

Fig. 2. The packing of the molecules within the unit cell. The contents of four cells are shown.  $\mathbf{a}$  and  $\mathbf{c}^* \times \mathbf{a}$  are parallel to the bottom and side of the page. The view is down  $\mathbf{c}^*$ .

[N(2)···Cl(1) 3.62 Å, N(1)···Cl(2) 3.61 Å] between adjacent molecules. The packing in this complex results in shortest Pt···Pt distances of 5.723 (2) and 5.828 (1) Å, considerably greater than the 3.4–3.5 Å typically found in *cis*-diamineplatinum(II) complexes (Lock, Speranzini & Zvagulis, 1980, and references therein). This difference in *trans* and *cis* complexes has already been noted by Srivasta, Froehlich & Eichhorn (1978).

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## Structure of Potassium Sucrose Octasulfate Heptahydrate

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**Abstract.**  $\text{C}_{12}\text{H}_{14}\text{O}_{35}\text{S}_8^{8-} \cdot 8\text{K}^+ \cdot 7\text{H}_2\text{O}$ ,  $M_r = 1413.58$ , orthorhombic,  $P2_12_12_1$ ,  $a = 16.865$  (12),  $b = 18.649$  (5),  $c = 14.051$  (3) Å,  $Z = 4$ , and  $D_x = 2.12$  Mg m $^{-3}$ . In the sucrose moiety, the furanosyl ring takes a  $^5T_4$  twist form while the pyranosyl ring takes a  $^4C_1$  chair. The  $\text{K}^+$  ion is surrounded by five to seven O

atoms including three to seven from the sulfate groups. The final  $R$  is 0.056.

**Introduction.** A basic aluminum salt of sucrose sulfate (I) accelerates the healing of gastric and duodenal ulcers (Mayberry, Williams, Rhodes & Lawrie, 1978).

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Table 1. Positional parameters ( $\times 10^4$ ) with e.s.d.'s in parentheses and equivalent isotropic thermal parameters

$$B_{eq} = \frac{1}{3}(a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + 2ab\beta_{12} + 2bc\beta_{23} + 2ac\beta_{13}).$$

	x	y	z	$B_{eq}$ ( $\text{\AA}^2$ )
K(1)	-643 (3)	-2250 (3)	599 (3)	4.82
K(2)	-208 (2)	2352 (2)	-2686 (2)	8.07
K(3)	796 (2)	-2107 (2)	3124 (2)	5.49
K(4)	428 (2)	-454 (2)	-3820 (2)	5.42
K(5)	3108 (2)	4844 (2)	1733 (2)	3.19
K(6)	3272 (2)	1779 (2)	4894 (2)	3.75
K(7)	3694 (1)	4798 (2)	-1097 (2)	3.50
K(8)	4957 (2)	4711 (2)	-3679 (2)	5.10
S(2)	2932 (2)	1679 (2)	2477 (2)	2.96
S(3)	1282 (2)	3625 (2)	2182 (2)	4.27
S(4)	1703 (2)	4605 (1)	-535 (2)	2.20
S(6)	3229 (2)	3505 (2)	-3037 (2)	3.57
S(1')	807 (2)	-630 (1)	1660 (2)	2.58
S(3')	-411 (2)	1667 (2)	-235 (2)	3.95
S(4')	-194 (2)	-920 (2)	-1200 (2)	2.03
S(6')	1219 (2)	1253 (2)	-3979 (2)	5.72
C(1)	2416 (5)	1771 (5)	73 (6)	1.13
C(2)	2471 (6)	2295 (5)	911 (6)	1.75
C(3)	1892 (6)	2901 (5)	768 (6)	1.96
C(4)	2055 (6)	3263 (5)	-209 (7)	1.94
C(5)	2002 (6)	2687 (5)	-980 (7)	1.91
C(6)	2137 (6)	2965 (6)	-1961 (7)	2.10
O(1)	1640 (4)	1500 (3)	68 (4)	1.89
O(5)	2575 (4)	2133 (3)	-788 (4)	2.38
C(1')	1641 (6)	387 (5)	914 (7)	2.76
C(2')	1508 (5)	748 (5)	-34 (6)	2.23
C(3')	640 (5)	643 (5)	-426 (7)	2.31
C(4')	737 (6)	178 (5)	-1303 (7)	1.64
C(5')	1605 (6)	293 (6)	-1586 (6)	2.97
C(6')	1704 (7)	927 (7)	-2267 (8)	3.31
O(2')	2013 (4)	441 (3)	-720 (5)	1.86
O(21)	2240 (4)	1927 (4)	1770 (5)	2.89
O(22)	2507 (5)	1269 (5)	3173 (6)	5.87
O(23)	3277 (5)	2324 (5)	2858 (6)	3.39
O(24)	3479 (5)	1281 (5)	1919 (6)	7.48
O(31)	2024 (4)	3414 (4)	1511 (5)	1.96
O(32)	919 (6)	2969 (5)	2494 (7)	8.29
O(33)	1660 (7)	3998 (7)	2929 (8)	4.13
O(34)	749 (6)	4011 (7)	1614 (8)	13.83
O(41)	1436 (4)	3783 (4)	-364 (5)	2.47
O(42)	961 (4)	4972 (4)	-403 (6)	3.36
O(43)	2017 (5)	4634 (4)	-1495 (5)	4.32
O(44)	2304 (4)	4768 (4)	156 (5)	2.14
O(61)	2918 (4)	3277 (4)	-1999 (5)	2.50
O(62)	2564 (6)	3767 (5)	-3540 (6)	6.27
O(63)	3546 (7)	2879 (6)	-3430 (7)	8.66
O(64)	3805 (7)	4029 (6)	-2810 (7)	4.13
O(11')	1405 (4)	-345 (4)	857 (5)	2.80
O(12')	1239 (5)	-658 (4)	2536 (5)	3.50
O(13')	616 (5)	-1334 (4)	1303 (6)	3.92
O(14')	157 (4)	-129 (4)	1681 (6)	5.11
O(31')	348 (4)	1332 (4)	-767 (5)	3.10
O(32')	-493 (5)	2333 (5)	-753 (7)	6.67
O(33')	-204 (6)	1746 (5)	742 (6)	5.98
O(34')	-1036 (5)	1169 (5)	-373 (7)	5.55
O(41')	674 (4)	-562 (4)	-1045 (5)	2.15
O(42')	-13 (6)	-1658 (4)	-957 (7)	4.12
O(43')	-387 (5)	-814 (6)	-2192 (6)	2.38
O(44')	-721 (5)	-572 (5)	-562 (6)	4.22
O(61')	1229 (6)	732 (5)	-3103 (6)	3.76
O(62')	1118 (6)	1954 (6)	-3607 (9)	7.75
O(63')	532 (6)	1016 (7)	-4483 (8)	6.42

Table 1 (cont.)

	x	y	z	$B_{eq}$ ( $\text{\AA}^2$ )
O(64')	1931 (6)	1155 (7)	-4455 (8)	10.51
O(W1)	-2253 (8)	-1901 (8)	335 (9)	7.11
O(W2)	316 (7)	-1465 (6)	4768 (9)	6.74
O(W3)	1331 (7)	-174 (9)	-5460 (8)	14.24
O(W4)	4327 (9)	3055 (8)	4830 (10)	8.09
O(W5)	5818 (6)	3507 (6)	-3171 (9)	5.72
O(W6)	-1165 (8)	1152 (6)	-2986 (10)	7.10
O(W7)	4785 (8)	1028 (8)	943 (9)	11.02

The atomic ratio of Al/S in (I) was found to be 2 and the number of basic hydroxy groups per Al to be 2.5 (Nagashima & Yoshida, 1979). (I) was obtained only as amorphous fine particles (Namekata, Tanaka, Sakamoto & Moro, 1967) and the three-dimensional structure of (I) remains unsolved. However, potassium sucrose octasulfate (Ochi, Watanabe, Okui & Shindo, 1980) was obtained as either monoclinic crystals (form I: space group  $C2$ ,  $a = 24.25$ ,  $b = 10.77$ ,  $c = 17.03$   $\text{\AA}$ ,  $\beta = 97.2^\circ$ ,  $Z = 4$ ), or orthorhombic crystals (form II, reported in the present paper). The crystal structure analysis was therefore undertaken to elucidate the structure of the sucrose sulfate moiety and the short-range atomic arrangement around the cations, which may provide useful information for the interpretation of the radial-distribution function of (I) in the amorphous state (Morikawa, Miyake, Iwai, Nawata & Shiba, 1980).

Crystals of potassium sucrose octasulfate heptahydrate were grown from a  $H_2O/CH_3OH$  solution. They deteriorated gradually by losing water of crystallization. The samples were coated with Vaseline and sealed in glass capillary tubes together with a small amount of mother liquor. Three fragments of single crystals of approximately equal dimensions ( $\sim 0.2 \times 0.1 \times 0.1$  mm) were employed to collect the intensity data. 3096 independent data were obtained above the  $2\sigma$  level on a Rigaku four-circle automatic diffractometer using Ni-filtered  $Cu K\alpha$  radiation. Intensities were corrected for Lorentz and polarization factors, but not for extinction or absorption. Attempts were made to solve the structure by use of the program *MULTAN* (Main, Woolfson & Germain, 1971), but the presence of 70 non-hydrogen atoms of various atomic weights in the asymmetric unit made the structure analysis difficult. A total of 512 sets of trials of phase calculations were carried out on 466 planes ( $|E_o| > 1.30$ ) using the starting phases of nine reflexions chosen by the program. 13 atoms, including seven  $K^+$  ions and six S atoms, were found on the  $E$  map of the most probable set [ $R(Karle) = 42.2\%$ , absolute figure of merit = 1.63]. Subsequent Fourier refinement revealed the positions of fifty non-hydrogen atoms. The structure was refined by the least-squares method of block-diagonal-matrix approximations using the program *HBLS IV* (Okaya & Ashida, 1967) including anisotropic temperature factors. Six water molecules

were found on the difference electron density map; their peak heights were as high as three to five times those of the background. The residual ( $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ) converged to 0.129; some of the principal-axis components of the thermal ellipsoids were negative for certain atoms [C(3), O(31), C(2'), *etc.*], probably because of the use of poor-quality data. Subsequent refinements were carried out with the reflexion data collected on a Philips PW 1100 diffractometer using Mo  $K\alpha$  radiation monochromated with a graphite plate; a crystal (0.50 × 0.25 × 0.20 mm), grown from an aqueous solution, coated with epoxy resin and sealed in a quartz-glass capillary tube, was used for the data collection (3575 planes above the  $2\sigma$  level). The calculations were continued with the atomic coordinates of 69 non-hydrogen atoms given isotropic temperature factors. After several cycles of refinement with anisotropic thermal parameters, the  $R$  index converged to 0.065 and one water molecule was recognized on the difference electron density map. In the final stage of the refinement, the contributions of 14 H atoms of the sucrose moiety were taken into account. They were placed at calculated positions. The final  $R$  was 0.056. The weighting scheme used was as follows:  $w^{1/2} = 293/|F_o|$  when  $|F_o| > 293$ ,  $w = 1.0$  when  $293 \geq |F_o| > 15$ , and  $w^{1/2} = 0.8$  when  $|F_o| \leq 15$ . The atomic scattering factors for  $K^+$ , S, O, C and H, and the dispersion corrections for  $K^+$  and S were those given in *International Tables for X-ray Crystallography* (1974). The approximate e.s.d.'s of the bond lengths and angles for non-hydrogen atoms were 0.005 ( $K^+ \cdots S$ ), 0.010 ( $K^+ \cdots O$ ), 0.009 (S—O), 0.012 Å (C—C, C—O), 0.5 (O—S—O) and 0.7° (C—O—C, C—C—O, C—C—C). Positional parameters are given in Table 1.\*

**Discussion.** A comparison of the structure of the sucrose moiety as observed in this study (SS) (Fig. 1) with that of the sucrose molecule (S) (Brown & Levy, 1973) and that in the sucrose sodium bromide dihydrate (SSBD) (Beever & Cochran, 1947) reveals some conformational changes in the fructofuranoside residue. The furanosyl rings in (SS) and (S) are both in the twist form (Stoddart, 1971), while that in (SSBD) is a  ${}^4E$  envelope. The conformation in (SS) can be described as  ${}^5T_4$ , that in (S) as  ${}^4T_3$ . The glucopyranosyl rings in (SS), (S) and in (SSBD), on the other hand, are all in the  ${}^4C_1$  chair conformation (Stoddart, 1971), with average endocyclic torsion angles of 60.3, 55.4 and 57.9°, respectively (Tables 2, 3). It should be noted that only small deviations (0.1 ~ 15.6°) of the torsion angles are observed for the

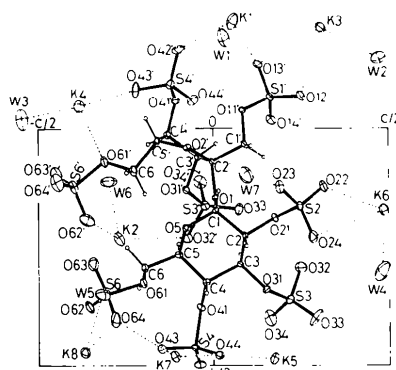


Fig. 1. ORTEP drawing (Johnson, 1970) of potassium sucrose octasulfate heptahydrate along [100], showing the numbering of the atoms and 15% probability thermal ellipsoids for the non-hydrogen atoms in the asymmetric unit. Dotted lines indicate some of the  $K^+ \cdots O$  bonds and hydrogen bonds (shorter than 3.1 Å) in the asymmetric unit.

Table 2. Displacements (Å) of the ring atoms out of the respective least-squares or reference planes

The equation of the plane is of the form  $Ax + By + Cz = D$ , where  $A$ ,  $B$  and  $C$  are the direction cosines of the normal to the plane for the orthogonal axes, and  $D$  (Å) is the perpendicular distance from the plane to the origin.  $E$  (°) is the angle between the least-squares plane of the glucopyranosyl ring and the reference plane of the fructofuranosyl ring.

	Potassium sucrose octasulfate	Sucrose	Sucrose sodium bromide
C(1)	-0.683 (7)	-0.628	-0.658
C(2)	-0.013 (8)*	0.015*	-0.054*
C(3)	0.013 (8)*	-0.015*	0.056*
C(4)	0.721 (8)	0.675	0.684
C(5)	-0.014 (8)*	0.016*	-0.056*
O(5)	0.014 (6)*	-0.016*	0.054*
A	0.7480	0.9410	0.0895
B	0.6624	0.2494	0.8745
C	-0.0404	0.2288	-0.4767
D	5.914	5.084	0.426
C(2')	0.000 (7)*	0.000*	-0.008*
C(3')	0.000 (7)*	-0.376	0.005*
C(4')	-0.174 (7)	0.206	0.531
C(5')	0.289 (8)	0.000*	-0.005*
O(2')	0.000 (6)*	0.000*	0.008*
A	0.0593	0.5212	-0.6295
B	0.8804	0.7943	0.7646
C	-0.4705	-0.3122	0.1385
D	1.401	1.220	-2.008
E	49.7	51.9	56.9

\* Atoms included in the calculation of the plane.

glycosidic linkage [C(1)—O(1)—C(2')] among the three molecules (Table 3 and Fig. 2), even though the intramolecular hydrogen bonds connecting the two moieties in (S) [O(2)  $\cdots$  O(1') and O(5)  $\cdots$  O(6')] are absent in (SS) and (SSBD) and bulky groups are introduced in (SS). Furthermore, in these crystals the environment of the sucrose molecule is quite different.

\* Lists of structure factors, anisotropic thermal parameters, bond lengths, bond angles and  $K^+ \cdots O$  distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35641 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Torsion angles ( $^{\circ}$ ) for the pyranosyl and furanosyl rings and the glycosidic linkage

	Potassium sucrose octasulfate	Sucrose	Sucrose sodium bromide
<b>D-Glucopyranosyl ring</b>			
O(5)—C(1)—C(2)—C(3)	58 (1)*	55.0	55.9
C(1)—C(2)—C(3)—C(4)	-56 (1)	-56.0	-51.3
C(2)—C(3)—C(4)—C(5)	56 (1)	56.3	53.9
C(3)—C(4)—C(5)—O(5)	-59 (1)	-54.9	-59.4
C(4)—C(5)—O(5)—C(1)	64 (1)	55.2	62.4
C(5)—O(5)—C(1)—C(2)	-69 (1)	-54.9	-64.5
<b>D-Fructofuranosyl ring</b>			
C(5')—O(2')—C(2')—C(3')	13 (1)	14.7	-1.5
O(2')—C(2')—C(3')—C(4')	7 (1)	-31.2	-21.4
C(2')—C(3')—C(4')—C(5')	-22 (1)	35.0	36.7
C(3')—C(4')—C(5')—O(2')	30 (1)	-27.3	-35.0
C(4')—C(5')—O(2')—C(2')	-27 (1)	8.1	23.2
<b>Glycosidic linkage</b>			
C(2)—C(1)—O(1)—C(2')	-133 (1)	-129.3	-136.7
O(5)—C(1)—O(1)—C(2')	107 (1)	107.8	92.2
C(1)—O(1)—C(2')—C(3')	-157 (1)	-159.8	-157.1
C(1)—O(1)—C(2')—O(2')	-42 (1)	-44.7	-47.2
C(1)—O(1)—C(2')—C(1')	80 (1)	73.7	75.4

\* E.s.d.'s are in parentheses.

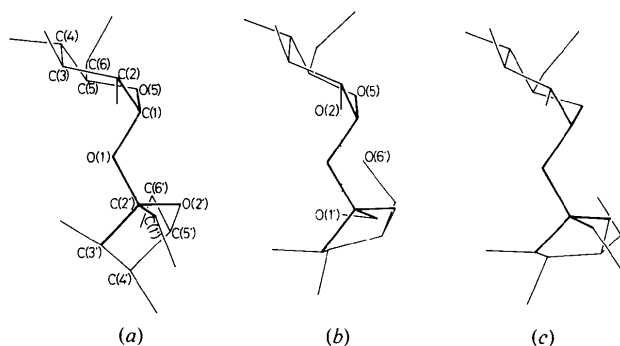


Fig. 2. Projection of sucrosyl moiety along the direction perpendicular to the plane formed by C(1), O(1), and C(2'): (a) sucrose octasulfate, (b) sucrose and (c) sucrose sodium bromide. The glycosidic linkage and its adjacent bonds are depicted by thick bonds.

The following observations are consistent with the most likely models of the short-range arrangement in the amorphous sodium salt and the aluminum hydroxide salt of sucrose sulfate (Morikawa, Miyake, Iwai,

Nawata & Shiba, 1980). In the present crystal structure, each of the eight  $K^+$  ions is found to be surrounded by five to seven O atoms, forming irregular coordination polyhedra. On average, each  $K^+$  ion, except for K(7), is surrounded by 4.7 O atoms from the sulfate groups and 1.7 O atoms from water molecules within 3.1 Å, the average  $K^+\cdots O$  distance being 2.832 Å. K(7) is surrounded by seven O atoms from sulfates (av.  $K^+\cdots O = 2.814$  Å). On average, 3.0 sulfate S atoms lie within 3.9 Å of the  $K^+$  ion. The average  $K^+\cdots S$  distance is 3.654 Å, except for K(7) which has four S atoms at 3.660 Å. Among the seven water molecules in the asymmetric unit, O(W7) does not participate in the coordination polyhedra of  $K^+$  ions but is surrounded by five O atoms of sulfate groups (at 2.64 ~ 3.10 Å).

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