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The sodium salt of 2-hydroxy-5-nitrobenzylsulfonic acid

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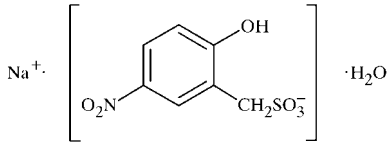
The structural data for sodium 2-hydroxy-5-nitrobenzylsulfonate monohydrate, $Na^+ \cdot C_7H_6NO_6S^- \cdot H_2O$, which mimics an artificial substrate for human arylsulfatase A, *viz*. *p*-nitrocatechol sulfate, reveal that the geometric parameters of the substrate and its analogue are very similar. Two water molecules, the phenolic O atom and three sulfonate O atoms form the coordination sphere of the Na^+ ion, which is a distorted octahedron. The Na^+ cations and the O atoms join to form a chain polymer.

Comment

The enzyme human arylsulfatase A (ASA) catalyses the *in vivo* desulfatation of cerebroside 3-sulfate, and a lack of ASA activity causes the rare disease metachromatic leukodystrophy. In this inherited disorder of myelin metabolism, cerebroside sulfate accumulates in the white matter of the central nervous system and in peripheral nerves (Kolodny & Fluharty, 1995). *p*-Nitrocatechol sulfate (NCS; Baum *et al.*, 1959) is used in the assay of ASA activity *in vitro*. Because of the structural similarity between NCS (Bülow & Usón, 2000) and 2-hydroxy-5-nitrobenzylsulfonic acid (NBSA), and the fact that ASA is not able to cleave the C—S bond, NBSA very strongly inhibits sulfatase activity (Zucker-Franklin & Nabi, 1985). The structure of sodium 2-hydroxy-5-nitrobenzylsulfonate monohydrate, (I), the sodium salt of NBSA, is reported here.



(I)

The molecular structure of (I) is shown in Fig. 1. The geometric parameters of NBSA and NCS are very similar. Only the geometries of the $-CH_2SO_3^-$ and $-OSO_3^-$ groups are slightly different, due to the replacement of carbon by oxygen (Table 1). A difference is also observed in the length of the bond between the phenolic O atom and the C atom belonging to the aromatic ring. In (I), the C2—O4 bond is longer than in NCS [1.350 (2) *versus* 1.285 (2) Å], indicating the different protonation state of the O atom, *i.e.* it is protonated in (I) and deprotonated in NCS.

Two water molecules, the phenolic O atom and three sulfonate O atoms form the coordination sphere of the Na^+ ion. These six O atoms create a distorted octahedron, with Na—O distances in the range 2.376 (1)–2.557 (2) Å. The Na^+ cations and the O atoms form a chain polymer, in which the $Na^+ \cdots Na^+$ distance is 3.927 (1) Å and atoms O1 and O7 belong to the coordination spheres of two neighbouring metal atoms.

There are no intramolecular hydrogen bonds, but contacts consistent with intermolecular hydrogen bonding (Table 2) are observed. The water molecule present in the structure bridges the Na^+ ions and also forms hydrogen bonds to the nitro and sulfonate groups. These connections enrich a network of possible interactions and stabilize the structure.

In the crystal structure of (I), molecules of NBSA form layers parallel to the (100) plane (Fig. 2). The hydrophobic interior of the layer is filled by aromatic rings arranged in antiparallel pairs and linked by face-to-face π-stacking, while sulfonate and carboxyl groups give the layer a polar surface. Contacts between the layers are stabilized by Na^+ ions and water molecules.

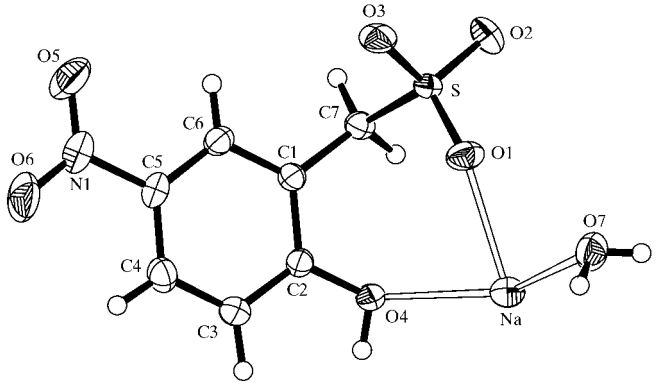


Figure 1
The molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

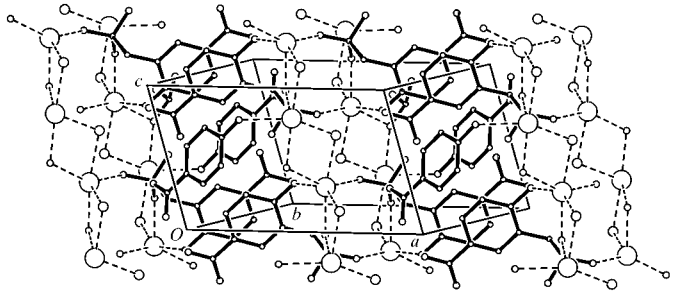


Figure 2
A packing diagram for (I), showing the hydrophobic and hydrophilic layers. Na^+ ions are shown as the largest spheres and H atoms have been omitted.

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Table 1
Selected geometric parameters (Å, °).

Na—O1	2.3756 (13)	C7—C1	1.502 (2)
Na—O1^{i}	2.4652 (13)	S—O1	1.4529 (12)
Na—O2^{ii}	2.3791 (14)	S—O2	1.4541 (12)
Na—O4	2.5293 (14)	S—O3	1.4582 (11)
Na—O7	2.4804 (15)	N1—C5	1.456 (2)
Na—O7^{i}	2.5573 (15)	N1—O5	1.213 (2)
S—C7	1.7842 (15)	N1—O6	1.231 (2)
O1—Na—O2^{ii}	89.28 (5)	O1—S—C7	107.67 (7)
O1—Na—O1^{i}	118.95 (5)	O2—S—C7	105.65 (7)
O1—Na—O7	75.37 (5)	O3—S—C7	106.76 (8)
O1—Na—O4	82.77 (4)	C1—C7—S	113.17 (11)
O1—Na—O7^{i}	168.52 (5)	O5—N1—O6	122.54 (16)
O7—Na—O7^{i}	105.67 (6)	O5—N1—C5	119.50 (16)
Na—O1—Na^{iii}	108.43 (5)	O6—N1—C5	117.95 (16)
Na—O7—Na^{iii}	102.43 (5)		

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O4—H5···O3^{i}	0.87 (3)	1.74 (3)	2.613 (2)	174 (3)
O7—H7···O6^{ii}	0.81 (3)	2.11 (3)	2.901 (2)	165 (3)
O7—H8···O2^{iii}	0.86 (5)	2.17 (5)	2.946 (2)	151 (4)

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

Experimental

Compound (I) was synthesized according to the procedure of Kaiser & Lo (1969), except 2-hydroxy-5-nitrobenzyl bromide (purchased from Fluka) was used instead of 2-hydroxy-5-nitrobenzyl chloride. The substrate (5.0 g) was mixed with anhydrous sodium sulfite (7.9 g) and distilled water (100 ml), and the colour of the mixture changed to yellow. The mixture was then heated under reflux for 1.5 h. Water was removed under reduced pressure and the residual sodium salts were dissolved in 0.1 *M* HCl. The solution was filtered and placed in Petri dishes. After evaporation of the water, two types of crystals were found in the dishes. A pale-yellow crystal, which was expected to be the salt of NBSA, was removed for X-ray analysis. The crystals of the second type were colourless and were assumed to be crystals of sodium bromide.

Crystal data

$Na^{+}\cdot C_7H_6NO_6S^{-}\cdot H_2O$
$M_r = 273.19$
Monoclinic, $P2_1/c$
$a = 12.4940$ (1) Å
$b = 12.0800$ (3) Å
$c = 7.1600$ (3) Å
$\beta = 105.264$ (1)°
$V = 1042.52$ (5) Å^3
$Z = 4$
$D_x = 1.741$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2893 reflections
$\theta = 1.0$–$30.0°$
$\mu = 0.38$ mm^{-1}
$T = 293$ (2) K
Prism, pale yellow
0.3 × 0.2 × 0.1 mm

Data collection

Nonius KappaCCD area-detector diffractometer
φ scans, and ω scans with κ offsets
5291 measured reflections
3026 independent reflections
2606 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 30°$
$h = 0 \rightarrow 17$
$k = -16 \rightarrow 15$
$l = -10 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.094$
$S = 1.10$
3026 reflections
186 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 0.6053P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.30$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

Refined distances involving H atoms are as follows: O—H = 0.81 (3)–0.87 (3) Å and C—H = 0.92 (2)–0.98 (2) Å.

Data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*III (Burnett & Johnson, 1996) and *ORTEP*-3 (Farrugia, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1096). Services for accessing these data are described at the back of the journal.

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