Table 3. *Comparison of pseudo and idealized hexagonal coordinates*

	Pseudohexagonal coordinates x,y,z	Idealized coordinates x,y,z	Difference (Å)
Rb(1)	0·0085, 0·0085, 0·0000	0·0000, 0·0000, 0·0000 0, 0, 0	0·050
Rb(2)	0·9721, 0·9819, 0·7949	0·0000, 0·0000, 0·7949 0, 0, z	0·199
O(1)	0·8413, 0·7121, 0·4349	0·8616, 0·7236, 0·4291 x, $2x$, z	0·166
O(3)	0·8388, 0·1235, 0·4344	0·8618, 0·1382, 0·4291 x, $-x$, z	0·166
O(4)	0·2441, 0·1198, 0·4180	0·2764, 0·1382, 0·4291 $-2x$, $-x$, z	0·296
O(2)	0·9075, 0·9521, 0·3423	0·0000, 0·0000, 0·3423 0, 0, z	0·470

deviation from hexagonal symmetry is for O(2), for which idealized coordinates correspond to those of a $3m$ special position. The pseudohexagonal structure is isotypic with $Ba_3(PO_4)_2$ (Zachariasen, 1948), a common structural type for trimetal sulfates, phosphates and chromates.

The observed structural features suggest that changes in the hydrogen bonds are present in the mechanisms of phase transitions above room temperature. They also suggest that the ammonium ions are involved in the phase transitions below room temperature, as they only occur for the triammonium salt.

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Structure of Silyl Fluoride, SiH_3F, at 96 K

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Abstract. $M_r = 50{\cdot}08$, monoclinic, $P2_1/n$, $a = 7{\cdot}7723\,(12)$, $b = 7{\cdot}76731\,(21)$, $c = 4{\cdot}6926\,(4)$ Å, $\beta = 96{\cdot}491\,(5)°$, $V = 281{\cdot}48\,(9)$ Å^3, $Z = 4$, $D_x = 1{\cdot}182$ Mg m^{-3}, $\lambda(\text{Mo }K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}462$ mm^{-1}, $F(000) = 104$, $T = 96$ K, $R = 0{\cdot}0572$ for 707 observed reflections. The structure comprises chains of molecules formed by intermolecular F···Si interactions. Perhaps surprisingly, there are no close F···H contacts. Concomitant with the 4 + 1 coordination at Si in the crystal a lengthening of the Si—F bond to 1·6045 (14) Å is observed, relative to the gas-phase value of 1·59465 (4) Å.

Introduction. As part of our continuing work in this department on the structures of low-melting inorganic compounds, we are interested in species whose vibrational spectra change significantly with phase, for example $N(CH_3)_2SiH_3$ (Blake, Ebsworth & Welch, 1984), SiH_3OSiH_3 (Barrow, Ebsworth & Harding, 1979) and SiH_3CN (Barrow, 1985). Here we report the crystal structure of silyl fluoride, in which the frequency of ν(Si—F) decreases sharply between the vapour (872 cm^{-1}) and solid (804 cm^{-1}).

Experimental. Colourless, cylindrical crystal, 0·04 × 0·04 × 0·03 cm, grown *in situ* on low-temperature-equipped Weissenberg goniometer from sample sealed in Pyrex capillary, space group identified by oscillation and Weissenberg photography. D_m and m.p. not determined – compound lacks well defined liquid phase at ambient pressure. Crystal transferred without melting as described previously (Blake, Cradock, Ebsworth,

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Rankin & Welch, 1984) to similarly equipped CAD-4 diffractometer, 96 K, 25 reflections ($17 < \theta < 18°$) centred, graphite-monochromated Mo $K\alpha$ X-radiation.

For data collection $\theta_{\max} = 30°$, ω–2θ scan in 96 steps, ω-scan width 0·8° + 0·35° tanθ, rapid pre-scan after which reflections with $I \geq 0{\cdot}5\sigma(I)$ remeasured such that final net intensity had $I > 33\sigma(I)$ subject to maximum measuring time of 60 s, crystal orientation checked every 60 reflections and reset if necessary, 2 standards, no significant crystal movement or decay, 800 unique reflections in four batches over 15 X-ray hours, h −10→10, k 0→10, l 0→6, no absorption correction.

For structure solution and refinement 707 amplitudes $[F > 2{\cdot}0\sigma(F)]$, Patterson and successive Fourier syntheses (Sheldrick, 1976), full-matrix least squares (F), $w^{-1} = [\sigma^2(F) + 0{\cdot}01508(F)^2]$, anisotropic thermal parameters for Si and F, isotropic for H, batch scaling factors refined, R 0·0572, wR 0·0807, S 0·646, data: variable ratio 20:1, $(\Delta/\sigma)_{\max}$ in final cycle < 0·01, max. peak and min. trough in final ΔF synthesis 0·44 and −0·25 e Å^{-3} respectively. No correction for secondary extinction. Neutral scattering factors for Si and F (Cromer & Liberman, 1970) and H (Stewart, Davidson & Simpson, 1965), computer programs *SHELX*76 (Sheldrick, 1976), *CALC* (Gould & Taylor, 1983), *ORTEP*II (Johnson, 1976) and *PLUTO* (Motherwell, 1976).

Accurate unit-cell parameters obtained by refinement (Pawley, 1981) against powder profiles generated by microdensitometry on Guinier–Simon films recorded at 96 K.

Discussion. Table 1 lists derived fractional coordinates and thermal parameters.* Fig. 1 is a view of a single molecule. Table 2 gives interatomic distances and interbond angles. As shown in Fig. 2, silyl fluoride crystallizes as infinite, zigzag chains formed by strong F···Si interactions characterized by F···Si–F and Si–F···Si angles of 178·65 (6) and 146·03 (7)° respectively. The F···Si distance of 2·8941 (14) Å is well within the sum of the van der Waals radii for F and Si (3·45 Å). The Si thus clearly has 4 + 1 coordination and we observe an associated lengthening of the Si–F bond in the crystal [1·6045 (14) Å] as compared with the gas-phase value of 1·59465 (4) Å (Cradock, 1984) derived from rotational constants (Georghiou, Baker & Jones, 1976; Robiette, Georghiou & Baker, 1976). There are, however, longer F···Si contacts [3·2421 (14) Å] which cross-link these chains to form layers.

Table 1. *Positional (fractional coordinates) and thermal* (Å^2) *parameters with standard deviations*

(*A*) Positional

	x	y	z	U or U_{eq}
Si	0·41117 (6)	0·27098 (8)	0·30044 (9)	0·0381
F	0·58863 (14)	0·33364 (21)	0·4781 (3)	0·0565
H(1)	0·435 (5)	0·099 (5)	0·240 (8)	0·080 (11)
H(2)	0·366 (7)	0·378 (5)	0·066 (9)	0·100 (13)
H(3)	0·287 (7)	0·277 (4)	0·481 (9)	0·069 (10)

(*B*) Thermal

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Si	0·0253 (4)	0·0535 (5)	0·0348 (4)	−0·0052 (1)	−0·0001 (3)	0·0012 (2)
F	0·0323 (6)	0·0669 (10)	0·0672 (8)	−0·0176 (6)	−0·0157 (5)	0·0067 (6)

The anisotropic temperature factor is defined as $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{23}b^*c^*kl + 2U_{13}a^*c^*hl + 2U_{12}a^*b^*hk)]$. The isotropic temperature factor is defined as $\exp[-8\pi^2U(\sin^2\theta)/\lambda^2]$.

Table 2. *Interatomic distances* (Å) *and interbond angles* (°)

Si–F	1·6045 (14)	Si–H(2)	1·39 (4)
Si–H(1)	1·38 (4)	Si–H(3)	1·35 (4)
F–Si–H(1)	105·6 (16)	H(1)–Si–H(2)	116·3 (25)
F–Si–H(2)	110·9 (18)	H(1)–Si–H(3)	106·4 (24)
F–Si–H(3)	107·2 (18)	H(2)–Si–H(3)	109·9 (26)

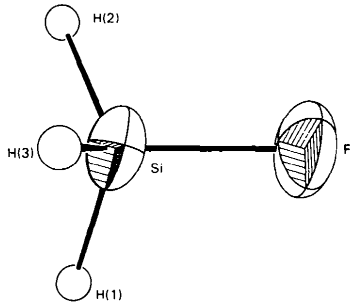

Fig. 1. Perspective view of the molecule.

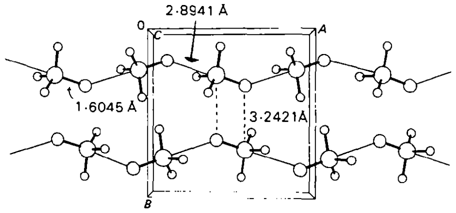

Fig. 2. Crystal packing in the unit cell viewed down **c**.

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* Lists of structure factors and Table 3 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42163 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

However, the microwave-derived results represent an $r_{\alpha o}$ structure whilst that determined in the crystal is an r_α structure. A common basis for comparison ($r_{\alpha o}$) can be achieved by correcting the latter structure for the effects of thermal motion. The observation that the U_{ij} values for Si do not follow the same pattern as those for F argues against the latter being the result of absorption or other systematic error. Also, the largest thermal motions of the F atom are, as expected, approximately normal to the Si—F bond. A librational analysis for an isolated molecule of SiH_3F, weighted on atomic mass, gives a generalized goodness-of-fit residual, R_g, of 0·124 and suggests a librational correction of 0·034 Å to the Si—F distance, giving a corrected value of 1·639 Å. The components of the librational tensors and the observed and calculated U_{ij} values are given in Table 3 (deposited). The rather high value of R_g arises from the necessary inclusion of the isotropically refined H atoms in the analysis (the libration is otherwise indeterminate): moreover, the assumption of an isolated molecule must be regarded as very approximate given the strong intermolecular F···Si contact. For these reasons, the librational correction should only be regarded as an order-of-magnitude estimate.

However, since these corrections are always positive, their application cannot result in shorter intramolecular bonds. The effect in this case can only be to emphasize the lengthening of the bonded Si—F distance on going from the gaseous to the crystalline phase.

The mean FSiH angle 111 (5)° is not significantly different from that observed in the gas phase [108·249 (6)°] and there is therefore no indication of a tendency towards trigonal-bipyramidal coordination at Si as observed in the dimethylsilylamine pentamer (Blake, Ebsworth & Welch, 1984). There are no close F···H contacts in the structure.

The secondary bonding in this crystal structure is reminiscent of that in SiH_3CN, but in the latter the C—N···Si angle was observed to be 176·1 (4)° (Barrow, 1985). We therefore became interested in addressing the question of the relative strengths of the secondary bonds in these two systems. Extended Hückel molecular-orbital (EHMO) calculations (Howell, Rossi, Wallace, Haraki & Hoffmann, 1977) on H_3SiCN (1), H_3SiF (2) and their secondary-bonded dimers were performed using parameters specified in Table 4. These calculations confirm that the acceptor orbitals of both molecules are of a_1 symmetry, localized largely on Si [36% 3*p* and 61% 3*d* for (1), 49% 3*p* and 49% 3*d* for (2)] and directed away from the bonded halide or pseudohalide. The σ-donor orbital of (1) is 52% N $2p_z$ with 14% N 2*s* character, with the sign of mixing such that this orbital is directed away from the bonded C. The σ-donor orbital of (2) is almost entirely F $2p_z$ (85%). However, the energy difference between donor and acceptor orbitals is *ca* 6·5 eV in (1) and 10·4 eV in (2), resulting in reduced overlap populations for a linear secondary bond of 0·1128 and 0·0194 respectively. These results suggest substantially stronger secondary bonding in (1) than in (2).

Table 4. *Parameters used in the EHMO calculations*

Geometric parameters

(*a*) Intramolecular geometries for all calculations

SiH_3CN		SiH_3F	
r(Si—H)	1·4757 Å	*r*(Si—H)	1·4757 Å
r(Si—C)	1·8400	*r*(Si—F)	1·6045
r(C—N)	1·1630		
∠(HSiC)	109·472°	∠(HSiF)	109·472°
∠(SiCN)	180		

(*b*) Intermolecular geometries for calculations on dimers; primed atoms belong to the second molecule

SiH_3CN		SiH_3F	
r(N···Si′)	2·8000 Å	*r*(F···Si′)	2·8941 Å
∠(CN···Si′)	180→110°*	∠(SiF···Si′)	180→110°†
∠(N···Si′C′)	180	∠(F···Si′F′)	180

Atomic orbital parameters

Orbital	Coulomb integral (eV)	Slater exponent
F2*s*	−40·0	2·425
F2*p*	−18·1	2·425
N2*s*	−26·0	1·950
N2*p*	−13·4	1·950
C2*s*	−21·4	1·625
C2*p*	−11·4	1·625
Si3*s*	−17·3	1·383
Si3*p*	−9·2	1·383
Si3*d*	−6·0	1·383
H1*s*	−13·6	1·300

* SiH_3 groups eclipsed at linearity.

† SiH_3 groups staggered by −28·01° at linearity.

Nevertheless, we do not necessarily believe that these results can explain entirely the contrast between the linear chains of (1) in the crystal and the zigzag chains of (2) described above; calculated potentials to bending of dimeric units about C—N···Si or Si—F···Si are very soft (destabilization less than 5 kJ mol^{-1} for angular deformations up to 45°). It is therefore likely that the observed differences in the shapes of these secondary-bonded chains are due primarily to crystal packing forces.

The decrease seen in $\nu(M$—F) for GeH_3F (158 cm^{-1}) on going from the gaseous to the solid state is more than twice that observed for SiH_3F (68 cm^{-1}) (Freeman, Rhee & Wilson, 1963), suggesting the involvement of the F atom in possibly stronger intermolecular interactions. It is therefore important to determine the crystal structure of GeH_3F (m.p. 238 K); however, the compound does not yield single crystals by standard growth techniques and we are currently investigating alternative methods.

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Redetermination of the Structure of Bismuth(III) Nitrate Pentahydrate, $Bi(NO_3)_3.5H_2O$

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Abstract. $M_r = 485{\cdot}067$, triclinic, $P\bar{1}$, $a = 6{\cdot}520$ (8), $b = 8{\cdot}642$ (8), $c = 10{\cdot}683$ (9) Å, $\alpha = 100{\cdot}82$ (6), $\beta = 80{\cdot}78$ (6), $\gamma = 104{\cdot}77$ (7)°, $V = 567{\cdot}7$ Å^3, $Z = 2$, $D_m = 2{\cdot}90$ (5), $D_x = 2{\cdot}837$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 150$ cm^{-1}, $F(000) = 452$, $T = 293$ (1) K; $R = 0{\cdot}087$ for 2228 observed diffractometer data. In the crystal structure each Bi^{3+} ion is coordinated bidentately by three NO_3^- ions and by four H_2O molecules, the fifth H_2O molecule is linked by weak hydrogen bonds [2·67 (2) and 2·78 (2) Å] to two other H_2O molecules. The NO_3^- ions are nearly planar.

Introduction. The crystal structure of bismuth(III) nitrate pentahydrate was determined by Herpin & Sudarsanan (1965) using the film technique. The visually estimated intensities were not corrected for absorption and a final R value of 0·14 was achieved for only 1600 reflexions. The redetermination of the crystal structure was undertaken to enable a precise comparison between the structure of this important bismuth compound and those of the related bismuth basic nitrates (Lazarini, 1978, 1979*a,b*) to be made.

Experimental. The crystals, grown from a saturated acid solution, decompose slightly in the air and in the X-ray beam as well. The refinement of a set of data, taken with a small and unprotected crystal, failed, therefore a new set of data was collected with a relatively big crystal, sealed together with a small amount of mother liquor into a glass capillary. D_m measured pycnometrically in CCl_4. The crystal was characterized by the following planes (in parentheses are the distances from the planes to the centre of the crystal): ±(010) (0·114 mm), ±(01$\bar{6}$) (0·472 mm), (515) (0·248 mm), ($\bar{5}1\bar{5}$) (0·248 mm), (011) (0·280 mm) and (01$\bar{1}$) (0·361 mm). Lattice parameters obtained from least-squares fit of the θ values of 30 reflexions. Intensities of 3002 independent reflexions ($-14 \le h \le 14$, $-12 \le k \le 12$, $-9 \le l \le 0$) measured, CAD-4 diffractometer (Mo $K\alpha$ radiation, ω–2θ scan, $0 < \theta < 30°$), 2228 with $I > 3\sigma(I)$ used in structural analysis. Intensities of three standard reflexions ($\bar{3}02$, $0\bar{3}5$, $\bar{3}\bar{1}2$) measured after every 237 reflections decreased by 7·5%. Absorption correction applied (Gaussian grid method, 3038 points), maximum and minimum transmission factors 0·0812 and 0·0110 respectively. Crystal structure determined by usual Patterson–Fourier procedure and refined by full-matrix least squares (based on F^2) with anisotropic thermal parameters for Bi and O and isotropic for N to an R value of 0·087 (150 parameters). Isotropic extinction parameter ($9{\cdot}7 \times 10^{-3}$), crystal-size parameter (1·22) and $\sigma(F)$ weighting function included in last stage of refinement ($wR = 0{\cdot}090$). Maximum and average parameter shift to error ratio in final cycle 1·9 (scale) and 0·30 respectively. Final difference Fourier map flat ($+2{\cdot}2 \ge \Delta\rho \ge -1{\cdot}8$ e Å^{-3}). Atomic scattering factors for neutral atoms of Cromer & Mann (1968) and anomalous-dispersion corrections of Cromer & Liberman (1970) used. All calculations performed on DEC-1091 computer at the University of Ljubljana using *SHELX*76 (Sheldrick, 1976).

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