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Structures of Thionyl Halides: $SOCl_2$ and $SOBr_2$

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Abstract. Thionyl chloride, $SOCl_2$, $M_r = 118{\cdot}97$, monoclinic, $P2_1/c$, $a = 8{\cdot}8373$ (9), $b = 5{\cdot}8033$ (6), $c = 7{\cdot}5862$ (8) Å, $\beta = 100{\cdot}064$ (8)°, $V = 383{\cdot}08$ (7) Å^3, $Z = 4$, $D_x = 2{\cdot}06$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71073$ Å, $\mu = 1{\cdot}97$ mm^{-1}, $F(000) = 232$, $T = 143$ K, $R = 0{\cdot}025$ for 1085 unique observed reflections. Thionyl bromide, $SOBr_2$, $M_r = 207{\cdot}88$, orthorhombic, $Pca2_1$, $a = 11{\cdot}512$ (5), $b = 4{\cdot}070$ (2), $c = 18{\cdot}166$ (5) Å, $V = 851{\cdot}1$ (6) Å^3, $Z = 8$, $D_x = 3{\cdot}24$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71073$ Å, $\mu = 19{\cdot}14$ mm^{-1}, $F(000) = 752$, $T = 133$ K, $R = 0{\cdot}063$ for 1234 unique observed reflections. In $SOBr_2$ two independent molecules form nearly centrosymmetric pairs. In both crystal structures the pyramidal molecules in general positions are arranged in double layers. Within these, three intermolecular distances between the S and other atoms are significantly smaller than the respective van der Waals radii sums [Pauling (1973). *Die Natur der chemischen Bindung*. Weinheim: Verlag Chemie].

Experimental. Samples of the compounds were sealed in thin-walled capillaries. 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 $SOCl_2$. A single crystal of $SOBr_2$ was obtained by slow cooling of the melt. Lattice parameters from setting angles of 15 reflections with $31 < 2\theta < 46°$.

Table 1. *Experimental details*

	$SOCl_2$	$SOBr_2$
Range of h	0→12	0→17
k	−8→8	0→6
l	−10→10	0→28
Standard reflections	522	$\bar{3}\bar{2}\bar{4}$
	$34\bar{3}$	$5\bar{1}\bar{8}$
	$34\bar{3}$	$5\bar{1}\bar{8}$
Reflections measured	2368	1980
unique	1111	1696
unobserved ($I < 1{\cdot}96\sigma_I$)	26	462
c in $w = [\sigma_F^2 + (cF_o)^2]^{-1}$	0·02	0·03
Parameters refined	37	73
R	0·025	0·063
wR	0·041	0·071
S	1·901	1·500
$(\Delta/\sigma)_{max}$ in final cycle	0·000	0·002
$(\Delta\rho)_{min}/(\Delta\rho)_{max}$, e Å^{-3}	−0·7/0·3	−3·0/2·1

Intensities by ω scan with $(\sin\theta)/\lambda$ up to 0·704 and 0·777 Å^{-1} for $SOCl_2$ and $SOBr_2$, respectively. Three standard reflections every 50 data with no significant variations.

A numerical absorption correction was applied for $SOBr_2$. The crystal grown with the crystallographic b axis parallel to the capillary axis was approximated by

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

	x	y	z	B_{eq}*(Å^2)
$SOCl_2$				
Cl(1)	0·25154 (4)	0·27957 (5)	0·40962 (4)	2·39 (1)
Cl(2)	0·37552 (3)	0·70469 (5)	0·23685 (4)	2·33 (1)
S	0·16514 (3)	0·56234 (4)	0·25725 (3)	1·51 (1)
O	0·09351 (10)	0·71064 (17)	0·37068 (14)	2·56 (2)
$SOBr_2$				
Br(11)	0·6576 (1)	0·3543 (6)	0·0	1·33 (4)
Br(12)	0·4402 (3)	−0·0124 (6)	−0·0969 (3)	1·66 (9)
S(1)	0·4817 (4)	0·1147 (13)	0·0180 (2)	0·94 (8)
O(1)	0·4006 (12)	0·359 (4)	0·0391 (7)	1·5 (3)
Br(21)	0·5893 (1)	0·1420 (6)	0·2033 (1)	1·50 (5)
Br(22)	0·8048 (3)	0·5038 (5)	0·3032 (3)	1·52 (7)
S(2)	0·7656 (4)	0·3839 (14)	0·1834 (2)	0·96 (9)
O(2)	0·8427 (12)	0·112 (4)	0·1607 (7)	1·5 (3)

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

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

$SOCl_2$			
S–O	1·4394 (10)	O–S–Cl(1)	107·30 (4)
S–Cl(1)	2·0745 (4)	O–S–Cl(2)	107·54 (4)
S–Cl(2)	2·0648 (4)	Cl(1)–S–Cl(2)	96·30 (2)
S···O^{i}	3·1761 (11)		
S···O^{ii}	3·0915 (10)		
S···Cl(1^{iii})	3·4898 (4)		

Symmetry code: (i) x, $1{\cdot}5-y$, $-0{\cdot}5+z$; (ii) $-x$, $-0{\cdot}5+y$, $0{\cdot}5-z$; (iii) x, $0{\cdot}5-y$, $-0{\cdot}5+z$.

$SOBr_2$			
S(1)–O(1)	1·42 (2)	S(2)–O(2)	1·48 (2)
S(1)–Br(11)	2·271 (5)	S(2)–Br(21)	2·284 (5)
S(1)–Br(12)	2·203 (6)	S(2)–Br(22)	2·276 (6)
O(1)–S(1)–Br(11)	108·9 (7)	O(2)–S(2)–Br(21)	104·8 (6)
O(1)–S(1)–Br(12)	106·2 (6)	O(2)–S(2)–Br(22)	107·9 (5)
Br(11)–S(1)–Br(12)	99·1 (2)	Br(21)–S(2)–Br(22)	96·7 (2)
S(1)···O(2^{i})	3·18 (1)	S(2)···O(2^{iii})	3·12 (2)
S(1)···Br(11^{ii})	3·713 (5)	S(2)···Br(11)	3·558 (4)
S(1)···Br(21)	3·590 (5)	S(2)···Br(21^{iii})	3·710 (6)

Symmetry code: (i) $-0{\cdot}5+x$, $-y$, z; (ii) x, $-1+y$, z; (iii) x, $1+y$, z.

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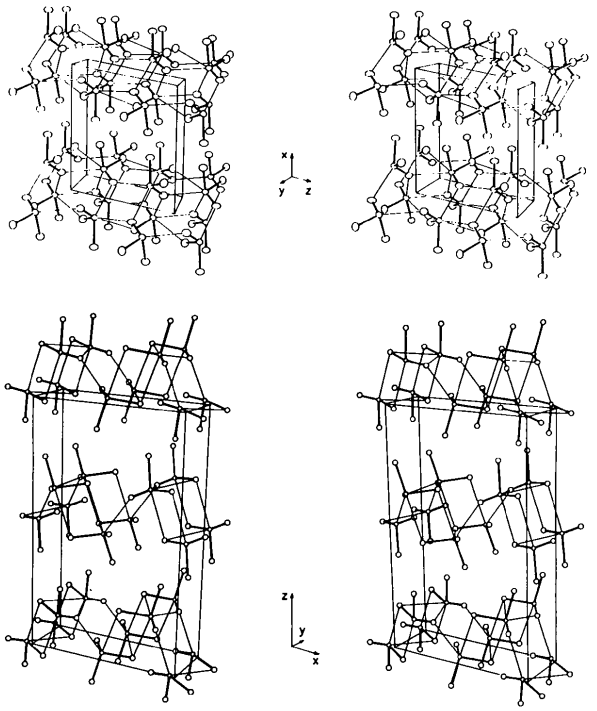

Fig. 1. Stereoplots of the crystal structures with short intermolecular contacts. Above: $SOCl_2$, below: $SOBr_2$.

an octagonal prism; $T_{max}/T_{min}=4{\cdot}67$. Direct methods; full-matrix least-squares refinement based on F magnitudes, observed reflections only. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Isotropic extinction parameter $F_c'=F_c/(1+0{\cdot}002gF_c^2/\sin 2\theta)^{1/4}$ with $g=0{\cdot}0013$ (2) for $SOBr_2$. Calculations with the program systems *XTLE* (Syntex, 1976) for $SOCl_2$, *SHELXTL* (Sheldrick, 1983) for $SOBr_2$ on Eclipse S/200 and S/140 minicomputers 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, and interatomic distances and relevant angles in Table 3.* Fig. 1 shows the stereo plots of the crystal structures.

Related literature. Molecular geometries from microwave spectroscopy (Suzuki, Yamaguchi, Onda, Sakaizumi, Ohashi & Yamaguchi, 1981; Mata & Carballo, 1983) and electron diffraction (Gregory, Hargittai & Kolonits, 1976; Brunvoll, Hargittai & Rozsondai, 1982), crystal structure of SOF_2 (Mootz & Korte, 1984).

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44703 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure of Bis(methanol)(*meso*-tetraphenylporphinato)manganese(III) Hexachloroantimonate Bis(tetrachloroethane) Solvate

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Abstract. $[Mn(C_{44}H_{30}N_4)(CH_3OH)_2][SbCl_6].2C_2H_2Cl_4$, $M_r=1401{\cdot}93$, triclinic, $P\bar{1}$, $a=11{\cdot}104$ (3), $b=12{\cdot}086$ (6), $c=12{\cdot}619$ (4) Å, $\alpha=115{\cdot}33$ (3), $\beta=104{\cdot}75$ (2), $\gamma=91{\cdot}75$ (3)°, $V=1461{\cdot}3$ Å^3, $Z=1$, $D_m=1{\cdot}58$, $D_x=1{\cdot}59$ Mg m^{-3}, $\bar{\lambda}$(Mo $K\alpha$) = 0·71073 Å, $\mu=1{\cdot}359$ mm^{-1}, $F(000)=698$, $T=$

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