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Chloramine-B sesquihydrate

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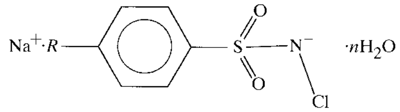
In the title compound, sodium *N*-chlorobenzenesulfonamide sesquihydrate, $Na^+\cdot C_6H_5ClNO_2S^-\cdot 1.5H_2O$, the sodium ion exhibits octahedral coordination by O atoms from three water molecules and by three sulfonyl O atoms of three different *N*-chlorobenzenesulfonamide anions. A two-dimensional polymeric layer consists of units, each comprising two face-sharing octahedra which share four corners with four other such units, the layer running parallel to the *ab* plane. The water molecules participate in hydrogen bonds of the types O—H···O, O—H···N and O—H···Cl.

Comment

The chemistry of *N*-haloarenesulfonamidates (NHAS) such as chloramine-T (*N*-chloro-*p*-toluenesulfonamide sodium salt trihydrate) and chloramine-B (*N*-chlorobenzenesulfonamide sodium salt hydrate) has made notable strides in diverse fields over the past century. They are good oxidants, efficient halogenators and versatile analytical and synthetic reagents. Their importance extends to wider scientific fields and technology, as is evident from their application to waste-water treatment, seed and grain protection, and the preparation of organic compounds. NHAS are also biologically and medicinally important and are used as antiseptics, disinfectants and fungicides. In industry, they are used in the dyeing and bleaching of cellular fabrics, and in the production of polymer latexes.



(I) *R* = H, n = 1.5
(II) *R* = Me, n = 3

Few crystallographic reports on NHAS compounds have been published except for that on chloramine-T, (II) (Olmstead & Power, 1986), which investigated the interaction with the sodium ion and reported that the expected Na···N ion interaction was not present. Moreover, the structure revealed the sodium ion coordination as octahedral, formed by one of the sulfonate O atoms, water O atoms and the Cl atom. These authors concluded that within the molecular anion, the negative charge is located on the sulfonyl O rather than on the N atom. As a part of our work on the solid-state and solution studies of NHAS, we have determined the crystal structure of the title compound, (I) (Fig. 1). It is also of importance to us to determine crystallographically the number of water molecules of hydration present in this compound.

Our results revealed that (I) is present as a sesqihydrate, in contrast with the trihydrate form found for (II). The bond distances involved in the phenyl ring are normal. The S=O distances in (I) [S1=O1 1.446 (3) and S1=O2 1.420 (4) Å] are different from those observed in (II) [1.455 (2) and 1.439 (2) Å]. The N1—Cl1 distance of 1.742 (4) Å is also shorter than in (II). The coordination around the sodium ion is octahedral, with all four available O atoms taking part and with the Na—O distances varying from 2.339 (4) to 2.486 (4) Å. We observed no interaction between nitrogen and sodium in (I), in agreement with the results of Olmstead & Power (1986) for (II) (see below). Moreover, in (I), the sodium ion is coordinated only by the O atoms from sulfonyl and water; the chlorine does not participate as in (II). As both the sulfonyl O atoms are coordinated to the sodium ions, our results establish that the negative charge is concentrated on the sulfonyl O atoms rather than on the nitrogen of the anion, as suggested for (II) by Olmstead & Power (1986).

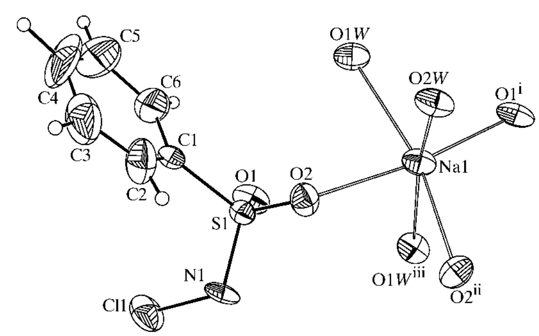


Figure 1
Displacement ellipsoid plot of (I) with the atom-numbering scheme, showing 50% probability ellipsoids. The H atoms on the water molecules could not be located and are therefore not shown [symmetry codes: (i) $\frac{3}{2}-x, y-\frac{1}{2}, 1-z$; (ii) $2-x, y, 1-z$; (iii) $\frac{3}{2}-x, \frac{1}{2}+y, 1-z$].

It is worth mentioning the sodium environment and the lattice formation in the two NHAS compounds (I) and (II). The salt (II) forms dimers, but these dimers are connected by long Na···Cl contacts to form polymeric chains along the crystallographic *b* axis, whereas in (I), the two-dimensional polymeric structure is formed parallel to the *ab* plane. The latter situation arises because the octahedral coordination around the sodium ion exclusively involves the sulfonyl and the water O atoms. The two-dimensional polymeric layer (Fig. 2) consists of face-sharing octahedra formed by two sodium ions and these twin octahedra are found to be corner sharing with other twin octahedra at four corners.

The Cl atom does not have any interaction with the sodium ion, suggesting that there is a smaller negative charge on Cl1 in (I) compared with (II). The electron-releasing methyl group in (II) may act to block the movement of charge from the chlorine to the sulfonyl O atoms, thereby keeping more negative charge on the chlorine than in (I). We believe that this explains the lack of interaction between Cl and Na in the latter structure.

The crystal structure contains O—H···O, O—H···N and O—H···Cl hydrogen bonds involving the water molecules. Since the water H atoms could not be located, only the donor-to-acceptor distances are given: O1W···O2^{iv} 3.125 (5), O1W···N1^{iv} 2.861 (5), O2W···N1^{v} 2.897 (5) and O1W···Cl1^{v} 3.430 (4) Å [symmetry codes: (iv) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (v) $x, y - 1, z$].

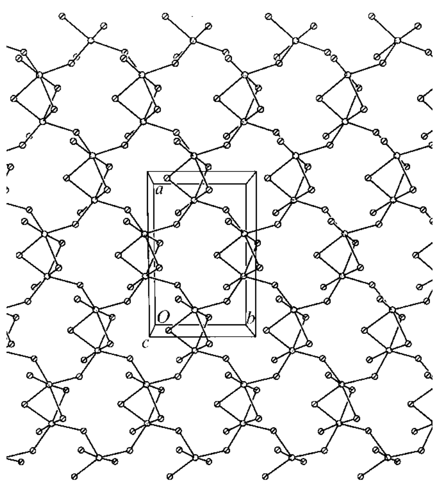


Figure 2
The polymeric structure viewed along the b axis, showing the Na—O—Na connectivity along the a axis.

Experimental

The title compound was purchased from Fluka and single crystals were obtained by slow evaporation from a saturated solution in distilled water.

Crystal data

$Na^+ \cdot C_6H_5ClNO_2S^- \cdot 1.5H_2O$	$D_x = 1.600$ Mg m^{-3}
$M_r = 240.63$	Mo $K\alpha$ radiation
Monoclinic, $C2$	Cell parameters from 25 reflections
$a = 10.450$ (3) Å	$\theta = 8$–22°
$b = 6.623$ (3) Å	$\mu = 0.614$ mm^{-1}
$c = 14.828$ (4) Å	$T = 293$ (2) K
$\beta = 103.31$ (3)°	Plate, colourless
$V = 998.7$ (6) Å^3	0.20 × 0.20 × 0.08 mm
$Z = 4$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.020$
$\theta/2\theta$ scans	$\theta_{max} = 25.02°$
Absorption correction: ψ scan (*MolEN*; Fair, 1990)	$h = -12 \rightarrow 12$
$T_{min} = 0.87$, $T_{max} = 0.98$	$k = -6 \rightarrow 7$
1536 measured reflections	$l = -14 \rightarrow 17$
963 independent reflections	3 standard reflections every 100 reflections intensity decay: <2%
902 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.028P)^2 + 0.979P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.035$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.080$	$\Delta\rho_{max} = 0.23$ e Å^{-3}
$S = 1.146$	$\Delta\rho_{min} = -0.24$ e Å^{-3}
963 reflections	Absolute structure: Flack (1983)
123 parameters	Flack parameter = 0.03 (15)
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Na1—O1^i	2.339 (4)	Na1—Na1^{ii}	3.295 (3)
Na1—O2	2.425 (4)	Cl1—N1	1.742 (4)
Na1—O2^{ii}	2.486 (4)	S1—O2	1.420 (4)
Na1—O1W	2.459 (4)	S1—O1	1.446 (3)
Na1—O1W^{iii}	2.416 (4)	S1—N1	1.592 (4)
Na1—O2W	2.428 (4)	S1—C1	1.771 (5)
O1^i—Na1—O1W^{iii}	91.08 (14)	O2—Na1—O1W	81.01 (13)
O1^i—Na1—O2	172.42 (15)	O2W—Na1—O1W	80.91 (12)
O1W^{iii}—Na1—O2	92.30 (16)	O1^i—Na1—O2^{ii}	109.69 (14)
O1^i—Na1—O2W	97.92 (14)	O1W^{iii}—Na1—O2^{ii}	79.19 (14)
O1W^{iii}—Na1—O2W	159.02 (13)	O2—Na1—O2^{ii}	77.63 (14)
O2—Na1—O2W	81.17 (13)	O2W—Na1—O2^{ii}	79.94 (13)
O1^i—Na1—O1W	91.42 (14)	O1W—Na1—O2^{ii}	153.17 (13)
O1W^{iii}—Na1—O1W	117.94 (11)	S1—N1—Cl1	109.5 (2)
O2—S1—N1—Cl1	176.1 (2)	C1—S1—N1—Cl1	60.3 (3)
O1—S1—N1—Cl1	−58.3 (3)		

Symmetry codes: (i) $\frac{3}{2} - x, y - \frac{1}{2}, 1 - z$; (ii) $2 - x, y, 1 - z$; (iii) $\frac{3}{2} - x, \frac{1}{2} + y, 1 - z$.

The H atoms in the benzene ring were geometrically fixed and allowed to ride on their respective C atoms with C—H distances of 0.93 Å and U_{iso} (H) = $1.2U_{eq}$(C). The water H atoms could not be located from difference maps.

Data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *MolEN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ZORTEP* (Zsolnai, 1997); software used to prepare material for publication: *SHELXL*97 and *PARST* (Nardelli, 1983).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1403). Services for accessing these data are described at the back of the journal.

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