SHORT-FORMAT PAPERS

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Acta Cryst. (1988). C**44**, 924–925

Structures of Sulfuryl Halides: SO_2F_2, SO_2ClF and SO_2Cl_2*

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(*Received* 3 *August* 1987; *accepted* 19 *January* 1988)

Abstract. Sulfuryl fluoride, SO_2F_2, $M_r = 102{\cdot}06$, tetragonal, $P4_12_12$, $a = 5{\cdot}176$ (1), $c = 11{\cdot}685$ (3) Å, $V = 313{\cdot}1$ (1) Å^3, $Z = 4$, $D_x = 2{\cdot}17$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71073$ Å, $\mu = 0{\cdot}88$ mm^{-1}, $F(000) = 200$, $T = 126$ K, $R = 0{\cdot}040$ for 433 unique observed reflections. Sulfuryl chloride fluoride, SO_2ClF, $M_r = 118{\cdot}51$, orthorhombic, $Pca2_1$, $a = 10{\cdot}795$ (3), $b = 7{\cdot}623$ (2), $c = 8{\cdot}989$ (3) Å, $V = 739{\cdot}7$ (4) Å^3, $Z = 8$, $D_x = 2{\cdot}13$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71073$ Å, $\mu = 1{\cdot}41$ mm^{-1}, $F(000) = 464$, $T = 123$ K, $R = 0{\cdot}024$ for 1620 unique reflections. Sulfuryl chloride, SO_2Cl_2, $M_r = 134{\cdot}97$, orthorhombic, $Fdd2$, $a = 15{\cdot}425$ (5), $b = 10{\cdot}336$ (3), $c = 5{\cdot}422$ (2) Å, $V = 864{\cdot}4$ (4) Å^3, $Z = 8$, $D_x = 2{\cdot}07$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 71073$ Å, $\mu = 1{\cdot}78$ mm^{-1}, $F(000) = 528$, $T = 153$ K, $R = 0{\cdot}025$ for 510 unique observed reflections. In SO_2F_2 and SO_2Cl_2 the molecules occupy special positions of point symmetry 2. In SO_2ClF two independent molecules in general positions form nearly centrosymmetric pairs. None of the crystal structures of these tetrahedral molecules could be correlated with close sphere packing.

Table 1. *Experimental details*

	SO_2F_2	SO_2ClF	SO_2Cl_2
Range of h	0→8	0→17	−24→24
k	0→5	0→12	−16→16
l	0→18	0→14	0→8
Standard reflections	$\bar{1}\bar{1}5$	$\bar{4}23$	$\bar{5}33$
	$\bar{2}22$	$4\bar{2}\bar{3}$	$\bar{6}4\bar{2}$
	$\bar{2}2\bar{2}$	$\bar{4}\bar{3}3$	$\bar{7}3\bar{1}$
Reflections measured	850	1888	2156
unique	453	1704	513
unobserved ($I < 1{\cdot}96\sigma_I$)	20	84	3
Parameters refined	24	90	23
R	0·040	0·024	0·025
wR	0·062	0·039	0·044
S	2·581	1·541	2·098
$(\Delta/\sigma)_{max}$ in final cycle	0·00	0·01	0·00
$(\Delta\rho)_{min}/(\Delta\rho)_{max}$, e Å^{-3}	−0·4/0·4	−0·5/0·5	−0·4/0·3

Table 2. *Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

	x	y	z	B_{eq}*(Å^2)
SO_2F_2				
S	0·07889 (9)	x	0	2·76 (1)
F	−0·1101 (3)	−0·0018 (6)	0·0922 (2)	6·83 (8)
O	0·3244 (3)	0·0094 (5)	0·03617 (13)	3·62 (4)
SO_2ClF				
S(1)	0·19636 (4)	0·51541 (5)	0·1	1·51 (1)
Cl(1)	0·07414 (4)	0·48657 (6)	−0·06000 (8)	2·27 (1)
F(1)	0·28878 (9)	0·37221 (14)	0·0531 (2)	2·37 (2)
O(11)	0·2577 (2)	0·6771 (2)	0·0837 (2)	2·78 (3)
O(12)	0·1441 (2)	0·4602 (2)	0·2361 (2)	2·45 (3)
S(2)	0·05277 (4)	−0·00531 (5)	0·19169 (5)	1·49 (1)
Cl(2)	0·17932 (4)	0·00504 (6)	0·34836 (8)	2·38 (1)
F(2)	−0·03607 (10)	0·1347 (2)	0·2536 (2)	2·54 (2)
O(21)	−0·0101 (2)	−0·1665 (2)	0·1977 (3)	2·76 (3)
O(22)	0·10285 (14)	0·0620 (2)	0·0585 (2)	2·47 (3)
SO_2Cl_2				
S	0	0	0	2·22 (1)
Cl	0·04546 (3)	0·13224 (5)	−0·23036 (13)	3·50 (1)
O	0·0715 (2)	−0·0551 (2)	0·1261 (6)	5·46 (6)

* $B_{eq} = \frac{1}{3}(B_{11}a^{*2}a^2 + \cdots + B_{23}b^*c^*bc\cos\alpha)$.

Experimental. Samples of the compounds were sealed in thin-walled capillaries (diameter *ca* 0·2 mm). Single crystals were grown on a Syntex $P2_1$ four-circle diffractometer equipped with a modified LT-1 low-temperature device. A miniature zone-melting technique using focused heat radiation (Brodalla, Mootz, Boese & Osswald, 1985) was applied for SO_2F_2 and SO_2ClF. A single crystal of SO_2Cl_2 was obtained by slow cooling of the melt. Lattice parameters from setting angles of 15 reflections with $30 < 2\theta < 44°$. Intensities by ω scan with $(\sin\theta)/\lambda$ up to 0·807 Å^{-1} for each crystal, three standard reflections every 50 data with no significant variations.

Direct methods for SO_2ClF and SO_2Cl_2, heavy-atom method for SO_2F_2. Full-matrix least-squares refinement based on F magnitudes, observed reflections only, weighted according to $w = [\sigma^2(F) + (0{\cdot}02\,|F_o|)^2]^{-1}$,

* Part 21 of the series *Fluorides and Fluoro Acids*. Part 20: Poll, Pawelke, Mootz & Appelman (1988).

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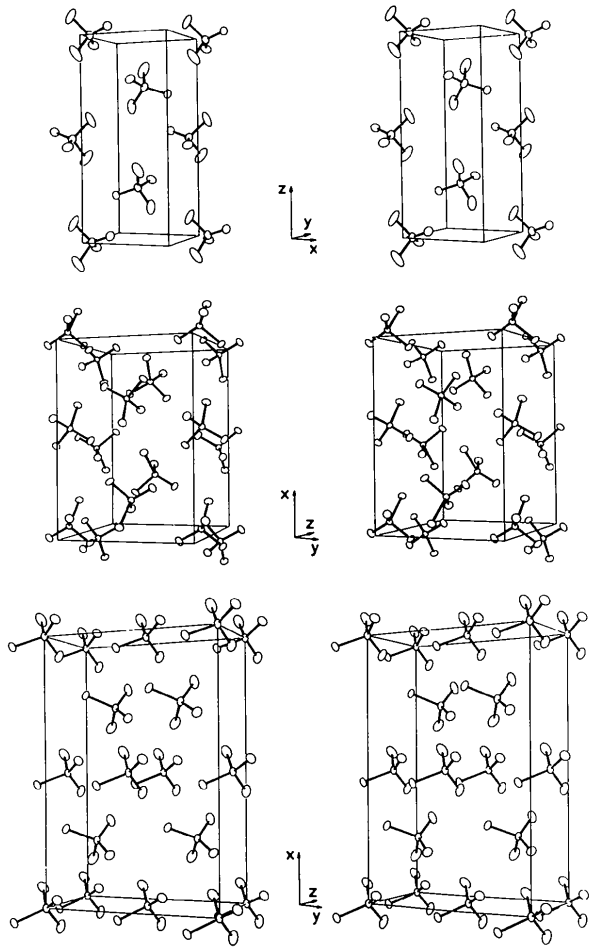

Fig. 1. Stereoplots of the crystal structures. Above: SO_2F_2; centre: SO_2ClF; below: SO_2Cl_2.

atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Calculations performed using the program systems *XTLE* (Syntex, 1976) and *SHELXTL* (Sheldrick, 1983) on an Eclipse S/200 minicomputer (Data General) and *ORTEP*II (Johnson, 1976) on a TR 445 computer (Telefunken).

Additional experimental details are given in Table 1, the atomic parameters in Table 2, interatomic distances and angles in Table 3.* Fig. 1 shows stereoplots of the crystal structures.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44702 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Interatomic distances* (Å) *and angles* (°)

SO_2F_2			
S–O	1·386 (2)	O–S–O^{i}	124·63 (11)
S–F	1·514 (2)	O–S–F	107·67 (12)
		O–S–F^{i}	107·60 (12)
		F–S–F^{i}	98·62 (13)
SO_2ClF			
S(1)–O(11)	1·407 (2)	S(2)–O(21)	1·4043 (14)
S(1)–O(12)	1·411 (2)	S(2)–O(22)	1·411 (2)
S(1)–Cl(1)	1·9639 (7)	S(2)–Cl(2)	1·9636 (8)
S(1)–F(1)	1·5377 (12)	S(2)–F(2)	1·5388 (13)
O(11)–S(1)–O(12)	122·68 (10)	O(21)–S(2)–O(22)	122·41 (10)
O(11)–S(1)–Cl(1)	109·77 (8)	O(21)–S(2)–Cl(2)	110·10 (8)
O(11)–S(1)–F(1)	106·72 (9)	O(21)–S(2)–F(2)	106·96 (10)
O(12)–S(1)–Cl(1)	109·42 (7)	O(22)–S(2)–Cl(2)	109·12 (7)
O(12)–S(1)–F(1)	106·57 (8)	O(22)–S(2)–F(1)	107·06 (9)
Cl(1)–S(1)–F(1)	98·96 (5)	Cl(2)–S(2)–F(2)	98·43 (6)
SO_2Cl_2			
S–O	1·418 (3)	O–S–O^{ii}	122·4 (2)
S–Cl	1·9799 (6)	O–S–Cl	107·82 (11)
		O–S–Cl^{ii}	107·60 (11)
		Cl–S–Cl^{ii}	101·77 (2)

Symmetry code: (i) $y, x, -z$; (ii) $-x, -y, z$.

Related literature. Molecular geometries from microwave spectroscopy (Lide, Mann & Fristrom, 1957; Holt & Gerry, 1971) and electron diffraction (Hagen, Cross & Hedberg, 1978; Hargittai & Hargittai, 1981).

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