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Structure of Tetraethylammonium Thiosulfate Dihydrate

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Abstract. $[(C_2H_5)_4N]_2S_2O_3.2H_2O$, $C_{16}H_{44}N_2O_5S_2$, M_r = 408·67, monoclinic, $P2_1$, a = 7·2356 (5), b = 16·5216 (6), c = 9·5964 (7) Å, β = 94·596 (4)°, V = 1143·50 (13) Å^3, Z = 2, D_x = 1·187 g cm^{-3}, λ(Mo $K\alpha_1$) = 0·70930 Å, μ = 2·5 cm^{-1}, $F(000)$ = 452, T = 295 K, R = 0·030 for 2855 reflections. The structure contains tetrahedral cations with approximate D_{2d} symmetry, tetrahedral anions with approximate C_{3v} symmetry, and water molecules which link the anions into chains along **a** *via* O—H···S and O—H···O hydrogen bonds. Mean N—C = 1·527 (2), C—C = 1·515 (2), S—S = 2·028 (1), S—O = 1·481 (2) Å (corrected for libration); O—(H)···S = 3·349 (3), 3·458 (2), O—(H)···O = 2·817 (3), and bifurcated 3·121 (4) and 3·154 (4) Å.

Introduction. The title compound was synthesized as part of a project to produce non-aqueous electrolytes, but proved unsuitable, since the present X-ray study showed that it contained water of crystallization.

Experimental. Colourless blocks, (001), $(\bar{2}21)$, ±(120), $\pm(01\bar{1})$ developed, uniform dimensions ~0·4 mm, Enraf–Nonius CAD-4F diffractometer, lattice parameters from 25 reflections with θ = 20–23°. Intensities for $\theta \le$ 32·5°, *hkl*: 0 to 10, 0 to 24, −14 to 14, ω–2θ scan, ω scan width (0·65 + 0·35tanθ)° at 1·2–10° min^{-1}, extended 25% on each side for background measurement, three standard reflections showed negligible variations in intensity, Lp but no absorption corrections, 4236 independent reflections measured, 2855 with $I \ge 3\sigma(I)$, where $\sigma^2(I) = S + 4(B_1 + B_2) + (0{\cdot}04I)^2$, S = scan, B_1 and B_2 = background counts. Structure by Patterson and Fourier methods, refined by full-matrix least squares on F, H atoms from a difference map, weights used $w = 1/\sigma^2(F)$, scattering factors and anomalous-dispersion corrections for S (f'' = 0·124) from *International Tables for X-ray Crystallography* (1974), locally written, or locally modified versions of standard computer programs, final R = 0·030, wR = 0·036 for 2855 reflections (the enantiomorph for the crystal used had R and wR ratios of 1·015, and could be rejected), S = 1·4, 225 parameters (non-hydrogen atoms, plus 176 H parameters), R = 0·058 for all 4236 reflections, Δ/σ = 0·10 (mean), 1·8 [maximum, for B of H(11*c*)], maximum final difference density ±0·18 e Å^{-3}.

The thermal motions of the anion and of the two independent cations were analysed separately in terms

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of rigid-body motion (Schomaker & Trueblood, 1968). The r.m.s. $\sigma(U_{ij})$ is 0·0013 Å^2, while the r.m.s. ΔU_{ij} are 0·0004 Å^2 for the anion, and 0·0025 and 0·0020 Å^2 for the two independent cations. The anion thermal motion is thus well described by the rigid-body model, as found for other thiosulfates (Armağan, 1983). The cations are also fairly well described as rigid bodies, with some additional motion of the outer methyl groups (Fig. 1). Bond lengths were corrected for libration on the basis of the rigid-body models.

Discussion. Positional parameters are given in Table 1.* The structure (Fig. 1) contains tetrahedral tetraethylammonium cations and thiosulfate anions, and water molecules.

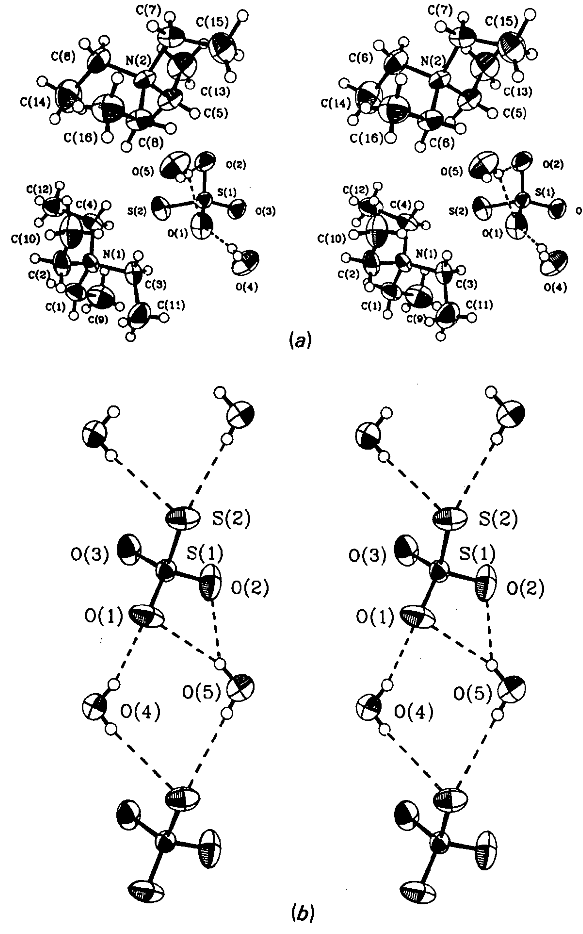

Fig. 1. (*a*) Stereoview of the two independent tetraethylammonium cations, the thiosulfate anion, and the two water molecules. (*b*) The hydrogen bonding scheme.

Table 1. *Positional (fractional) and equivalent isotropic thermal parameters (U_{eq}, Å^2), with e.s.d.'s in parentheses*

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S(1)	0·88450 (6)	0·55720	0·52218 (4)	0·035
S(2)	1·06637 (8)	0·46969 (5)	0·48409 (8)	0·057
O(1)	0·72470 (24)	0·51871 (13)	0·57933 (24)	0·065
O(2)	0·82672 (33)	0·59860 (14)	0·39149 (17)	0·069
O(3)	0·97269 (26)	0·61413 (11)	0·62320 (16)	0·057
O(4)	0·40545 (30)	0·54672 (16)	0·72213 (19)	0·065
O(5)	0·43484 (36)	0·52435 (19)	0·31599 (23)	0·077
N(1)	0·58043 (22)	0·27970 (8)	0·47550 (17)	0·035
N(2)	−0·09896 (23)	0·53336 (11)	0·00921 (14)	0·039
C(1)	0·70967 (35)	0·21901 (14)	0·55283 (27)	0·050
C(2)	0·41672 (33)	0·23253 (15)	0·40982 (31)	0·050
C(3)	0·51753 (37)	0·34414 (13)	0·57360 (28)	0·048
C(4)	0·68119 (30)	0·32348 (13)	0·36546 (25)	0·044
C(5)	0·06487 (29)	0·56242 (20)	0·10449 (19)	0·048
C(6)	−0·03376 (43)	0·48124 (18)	−0·10860 (24)	0·056
C(7)	−0·20499 (39)	0·60332 (16)	−0·05981 (24)	0·052
C(8)	−0·22155 (31)	0·48571 (15)	0·10054 (22)	0·046
C(9)	0·87362 (53)	0·25614 (27)	0·63537 (44)	0·077
C(10)	0·27812 (40)	0·28210 (21)	0·32134 (42)	0·071
C(11)	0·42351 (56)	0·31234 (25)	0·69752 (38)	0·073
C(12)	0·74656 (42)	0·26920 (20)	0·25208 (29)	0·058
C(13)	0·19515 (48)	0·61904 (26)	0·03650 (39)	0·073
C(14)	0·06554 (61)	0·40480 (25)	−0·06310 (47)	0·080
C(15)	−0·26904 (50)	0·66571 (20)	0·04117 (38)	0·069
C(16)	−0·38597 (46)	0·44505 (24)	0·02447 (36)	0·065

Table 2. *Summary of bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

	Uncorrected	Corrected
N—C	1·511–1·526 (3), mean 1·517 (2)	1·521–1·536, mean 1·527
C—C	1·501–1·515 (4), mean 1·508 (2)	1·508–1·522, mean 1·515
S—S	2·008 (2)	2·028
S—O	1·460–1·464 (2), mean 1·461 (2)	1·480–1·483, mean 1·481

C—N—C	106·3–107·1 (2), mean 106·6 (2)	(around S_4 axis)
	110·1–111·5 (2), mean 110·9 (2)	(around C_2 axis)
N—C—C	114·3–115·4 (2), mean 114·8 (1)	

	O···O/S	O—H	H···O/S	O—H···O/S
O(4)—H(O4*a*)···S(2$^{\rm i}$)	3·458 (2)	0·74 (4)	2·74 (4)	165 (3)
O(4)—H(O4*b*)···O(1)	2·817 (3)	0·80 (5)	2·04 (5)	165 (4)
O(5)—H(O5*a*)···O(1)	3·154 (4)	0·86 (5)	2·39 (5)	148 (4)
O(5)—H(O5*a*)···O(2)	3·121 (4)	0·86 (5)	2·37 (5)	146 (4)
O(5)—H(O5*b*)···S(2$^{\rm i}$)	3·349 (3)	0·76 (4)	2·59 (4)	170 (4)

Symmetry code: (i) $-1+x, y, z$.

The two independent cations have similar conformations, with symmetry close to D_{2d}; the C—N—C—C torsion angles* differ by a maximum of 7° from the ideal ±60, 180° values. There are many previous studies of the tetraethylammonium cation, mainly as a counter cation, with the main interest being in the anion; S_4, D_{2d}, and disordered conformations are found (*e.g.* Schomaker & Marsh, 1979). The mean (libration-corrected) bond distances (Table 2) are N—C =

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* Method of synthesis of the compound, and lists of anisotropic thermal parameters, H-atom positions, bond lengths and angles, torsion angles, and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51035 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

* See deposition footnote.

1·527 (2), C—C = 1·515 (2) Å. The bond angles at the N atoms show a significant deviation from tetrahedral geometry, with the angles in each cation bisected by the S_4 axis being compressed to an average of 106·2 (2)°, possibly as a result of $CH_3\cdots CH_2$ intra-ion repulsions; the other C—N—C angles average 110·9 (2)°, and the N—C—C angles average 114·8 (1)°, perhaps a little larger than normal values as a result of the repulsions.

The thiosulfate anion has symmetry close to C_{3v} (Table 2), with S—S = 2·028 (1), mean (standard deviation of mean calculated from r.m.s. differences) S—O = 1·481 (2) Å (corrected for libration), S—S—O = 108·6 (5), O—S—O = 110·3 (1)°; the values are within the ranges normally found in thiosulfates (*e.g.* Teng, Fuess & Bats, 1984): S—S = 1·987–2·031, S—O = 1·473–1·489 Å. The anions are linked into chains along **a** by hydrogen bonds from the water molecules (Fig. 1, Table 2). O(4) forms two normal nearly linear bonds, O—(H)···O = 2·817 (3) Å and O—(H)···S = 3·458 (2) Å [an additional O(4)—H(O4*a*)···O(3$^{\rm i}$) contact of 3·387 (3) Å and 134 (3)° may represent some minor bifurcation of the O—(H)···S bond]; O(5) forms a normal nearly linear O—(H)···S bond, 3·349 (3) Å, and a bifurcated $\mathrm{O{-}H}\genfrac{}{}{0pt}{}{\cdot\cdot\,\mathrm{O}}{\cdot\cdot\,\mathrm{O}}$ bond, O···O = 3·121 (4) and 3·154 (4) Å. The shortest interionic distances involving the cation are H···S(2) = 2·86 (4), H···O = 2·52 (4), H···H = 2·10 (5) Å.

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Structure of Diethyl 9-Hydroxy-7-methyl-2,4-diphenyl-3-oxa-7-aza-1,5-bicyclo[3.3.1]nonanedicarboxylate

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Abstract. $C_{26}H_{31}NO_6$, $M_r = 453·5$, monoclinic, $P2_1/c$, $a = 11·504$ (4), $b = 14·009$ (3), $c = 15·564$ (4) Å, $\beta = 109·80$ (3)°, $V = 2360·0$ Å^3, $Z = 4$, $D_x = 1·276$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 0·844$ cm^{-1}, $F(000) = 968$, room temperature, $wR = 0·037$ for 4701 reflections [$I > 1·5\sigma(I)$]. The oxacyclohexanone part of the molecule is in a boat conformation, and the piperidine part shows a chair conformation. The OH group is inclined towards the phenyl-substituted part of the molecule and forms an intramolecular hydrogen bond [O···O = 2·726 (2) Å] to one of the carboxylate groups.

Introduction. Heterocyclic bicyclo[3.3.1]nonan-9-ols containing a piperidinol ring are of pharmacological interest because of their relation to opioid analgesics (Casy & Parfitt, 1986). To understand the pharmacological properties, it is important to know the stereogeometry of the molecule. 3-Oxa-7-aza-bicyclo[3.3.1]nonan-9-ones are obtained through a Mannich reaction by condensing a diethyl 4-oxo-2,6-diphenyl-1-oxa-3,5-cyclohexanedicarboxylate with formaldehyde and methylamine (Mannich & Mück, 1930; Haller & Unholzer, 1971). Two isomers are isolated (see Fig. 1), one showing a boat–chair conformation with the boat structure in the oxacyclohexanone ring containing the two benzene rings in a quasi-equatorial position, and the other isomer showing a chair–chair structure with the benzene rings in equatorial position (Küppers, Hesse, Ashauer-Holzgrabe, Haller & Boese,