

# The Crystal Structure of Tetraaqua(1,2-naphthoquinone-1-oximato-6-sulfonate)nickel(II) Sesquihydrate: $[\text{Ni}(\text{H}_2\text{O})_4(\text{C}_{10}\text{H}_5\text{NO}_5\text{S})] \cdot 1\frac{1}{2}\text{H}_2\text{O}$

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The crystal structure of the title compound has been determined from X-ray data. The space group is  $C2/c$ ,  $Z=8$ ,  $a=28.895(15)$ ,  $b=10.637(4)$ ,  $c=9.831(4)$  Å,  $\beta=91.97(5)^\circ$ . The structure was solved by direct methods and refined by least-squares procedures to a final  $R$  value of 0.062 for 1467 observed reflections. The estimated standard deviation in the bond lengths for the non-hydrogen atoms was in the range 0.005–0.012 Å. In the structure the octahedron around nickel consists of one nitrogen and one oxygen atom from the ligand, and of four aqua water oxygens.

In the course of our structural studies on 1,2-nitronaphthols ( $\rightleftharpoons$  1,2-naphthoquinone monoximes) and the metal complexes formed by them we have recently characterized a number of compounds by X-ray methods.<sup>1,2</sup> The title compound has been specially selected for analysis in order to ascertain the way in which divalent nickel coordinates to such chelating agents. Nickel as the central metal ion and 1-nitroso-2-naphthol-6-sulfonic acid anion as the ligand are both new in this series of investigations.

## EXPERIMENTAL

**Crystal preparation.** The complex was obtained by addition of an aqueous solution of  $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$  (1 mol equiv.) to a hot aqueous solution of sodium 1-nitroso-2-naphthol-6-sulfonate (1 mol equiv., prepared from sodium 2-naphthol-6-sulfonate on nitrosation<sup>3</sup>). The crude product that separated on cooling was dissolved into water, from which the dark brown crystals were formed on gradual cooling during two weeks. Anal. C, H, N, S, Ni.

**Crystal and intensity data.** Weissenberg photographs indicated monoclinic symmetry. Systematic absences were characteristic for the space groups  $Cc$  (No. 9) and  $C2/c$  (No. 15), but the space group  $Cc$  was excluded on the basis of statistical tests favouring a centrosymmetric structure. The unit cell dimensions were determined from powder photographs taken with a Hägg-Guinier camera, with  $\text{CuK}\alpha$  radiation and calcium fluoride ( $a=5.4630$  Å) as an internal standard. The cell parameters were refined by a least-squares program. The density was determined by the flotation method. Crystal data for  $[\text{Ni}(\text{H}_2\text{O})_4(\text{C}_{10}\text{H}_5\text{NO}_5\text{S})] \cdot 1\frac{1}{2}\text{H}_2\text{O}$  are: Space group:  $C2/c$   
 $a=28.895(15)$  Å,  $b=10.637(4)$  Å,  $c=9.831(4)$  Å  
 $\beta=91.97(5)^\circ$ ,  $Z=8$ ,  $D_m=1.79$  g cm<sup>-3</sup>,  $D_x=1.799$  g cm<sup>-3</sup>,  $\mu(\text{CuK}\alpha)=35.8$  cm<sup>-1</sup>

The crystals were unstable in the X-ray beam and decomposed after a couple of days. The intensities from levels  $h0l-h4l$  and  $h5l-h8l$  were measured from two separate crystals, both with approximate dimensions  $0.3 \times 0.4 \times 0.3$  mm. The data were collected with a Stoe-Güttinger diffractometer using Ni-filtered Cu radiation ( $\text{CuK}\alpha$ ,  $\lambda=1.5418$  Å). The total number of reflections was 2137, of which the 1467 stronger than  $3\sigma(I)$  were considered observed. The data set was corrected for Lorentz and polarization effects but not for absorption.

**Structure determination.** Attempts to solve the structure by direct methods with the X-RAY 76 program system<sup>4</sup> were not successful but initial coordinates for 17 non-hydrogen atoms were obtained from an  $E$  map by use of the MULTAN 74 program.<sup>5</sup> The positions of the remaining non-hydrogen atoms were found from a difference map. At last a difference Fourier synthesis revealed the positions of the hydrogen atoms.

The final refinement was carried out by full-matrix least-squares methods, with anisotropic temperature factors for the non-hydrogen atoms and the fixed value ( $B=2.9$  Å<sup>2</sup>) for the

Table 1. Fractional atomic coordinates for the non-hydrogen atoms.

Atom	X/a	Y/b	Z/c	Atom	X/a	Y/b	Z/c
C1	0.1885(3)	0.3266(9)	0.3270(8)	O2	0.1302(2)	0.4112(6)	0.4625(5)
C2	0.1733(3)	0.3971(8)	0.4394(8)	O3	0.0307(2)	0.4199(6)	0.3879(6)
C3	0.2074(3)	0.4551(10)	0.5288(7)	O4	0.0537(2)	0.2760(6)	0.1287(5)
C4	0.2526(3)	0.4488(9)	0.5013(8)	O5	0.0721(2)	0.1811(6)	0.4020(6)
C5	0.3160(3)	0.3844(9)	0.3574(8)	O6	0.0980(3)	0.5097(6)	0.2074(6)
C6	0.3325(3)	0.3200(8)	0.2443(8)	O7	0.5233(2)	0.4613(7)	0.6286(7)
C7	0.3004(3)	0.2488(9)	0.1616(8)	O8	0.0000	0.3545(9)	0.7500
C8	0.2544(3)	0.2468(10)	0.1885(8)	S	0.3905(1)	0.3304(2)	0.1954(2)
C9	0.2370(3)	0.3164(8)	0.2996(8)	O9	0.4190(2)	0.3328(7)	0.3213(5)
C10	0.2693(3)	0.3823(9)	0.3832(8)	O10	0.3938(2)	0.4434(7)	0.1165(6)
N	0.1515(2)	0.2780(8)	0.2509(6)	O11	0.3995(2)	0.2164(7)	0.1174(6)
O1	0.1586(2)	0.2048(7)	0.1530(6)	Ni	0.0894(1)	0.3424(1)	0.3039(1)

hydrogen atoms. The weighting scheme was  $w = 1/(60.0 + |F_o| + 0.05|F_o|^2)$ . Atomic scattering factors for the non-hydrogen and hydrogen atoms were taken from Refs. 6 and 7, respectively, and the dispersion corrections ( $\Delta f'$ ,  $\Delta f''$ ) were applied for Ni and S.<sup>8</sup> The final  $R$  value was 0.062 for 1467 observed reflections.

The atomic coordinates for the non-hydrogen atoms are given in Table 1 and for hydrogen atoms in Table 2. Lists of the structure factors and thermal parameters are available on request from the authors.

## DESCRIPTION OF THE STRUCTURE

The complex molecule is visualized in Fig. 1 where the bond lengths are also shown. The

Table 2. Fractional atomic coordinates for the hydrogen atoms.

Atom	X/a	Y/b	Z/c
H(C3)	0.203(3)	0.495(9)	0.601(8)
H(C4)	0.277(3)	0.504(9)	0.570(8)
H(C5)	0.342(3)	0.435(8)	0.419(8)
H(C7)	0.315(3)	0.198(8)	0.071(8)
H(C8)	0.232(3)	0.185(8)	0.136(9)
H1(O3)	0.133(3)	0.486(8)	0.334(8)
H2(O3)	0.005(3)	0.366(9)	0.394(9)
H1(O4)	0.034(3)	0.153(8)	0.114(9)
H2(O4)	0.061(3)	0.309(8)	0.055(9)
H1(O5)	0.091(3)	0.087(9)	0.405(9)
H2(O5)	0.076(3)	0.189(9)	0.452(9)
H1(O6)	0.101(3)	0.528(9)	0.157(9)
H2(O6)	0.097(3)	0.578(9)	0.250(9)
H1(O7)	0.548(3)	0.526(9)	0.648(8)
H2(O7)	0.509(3)	0.486(9)	0.570(8)
H1(O8)	0.023(3)	0.323(9)	0.727(8)

bond angles can be found in Table 3. It can be seen from the figure that the coordination octahedron around nickel is formed of one nitrogen and one oxygen atom from the ligand, and of the four aqua water oxygens. The chelate ring is thus five-membered, which is consistent with the copper(II) and zinc(II) chelates of the isomeric nitrosophthal ligands studied previously.<sup>1,2</sup> The five Ni—O distances, ranging from 2.036(7) to 2.099(6) Å, are somewhat longer than the Ni—N distance 2.007(7) Å, which together with the respective O—Ni—O and O—Ni—N angles (Table 3) display the expected distortions from true octahedron.

As in the earlier reported 1:1 copper complex of 2-nitroso-1-naphthol-4-sulfonic acid,<sup>9</sup> the electrically neutral complex molecule is a zwitter-

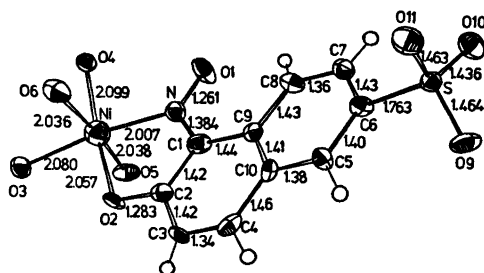


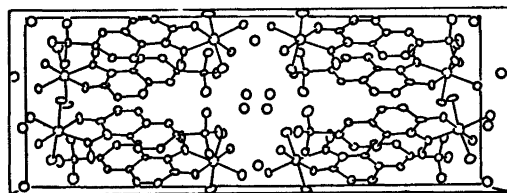
Fig. 1. ORTEP drawing of the complex molecule including bond lengths. The thermal ellipsoids are drawn at the 50% probability level. The e.s.d.'s for the C—C bonds are 0.011–0.012 Å and for the rest of the bonds 0.005–0.009 Å. The observed C—H and O—H bond lengths are 0.86–1.14 Å and 0.54–1.44 Å, respectively, the average e.s.d. being 0.09 Å.

Table 3. Bond angles ( $^\circ$ ) and their standard deviations.

The nickel environment			
N-Ni-O2	79.8(2)	O2-Ni-O4	88.0(2)
N-Ni-O3	170.5(2)	O3-Ni-O4	94.3(2)
N-Ni-O4	95.2(2)	O3-Ni-O5	86.0(3)
N-Ni-O5	94.1(3)	O3-Ni-O6	87.3(3)
N-Ni-O6	93.0(3)	O4-Ni-O5	89.1(2)
O2-Ni-O3	90.7(2)	O4-Ni-O6	88.6(3)
O2-Ni-O4	173.8(2)	O5-Ni-O6	172.7(3)
O2-Ni-O5	94.8(2)		
The ligand molecule			
C2-C1-C9	121.0(7)	C8-C9-C10	117.5(7)
C2-C1-N	111.4(7)	C4-C10-C5	119.4(8)
C9-C1-N	127.6(8)	C4-C10-C9	118.5(7)
C1-C2-C3	118.2(8)	C5-C10-C9	122.2(8)
C1-C2-O2	121.9(7)	C1-N-O1	120.0(6)
C3-C2-O2	119.9(7)	C5-C6-S	122.5(6)
C2-C3-C4	121.6(8)	C7-C6-S	118.8(6)
C3-C4-C10	121.7(8)	C6-S-O9	106.5(3)
C6-C5-C10	120.0(8)	C6-S-O10	106.4(4)
C5-C6-C7	118.6(7)	C6-S-O11	106.3(4)
C6-C7-C8	121.0(8)	O9-S-O10	113.3(4)
C7-C8-C9	120.8(8)	O9-S-O11	110.6(4)
C1-C9-C8	123.6(7)	O10-S-O11	113.2(4)
C1-C9-C10	118.8(7)		

Table 4. Possible hydrogen bonding.

X-H...Y	Position of acceptor atom			X...Y	X-H...Y
O3-H1(O3)...O8	-x	1-y	1-z	2.88	159
O3-H2(O3)...O4	-x	y	$\frac{1}{2}$ -z	2.88	167
O4-H1(O4)...O7	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z$	2.67	164
O4-H2(O4)...O11	$\frac{1}{2}-x$	$\frac{1}{2}-y$	-z	2.81	143
O5-H1(O5)...O10	$\frac{1}{2}-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	2.73	164
O5-H2(O5)...O9	$\frac{1}{2}-x$	$\frac{1}{2}-y$	1-z	2.72	162
O6-H1(O6)...O2	x	1-y	$-\frac{1}{2}+z$	2.74	166
O6-H2(O6)...O11	$\frac{1}{2}-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$	2.79	167
O7-H1(O7)...O9	1-x	1-y	1-z	2.79	167
O7-H2(O7)...O7	1-x	y	$1\frac{1}{2}-z$	2.78	169

Fig. 2. Molecular packing looking down the *c* axis.

terion type of compound, being composed of the positive nickel part and negative sulfonate part. The unit cell packing illustrated in Fig. 2 indicates that the structure may be described as built up from pairs of such zwitterions. The orientation of the molecules within the pairs is typically dipolar: the similarly charged parts of the dipoles repel and oppositely charged parts attract each other.

The decisive features for the packing arise from hydrogen bond formation. As the hydrogen atoms in the structure could be located only with relatively low accuracy (*cf.* Fig. 1), some of the hydrogen bonding details are partly uncertain. It is probable, however, that bonding between the molecules of the aforementioned pairs is effected by an aqua water molecule which donates a hydrogen bond to the adjacent sulfonate oxygen, and the separate pairs are chiefly connected through hydrogen bonds from aqua waters to sulfonate oxygens and to the oxygens of the "free" water molecules. In this way the aqua waters of separate complex pairs are joined together in the direction of the *a* axis *via* the water molecule in the special position. It is further evident that the remaining "free" waters in the structure are also hydrogen bonded to each other. The proposed hydrogen bonds which are mostly of medium strength, varying from 2.7 to 2.9 Å, are collected in Table 4.

In the previous studies we have indicated that uncoordinated 1,2-nitrosonaphthols exist in their tautomeric 1,2-naphthoquinone oxime forms in the solid state.<sup>1</sup> Comparison of the bond lengths and angles of ligands in "free" and copper and zinc coordinated states has shown some systematic changes to occur upon coordination, but the quinonoid nature is still important in describing the structure of the metal complex. As the characteristic C—N, N—O, and C3—C4 bond distances of the present molecule (Fig. 1) do not significantly differ from those previously found for the copper and zinc chelates of this type of ligand,<sup>1,2</sup> the designation of the complex as naphthoquinone oximate has been preferred to the alternative nitrosonaphtholato.

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## REFERENCES

1. Saarinen, H., Korvenranta, J. and Näsäkkälä, E. *Acta Chem. Scand. A* 31 (1977) 213.
2. Saarinen, H., Korvenranta, J. and Näsäkkälä, E. *Finn. Chem. Lett.* (1977) 155.
3. Mäkitie, O. and Saarinen, H. *Anal. Chim. Acta* 46 (1969) 314.
4. X-Ray 76, Program System for X-Ray Crystallography, *Technical Report TR-446 of the Computer Science Center*, University of Maryland.
5. Main P., Woolfson, M. M., Lessinger, L., Germain, G. and Declercq, J.-P. MÜLTAN 74, A System of Computer Programmes for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data.
6. Cromer, D. T. and Mann, J. B. *Acta Crystallogr. A* 24 (1968) 321.
7. Stewart, R. F., Davidson, E. and Simpson, W. *J. Chem. Phys.* 42 (1968) 3175.
8. *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham 1974, Vol. IV, p. 149.
9. Korvenranta, J. and Saarinen, H. *Finn. Chem. Lett.* (1975) 314.

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