Acta Cryst. (1991). C47, 2231–2232

Structures of Trimethyloxosulfonium Salts. IV. The Chromate

BY CHRISTINE DE BRAUER, MICHEL JANNIN, RENÉ PUGET AND RENÉ PERRET

Laboratoire de Physique du Solide, associé au CNRS (URA 785), Université de Bourgogne, BP 138, 21004 Dijon CEDEX, France

(*Received* 27 *June* 1990; *accepted* 23 *October* 1990)

Abstract. Trimethyloxosulfonium chromate, $[(CH_3)_3SO]_2CrO_4$, $M_r = 302{\cdot}33$, orthorhombic, *Pbca*, $a = 10{\cdot}808$ (3), $b = 10{\cdot}731$ (3), $c = 21{\cdot}647$ (3) Å, $V = 2511$ (2) Å^3, $Z = 8$, $D_m = 1{\cdot}57$ (5), $D_x = 1{\cdot}600$ (5) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1{\cdot}2137$ mm^{-1}, $F(000) = 1264$, $T = 293$ K, final $R = 0{\cdot}022$ for 1568 independent observed reflections. The structure contains quasi-tetrahedral CrO_4^{2-} anions and pyramidal $[(CH_3)_3SO]^+$ thiocations which closely approximate to symmetry 3*m*, as found previously in almost all the other salts of this family. The H atoms have been located.

Experimental. The preparation is described elsewhere (de Brauer & Perret, 1991). Prismatic yellow crystals, density measured by pycnometry in xylene, $D_m = 1{\cdot}57$ (5) Mg m^{-3}. Crystal size: 0·19 × 0·20 × 0·22 mm. Enraf–Nonius CAD-4 diffractometer, monochromated. Mo $K\alpha$. Systematic absences: $hk0$ ($h = 2n$), $0kl$ ($k = 2n$), $h0l$ ($l = 2n$). Unit-cell constants from least-squares refinement of 25 reflections with $5 < \theta < 13°$. $\omega/2\theta$ scan, scan width 1·2°, $1 < \theta < 32°$, $-12 < h < 12$, $-12 < k < 12$, $-15 < l < 15$. Four orientation reference reflections every 200 scans (414, 604, 424, 326): no significant variation. Intensities of four reference reflections (424, 326, 004, 424) recorded every 2 h, fading of 3·1% during 328 h, decay correction. 10 816 measured reflections, 6698 reflections with $I > 3\sigma(I)$. Lorentz and polarization corrections. Absorption correction from ψ scan: relative transmission factor between 96·22 and 99·97%. After averaging, 1575 independent unique reflections, $R_{int} = 0{\cdot}015$.

Crystal structure solved in *Pbca* (No. 61) by a direct method: *MULTAN* (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: $g = 3{\cdot}401 \times 10^{-7}$ (Stout & Jensen, 1968). 209 variables. Final refinement with 1568 independent reflections (three rejected as unobserved, four rejected as bad): final $R = 0{\cdot}022$ ($wR = 0{\cdot}021$). Max. and min. peak heights in final Fourier synthesis 0·253 and −0·226 e Å^{-3}; $S = 1{\cdot}158$; max $\Delta/\sigma = 0{\cdot}00$, $w = 1$.

Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974). Enraf–Nonius (1979) *Structure Determination Package* used for all calculations, computer VAX 730.

Table 1. *Final atomic coordinates for* $[(CH_3)_3SO]_2CrO_4$ *and isotropic thermal parameters with e.s.d.'s in parentheses*

$B_{eq} = (1/3)\sum_i\sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	B_{eq}(Å^2)
Cr	0·46534 (3)	0·24628 (3)	0·12515 (3)	1·917 (6)
O(11)	0·521 (2)	0·3872 (2)	0·1247 (1)	3·82 (4)
O(22)	0·5129 (3)	0·1739 (2)	0·0637 (1)	6·10 (6)
O(33)	0·5089 (2)	0·1745 (2)	0·1875 (1)	5·51 (6)
O(44)	0·3137 (2)	0·2521 (2)	0·1246 (2)	4·23 (4)
S(1)	0·25337 (6)	−0·02119 (5)	0·26019 (3)	2·09 (1)
O(1)	0·1785 (2)	−0·1083 (2)	0·29414 (9)	3·20 (4)
C(11)	0·3771 (3)	−0·0935 (3)	0·2229 (1)	3·06 (6)
C(12)	0·3166 (3)	0·0951 (3)	0·3070 (1)	2·92 (6)
C(13)	0·1692 (2)	0·0559 (3)	0·2033 (1)	2·78 (5)
S(2)	0·22971 (5)	−0·00182 (6)	−0·00990 (3)	2·25 (1)
O(2)	0·1661 (2)	−0·0997 (2)	0·0423 (1)	3·27 (4)
C(21)	0·1295 (3)	0·0954 (3)	0·0311 (1)	3·37 (6)
C(22)	0·3142 (3)	0·0956 (3)	0·0588 (1)	3·76 (7)
C(23)	−0·3351 (3)	−0·0588 (3)	0·0440 (1)	2·83 (5)

Table 2. *Main interatomic distances* (Å) *and bond angles* (°) *for* $[(CH_3)_3SO]_2CrO_4$

Tetrahedral chromate anion				
Cr	O(11)	O(22)	O(33)	O(44)
O(11)	1·630 (2)	2·643 (3)	2·661 (3)	2·676 (3)
O(22)	108·6 (1)	1·624 (3)	2·680 (4)	2·660 (4)
O(33)	109·7 (1)	111·2 (1)	1·624 (3)	2·646 (3)
O(44)	109·8 (2)	109·2 (1)	108·3 (1)	1·641 (2)
Trimethyloxosulfonium cation				
S(1)	O(1)	C(11)	C(12)	C(13)
O(1)	1·439 (3)	2·648 (3)	2·658 (3)	2·643 (3)
C(11)	112·3 (1)	1·745 (3)	2·800 (4)	2·793 (4)
C(12)	112·8 (1)	106·7 (1)	1·746 (3)	2·784 (4)
C(13)	112·1 (1)	106·5 (1)	106·0 (1)	1·741 (3)
S(2)	O(2)	C(21)	C(22)	C(23)
O(2)	1·438 (3)	2·657 (4)	2·631 (4)	2·650 (4)
C(21)	112·9 (1)	1·747 (4)	2·788 (4)	2·784 (4)
C(22)	113·2 (1)	106·0 (1)	1·745 (3)	2·784 (4)
C(13)	112·5 (1)	105·9 (1)	105·9 (1)	1·742 (3)

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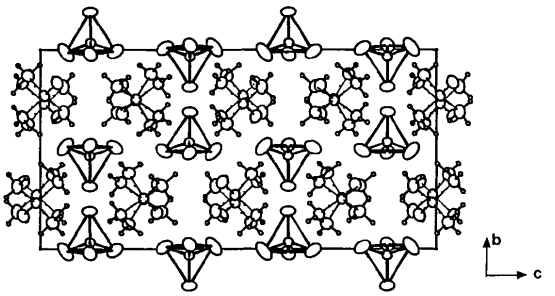

Fig. 1. Projection along the *a* axis of the atomic arrangement of $[(CH_3)_3SO]_2CrO_4$.

Table 1* reports the final atomic coordinates. The main interatomic distances and bond angles are given in Table 2. The CrO_4^{2-} anion, which has no symmetry element in this cell, is quasi-tetrahedral, as usual. The two pyramidal thiocations $(CH_3)SO^+$ also have neither symmetry plane nor axis; nevertheless, they closely approximate the $3m$ symmetry assumed for the free cation, as found in almost all the other salts studied. The projection of the atomic arrangement of $[(CH_3)_3SO]_2CrO_4$ along the *a* axis is given in Fig. 1.

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. We have reported the structure of some other trimethyloxosulfonium salts, *e.g.* iodide, bromide, chloride and nitrate (Jannin, Puget, de Brauer & Perret, 1991).

* Lists of structure factors, anisotropic thermal parameters, bond angles, bond lengths and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53681 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1991). C**47**, 2232–2234

Structures of Trimethyloxosulfonium Salts. VI. The Thiocyanate

BY RENÉ PUGET, MICHEL JANNIN, RENÉ PERRET AND CHRISTINE DE BRAUER

Laboratoire de Physique du Solide, associé au CNRS (URA 785), Université de Bourgogne, BP 138, 21004 Dijon CEDEX, France

(*Received* 1 *August* 1990; *accepted* 21 *December* 1990)

Abstract. $[(CH_3)_3SO]SCN$, $M_r = 151{\cdot}25$, orthorhombic, $Pmn2_1$, $a = 7{\cdot}260\ (2)$, $b = 5{\cdot}951\ (2)$, $c = 8{\cdot}757\ (2)$ Å, $V = 378\ (1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}30$, $D_m = 1{\cdot}30\ (1)$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·7173 Å, μ(Mo $K\alpha$) = 5·93 cm^{-1}, $F(000) = 160$, $T = 293$ K, final $R = 0{\cdot}023$, $wR = 0{\cdot}033$ for 760 independent observed reflections. The structure contains linear anions SCN^- and pyramidal thiocations $[(CH_3)_3SO]^+$, which approximate to $3m$ symmetry: these cations possess only one symmetry plane ($x = 0{\cdot}500$) where the anions are also located. The H atoms were located.

Experimental. The preparation of the crystals will be described elsewhere (de Brauer & Perret, 1991). Prismatic colorless crystals, density measured by pycnometry in xylene, $D_m = 1{\cdot}30\ (1)$ Mg m^{-3}, crystal size 0·21 × 0·23 × 0·24 mm. Enraf–Nonius CAD-4 diffractometer, graphite monochromator. Unit-cell constants from least-squares refinement of 25 reflections with $5 < \theta < 13°$. Systematic absences $h0l$ ($h + l = 2n$). Space group $Pmn2_1$, $P2_1nm$ (No. 31) or $Pmnm$ (No. 59). $\omega/2\theta$ scan, scan width 1·2°. $1 < \theta < 33°$, $-10 < h < 10$, $-13 < k < 13$, $-9 < l < 9$. Four orientation reference reflections ($\bar{1}05$, $1\bar{2}2$, $2\bar{1}\bar{1}$, $\bar{2}00$)

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