + Z \cos \beta$, $Y' = Y$, and $Z' = Z \sin \beta$. Plane C1-C10: $0.9946X' + 0.0960Y' + 0.0408Z' - 2.8570 = 0$

Atom	Distance	Atom	Distance	Atom	Distance
C1	0.003	C6	0.017	N	0.075
C2	0.009	C7	0.018	O1	0.084
C3	0.005	C8	-0.022	O2	0.043
C4	0.002	C9	-0.004	S	0.055
C5	-0.015	C10	-0.014		

potassium ions. The bond contacts about the potassium ion fall in the range 2.79–3.05 Å (Table 5).

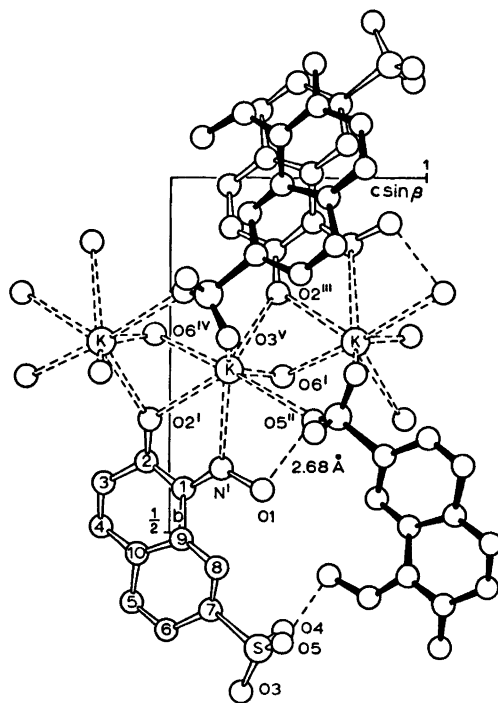


Fig. 2. Partial packing diagram of $KC_{10}H_6NO_6 \cdot S \cdot H_2O$ as viewed down the a axis. Symmetry operations used in Fig. 2 and Table 5 are: I x, y, z II $1-x, 1-y, 1-z$ III $x, \frac{1}{2}-y, \frac{1}{2}+z$ IV $x, \frac{1}{2}-y, -\frac{1}{2}+z$ V $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$.

Table 5. Interatomic distances (Å) of the potassium ion environment.

K-O2 ^I	2.89	K-N ^I	2.90	K-O6 ^I	2.79
K-O5 ^{II}	3.05	K-O2 ^{III}	2.90	K-O6 ^{IV}	2.81
K-O3 ^V	3.00				

The role of the water molecule in the structure is distinct: besides the K-O contact mentioned it also takes part in hydrogen bonding by accepting two hydrogen bonds from sulfonate oxygens. These bond lengths are both 2.86 Å. A third and somewhat shorter hydrogen bond is formed through the oxime hydrogen atom which is bound to the remaining sulfonate oxygen. Each sulfonate oxygen atom is thus active in hydrogen bonding. It may be noted that the last-mentioned $\text{NOH}\cdots\text{O}$ contact has always been found to be the shortest hydrogen bond in these compounds. Details of the hydrogen bonding can be found in Table 6 and the packing of the structure is illustrated in Fig. 2.

As mentioned above, the free 1,2-naphthoquinone oximes studied are clearly similar in structure, and the minor differences to be found in separate ligands (Table 3) are not significant. Due to the different positions of the substituents on the naphthalene carbon ring and to the different packing effects, exact similarity could hardly be expected.

Selected bond lengths and angles of the ligand anions coordinated to copper(II) ion are also included in Table 3. On comparing the bond distances with those of the free oximes supposed to exist in the alkali salts and in the salt of the nickel hexaaqua ion,⁴⁻⁶ some general observations can be made: (i) the N-O distance is significantly shortened from *ca.* 1.37 to *ca.* 1.26 Å on complex formation, (ii) the C-O

bond is significantly lengthened from *ca.* 1.21 to 1.28 Å, (iii) the C-N bond may be slightly lengthened (from *ca.* 1.31 to 1.35 Å, and (iv) the C-N-O angle is opened up by about 8° from the average free ligand value of 113°. Another result is that on complex formation the C1-C2 bond distance shortens to some extent and the C3-C4 bond is only slightly affected (Table 3).

Clearly, these alternations all lead to a resonance structure that can well be regarded as a metal-nitrosophthalato structure. On this view, it is understandable that unambiguous conclusions about the tautomeric form of these uncoordinated ligand acids are not possible merely from a consideration of structures of their metal chelates.

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Table 6. Hydrogen bonding details.

X-H \cdots Y	X \cdots Y Å	X-H Å	H \cdots Y Å	X-H \cdots Y (°)
O1-H(O1) \cdots O5 ^I	2.68	0.92	1.77	166
O6-H1(O6) \cdots O3 ^{II}	2.86	1.03	1.85	167
O6-H2(O6) \cdots O4 ^{III}	2.86	0.87	1.99	173

^I1-x, 1-y, 1-z

^{II}-x, - $\frac{1}{2}$ +y, $\frac{1}{2}$ -z

^{III}-x, 1-y, 1-z

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