Program used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program used to refine structure: *LSFM* (B. A. Frenz & Associates Inc., 1985). Molecular graphics: *ORTEP*II (Johnson, 1976).

This work was partly supported by a National Natural Scientific Foundation of China.

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: AB1192). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Sodium 4-Hydroxy-3-nitrobenzenesulfonate Trihydrate

Philip J. Squattrito

Department of Chemistry, Central Michigan University, Mt. Pleasant, Michigan 48859, USA

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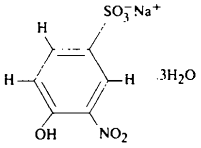
Abstract

The title compound, $Na^+.C_6H_4NO_6S^-.3H_2O$, crystallizes in double layers with the nearly planar organic anions oriented parallel to one another and the sulfonate groups directed towards the center of the sandwich, where they are bonded to Na^+ cations. Each Na^+ cation bonds to six O atoms in a distorted octahedral geometry. The coordination sphere contains two sulfonate O atoms, one nitro O atom from a different anion and three water molecules. There are hydrogen bonds involving the water molecules, the sulfonate O atoms and the hydroxyl groups.

Comment

In an earlier study of layered metal–arylsulfonate compounds (Shubnell, Kosnic & Squattrito, 1994), sodium 4-hydroxy-3-nitrobenzenesulfonate hemihydrate, $C_6H_4NO_6NaS.\frac{1}{2}H_2O$, was identified as a minor reaction product. We subsequently confirmed that the reported trihydrate (King, 1921) is the usual product of the nitration of sodium 4-hydroxybenzenesulfonate in aqueous nitric acid. Having determined the structure of the hemihydrate, it was of interest to see how the structure of the trihydrate, (I), would differ.



(I)

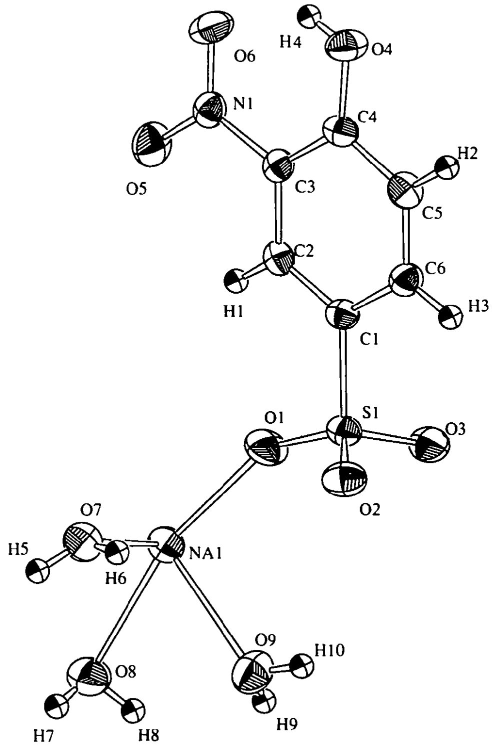


Fig. 1. *ORTEP*II (Johnson, 1976) diagram of the title compound showing the atom-labeling scheme. In this and Fig. 2, the displacement ellipsoids of the non-H atoms are shown at the 50% probability level.

The structure of the hemihydrate also contains double layers of sulfonate anions held together by Na^+ ions. It differs from the present structure in that there are four independent Na^+ ions, three of which bond only to sulfonate groups with no water molecules in the coordination sphere. The fourth Na^+ ion is in an octahedral environment composed of four sulfonate O atoms and two water molecules. There are also four independent sulfonate anions which are approximately parallel.

The trihydrate, shown in Figs. 1 and 2, has a more regular structure in which the anions are constrained by symmetry to be parallel. There is only one Na^+ ion which bonds to the three water molecules and three O atoms of the sulfonate and nitro groups. As a result of the increased hydration, the layers are further reinforced by hydrogen bonds between the water molecules and the sulfonate and hydroxyl groups (see Table 2). There is also an intramolecular hydrogen bond between atoms H(4) and O(6) which apparently forces the hydroxyl group to bend slightly away from the nitro group.

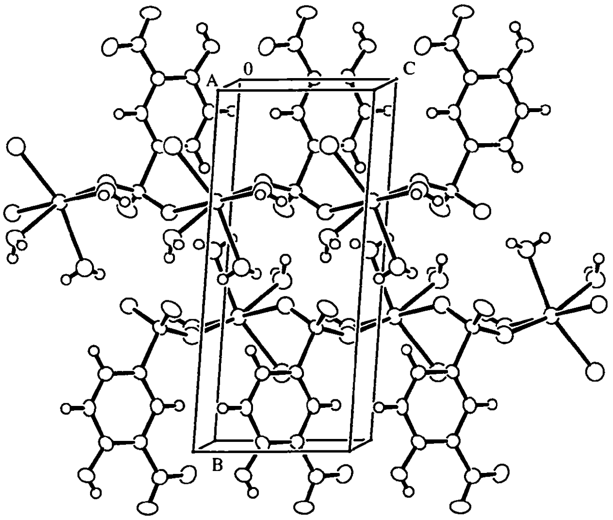


Fig. 2. *ORTEPII* (Johnson, 1976) packing diagram showing the outline of the unit cell, viewed down the *a* axis.

Experimental

The synthesis of the title compound was carried out by reaction of 2 g of sodium 4-hydroxybenzenesulfonate in a solution of 25 ml of water and 2 ml of concentrated nitric acid. The solution was initially colorless but turned red–orange within 24 h and was allowed to stand at room temperature for 15 d. Orange plate-shaped crystals grew upon evaporation of solvent.

Crystal data

$Na^+.C_6H_4NO_6S^-.3H_2O$
$M_r = 295.20$
Triclinic
$P\bar{1}$
$a = 7.986\,(1)$ Å
$b = 12.798\,(3)$ Å
$c = 5.481\,(1)$ Å
$\alpha = 94.08\,(2)°$
$\beta = 95.45\,(1)°$
$\gamma = 95.81\,(1)°$
$V = 553.0\,(2)$ Å^3
$Z = 2$
$D_x = 1.77$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 18 reflections
$\theta = 18–22°$
$\mu = 0.357$ mm^{-1}
$T = 296$ K
Plate
0.35 × 0.20 × 0.06 mm
Orange

Data collection

Rigaku AFC-6*S* diffractometer
ω scans
Absorption correction: none
2087 measured reflections
1934 independent reflections
1441 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.028$
$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 9$
$k = -15 \rightarrow 15$
$l = -6 \rightarrow 6$
3 standard reflections monitored every 150 reflections
intensity decay: <2%

Refinement

Refinement on F
$R = 0.031$
$wR = 0.032$
$S = 1.74$
1441 reflections
193 parameters
$w = 4F_o^2/\sigma^2(F_o^2)$

$(\Delta/\sigma)_{\rm max} = 0.02$
$\Delta\rho_{\rm max} = 0.27$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.28$ e Å^{-3}
Atomic scattering factors from Cromer & Waber (1974) and Cromer (1974)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{\rm eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
S(1)	0.9087 (1)	0.31399 (6)	0.3896 (1)	1.95 (3)
Na(1)	1.2099 (1)	0.33349 (9)	−0.0677 (2)	2.38 (5)
O(1)	1.0101 (3)	0.2881 (2)	0.1961 (4)	3.2 (1)
O(2)	1.0029 (3)	0.3704 (2)	0.6084 (4)	2.69 (8)
O(3)	0.7640 (2)	0.3686 (2)	0.3054 (4)	2.94 (9)
O(4)	0.6124 (3)	−0.0813 (2)	0.7511 (4)	2.63 (9)
O(5)	0.8938 (3)	−0.0890 (2)	0.1424 (4)	3.1 (1)
O(6)	0.7309 (3)	−0.1772 (2)	0.3626 (4)	3.3 (1)
O(7)	1.4145 (3)	0.2975 (2)	0.2497 (4)	2.9 (1)
O(8)	1.4106 (3)	0.4283 (2)	−0.3053 (5)	3.3 (1)
O(9)	1.2324 (3)	0.5161 (2)	0.1235 (4)	3.2 (1)
N(1)	0.8015 (3)	−0.0929 (2)	0.3071 (4)	2.2 (1)
C(1)	0.8199 (3)	0.1926 (2)	0.4855 (5)	1.8 (1)
C(2)	0.8433 (3)	0.0985 (2)	0.3638 (5)	1.9 (1)
C(3)	0.7737 (3)	0.0038 (2)	0.4453 (5)	1.8 (1)
C(4)	0.6830 (3)	0.0031 (2)	0.6509 (5)	1.9 (1)
C(5)	0.6607 (4)	0.1005 (2)	0.7705 (5)	2.1 (1)
C(6)	0.7272 (4)	0.1928 (2)	0.6898 (5)	2.1 (1)

Table 2. *Selected geometric parameters* (Å, °)

Na(1)—O(1)	2.312 (2)	S(1)—O(2)	1.456 (2)
Na(1)—O(2$^{\rm i}$)	2.414 (2)	S(1)—O(3)	1.464 (2)
Na(1)—O(6$^{\rm ii}$)	2.591 (2)	S(1)—C(1)	1.777 (3)
Na(1)—O(7)	2.374 (3)	C(3)—N(1)	1.452 (3)
Na(1)—O(8)	2.442 (3)	C(4)—O(4)	1.344 (3)
Na(1)—O(9)	2.474 (3)	N(1)—O(5)	1.219 (3)
S(1)—O(1)	1.435 (2)	N(1)—O(6)	1.237 (3)

O(2^i)—Na(1)—O(7)	179.74 (9)	O(1)—S(1)—O(2)	114.6 (1)
O(1)—Na(1)—O(8)	164.92 (9)	O(1)—S(1)—O(3)	112.8 (1)
O(6^{ii})—Na(1)—O(9)	158.41 (9)	O(1)—S(1)—C(1)	106.6 (1)
O(7)—Na(1)—O(9)	87.90 (9)	O(2)—S(1)—O(3)	110.8 (1)
O(8)—Na(1)—O(9)	77.14 (9)	O(2)—S(1)—C(1)	105.8 (1)
O(7)—Na(1)—O(8)	95.83 (9)	O(3)—S(1)—C(1)	105.4 (1)
O(1)—Na(1)—O(7)	86.28 (9)	O(4)—C(4)—C(3)	127.5 (3)
O(1)—Na(1)—O(9)	88.04 (9)	O(4)—C(4)—C(5)	114.7 (3)

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

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*—H···*A*
O(9)—H(10)···O(2^i)	0.80 (3)	2.15 (3)	163 (3)
O(7)—H(5)···O(3^{ii})	0.81 (3)	2.04 (3)	162 (3)
O(9)—H(9)···O(3^{iii})	0.79 (3)	2.09 (3)	166 (3)
O(4)—H(4)···O(7^{iv})	0.75 (3)	2.18 (3)	134 (3)
O(8)—H(7)···O(9^v)	0.79 (3)	2.14 (3)	176 (3)
O(7)—H(6)···O(8^{vi})	0.79 (3)	2.09 (3)	165 (3)
O(4)—H(4)···O(6)	0.75 (3)	2.07 (3)	138 (3)

Symmetry codes: (i) $2-x, 1-y, 1-z$; (ii) $1+x, y, z$; (iii) $2-x, 1-y, -z$; (iv) $2 - x, -y, 1 - z$; (v) $3 - x, 1 - y, -z$; (vi) $x, y, 1 + z$.

All H atoms were located on difference electron density maps and assigned isotropic displacement parameters equal to 1.2*B* of the attached atom at the time of their inclusion in the model.

Data collection and cell refinement: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Data reduction: *TEXSAN* (Molecular Structure Corporation, 1991). Structure solution: *MITHRIL* (Gilmore, 1983), *DIRDIF* (Beurskens *et al.*, 1984). Structure refinement: *TEXSAN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, including H-atom geometry, intermolecular distances involving H atoms and least-squares-planes data have been deposited with the IUCr (Reference: CR1155). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Isothiocyanato Complexes of Rhenium. V. *trans*-Bis(isothiocyanato)(methoxy)(phenylimido)bis(triphenylphosphine)rhenium(V)[†]

Rainer Hübener,* Ulrich Abram and Joachim Strähle

University of Tübingen, Institute of Inorganic Chemistry, Auf der Morgenstelle 18, D-72076 Tübingen, Germany

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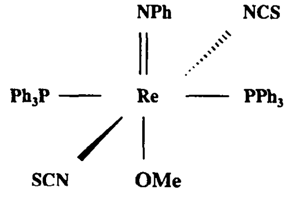
Abstract

The title compound consists of well separated molecules of $[Re(C_6H_5N)(CH_3O)(NCS)_2(C_{18}H_{15}P)_2]$. The Re atom is six-coordinate in a distorted octahedral environment. The two triphenylphosphine ligands are arranged *trans* to each other and there is a methoxy group in the position *trans* to the phenylimido group. The Re—NPh distance is 1.744 (4) Å and the NCS ligands are coordinated *via* the N atom.

Comment

The title compound, (I), consists of discrete monomeric molecules. An *ORTEP*II plot (Johnson, 1976) together with the atomic numbering scheme is shown in Fig. 1.



(I)

The Re atom is six-coordinate, the two *trans* triphenylphosphine ligands are bonded to the Re atom in an approximately linear fashion with a P—Re—P angle of 178.78 (4)°. The Re—P bond distances, 2.506 (1)

[†] Part IV: see Hübener, Abram & Strähle (1995).