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Structures of Trimethyloxosulfonium Salts. II. The Chloride

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Abstract. $(CH_3)_3SOCl.H_2O$, $M_r = 146{\cdot}64$, cubic, $P2_13$, $a = 9{\cdot}023\ (2)$ Å, $V = 734\ (1)$ Å^3, $Z = 4$, D_x (anhydrous) $= 1{\cdot}326$ Mg m^{-3}, D_m not measured, λ(Mo $K\alpha$) = 0·71073 Å, μ(Mo $K\alpha$) = 0·71067 mm^{-1}, $F(000) = 312$, $T = 295$ K, final $R = 0{\cdot}023$, $wR = 0{\cdot}022$ for 527 independent observed reflections. The structure is made up of stacks of Cl^- anions and pyramidal thiocations $[(CH_3)_3SO]^+$, which, in this compound, have $3m$ symmetry. S and O atoms (as well as Cl atoms) are located on ternary axes. The cell encloses four large cavities partially occupied by a very mobile water molecule, $H_2O(w)$ (averaged occupation about 0·8), whose H atoms were not located.

Experimental. The crystals were obtained by the preparative method described elsewhere (de Brauer & Perret, 1991). Prismatic colorless crystals, density not measured, crystal size 0·23 × 0·21 × 0·24 mm. Nonius CAD-4 diffractometer, graphite monochromator, monochromated Mo $K\alpha$. Unit-cell constants from least-squares refinement of 25 reflections with $5 < \theta < 13°$, systematic absences $h00$ ($h = 2n$), space group $P2_13$ (No. 198). $\omega/2\theta$ scan, scan width 1·2°, $1 < \theta < 30°$, $0 < h < 12$, $-12 < k < 12$, $-12 < l < 12$. Four orientation reference reflections (202, 312, 123, 113) measured every 200 scans: no significant variations. Intensities of the same reference reflections recorded every 2 h: fading of 1·6% during 139·4 h; decay correction. 4477 measured reflections, 2872 reflections with $I > 3\sigma(I)$. Lorentz and polarization corrections, absorption corrections from ψ scan: relative transmission factor between 0·958 and 0·998. 527 reflections after averaging: $R_{\text{int}} = 0{\cdot}021$.

Crystal structure solved by direct methods: *MULTAN*77 (Main, Lessinger, Woolfson, Germain & Declercq, 1977). H atoms located by difference Fourier synthesis. Anisotropic full-matrix least-squares refinement (on F) for non-H atoms, isotropic for H atoms, extinction coefficient refined: $g = 1{\cdot}221 \times 10^{-6}$ (Stout & Jensen, 1968), 36 variables, unit weights. Final refinement with 527 reflections: final $R = 0{\cdot}023$, $wR = 0{\cdot}022$, $S = 0{\cdot}287$. Maximum and minimum peak heights in final Fourier synthesis 0·276 and $-0{\cdot}214$ e Å^{-3}, maximum $\Delta/\sigma = 0$. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV). Enraf–Nonius (1977) *SDP* used for all calculations. Computer used: VAX 730.

Table 1. *Final atomic coordinates for* $(CH_3)_3SOCl.H_2O$ *with e.s.d.'s in parentheses*

$$B_{\text{eq}} = (4/3)\textstyle\sum_i\sum_j \beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Cl	0·7039 (1)	0·7039	0·7039	6·856 (6)
S	0·4507 (1)	0·4507	0·4507	4·048 (3)
O	0·3588 (2)	0·3588	0·3588	5·58 (1)
C	0·0858 (2)	0·1501 (2)	0·4551 (2)	5·54 (5)
O(w)	0·0407 (3)	0·0407	0·0407	10·97 (4)

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *for* $(CH_3)_3SOCl.H_2O$

Trimethyloxosulfonium ion			
S—O	1·742 (3)	O—S—C	106·2 (1)
S—C	1·436 (8)	C—S—C	112·6 (1)
Chloride coordination			
Cl—S	3·9567 (4)	4·0766 (5)	
Cl—O	4·2242 (13)		
Cl—C	3·648 (2)	3·701 (2)	
O(w) atom coordination			
O(w)—Cl	3·513 (2)		
O(w)—C	3·707 (3)	3·862 (3)	3·886 (3)

Table 1 gives the final atomic coordinates and some interatomic distances and bond angles are listed in Table 2.* The structure is formed by stacks of Cl^- anions and pyramidal thiocations $(CH_3)_3SO^+$. In this compound, the thiocation really has $3m$ symmetry: the two atoms S and O (as is Cl) are located on a ternary axis. The cell contains four large cavities, each of which is partially occupied (average occupation 0·792) by a very mobile O(w) ($B_{\text{eq}} = 11{\cdot}6$ Å^2) of a water molecule $H_2O(w)$ whose two H atoms were not located; Table 2 gives the distances between this O(w) atom and the surrounding C and Cl atoms. The cell packing is shown in

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and intermolecular contacts have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53844 (7 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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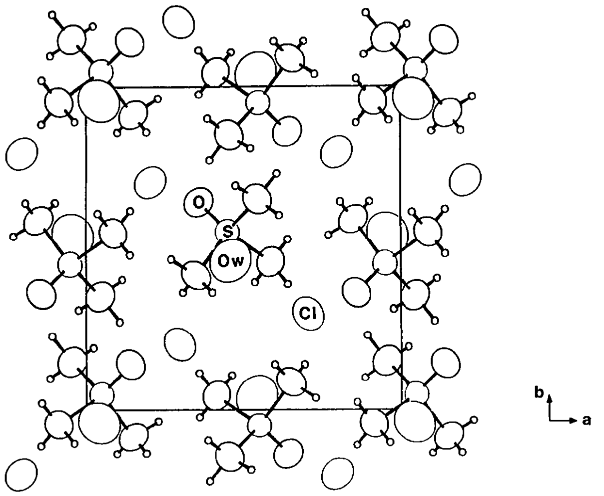

Fig. 1. Projection along the c axis of the atomic arrangement of $(CH_3)_3SOCl.H_2O$.

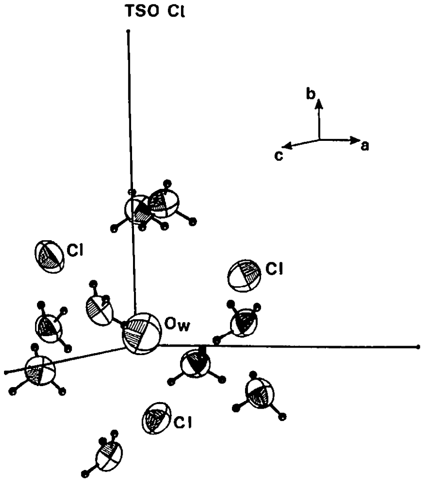

Fig. 2. The surroundings of the O(w) atom.

Fig. 1 and the environment of the O(w) atom is in Fig. 2.

Related literature. Very little is known about the structures of trimethyloxosulfonium salts, only the structures of the perchlorate (Coulder, Gantzel & McCullough, 1963) and the fluoroborate (Zimmermann, Barlow & McCullough, 1963) have been described at 293 K. In a previous paper, we reported the structure of the isotypic iodide and bromide salts (Jannin, Puget, de Brauer & Perret, 1991).

This work was carried out at the Centre de Diffractométrie de l'Université de Bourgogne.

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Structures of Trimethyloxosulfonium Salts. III. The Nitrate

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Abstract. $[(CH_3)_3SO]NO_3$, $M_r = 155{\cdot}7$, orthorhombic, $Pbca$, $a = 11{\cdot}048\,(2)$, $b = 11{\cdot}238\,(2)$, $c = 11{\cdot}549\,(2)$ Å, $V = 1434{\cdot}0\,(6)$ Å^3, $Z = 8$, $D_m = 1{\cdot}42\,(1)$, $D_x = 1{\cdot}437$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu(\text{Mo } K\alpha) = 0{\cdot}3852$ mm^{-1}, $F(000) = 656$, $T = 293$ K, final $R = 0{\cdot}034$ and $wR = 0{\cdot}032$ for 683 independent observed reflections. The structure contains the planar anions NO_3^- and pyramidal cations $[(CH_3)_3OS]^+$, which closely approximate to symmetry $3m$. The H atoms were located.

Experimental. The preparation of the crystals is described elsewhere (de Brauer & Perret, 1991). Prismatic colorless crystals, density measured by pycnometry in xylene, $D_m = 1{\cdot}42\,(1)$ Mg m^{-3}, crystal size $0{\cdot}22 \times 0{\cdot}27 \times 0{\cdot}25$ mm. Enraf–Nonius CAD-4

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