Acta Cryst. (1977). B**33**, 2751–2756

The Crystal Structure of the Hexasodium Salt of Benzenehexasulphonic Acid Octahydrate

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(*Received* 17 *January* 1977; *accepted* 25 *February* 1977)

The hexasodium salt of benzenehexasulphonic acid, $C_6(SO_3Na)_6$, forms an octahydrate which is stable in air. The compound is monoclinic with $a = 8{\cdot}360$ (1), $b = 13{\cdot}981$ (1), $c = 12{\cdot}692$ (1) Å, $\gamma = 118°\,36\,(1)'$, $Z = 2$, space group $P2_1/b$. The intensities were measured on an automatic Syntex $P\bar{1}$ diffractometer. The structure was solved by direct methods and refined by the least-squares technique to a final R of 0·053. The configuration of the anion is determined by steric forces between the large SO_3 groups. The observed average values of the bond lengths and angles are C–C 1·415, S–C 1·835, S–O 1·453 Å; CCC 119·8, OSO 112·8, CSO 102·4 and 112·7°. The coordination of the Na(1) and Na(2) ions is distorted octahedral; the Na(3) ion environment forms a very distorted pentagonal bipyramid. The Na–O distances are in the range 2·253 to 2·637 Å. In the crystal there are weak hydrogen bonds (2·817 to 2·926 Å).

Introduction

It is known that the unmixed substituted benzenes C_6X_6, where X is a substituent such as Cl, Br, I or CH_3, belong to the class of overcrowded compounds (Avoyan, Struchkov & Dashevski, 1966; Coulson & Stocker, 1959). The crystal structures of C_6F_6 (Boden, Davis, Stam & Wesselink, 1973), C_6Cl_6 (Streltsova & Struchkov, 1961; Brown & Strydom, 1974), C_6Br_6 (in the molecular complex with 1,2,4,5-tetrabromobenzene) (Gafner & Herbstein, 1964), C_6I_6 (Khotsyanova & Smirnova, 1968; Steer, Watkins & Woodward, 1970) and $C_6(CH_3)_6$ (Brockway & Robertson, 1939; Hamilton, Edmonds, Tippe & Rush, 1969) showed that all these molecules are practically planar, but that in some the small deviations of the atoms from the best molecular plane qualitatively agree with the predictions of Coulson & Stocker (1959). In another group of unmixed hexa-substituted benzenes (*e.g.* $X = NO_2$, COOH) the molecules are not planar because the substituents are tilted around the C–X bond. Thus in hexanitrobenzene the angle between the normals to the NO_2 groups and the C atom framework is 53° (Akopyan, Struchkov & Dashevski, 1966); in benzenehexacarboxylic acid the corresponding angles range from 24·6 to 80·7° (Darlow, 1961).

Dokunikhin, Gaeva & Mezentseva (1972) synthesized the first aromatic persulphonic acid – benzenehexasulphonic acid. This compound is an extremely overcrowded derivative of benzene with very large substituents, and has unusual properties (Dokunikhin & Mezentseva, 1973).

The hexasodium salt of benzenehexasulphonic acid forms a variety of hydrates $[C_6(SO_3Na)_6 . nH_2O]$. The large crystals of the hydrate with $n = 14$ in the form of transparent colourless orthorhombic prisms exist only in contact with the solution. However, the hydrate with $n = 8$ is stable in air for several weeks. Dokunikhin, Gaeva & Mezentseva (1972) showed that the hexasodium salt of benzenehexasulphonic acid retains firmly only three molecules of the crystal water.

We have determined the structure of the hexasodium salt of benzenehexasulphonic acid octahydrate (HSB) in order to discover the structural features connected with the large steric hindrance in the benzenehexasulphonic acid ion. Brief reports have been published (Chetkina, Sobolev, Mezentseva & Dokunikhin, 1975; Chetkina & Sobolev, 1975).

Experimental

The bright colourless transparent crystals of HSB were obtained by crystallization from water. The parameters of the unit cell and the intensities were measured on an automatic Syntex $P\bar{1}$ diffractometer. The number of water molecules was determined from the cell volume and from the density, measured by flotation. The crystals are monoclinic with $a = 8{\cdot}360\,(1)$, $b = 13{\cdot}981\,(1)$, $c = 12{\cdot}692$ (1) Å, $\gamma = 118°\,36\,(1)'$; space group $P2_1/b$, $Z = 2$, $V = 1302{\cdot}4\,(3)$ Å^3; $C_6H_{16}O_{26}S_6Na_6$, $d_o = 2{\cdot}15$, $d_c = 2{\cdot}13$ g cm^{-3}, $M_r = 834{\cdot}5$; $F(000) = 844$, $\mu(\text{Mo } K\alpha) = 7{\cdot}8$ cm^{-1}.

During data collection it was discovered that the crystal had begun to break: the intensities of the control reflexions decreased by 50%. This crystal was under X radiation for 50 h and exposed to air for about two months. 2997 observed independent reflexions were recorded [λ(Mo $K\alpha$), graphite monochromator, $\theta/2\theta$ method, $2\theta_{\max} = 58°$, $h = -11$ to $+6$, $k = 0$ to 18, $l = 0$ to 16]; of these only 2530 with $I \geq 3\sigma(I)$ were used in the calculations. Lorentz and polarization factors were applied but no correction was made for absorption or extinction.

Structure determination and refinement

The structure was solved by direct methods (Sayre, 1952; Zachariasen, 1952; Cochran, 1952) with the automatic program *XRAY*-69 (Andrianov, Tarnopolski & Shibaeva, 1969; Andrianov, Safina & Tarnopolski, 1971). For 462 normalized structure amplitudes with $|E| \geq 1{\cdot}3$, 1648 triple products were formed with a probability $P \geq 0{\cdot}83$ (expected value 0·884, $\sigma = 0{\cdot}124$). In addition to three origin-defining reflexions, the basic group contained eight reflexions with the maximum number of connexions. All possible combinations of signs ($2^8 = 256$ combinations) were assigned to these eight reflexions with high E values. Each combination was used independently to define the signs of all the normalized amplitudes. Estimates of the two best sign combinations are given below:

Q_1	R_1	Q_2	R_2
461	0·992	12	0·523
458	0·966	50	0·520.

Q_1 is the number of defined signs; $R_1 = \Sigma^+|E_{\mathbf{h}}E_{\mathbf{h}'}E_{\mathbf{h}''}|/\Sigma|E_{\mathbf{h}}E_{\mathbf{h}'}E_{\mathbf{h}''}|$, where Σ^+ is the sum of the triple products for which $S(E_{\mathbf{h}}) \times S(E_{\mathbf{h}'}) \times S(E_{\mathbf{h}''}) > 0$ and $\Sigma|E_{\mathbf{h}}E_{\mathbf{h}'}E_{\mathbf{h}''}|$ is the sum of all the triple products; Q_2 is the number of negative triple products; and R_2 is the number of positive signs divided by the total number of signs determined. The E synthesis for the best solution revealed the positions of all the nonhydrogen atoms. For these atoms and the 2530 reflexions R was 0·396.

Table 1. *Positional parameters* ($\times 10^5$) *for HSB with standard deviations*

	x	y	z
Na(1)	425 (26)	27984 (14)	29903 (14)
Na(2)	46544 (26)	28656 (16)	−38344 (15)
Na(3)	33710 (28)	638 (17)	−40566 (17)
S(1)	7431 (14)	6065 (8)	24422 (8)
S(2)	19298 (14)	25595 (8)	5553 (8)
S(3)	31805 (14)	15786 (8)	−15595 (8)
O(1)	4175 (45)	−4629 (24)	28187 (24)
O(2)	−3171 (49)	9993 (26)	30455 (25)
O(3)	26366 (45)	13803 (27)	23657 (26)
O(4)	5765 (45)	24987 (25)	13149 (25)
O(5)	37761 (43)	31171 (24)	9573 (26)
O(6)	17357 (45)	29741 (24)	−4618 (24)
O(7)	45745 (43)	21316 (27)	−7618 (26)
O(8)	29088 (46)	23181 (26)	−22407 (25)
O(9)	34352 (46)	7659 (26)	−21468 (27)
C(1)	507 (55)	3251 (31)	10609 (30)
C(2)	11208 (53)	11039 (31)	2900 (30)
C(3)	11624 (53)	7568 (31)	−7499 (29)
(H_2O)(1)	41976 (51)	3882 (28)	−60092 (32)
(H_2O)(2)	19972 (50)	12636 (32)	−45399 (30)
(H_2O)(3)	32347 (59)	39323 (33)	−40665 (34)
(H_2O)(4)	29071 (60)	38632 (43)	−63070 (41)

The structure was refined by the isotropic full-matrix least-squares method to $R = 0{\cdot}080$ with the program of Andrianov, Safina & Tarnopolski (1971). The H atoms of the water molecules could not be located from a difference synthesis. Refinement with anisotropic temperature factors was performed by the block-diagonal least-squares method to the final R of 0·053, with a program written by A. B. Tovbis. Scattering factors were taken from Hanson, Herman, Lea & Skillman (1964). The atomic coordinates are given in Table 1. Using the program of Muradyan & Simonov (1973) we calculated the thermal-vibration characteristics of the atoms. The half-axes of the thermal ellipsoids for probability values $p = 0{\cdot}5$ and $p = 0{\cdot}9$, and their orientation with respect to the crystallographic axes are shown in Table 2.*

Discussion

The structure contains the HSB ions in special positions at centres of symmetry. Bond lengths and angles are shown in Fig. 1, together with deviations from a least-squares plane through the six C atoms. Table 3 gives the intramolecular distances and angles, the equations of planes, and the distances of various atoms from these planes.

There are considerable steric forces between the SO_3 groups, which are the largest in the hexa-substituted

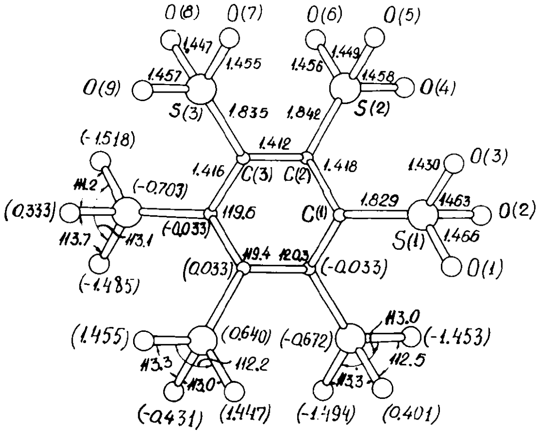

Fig. 1. Bond lengths (Å) and angles (°) in the benzenehexasulphonic acid ion; the deviations of the atoms from the plane are given in parentheses.

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* Lists of structure factors, anisotropic thermal parameters and Table 2 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32559 (29 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

benzenes. The configuration of the anion can be described by considering the deviations of the atoms from the plane through the ring [plane 1, Table 3(*c*)]. The SO_3 groups deviate alternately in opposite directions, the deviations of the S atoms having a mean of 0·672 Å and the S–C bonds a tilt of about 22°. The O atoms of the pyramidal SO_3 groups are arranged regularly: two O atoms deviate by equal amounts in the same direction (the average values of this deviation and the CSO bond angles are 1·475 Å and 102·4°); however, the other O atom deviates by a smaller amount in the opposite direction (the mean deviation is 0·388 Å, the CSO bond angle is 112·7°). In neighbouring SO_3 groups the signs of the deviations of the O atoms alternate. Such an arrangement of the SO_3 groups leads to a diminishing of the steric interactions between neighbours.

The deviation of each S atom and its bonded C atom is in the same direction: the C atoms deviate alternately in opposite directions from the best molecular plane by 0·033 Å: the bend angle is 5° [plane 1, Table 3(*c*)]. With respect to a plane through any four C atoms

Table 3. *The geometry of the benzenehexasulphonic acid ion*

E.s.d.'s are given in parentheses.

(*a*) Bond lengths and non-bonding intramolecular O···O and S···S distances (Å)

C(1)–S(1)	1·829 (4)	S(1)–O(1)	1·466 (4)	O(1)···O(2)	2·417 (6)
C(2)–S(2)	1·842 (4)	S(1)–O(2)	1·463 (5)	O(1)···O(3)	2·416 (4)
C(3)–S(3)	1·835 (4)	S(1)–O(3)	1·430 (3)	O(2)···O(3)	2·422 (6)
Average	1·835	S(2)–O(4)	1·458 (4)	O(4)···O(5)	2·428 (5)
		S(2)–O(5)	1·449 (4)	O(4)···O(6)	2·418 (5)
C(1)–C(2)	1·418 (5)	S(2)–O(6)	1·456 (4)	O(5)···O(6)	2·422 (5)
C(2)–C(3)	1·412 (6)	S(3)–O(7)	1·455 (3)	O(7)···O(8)	2·424 (5)
C(3)–C′(1)	1·416 (5)	S(3)–O(8)	1·447 (4)	O(7)···O(9)	2·429 (5)
Average	1·415	S(3)–O(9)	1·457 (4)	O(8)···O(9)	2·415 (6)
		Average	1·453		
S(1)···S(2)	3·403 (2)				
S(2)···S(3)	3·399 (2)				
S(3)···S′(1)	3·428 (2)				

(*b*) Bond angles (°)

O(1)S(1)O(2)	111·2 (2)	C(1)C(2)C(3)	119·4 (4)	C(1)S(1)O(2)	113·3 (3)
O(1)S(1)O(3)	113·1 (3)	C(2)C(3)C′(1)	120·3 (3)	C(2)S(2)O(5)	113·1 (3)
O(2)S(1)O(3)	113·7 (2)	C(2)C(1)C′(3)	119·6 (4)	C(3)S(3)O(8)	111·7 (3)
O(4)S(2)O(5)	113·3 (2)	Average	119·8	Average	112·7
O(4)S(2)O(6)	112·2 (3)				
O(5)S(2)O(6)	113·0 (2)	C(1)S(1)O(1)	102·0 (2)	S(1)C(1)C(2)	118·6 (3)
O(7)S(3)O(8)	113·3 (3)	C(1)S(1)O(3)	102·7 (2)	S(1)C(1)C′(3)	119·2 (3)
O(7)S(3)O(9)	113·0 (3)	C(2)S(2)O(4)	101·1 (2)	S(2)C(2)C(1)	119·0 (3)
O(8)S(3)O(9)	112·5 (3)	C(2)S(2)O(6)	103·1 (2)	S(2)C(2)C(3)	119·6 (3)
Average	112·8	C(3)S(3)O(7)	101·9 (2)	S(3)C(3)C(2)	118·3 (3)
		C(3)S(3)O(9)	103·4 (2)	S(3)C(3)C′(1)	119·1 (3)
		Average	102·4	Average	119·0

(*c*) Equations of the $Ax + By + Cz = D$ planes

Plane	*A*	*B*	*C*	*D*	Atoms defining the plane	Distances of individual atoms from the plane (Å)			
1	7·953	−9·087	2·715	0	C(1),C(2),C(3)	C(1)	+0·033	C(2)	−0·033
					C′(1),C′(2),C′(3)	C(3)	+0·033	S(1)	+0·703
						S(2)	−0·640	S(3)	+0·672
						O(1)	+1·518	O(2)	−0·333
						O(3)	+1·485	O(4)	−1·455
						O(5)	+0·431	O(6)	−1·447
						O(7)	+1·494	O(8)	−0·401
						O(9)	+1·453		
2	2·779	−0·438	11·827	3·470	O(1),O(2),O(3)	S(1)	−0·402		
3	−2·379	13·502	2·061	3·508	O(4),O(5),O(6)	S(2)	−0·396		
4	5·836	1·594	−6·372	3·495	O(7),O(8),O(9)	S(3)	−0·393		
5	8·065	−8·795	2·310	0	C(1),C′(1),C(2),C′(2)	C(3)	+0·099		
6	7·887	−8·868	3·276	0	C(2),C′(2),C(3),C′(3)	C(1)	+0·099		
7	7·881	−9·572	2·557	0	C(1),C′(1),C(3),C′(3)	C(2)	−0·099		

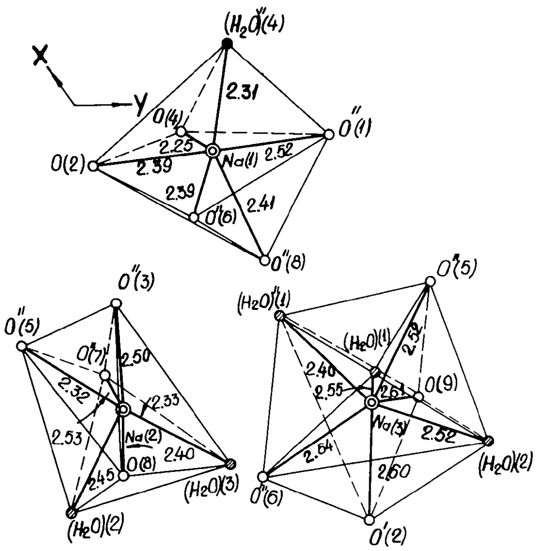


Fig. 2. The coordination polyhedra of the sodium ions.

related in pairs by the centre of symmetry, the other two C atoms deviate in opposite directions by 0·099 Å; the bend angle is 8° [planes 5 to 7, Table 3(*c*)]. Thus the ring has a flattened chair conformation. The average C–C length in the benzene ring (1·415 Å) is somewhat larger than the value found in benzene, 1·392 Å (Cox, Cruickshank & Smith, 1958). The values of the bond angles in the ring are close to 120°.

In hexa-substituted benzenes, substituents such as Cl (R_{Cl} = 1·80 Å), Br (R_{Br} = 1·95 Å), I (R_{I} = 2·10 Å), and CH_3 (R_{Me} ~ 2 Å) do not influence the structure of the benzene ring. In HSB the substituents are larger (R_{SO_3} ~ 2·5 Å). The conformational features of the anion closely resemble those of hexaiodobenzene (Khotsyanova & Smirnova, 1968; Steer, Watkins & Woodward, 1970), where the I atoms deviate alternately on opposite sides by 0·04 Å and the benzene ring is practically planar. The deviations of the SO_3 groups from the plane through the six ring atoms agree qualitatively with the theoretical predictions of Coulson & Stocker (1959) for the unmixed hexahalogen-substituted benzenes.

Table 4. *The coordination polyhedra of the* Na *ions*

The sodium atoms are in the position [I-100]. E.s.d.'s are in parentheses.

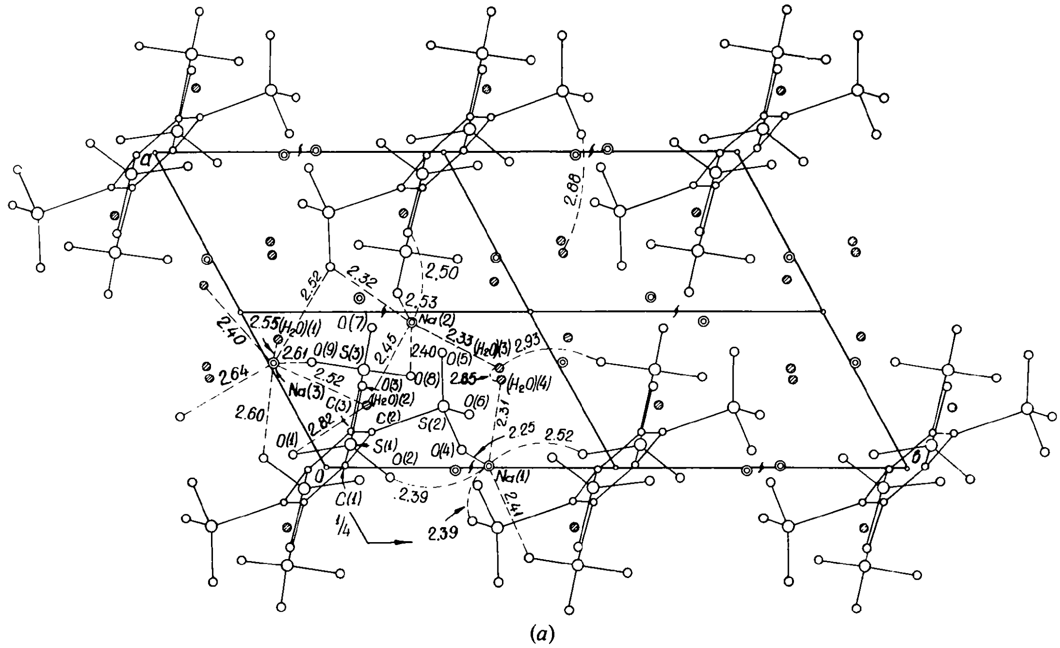
(*a*) Interatomic distances (Å)

Na(1)–O″(1)[O(1)III-000]	2·516 (4)	Na(2)–$(H_2O)(2)[(H_2O)(2)$ I-000]	2·447 (4)
Na(1)–O(2)[O(2) I-000]	2·387 (5)	Na(2)–$(H_2O)(3)[(H_2O)(3)$ I-000]	2·327 (6)
Na(1)–O(4)[O(4) I-000]	2·253 (4)	Na(3)–O′(2)[O(2) II-000]	2·596 (4)
Na(1)–O″(6)[O(6) IV-000]	2·387 (4)	Na(3)–O″(5)[O(5) IV-10$\bar{1}$]	2·520 (3)
Na(1)–O″(8)[O(8) IV-000]	2·412 (5)	Na(3)–O‴(6)[O(6) III-0$\bar{1}\bar{1}$]	2·637 (4)
Na(1)–$(H_2O)''(4)[(H_2O)(4)$ I-00$\bar{1}$]	2·309 (5)	Na(3)–O(9)[O(9) I-000]	2·606 (4)
Na(2)–O″(3)[O(3) IV-10$\bar{1}$]	2·505 (4)	Na(3)–$(H_2O)(1)[(H_2O)(1)$ I-000]	2·554 (5)
Na(2)–O″(5)[O(5) IV-10$\bar{1}$]	2·325 (5)	Na(3)–$(H_2O)''(1)[(H_2O)(1)$ II-10$\bar{1}$]	2·402 (6)
Na(2)–O″(7)[O(7) IV-10$\bar{1}$]	2·529 (4)	Na(3)–$(H_2O)(2)[(H_2O)(2)$ I-000]	2·521 (6)
Na(2)–O(8)[O(8) I-000]	2·395 (4)		

(*b*) Interbond angles (°)

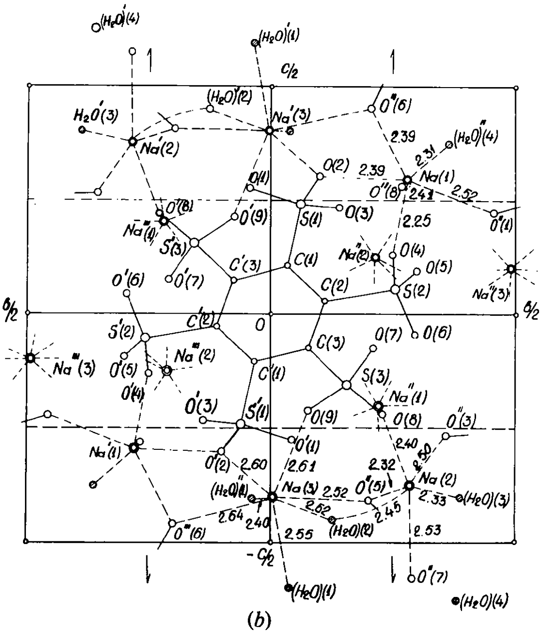
O″(1)–Na(1)–$(H_2O)''(4)$	85·6 (2)	O″(3)–Na(2)–$(H_2O)(3)$	116·3 (2)	O‴(6)–Na(3)–$(H_2O)(2)$	121·4 (2)
O(4)–Na(1)–$(H_2O)''(4)$	104·3 (2)	O″(3)–Na(2)–O(8)	84·9 (2)	O‴(6)–Na(3)–O′(2)	68·5 (2)
O(2)–Na(1)–$(H_2O)''(4)$	103·7 (2)	$(H_2O)(2)$–Na(2)–O″(5)	86·5 (2)	O‴(6)–Na(3)–$(H_2O)(1)$	85·7 (2)
O″(6)–Na(1)–$(H_2O)''(4)$	101·7 (2)	$(H_2O)(2)$–Na(2)–O″(7)	76·5 (2)	O‴(6)–Na(3)–$(H_2O)''(1)$	76·8 (2)
O″(1)–Na(1)–O″(8)	70·5 (2)	$(H_2O)(2)$–Na(2)–$(H_2O)(3)$	91·3 (2)	$(H_2O)(1)$–Na(3)–$(H_2O)''(1)$	83·7 (2)
O(4)–Na(1)–O″(8)	99·2 (2)	$(H_2O)(2)$–Na(2)–O(8)	82·5 (2)	O(9)–Na(3)–$(H_2O)(2)$	84·8 (2)
O(2)–Na(1)–O″(8)	108·9 (2)	O″(5)–Na(2)–O″(7)	71·1 (2)	O(9)–Na(3)–O′(2)	66·0 (2)
O″(6)–Na(1)–O″(8)	71·0 (2)	O″(5)–Na(2)–O(8)	109·7 (2)	$(H_2O)''(1)$–Na(3)–O(9)	101·5 (2)
O″(1)–Na(1)–O″(6)	122·4 (2)	$(H_2O)(3)$–Na(2)–O″(7)	94·8 (2)	$(H_2O)''(1)$–Na(3)–O′(2)	123·8 (2)
O″(1)–Na(1)–O(4)	81·4 (2)	$(H_2O)(3)$–Na(2)–O(8)	83·8 (2)	$(H_2O)(2)$–Na(3)–$(H_2O)(1)$	79·4 (2)
O(4)–Na(1)–O(2)	76·6 (2)	O″(3)–Na(2)–$(H_2O)(2)$	148·2 (2)	$(H_2O)(2)$–Na(3)–O′(2)	82·2 (2)
O(2)–Na(1)–O″(6)	76·2 (2)	O″(7)–Na(2)–O(8)	158·9 (2)	$(H_2O)(2)$–Na(3)–$(H_2O)''(1)$	153·7 (2)
O(4)–Na(1)–O″(6)	146·0 (2)	O″(5)–Na(2)–$(H_2O)(3)$	165·9 (2)	O′(2)–Na(3)–O″(5)	140·4 (2)
O″(1)–Na(1)–O(2)	157·6 (2)	O″(5)–Na(3)–$(H_2O)(1)$	77·5 (2)	O′(2)–Na(3)–$(H_2O)(1)$	133·6 (2)
$(H_2O)''(4)$–Na(1)–O″(8)	143·4 (2)	O″(5)–Na(3)–$(H_2O)''(1)$	75·8 (2)	O″(5)–Na(3)–O‴(6)	149·1 (2)
O″(3)–Na(2)–O″(5)	70·5 (2)	O″(5)–Na(3)–O(9)	77·0 (2)	O‴(6)–Na(3)–O(9)	122·6 (2)
O″(3)–Na(2)–O″(7)	114·2 (2)	O″(5)–Na(3)–$(H_2O)(2)$	81·0 (2)	O(9)–Na(3)–$(H_2O)(1)$	151·7 (2)

Symmetry code: (I) x,y,z; (II) $\bar{x},\bar{y},\bar{z}$; (III) $x, \frac{1}{2}+y, \frac{1}{2}-z$; (IV) $\bar{x}, \frac{1}{2}-y, \frac{1}{2}+z$.



(a)

Fig. 3. (a) Projection of the crystal structure along c.



(b)

Fig. 3 (cont.). (b) Projection along a.

Table 5. *The hydrogen-bond distances* (Å)

For the labelling of the atoms see Table 4.

$(H_2O)(2)$–O(1)[II-000]	2·817 (5)
$(H_2O)(3)$–O(4)[IV-00$\bar{1}$]	2·879 (5)
$(H_2O)(3)$–O(9)[III-00$\bar{1}$]	2·926 (6)
$(H_2O)(3)$–$(H_2O)(4)$[I-000]	2·854 (7)

The observed mean (1·835 Å) for S—C is larger than the standard S—C(sp^2) single-bond distance of 1·78 Å, and the lengths in benzenemonosulphonate structures (Arora & Sundaralingam, 1971; Attig & Mootz, 1976), where the mean is 1·77 Å. A similar increase of the S—C length was found by Barnes & Sundaralingam (1973) in the 2,4,6-trinitrobenzenesulphonate ion (1·810 Å) and was ascribed to steric effects. The SO_3 groups have a trigonal-pyramidal coordination and are tilted towards the S—C bond since there are two types of CSO bond angles (102·4 and 112·7°). The values of the OSO bond angles (mean 112·8°) and the practically equal S—O lengths (mean 1·453 Å) closely resemble those in other benzenesulphonate structures (Arora & Sundaralingam, 1971; Attig & Mootz, 1976; Barnes & Sundaralingam, 1973; Huber, 1969). Table 3(*c*) (planes 2 to 4) shows that the deviation of the S atoms from the base of the pyramid is 0·397 Å on average.

All O atoms of the SO_3 groups have close contacts with Na^+ ions and water molecules. The coordination polyhedra of the three independent Na^+ ions are shown in Fig. 2. The interatomic distances and angles in the coordination polyhedra of the Na^+ ions are given in Table 4. The coordination of the six closest O atoms about Na(1) and Na(2) is approximately octahedral. Na(3) has seven closest neighbours. The values of the Na—O interactions are in the range 2·253 to 2·637 Å (the sum of the atomic radii is 2·34 Å). The Na(1) environment consists of five O atoms from SO_3 groups and one from a water molecule: O(2), O(4), O″(1) and

O″(6) are in an equatorial position with a deviation from the plane through these atoms of d(max.) = ±0·15 Å; O″(8) and (H$_2$O)″(4) are in axial positions (Fig. 2). The polyhedron of Na(2) consists of four O atoms from SO$_3$ groups and two from water molecules: O(8), O″(7), O″(5) and (H$_2$O)(3) are in an equatorial position with d(max.) = ±0·21 Å; O″(3) and (H$_2$O)(2) are in axial positions. The seven O atoms surrounding Na(3) form a highly distorted pentagonal bipyramid with O(9) and (H$_2$O)(1) at the vertices (Fig. 2).

The crystal structure is shown in Fig. 3 with the closest Na$^+$ contact distances. Each SO$_3$ group has contacts with all three Na$^+$ ions. In addition, the O atoms of the SO$_3$ groups form weak hydrogen bonds with water molecules. These O···O distances are listed in Table 5 and vary between 2·817 and 2·926 Å.

We thank Professor N. S. Dokunikhin and Dr G. A. Mezentseva for suggesting this investigation, providing the crystals and for useful discussions; Mrs Z. S. Loginova for the determination of the density; and Dr L. A. Muradyan for help with the calculation of the thermal vibration ellipsoids.

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