References

Hall, L. D., Steiner, P. R. & Pedersen, C. (1970). *Can. J. Chem.* **48**, 1155–1165.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

Malmros, G. & Werner, P. E. (1973). *Acta Chem. Scand.* **27**, 493–502.

Messmer, A., Pintér, I. & Soliman, F. M. (1970). *Hung. Acta Chim.* **65**, 397–402.

Pauling, L. (1960). *The Nature of the Chemical Bond.* Ithaca: Cornell Univ. Press.

Schiele, C. (1967). *Chimia*, **21**, 413–448.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Zsoldos-Mády, V., Messmer, A., Pintér, I. & Neszmélyi, A. (1978). *Carbohydr. Res.* **62**, 105–116.

Acta Cryst. (1978). B**34**, 3486–3488

The Structure of 4-Methyl-5-sulphosalicylic Acid Tetrahydrate

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Abstract. $C_8H_8O_6S.4H_2O$, monoclinic, space group $P2_1/c$, $a = 7{\cdot}60\ (1)$, $b = 25{\cdot}30\ (2)$, $c = 8{\cdot}48\ (1)$ Å, $\beta = 119{\cdot}0\ (1)°$. $D_m = 1{\cdot}43$, $D_x = 1{\cdot}41$ g cm^{-3}, $Z = 4$; μ(Cu $K\alpha$) = 23 cm^{-1}. The three-dimensional crystal structure analysis revealed that the compound, in the crystalline state, exists in an ionized form as $H_7O_3^+H_3O^+.C_6H_2(COO^-)OHSO_3^-CH_3$, diaquaoxonium oxonium 4-methyl-5-sulphonatosalicylate. A short intramolecular contact of 3·04 Å between the methyl C and sulphonate O atoms suggests the presence of a C—H···O type hydrogen bond. The crystal structure is stabilized through intermolecular hydrogen bonds formed between the anionic molecules and cationic water species.

Introduction. Intensities of 965 non-zero independent reflections, recorded by usual X-ray diffraction photographic techniques, were estimated visually and corrected for the Lorentz–polarization effects and spot-extension factors. Absorption was neglected (crystal cross-section = 0·2 × 0·3 mm). The coordinates of the heavy atom (S) were determined from a sharpened Patterson map ($E^2 - 1$ map, where E is the normalized structure factor). Starting with the phases of the S atom alone, successive Fourier syntheses revealed all the non-hydrogen atoms. The structure was then refined isotropically to an R value of 0·143 and anisotropically to an R value of 0·113, using a full-matrix least-squares program (Busing, Martin & Levy, 1962). Scale factors and anisotropic temperature factors were refined in alternate cycles (Lingafelter & Donohue, 1966) along with positional parameters. The variations in parameters in the last cycle of anisotropic refinement were less than a tenth of their e.s.d.'s. The final atomic parameters are given in Table 1.* Bond lengths (with e.s.d.'s) and bond angles are shown in Fig. 1. The average e.s.d. of the bond angles is of the order of 1·5°.

Discussion. As part of our programme to study the effects of substituents on the geometry and biological

Table 1. *Atomic parameters* (×10^4) *of non-hydrogen atoms with their e.s.d.'s in parentheses*

	x	y	z
S	1614 (7)	3424 (1)	5395 (7)
O(1)	3799 (16)	5840 (4)	5821 (19)
O(2)	5066 (17)	5241 (5)	8018 (19)
O(3)	1072 (17)	5588 (5)	2661 (18)
O(4)	−287 (16)	3332 (4)	5455 (17)
O(5)	1862 (18)	3058 (5)	4146 (22)
O(6)	3328 (19)	3425 (5)	7219 (21)
O(*W*1)	−495 (20)	2842 (5)	8269 (30)
O(*W*2)	2700 (20)	4013 (5)	9970 (19)
O(*W*3)	4755 (22)	3136 (5)	3009 (29)
O(*W*4)	6342 (21)	2710 (6)	8366 (29)
C(1)	2588 (23)	4958 (6)	5065 (21)
C(2)	1208 (23)	5087 (6)	3268 (24)
C(3)	−22 (26)	4713 (7)	3074 (27)
C(4)	5 (25)	4189 (6)	2689 (26)
C(5)	1447 (23)	4067 (6)	4547 (26)
C(6)	2667 (24)	4441 (6)	5741 (26)
C(7)	3909 (23)	5400 (6)	6322 (26)
C(8)	−1382 (31)	3773 (8)	1343 (33)

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* Lists of structure factors, anisotropic thermal parameters and deviations from the least-squares plane have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33759 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

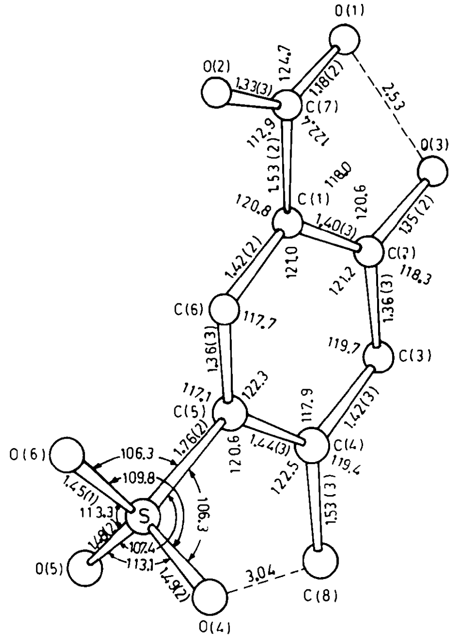
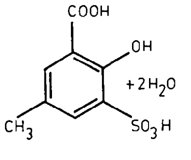
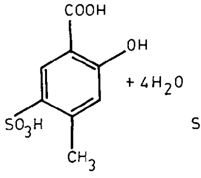


Fig. 1. Intramolecular bond lengths (Å) and angles(°).

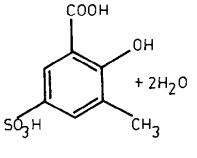
activity of the salicylic acid moiety, we have undertaken the structural analysis of sulpho-methyl derivatives of salicyclic acid. The structure of 5-methyl-3-sulphosalicyclic acid dihydrate (hereafter 5,3-MSSA, I) has been reported earlier (Vyas, Sakore & Biswas, 1978). This paper communicates our work on 4-methyl-5-sulphosalicylic acid tetrahydrate (hereafter 4,5-MSSA, II). The structure determination of 3-methyl-5-sulphosalicylic acid dihydrate (hereafter 3,5-MSSA, III) is in progress in our laboratory.



(I)



(II)



(III)

The structure of 4,5-MSSA is planar within 0·02 Å except for O(1), O(2) and O(3) which are respectively 0·07, 0·08 and 0·05 Å out of the plane. In the carboxylic acid group, the difference in C—O bond lengths (Δr = 0·15 Å) and in C—C—O angles ($\Delta\theta$ = 11·8°) shows that there is no orientational disorder (Leiserowitz, 1976). The intramolecular hydrogen bond [O(1)···O(3) = 2·53 Å] is short compared with that found in salicylic acid (2·62 Å, Sundaralingam & Jensen, 1965), 5-sulphosalicylic acid trihydrate (2·64 Å, Mootz & Fayos, 1970) and 5,3-MSSA (2·62 Å).

In the sulpho group, the three S—O bond lengths suggest that there is no covalently attached H atom to any of the sulphonyl O atoms. The difference between the C—S—O (average 106·7°) and O—S—O (average 112·2°) angles is 5·5°, such a difference has been observed in several other similar structures (Greenberg & Okaya, 1969; Arora & Sundaralingam, 1971) and could be a general property of the deprotonated sulpho group. The short contacts (2·47 and 2·40 Å) between O(W1) and O(W4), O(W4) and O(W3) reveal that the acid proton (from the SO_3H group) is shared by three water molecules [O(W1), O(W3) and O(W4)], yielding a diaquaoxonium ($H_7O_3^+$), cationic water species. The aromatic sulphonic acids, in the crystalline state, are generally found to exist in an ionic form yielding different types of cationic water species (Mootz & Fayos, 1970; Arora & Sundaralingam, 1971; Lundgren, 1972; Lundgren & Lundin, 1972; Attig & Mootz, 1976; Vyas, Sakore & Biswas, 1978). One O atom, O(4) of the sulphonate group, forms a short contact (3·04 Å) with the methyl C atom C(8), which may be a C—H···O type of intramolecular hydrogen bond. The two short contacts [O(1)···O(3) = 2·53 Å and O(2)···O(3) = 2·55 Å] and the formation of the C(8)—H··· O(4) = 3·04 Å hydrogen bond suggest that the carboxylic acid group in this compound is deprotonated yielding another cationic water species (H_3O^+), oxonium, in the crystalline form. Such deprotonation of the carboxylic acid group is not observed in crystal structures of 5,3-MSSA (Vyas, Sakore & Biswas, 1978) and 5-sulphosalicylic acid trihydrate (Mootz & Fayos, 1970), where molecules are dimerized through the carboxyl groups and through the carboxyl group and sulphonate group respectively. This means that 4,5-MSSA in the crystal structure exists as $H_7O_3^+H_3O^+.C_6H_2(COO^-)OHSO_3^-CH_3$, diaquaoxonium oxonium 4-methyl-5-sulphonatosalicylate.

The crystal structure of 4,5-MSSA as viewed down the *c* axis is shown in Fig. 2, in which hydrogen bonds are shown by broken lines. All the O atoms of the sulphonate group form hydrogen bonds with the

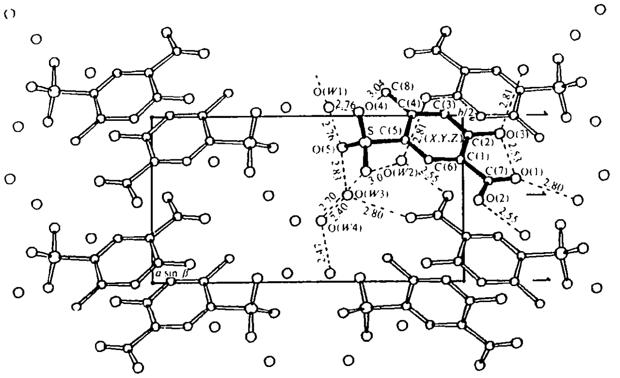


Fig. 2. Molecular packing viewed down *c*. The molecule corresponding to the coordinates in Table 1 is shown by solid lines, and important hydrogen bonds are shown as broken lines.

cationic water species. The crystal structure of this compound is stabilized by the hydrogen bonds formed between anionic molecules and cationic water species.

References

ARORA, S. K. & SUNDARALINGAM, M. (1971). *Acta Cryst.* B**27**, 1293–1298.

ATTIG, R. & MOOTZ, D. (1976). *Acta Cryst.* B**32**, 435–439.

BUSING, W. R., MARTIN, K. O. & LEVY, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Tennessee.

GREENBERG, B. & OKAYA, Y. (1969). *Acta Cryst.* B**25**, 2101–2108.

LEISEROWITZ, L. (1976). *Acta Cryst.* B**32**, 775–802.

LINGAFELTER, E. O. & DONOHUE, J. (1966). *Acta Cryst.* **20**, 321.

LUNDGREN, J. O. (1972). *Acta Cryst.* B**28**, 475–481.

LUNDGREN, J. O. & LUNDIN, P. (1972). *Acta Cryst.* B**28**, 486–491.

MOOTZ, D. & FAYOS, J. (1970). *Acta Cryst.* B**26**, 2046–2054.

SUNDARALINGAM, M. & JENSEN, L. H. (1965). *Acta Cryst.* **18**, 1053–1058.

VYAS, N. K., SAKORE, T. D. & BISWAS, A. B. (1978). *Acta Cryst.* B**34**, 2892–2893.

Acta Cryst. (1978). B**34**, 3488–3490

Tetraethylammonium Chloride Monohydrate*

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Abstract. $C_8H_{20}ClN.H_2O$, monoclinic, $C2/c$, $a = 13{\cdot}684\,(3)$, $b = 14{\cdot}144\,(3)$, $c = 12{\cdot}372\,(4)$ Å, $\beta = 110{\cdot}75\,(2)^\circ$ at 24°C, $Z = 8$, $D_x = 1{\cdot}0899\,(5)$ g cm^{-3}. The asymmetric unit consists of one formula unit. Pairs of Cl^- ions and water molecules form a centrosymmetric hydrogen-bonded ring. The tetraethylammonium ions lie on a twofold axis and have two different orientations. One conforms to the crystallographic symmetry while the other is in a general orientation with a twofold disorder.

Introduction. Several prismatic crystals grew slowly from a chloroform–ether solution of tetraethylammonium chloride (Et_4NCl) during attempts to grow crystals of $Et_4NCl.CHCl_3$. The composition of these crystals was established by the present structural analysis. Since dried solvents and vacuum-dried salt were used, the water must have entered from the atmosphere. The crystal used for data collection was placed in a glass capillary from which all solvent was removed prior to sealing.

Data were collected using Mo $K\alpha$ radiation on a Nonius CAD-4 diffractometer fitted with a graphite monochromator. 24 independent reflections were used to determine the lattice parameters by a least-squares fit with the diffraction angle θ, measured as 4θ $[2\theta-(-2\theta)]$. Systematic extinctions were observed for all reflections with $h + k$ odd and for $h0l$ reflections with h odd. The choice of space group $C2/c$ rather than Cc was made after determination of the structure. All unique reflections (1976) were measured out to $\theta = 25^\circ$ ($\sin\theta/\lambda = 0{\cdot}595$ Å^{-1}) using a θ–2θ scan technique. No significant changes were observed in four standard reflections monitored at regular intervals. Background corrections were made using the profile-analysis method of Lehmann & Larsen (1974) following which the data were corrected for Lorentz and polarization effects and for absorption ($\mu = 3{\cdot}01$ cm^{-1}) using the Gaussian integration method with a grid of 360 points. The crystal had faces of the forms $\{110\}$ and $\{111\}$ and measured $0{\cdot}013 \times 0{\cdot}013 \times 0{\cdot}024$ cm with the long axis coinciding with c. Of the 1976 unique reflections measured, 834 with observed intensities greater than $1{\cdot}5\sigma(I)$ were used in the refinement.

The position of the Cl^- ion was found using both heavy-atom and direct methods.† The non-hydrogen

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* Hydrogen Bond Studies. CXXVIII.

† The program *MULTAN* (Declercq, Germain, Main & Woolfson, 1973) was used for direct methods. All other programs used in this work, including *ORTEP* (Johnson, 1965) used in preparing Fig. 1, are described by Lundgren (1975) or were written by the authors.