The crystal structure of (II) with the newly assigned space-group symmetry *P*2/*c* is illustrated in Fig. 3. Infinite chain-like polyanions $[AlF_4F^{2-}_{2/2}]_n$ with distorted octahedral coordination at the Al atoms and the bridging F atoms in *trans* positions (point symmetry 2 for both kinds of atoms) are extended parallel to the *b* axis. They are linked *via* hydrogen bonds with $H_5O_2^+$ cations as well as chains of alternating $H_5O_2^+$ cations and neutral water molecules (point symmetry 2) which run parallel to the *c* axis. The two independent cations lie on inversion centres of the space group. Interatomic distances and angles of (II) are listed in Table 4. They show a much better internal consistency than those of the reported *Pc* model of the structure (Trunov *et al.*, 1980), although in *P*2/*c* the atomic coordinates have not been further refined.

Each of the three independent $H_5O_2^+$ cations [one in (I) and two in (II)] has a very short central hydrogen bond O—H···O, in which the H atom is disordered between two positions. In its four outer hydrogen bonds, to O and/or F atoms, each cation, in compliance with its positive charge, acts as the donor only, never as an acceptor, of the respective H atom. The behavior described is characteristic of this kind of cationic water species, which also occurs in many other hydrates of strong acids (Lundgren & Olovsson, 1976; Ratcliffe & Irish, 1986).

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Structure of Silyl Iodide at 116 K

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Abstract. SiH_3I, $M_r = 158{\cdot}01$, monoclinic, $P2_1/c$, $a = 4{\cdot}564\ (5)$, $b = 8{\cdot}3878\ (21)$, $c = 10{\cdot}5086\ (21)$ Å, $\beta = 103{\cdot}13\ (7)°$, $U = 391{\cdot}8$ Å^3, $Z = 4$, $D_x = 2{\cdot}678$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71073$ Å, $\mu = 8{\cdot}282$ mm^{-1}, $F(000) = 280$, $T = 116$ K, $R = 0{\cdot}0238$ for 661 unique observed reflections. Molecules of silyl iodide are linked by short, 3·8030 (13) Å, I···Si intermolecular contacts into infinite zigzag chains characterized by Si—I···Si and I···Si—I angles of 84·14 (4) and 178·13 (5)° respectively. At 2·4533 (13) Å, the Si–I bond is significantly longer than the gas-phase value of 2·4384 (6) Å. Comparisons are drawn between the intermolecular geometries of the simple silyl halides SiH_3X (X = F, Cl, Br, I) and with the intramolecular geometries of the disilyl chalcogenides $(SiH_3)_2E$ (E = O, S, Se, Te).

Introduction. As part of our continuing programme of work on the solid-state structures of low-melting silyl compounds, we undertook a study of the simple silyl halides SiH_3X (X = F, Cl, Br, I). Of these four compounds, only the last presented no serious difficulties: the fluoride has no well defined liquid phase at ambient pressure and both the chloride and the bromide exhibit phase transformations near their freezing points which prevent the growth, stabilization or transfer of single crystals. Nevertheless, we were able to obtain a single crystal of SiH_3F and to determine its structure (Blake, Ebsworth, Henderson & Welch, 1985). Here we describe low-temperature X-ray powder diffraction studies which have established the gross structures of SiH_3Cl and SiH_3Br and a low-temperature single-crystal diffraction study of SiH_3I.

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Experimental. *Powder diffraction studies.* Samples sealed in Pyrex capillaries cooled on Guinier–Simon powder camera fitted with low-temperature attachment. Patterns recorded using quartz-monochromated Cu $K\alpha_1$ radiation ($\lambda = 1{\cdot}54051$ Å), either at fixed temperature using static cassette or as variable-temperature runs using moving cassette. Patterns calibrated against silicon as internal standard, temperatures measured using a Pt 100 thermoresistor calibrated against melting points of trimethylamine (156 K) and chlorobenzene (227 K).

Single-crystal study. Colourless cylindrical crystal, 0·3 × 0·3 × 0·2 mm, grown *in situ* by zone refining from sample sealed in Pyrex capillary on Weissenberg camera equipped with low-temperature device, m.p. 216 K, transferred without melting as described previously (Blake, Cradock, Ebsworth, Rankin & Welch, 1984) to similarly equipped CAD-4 diffractometer, 116 K, 25 reflections ($13{\cdot}8 < \theta < 16{\cdot}0°$) for refinement of orientation matrix. For data collection, $\theta_{\max} = 25°$, ω–2θ scans with ω-scan width $(0{\cdot}80 + 0{\cdot}30\tan\theta)°$, h 0→5, k 0→9, l −12→12, 845 reflections, 691 unique ($R_{\text{int}} = 0{\cdot}053$) in 11 X-ray hours.

For structure solution and refinement 661 reflections with $F > 2\sigma(F)$, Patterson (I) and successive difference Fourier syntheses (Sheldrick, 1976), full-matrix least squares (F), at isotropic convergence data corrected empirically for absorption, max. and min. corrections 1·088 and 0·926 respectively (Walker & Stuart, 1983), $w^{-1} = \sigma^2(F) + 0{\cdot}000155F^2$, anisotropic thermal parameters for I, Si, isotropic for H. At final convergence R, wR 0·0238, 0·0346, S 1·093, data:variable ratio 21:1, max. shift/e.s.d. in final cycle 0·01, max. peak and min. trough in final difference Fourier synthesis 0·78 and $-0{\cdot}79$ e Å^{-3} respectively. No correction for secondary extinction. Neutral-atom scattering factors for Si, H (Sheldrick, 1976) and I (Cromer & Mann, 1968), computer programs *SHELX*76 (Sheldrick, 1976), *DIFABS* (Walker & Stuart, 1983), *ORTEP*II (Mallinson & Muir, 1985), *PLUTO* (Motherwell, 1976) and *CALC* (Gould & Taylor, 1985).

Table 1. *Fractional coordinates and anisotropic vibration parameters of atoms with e.s.d.'s*

	x	y	z	U_{eq}(Å^2)
I	0·13286 (7)	0·23311 (4)	0·05679 (3)	0·0280 (3)
Si	0·4295 (3)	0·42832 (14)	0·20642 (12)	0·0231 (6)
H(1)	0·257 (13)	0·508 (7)	0·277 (5)	0·057 (16)
H(2)	0·568 (11)	0·516 (7)	0·138 (5)	0·052 (16)
H(3)	0·662 (11)	0·352 (7)	0·301 (5)	0·042 (16)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I	0·0287 (3)	0·0272 (3)	0·0266 (3)	−0·0016 (1)	0·0060 (2)	−0·0072 (1)
Si	0·0236 (6)	0·0225 (7)	0·0224 (6)	−0·0005 (4)	0·0070 (5)	−0·0018 (5)

Table 2. *Molecular geometry parameters with e.s.d.'s*

I–Si	2·4533 (13) Å	Si–H(2)	1·29 (5) Å
Si–H(1)	1·38 (6)	Si–H(3)	1·43 (5)
I–Si–H(1)	111·8 (23)°	H(1)–Si–H(2)	116 (3)°
I–Si–H(2)	106·9 (24)	H(1)–Si–H(3)	106 (3)
I–Si–H(3)	111·1 (21)	H(2)–Si–H(3)	105 (3)

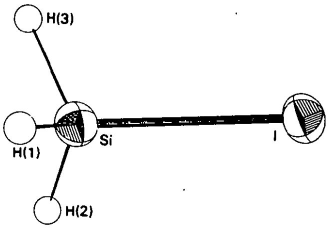

Fig. 1. View of a single molecule of silyl iodide.

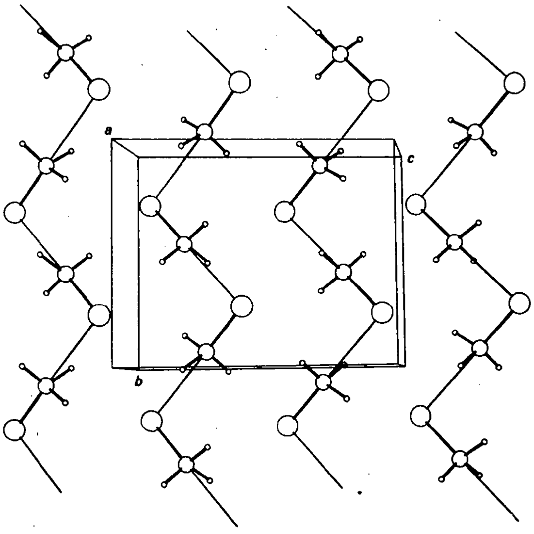

Fig. 2. Packing of molecules viewed along the crystallographic **a** axis, showing the zigzag chains running parallel to **b**.

Discussion. Table 1 lists refined fractional coordinates and thermal parameters.* Fig. 1 is a view of a single molecule. Table 2 gives interatomic distances and interbond angles. As Fig. 2 shows, silyl iodide crystallizes as infinite zigzag chains of molecules linked by close I···Si interactions. The chains are characterized by Si—I···Si and I···Si—I angles of 84·14 (4) and 178·13 (5)° respectively. The I···Si distance of 3·8030 (13) Å compares with the sum of the corresponding van der Waals radii of 4·25 Å. The 4 + 1 coordination of the Si is associated with a small but significant lengthening of the Si—I bond from 2·4384 (6) Å in the gas phase (Duncan, Harvie, McKean & Cradock, 1986) to 2·4533 (13) Å in the crystal. In contrast to silyl fluoride, there is no significant cross-linking between adjacent chains.

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* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44723 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Crystal data for the silyl halides*

	SiH$_3$F*	SiH$_3$Cl†	SiH$_3$Br‡	SiH$_3$I‡
Space group	$P2_1/n$	$Cmc2_1$	$Cmc2_1$	$P2_1/c$
a (Å)	7·772	7·119	7·262	4·564
b (Å)	7·767	5·568	5·703	8·388
c (Å)	4·693	8·453	8·456	10·509
β (°)	96·49	—	—	103·13
V (Å^3)	281·5	335·1	350·2	391·8
Z	4	4	4	4
D_x (Mg m^{-3})	1·182	1·323	2·106	2·678

* Blake, Ebsworth, Henderson & Welch (1985).
† Blake, Ebsworth & Dyrbusch (1987).
‡ Present work.

Table 4. *Comparison of subtended angles* (°)

Si—F···Si in SiH$_3$F	146·03 (7)*	Si—O—Si in (SiH$_3$)$_2$O	142·2 (3)§
Si—Cl···Si in SiH$_3$Cl	~97†	Si—S—Si in (SiH$_3$)$_2$S	98·4 (3)¶
Si—Br···Si in SiH$_3$Br	~97‡	Si—Se—Si in (SiH$_3$)$_2$Se	95·7 (5)¶
Si—I···Si in SiH$_3$I	84·14 (4)‡	Si—Te—Si in (SiH$_3$)$_2$Te	~90**

* Blake, Ebsworth, Henderson & Welch (1985).
† Blake, Ebsworth & Dyrbusch (1987).
‡ Present work.
§ Barrow, Ebsworth & Harding (1979).
¶ Barrow & Ebsworth (1982).
** Rankin (1987).

Our attempts to grow single crystals of silyl chloride and bromide were frustrated by the presence of phase changes which occurred close to the freezing points of these compounds. However, it proved possible to record powder patterns of these compounds which showed, both visually and by refinement of unit-cell parameters, that both were isostructural with germyl chloride, whose structure we were able to determine (Blake, Ebsworth & Dyrbusch, 1987). Although the identification of isostructuralism cannot provide the fine details of the structures of the silyl compounds, it does indicate that the structure of their chains – approximately linear at Si and with angles of *ca* 97° at the halogen – must be similar. Space-group and unit-cell data for the four members of the series SiH$_3X$ (X = F, Cl, Br, I) are given in Table 3.

We have observed striking similarities between the intramolecular Si—E—Si angles in disilyl chalcogenides and the Si—X···Si angles in the crystal structures of the silyl halides where E and X are elements of the same period (Table 4). The parallel trends seen in the two series may be explained by regarding E and X of the same period as isoelectronic: given that the X···Si interactions are both significant and directional in nature, simple VSEPR theory accounts for the observed similarities. Thus we find, for example, that the Si—O—Si angle in disiloxane, 142·2 (3)° (Barrow, Ebsworth & Harding, 1979), lies close to the Si—F···Si angle in SiH$_3$F (Blake, Ebsworth, Henderson & Welch, 1985).

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Structure du Sulfure d'Indium et d'Etain In$_{11}$Sn$_{5,5}$S$_{22}$

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Abstract. In$_{11}$Sn$_{5.5}$S$_{22}$, $M_r = 2621{\cdot}1$, monoclinic, $P2/m$, $a = 15{\cdot}636$ (6), $b = 14{\cdot}627$ (7), $c = 3{\cdot}847$ (1) Å, $\gamma = 97{\cdot}38$ (4)°, $V = 872{\cdot}5$ (6) Å^3, $Z = 1$, $D_m = 4{\cdot}98$, $D_x = 4{\cdot}99$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, μ = 121·6 cm^{-1}, $F(000) = 1166$, $T = 293$ K, final R = 0·054 for 1825 independent reflections. In^{3+} atoms have octahedral environments and Sn^{2+} atoms lie inside dicapped trigonal prisms of S atoms. Six contiguous

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