anisotropen Temperaturfaktoren erzielte Zwischenergebnis mit $R = 0{,}036$ war bereits so gut, daß auf weitere Verfeinerungsversuche in *Cm* oder *C*2 von vornherein verzichtet werden dürfte. Eine Differenz-Fouriersynthese Fig. 1(*a*) wies jedoch darauf hin, daß für das Cu-Atom ein anharmonischer Charakter der thermischen Schwingung in Betracht geazogen werden mußte. Der Temperaturfaktor des Cu-Atoms wurde daher wie folgt umformuliert (Johnson, 1969; *International Tables for X-ray Crystallography,* 1974) und die freien Koeffizienten zusammen mit anderen Parametern verfeinert:

$$\exp\Bigg(-\sum_{p,q=1}^{3}\beta^{pq}h_ph_q - i\sum_{p,q,r=1}^{3}c^{pqr}h_ph_qh_r + \sum_{p,q,r,s=1}^{3}d^{pqrs}h_ph_qh_rh_s\Bigg).$$

Die große Differenz des AIC zeigt, daß dieses Modell dem früheren gegenüber eine Verbesserung darstellt. Die zur Kontrolle berechnete Differenz-Fouriersynthese offenbart jedoch, daß das Verhalten des Cu-Atoms durch den eben aufgeführten Temperaturfaktor nicht vollständig auszugleichen ist. Ähnlich verhält sich auch das Cu-Atom in $Cu_xV_{12}O_{29}$ (Kato *et al.*, 1989).

Die verfeinerten Lageparameter sowie die interatomaren Abstände sind in den Tabellen 1 und 2 aufgeführt. Fig. 2 zeigt die projektion der Struktur parallel [010]. Alle Atome liegen auf der Spiegelebene der Raumgruppe *C*2/*m*. Die $VO_6$-Oktaeder und die $VO_5$-Pyramiden sind durch gemeinsame Kanten miteinander verknüpft und bilden eine Schicht parallel (100), welche gemeinsame Baueinheit der homologen Strukturen von $Cu_xV_{6n}O_{15n-m}$ ($m \leq n$) darstellt. Die vorliegende Verbindung ist als ein Vertreter dieser Struktur-Reihe dadurch gekennzeichnet, daß die ebengenannte Schicht beidseitig über ein Brüken-Sauerstoffatom mit den benachbarten Schichten verbunden ist. Das Cu-Atom ist annähernd trigonal-dipyramidal von fünf O-Atomen umgeben (Fig. 3).

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*Acta Cryst.* (1989). C45, 1847–1853

# Structures of Nonadecasulfur(2+) Bis[hexafluoroantimonate(1−)] $S_{19}(SbF_6)_2$, Octasulfur(2+) Di-$\mu$-fluoro-dodecafluorotriantimonate(1−) Hexafluoroantimonate(1−) $S_8(Sb_3F_{14})(SbF_6)$, and Tetrasulfur(2+) Di-$\mu$-fluoro-difluorodiantimony(2+) $\mu$-Fluoro-tetrafluorodiantimony(1+) Pentakis[hexafluoroantimonate(1−)] $S_4(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$

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**Abstract.** $S_{19}(SbF_6)_2$ (1), $M_r = 1080{\cdot}6$, monoclinic, $P2_1/a$, $a = 15{\cdot}423\ (5)$, $b = 13{\cdot}288\ (4)$, $c = 14{\cdot}408\ (2)$ Å, $\beta = 105{\cdot}33\ (2)°$, $V = 2848\ (1)$ Å$^3$, $Z = 4$, $D_x = 2{\cdot}52$ g cm$^{-3}$, Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å), $\mu = 33{\cdot}3$ cm$^{-1}$, $F(000) = 2056$, $T = 298$ K, $R = 0{\cdot}045$ for 2227 observed [$I > 3\sigma(I)$] reflections. $S_8(Sb_3F_{14})(SbF_6)$ (2), $M_r = 1123{\cdot}3$, orthorhombic, *Pbca*, $a = 15{\cdot}140\ (3)$, $b = 17{\cdot}402\ (4)$, $c = 17{\cdot}309\ (4)$ Å,

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Table 1. *Experimental details*

| | (1) | (2) | (3) |
|---|---|---|---|
| Crystal size (mm) | Irregular block cut from larger crystal (max. dimension *ca* 0·2) | Dark-blue block *ca* 0·10 × 0·14 × 0·16 | Approximately spherical 0·1 radius |
| No. of reflections used in cell determination, and $2\theta$ range (°) | 15<br>20·3–28·5 | 15<br>24·6–32·7 | 15<br>20·5–25·9 |
| Scan rates (° $min^{-1}$)* | 6·0–29·3 | 6·0–29·3 | 5·0–29·3 |
| Standard reflections [No./interval (reflections)]† | 2/48 | 2/48 | 2/48 |
| Max. $2\theta$(°) | 45 | 55 | 50 |
| Quadrants | $h, k, \pm l$<br>$h_{max} = 16$<br>$k_{max} = 14$<br>$\|l\|_{max} = 15$ | $h, k, \pm l$<br>$h_{max} = 22$<br>$k_{max} = 22$<br>$\|l\|_{max} = 19$ | $h, k, \pm l$<br>$h_{max} = 18$<br>$k_{max} = 15$<br>$\|l\|_{max} = 20$ |
| No. of observed data | 2227 | 2131 | 4805 |
| $R$ ($wR$) | 0·045 (0·042) | 0·036 (0·043) | 0·038 (0·044) |
| Max. $\Delta/\sigma$ in final cycle | 0·02 | 0·24 | 0·09 |
| Weights | $[\sigma^2(F) + 0{\cdot}00025F^2]^{-1}$ | $[\sigma^2(F) + 0{\cdot}0004F^2 + 0{\cdot}00003F^3]^{-1}$ | $[\sigma^2(F) + 0{\cdot}0338F^2]^{-1}$ |
| Max. peak (e $Å^{-3}$) in final $\Delta F$ map | 0·9 (near Sb) | 3·0 (near Sb) | 1·7 [near Sb(3)] |

*Dependent on intensity of a 2 s prescan.

†No large declines in intensities of standards of any of the crystals. Data rescaled for fluctuations in intensities of standards at data reduction.

$V = 4560$ (2) $Å^3$, $Z = 8$, $D_x = 3{\cdot}27$ g $cm^{-3}$, Mo $K\alpha$ radiation, $\mu = 55{\cdot}9$ $cm^{-1}$, $F(000) = 4096$, $T = 298$ K, $R = 0{\cdot}036$ for 2131 observed $[I > 3\sigma(I)]$ reflections. $S_4(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$ (3), $M_r = 1965{\cdot}0$, monoclinic, $P2_1/c$, $a = 15{\cdot}658$ (4), $b = 13{\cdot}268$ (3), $c = 16{\cdot}974$ (3) Å, $\beta = 91{\cdot}59$ (2)°, $V = 3525$ (1) $Å^3$, $Z = 4$, $D_x = 3{\cdot}70$ g $cm^{-3}$, Mo $K\alpha$ radiation, $\mu = 72{\cdot}7$ $cm^{-1}$, $F(000) = 3496$, $T = 298$ K, $R = 0{\cdot}038$ for 4805 observed $[I > 3\sigma(I)]$ reflections. All three structures contain previously known sulfur cations $S_{19}^{2+}$, $S_8^{2+}$ and $S_4^{2+}$ with hexafluoroantimonate(V) and, in compounds (2) and (3), mixed fluoroantimony(III,V) counter-ions. The $S_{19}^{2+}$ cation in (1) consists of two seven-membered rings with chair conformations bridged by a five-atom chain. Unlike the corresponding $AsF_6^-$ salt, the cation in (1) is completely ordered and prominently displays the S—S bond length alternation around the cation which was commented upon previously. Similarly, the $S_8^{2+}$ cation in (2) has the characteristic *exo-endo* conformation due to a transannular S···S interaction of length 2·906 (6) Å. The packing in (2) is determined by several $Sb^{III}$···F interactions surrounding the lone pair on $Sb^{III}$ in the $Sb_3F_{14}^-$ anion, which are up to 0·69 Å less than van der Waals distances (3·55 Å). Finally, compound (3) is isomorphous with a previously reported tetraselenium analogue. The ⟨S—S⟩ distance in the two independent centrosymmetric $S_4^{2+}$ cations in the asymmetric unit is 1·988 (8) Å and both cations are involved in several S···F contacts bridging edges or along the diagonals of the cations. Like the Se analogue, the $Sb_2F_4^{2+}$ and $Sb_2F_5^+$ cations are involved in numerous stereospecific $Sb^{III}$···F interactions over a range of distances which help to define the position of the lone pair on each $Sb^{III}$.

**Introduction.** The oxidation of sulfur in $SO_2$ solutions with a number of different oxidizing agents such as $SbF_5$ and $AsF_5$ has been shown to produce the dipositive ions $S_{19}^{2+}$, $S_8^{2+}$ and $S_4^{2+}$ which have been characterized in the solid state and in solution (Davies, Gillespie, Park & Passmore, 1971; Burns, Gillespie & Sawyer, 1980; Passmore, Sutherland & White, 1980). During attempts to prepare further $S_n^{2+}$ cations in the range $19 < n < 8$ using $SbF_5$ as oxidant we have isolated several crystalline materials which have been shown by X-ray crystallography to be the compounds $S_{19}(SbF_6)_2$, $S_8(Sb_3F_{14})(SbF_6)$ and $S_4(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$.

**Experimental.** Reaction vessels and the preparations and purifications of starting materials have been previously described (Cardinal, Gillespie, Sawyer & Vekris, 1982).

### *Preparation*

(*a*) $S_8(Sb_3F_{14})(SbF_6)$ *and* $S_{19}(SbF_6)_2$. S (15·2 mmol, 0·4857 g) was allowed to react with 50 ml of an $SO_2/SbF_5$ (3·25 mmol, 0·7041 g) solution at 298 K. The reaction initially gave a blue solution but after 1 h of stirring the color changed to dark-brown and a light colored precipitate appeared. After stirring for 48 h, the volatile components of the reaction were slowly removed to give small quantities of dark grey-blue crystals of $S_8Sb_4F_{20}$ and colorless crystals of a presumed $SbF_3(SbF_5)_x$ adduct together with a larger quantity of red-brown $S_{19}(SbF_6)_2$ crystals.

(*b*) $S_4(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$. S (7·21 mmol, 0·2311 g) was allowed to react with 50 ml of an $SO_2/SbF_5$ (6·02 mmol, 1·3045 g) solution to which a trace of bromine had been added at 298 K. A dark solution and a dark precipitate formed. After stirring the mixture for 48 h, the supernatant liquid was filtered to the other side of the double ampoule. Volatile components were removed over 48 h to give well formed colorless crystals coated with a film of dark material which was washed off with $SO_2$.

All crystals were sealed in Lindemann capillaries in a dry box equipped with a microscope. Preliminary cell and space-group information was obtained using precession photographs. Further work on a Nicolet *R*3 diffractometer using Zr-filtered Mo $K\alpha$ radiation. Accurate unit-cell dimensions by least-squares refinement of $2\theta$, $\omega$ and $\chi$ for 15 high-angle reflections. Intensity data on each compound were collected by use of $\omega$:$2\theta$ scans over scan ranges ($K\alpha_1 - 1{\cdot}0°$) to ($K\alpha_2 + 1{\cdot}0°$). Variable scan rates were dependent on the intensity of preliminary counts. Stationary background counts at each end of the scan, each for half the scan time. Intensities of standard reflections collected at regular intervals to monitor crystal and instrument stability showed no systematic variations with time for any of the compounds. All other experimental details are given in Table 1. All reflections collected were corrected for Lorentz and polarization effects, but not for absorption.

### *Structure solution*

For (1) and (2), Sb atoms were located by Patterson methods, S and F atoms in successive cycles of least-squares and Fourier calculations. Compound (3) is isomorphous with a tetraselenium analogue (Cardinal *et al.*, 1982) and these positional parameters were used with the scattering curve of S replacing that of Se. Least-squares refinements of all three structures with all atoms anisotropic and minimizing $\sum w\Delta F^2$ converged to the indicated final agreement indices (Table 1). Weights were given by the indicated expressions and the $\langle w\Delta F^2\rangle$ as a function of $F$ and $\sin\theta$ after the use of these schemes revealed no systematic trends. Final $\Delta F$ maps usually contained peaks up to *ca* 3·0 e Å$^{-3}$ close to the Sb atoms due in part to the absence of any absorption corrections.

Computing was on a CDC6400 computer using the *XRAY76* system (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976), *SHELX* (Sheldrick, 1976) and local programs. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The final atomic positional and thermal parameters, and selected bond lengths/bond angles for all three compounds are given in Tables 2 and 3.*

**Discussion.** (1) $S_{19}(SbF_6)_2$. This compound is not isomorphous with the corresponding hexafluoro-

Table 2. *Final atomic positional* ( × 10$^4$) *and thermal parameters* ( × 10$^3$)

$U_{eq} = \frac{1}{3}$ trace **U**.

| | *x* | *y* | *z* | $U_{eq}$ (Å$^2$) |
|---|---|---|---|---|
| (1) | | | | |
| Sb(1) | 948·1 (6) | 2174·0 (7) | 9720·6 (7) | 45·3 (7) |
| Sb(2) | 257·9 (6) | 2458·6 (7) | 5239·8 (6) | 42·1 (6) |
| S(1) | 2792 (3) | 4097 (3) | 4057 (3) | 65 (3) |
| S(2) | 2003 (3) | 5177 (3) | 4248 (3) | 62 (3) |
| S(3) | 814 (3) | 4938 (3) | 3225 (3) | 76 (3) |
| S(4) | 817 (3) | 6091 (3) | 2330 (4) | 79 (4) |
| S(5) | 1698 (3) | 5691 (3) | 1561 (3) | 75 (3) |
| S(6) | 2908 (3) | 6017 (3) | 2448 (3) | 57 (3) |
| S(7) | 3473 (2) | 4645 (3) | 2989 (2) | 47 (2) |
| S(8) | 2940 (3) | 3619 (3) | 1902 (3) | 61 (3) |
| S(9) | 3994 (3) | 3390 (3) | 1342 (3) | 60 (3) |
| S(10) | 4596 (3) | 2113 (3) | 2017 (3) | 57 (3) |
| S(11) | 771 (2) | 6007 (3) | 8989 (2) | 47 (3) |
| S(12) | 3021 (2) | 467 (3) | 1095 (2) | 47 (2) |
| S(13) | 3402 (2) | − 598 (2) | 2163 (2) | 41 (2) |
| S(14) | 2159 (3) | − 1490 (3) | 1701 (3) | 56 (3) |
| S(15) | 1550 (3) | − 1391 (3) | 2723 (3) | 65 (3) |
| S(16) | 767 (3) | − 107 (4) | 2353 (4) | 90 (4) |
| S(17) | 1385 (3) | 826 (4) | 3412 (3) | 84 (4) |
| S(18) | 2538 (3) | 1296 (3) | 3081 (3) | 63 (3) |
| S(19) | 1602 (3) | 5141 (3) | 6549 (2) | 54 (3) |
| F(11) | 749 (6) | 2366 (8) | 8422 (6) | 107 (8) |
| F(12) | 891 (8) | 3550 (7) | 9884 (8) | 124 (10) |
| F(13) | 2166 (6) | 2269 (9) | 9885 (7) | 121 (9) |
| F(14) | − 258 (6) | 2143 (8) | 9572 (6) | 103 (8) |
| F(15) | 1023 (8) | 830 (7) | 9566 (8) | 125 (10) |
| F(16) | 1158 (7) | 2022 (8) | 1020 (6) | 110 (9) |
| F(21) | 918 (7) | 2984 (6) | 6393 (5) | 94 (7) |
| F(22) | − 390 (6) | 1940 (7) | 4072 (6) | 90 (7) |
| F(23) | 676 (11) | 1226 (7) | 5597 (8) | 191 (14) |
| F(24) | 1168 (10) | 2709 (12) | 4727 (11) | 211 (17) |
| F(25) | − 689 (9) | 2327 (14) | 5692 (10) | 236 (18) |
| F(26) | − 105 (13) | 3726 (9) | 4892 (10) | 216 (16) |
| (2) | | | | |
| Sb(1) | 317·5 (5) | 5319·9 (5) | 2496·2 (7) | 31·9 (4) |
| Sb(2) | 861·0 (5) | 3076·9 (5) | 2558·1 (6) | 27·6 (4) |
| Sb(3) | 2984·2 (5) | 2113·4 (5) | 2623·1 (6) | 30·1 (4) |
| Sb(4) | 48·6 (5) | 2310·9 (5) | 101·7 (6) | 33·2 (5) |
| S(1) | 3838 (2) | 611 (2) | 614 (3) | 44 (2) |
| S(2) | 2997 (3) | 1015 (2) | − 207 (3) | 49 (2) |
| S(3) | 2077 (2) | 615 (3) | 457 (3) | 53 (2) |
| S(4) | 1395 (2) | 117 (3) | − 493 (3) | 64 (2) |
| S(5) | 2175 (2) | − 548 (2) | − 1141 (2) | 45 (2) |
| S(6) | 2208 (2) | − 1367 (2) | − 176 (3) | 52 (2) |
| S(7) | 2854 (2) | − 839 (2) | 769 (2) | 48 (2) |
| S(8) | 3781 (2) | − 468 (2) | 107 (3) | 45 (2) |
| F(11) | 352 (5) | 6380 (5) | 2470 (7) | 68 (6) |
| F(12) | 277 (4) | 4197 (4) | 2469 (6) | 40 (4) |
| F(13) | − 741 (4) | 5298 (5) | 2524 (8) | 68 (6) |
| F(14) | 375 (7) | 5251 (5) | 3720 (6) | 78 (8) |
| F(15) | 1382 (5) | 5233 (6) | 2446 (9) | 82 (7) |
| F(16) | 269 (6) | 5251 (5) | 1265 (6) | 64 (6) |
| F(21) | 1459 (5) | 3487 (4) | 1633 (5) | 42 (5) |
| F(22) | 1484 (5) | 3612 (5) | 3379 (5) | 48 (5) |
| F(31) | 4039 (4) | 1987 (5) | 2617 (7) | 65 (6) |
| F(32) | 1873 (4) | 2237 (4) | 2636 (6) | 47 (5) |
| F(33) | 3064 (5) | 3156 (5) | 2593 (6) | 57 (5) |
| F(34) | 2940 (6) | 2083 (6) | 1400 (5) | 73 (7) |
| F(35) | 2818 (5) | 1069 (5) | 2669 (8) | 79 (7) |
| F(36) | 2919 (5) | 2151 (6) | 3842 (5) | 77 (7) |
| F(41) | − 37 (5) | 3073 (5) | 976 (5) | 59 (5) |
| F(42) | 690 (6) | 2964 (5) | − 525 (6) | 72 (7) |
| F(43) | 127 (7) | 1558 (5) | − 767 (7) | 83 (7) |
| F(44) | 883 (5) | 1911 (6) | 697 (7) | 76 (7) |
| F(45) | − 601 (6) | 1693 (6) | 747 (6) | 68 (6) |
| F(46) | − 797 (6) | 2718 (6) | − 507 (6) | 72 (6) |
| (3) | | | | |
| Sb(1) | − 326·7 (4) | 4488·4 (5) | 888·0 (4) | 21·4 (3) |
| Sb(2) | 5354·2 (4) | 5624·7 (5) | 849·0 (4) | 21·8 (3) |
| Sb(3) | 1957·7 (4) | 3742·3 (5) | 2145·4 (4) | 19·3 (3) |
| Sb(4) | 3112·6 (4) | 6485·2 (5) | 2081·5 (4) | 19·8 (3) |
| Sb(5) | 5328·2 (4) | 8142·5 (5) | 2464·9 (4) | 27·6 (4) |
| Sb(6) | − 321·9 (4) | 2196·8 (5) | 2670·9 (4) | 23·5 (4) |
| Sb(7) | − 2690·2 (5) | 2833·3 (5) | 577·4 (4) | 24·5 (4) |
| Sb(8) | 7669·6 (4) | 7212·7 (5) | 470·6 (4) | 23·3 (3) |
| Sb(9) | 2451·7 (6) | 178·4 (6) | 1858·4 (5) | 40·9 (5) |
| S(1) | 135 (3) | 3999 (3) | 5243 (2) | 53 (2) |
| S(2) | 598 (3) | 4866 (3) | 4403 (2) | 60 (2) |
| S(3) | 4895 (2) | 4167 (3) | 5503 (2) | 48 (2) |

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* Lists of anisotropic thermal parameters, bond lengths and bond angles for the anions, final structure factor amplitudes for all three compounds and a supplementary figure have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52046 (72 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2 (*cont.*)

| | *x* | *y* | *z* | $U_{eq}$(Å$^2$) |
|---|---|---|---|---|
| S(4) | 4153 (2) | 5289 (3) | 5107 (2) | 49 (2) |
| F(11) | 669 (4) | 5208 (5) | 321 (3) | 29 (3) |
| F(12) | 68 (5) | 3261 (5) | 473 (4) | 44 (4) |
| F(21) | 4337 (4) | 4817 (5) | 313 (3) | 33 (3) |
| F(22) | 4947 (4) | 6788 (5) | 341 (4) | 42 (4) |
| F(31) | 900 (4) | 4322 (5) | 1664 (4) | 38 (4) |
| F(32) | 1701 (4) | 4472 (5) | 3052 (4) | 40 (4) |
| F(34) | 2509 (4) | 5091 (4) | 1783 (4) | 29 (3) |
| F(41) | 4106 (4) | 5925 (5) | 1549 (4) | 34 (4) |
| F(42) | 3482 (5) | 5802 (5) | 2995 (4) | 46 (4) |
| F(51) | 4199 (5) | 7649 (7) | 2404 (6) | 80 (7) |
| F(52) | 6442 (4) | 8648 (7) | 2505 (6) | 71 (6) |
| F(53) | 5691 (5) | 7008 (6) | 1941 (5) | 61 (5) |
| F(54) | 4925 (5) | 9272 (7) | 2953 (7) | 94 (8) |
| F(55) | 5546 (9) | 7476 (11) | 3395 (7) | 121 (11) |
| F(56) | 5115 (8) | 8778 (9) | 1511 (6) | 99 (8) |
| F(61) | 821 (4) | 2621 (6) | 2526 (5) | 55 (5) |
| F(62) | −1431 (5) | 1751 (7) | 2839 (6) | 67 (6) |
| F(63) | −267 (7) | 1361 (7) | 1791 (6) | 81 (7) |
| F(64) | −359 (8) | 3057 (9) | 3520 (5) | 95 (8) |
| F(65) | −698 (4) | 3234 (6) | 2001 (4) | 46 (4) |
| F(66) | 90 (5) | 1171 (7) | 3312 (7) | 79 (7) |
| F(71) | −2793 (6) | 3081 (7) | −503 (4) | 59 (5) |
| F(72) | −2591 (5) | 2596 (6) | 1663 (4) | 48 (4) |
| F(73) | −3630 (5) | 1950 (6) | 502 (5) | 60 (5) |
| F(74) | −1749 (5) | 3728 (6) | 642 (4) | 51 (5) |
| F(75) | −1935 (6) | 1790 (7) | 419 (6) | 74 (6) |
| F(76) | −3419 (5) | 3888 (6) | 782 (5) | 59 (5) |
| F(81) | 6920 (6) | 8240 (7) | 204 (6) | 69 (6) |
| F(82) | 8380 (5) | 6148 (6) | 741 (5) | 55 (5) |
| F(83) | 6726 (4) | 6343 (6) | 572 (4) | 45 (4) |
| F(84) | 8596 (5) | 8088 (6) | 366 (6) | 68 (6) |
| F(85) | 7599 (5) | 7557 (6) | 1531 (4) | 53 (5) |
| F(86) | 7743 (6) | 6822 (7) | −583 (4) | 62 (6) |
| F(91) | 1853 (12) | 120 (10) | 904 (9) | 163 (14) |
| F(92) | 3091 (10) | 253 (9) | 2784 (6) | 117 (11) |
| F(93) | 2649 (7) | −1193 (6) | 1778 (6) | 88 (8) |
| F(94) | 2286 (8) | 1560 (7) | 1884 (7) | 97 (8) |
| F(95) | 3439 (8) | 433 (9) | 1283 (8) | 109 (9) |
| F(96) | 1507 (9) | −38 (11) | 2428 (12) | 172 (17) |

Table 3. *Comparison of some principal* $Sb^{III}$—F *distances* (Å) *and related bond angles* (°) *in the compounds* $M_4(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$ ($M$ = S, Se)

| | Se | S | | Se | S |
|---|---|---|---|---|---|
| Sb(1)—F(11) | 2·09 (1) | 2·086 (6) | Sb(2)—F(21) | 2·10 (1) | 2·105 (6) |
| —F(11$^{vi}$) | 2·15 (1) | 2·145 (6) | —F(21$^{iv}$) | 2·11 (1) | 2·125 (6) |
| —F(12) | 1·89 (1) | 1·886 (7) | —F(22) | 1·87 (1) | 1·871 (7) |
| —F(31) | 2·33 (1) | 2·309 (6) | —F(41) | 2·41 (1) | 2·350 (6) |
| —F(65) | 2·64 (2) | 2·596 (7) | —F(53) | 2·65 (2) | 2·651 (8) |
| —F(74) | 2·47 (2) | 2·470 (8) | —F(83) | 2·37 (1) | 2·409 (7) |
| —F(66$^{ix}$) | 2·68 (2) | 2·633 (10) | —F(54$^{viii}$) | 2·79 (2) | 2·756 (11) |
| —F(82$^{ii}$) | 2·95 (2) | 2·997 (8) | —F(76$^{i}$) | 2·97 (2) | 3·004 (8) |
| —F(96) | — | 3·504 (19) | —F(92) | — | 3·354 (13) |
| Sb(3)—F(31) | 1·98 (1) | 1·982 (6) | Sb(4)—F(34) | 2·15 (1) | 2·132 (6) |
| —F(32) | 1·88 (1) | 1·871 (7) | —F(41) | 1·95 (1) | 1·966 (6) |
| —F(34) | 2·09 (1) | 2·086 (6) | —F(42) | 1·86 (1) | 1·874 (7) |
| —F(61) | 2·47 (2) | 2·421 (8) | —F(51) | 2·38 (2) | 2·351 (9) |
| —F(86$^{iv}$) | 2·82 (2) | 2·808 (7) | —F(71$^{vi}$) | 2·79 (2) | 2·772 (7) |
| —F(52$^{viii}$) | 2·59 (2) | 2·563 (7) | —F(62$^{ix}$) | 2·74 (2) | 2·665 (7) |
| —F(85$^{viii}$) | 2·91 (1) | 2·813 (8) | —F(72$^{ix}$) | 2·82 (1) | 2·734 (7) |
| —F(94) | 3·03 (2) | 2·976 (9) | | | |
| | | | | | |
| Sb(3)—F(34)—Sb(4) | 149·8 (6) | 149·1 (3) | F(11)—Sb(1)—F(11$^{vi}$) | 69·0 (4) | 69·1 (2) |
| Sb(1)—F(31)—Sb(3) | 158·4 (7) | 160·9 (4) | —F(12) | 87·0 (5) | 88·1 (3) |
| Sb(4)—F(41)—Sb(2) | 166·2 (6) | 167·5 (4) | F(11$^{vi}$)—Sb(1)—F(12) | 83·3 (5) | 83·1 (3) |
| Sb(1)—F(11)—Sb(1$^{vi}$) | 111·0 (5) | 110·9 (3) | F(21)—Sb(2)—F(21$^{iv}$) | 68·4 (4) | 69·3 (2) |
| Sb(2)—F(21)—Sb(2$^{iv}$) | 111·6 (5) | 110·7 (3) | —F(22) | 88·1 (5) | 88·7 (3) |
| | | | F(22$^{iv}$)—Sb(2)—F(22) | 84·0 (5) | 83·3 (3) |
| F(31)—Sb(3)—F(32) | 86·8 (5) | 86·7 (3) | F(41)—Sb(4)—F(42) | 88·6 (5) | 88·1 (3) |
| —F(34) | 82·9 (5) | 83·9 (3) | —F(34) | 84·3 (5) | 85·1 (3) |
| —F(61) | 74·3 (5) | 74·7 (3) | —F(51) | 77·8 (6) | 77·2 (3) |
| F(32)—Sb(3)—F(34) | 84·4 (5) | 84·2 (3) | F(42)—Sb(4)—F(34) | 84·4 (5) | 84·4 (3) |
| F(61) | 84·8 (6) | 85·6 (3) | —F(51) | 83·6 (6) | 85·4 (3) |
| F(34)—Sb(3)—F(61) | 155·3 (5) | 156·7 (2) | F(34)—Sb(4)—F(51) | 158·6 (5) | 159·8 (3) |

Symmetry codes [from Cardinal *et al.* (1982)]: (i) $1 + x, y, z$; (ii) $-1 + x, y, z$; (iv) $1 - x, 1 - y, -z$; (vi) $-x, 1 - y, -z$; (viii) $1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$; (ix) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

arsenate salt (Burns *et al.*, 1980). Unlike the corresponding $AsF_6^-$ salt, which contains some disorder in one of the seven-membered rings of the $S_{19}^{2+}$ cation, the $S_{19}^{2+}$ cation in this compound (Figs. 1 and 2) is completely ordered and contains two seven-membered rings with very similar chair conformations. These two rings are linked by a five S atom chain. Due to the much improved e.s.d.'s for the S—S distances in the present structure determination, the very noticeable short–long S—S bond length alternation around the cation, which was commented upon previously, is significantly more pronounced than that in $S_{19}(AsF_6)_2$. As discussed previously, both the S(1)—S(7) [2·203(6) Å] and S(13)—S(14) [2·202(5) Å] bonds are significantly elongated since bonding and lone pairs of electrons on these atoms are virtually eclipsed.

In the anions some Sb—F bond lengths are significantly shortened by thermal effects [Sb—F = 1·758 (15)–1·848 (8) Å] and there are some significant S···F contacts involving these anions. The shortest of these contacts are S(7)···F(23′) = 2·92 (1), S(7)···F(23″) = 2·98 (1) and S(13)···F(21′) = 2·797 (8) Å involving the two three-coordinate S atoms (other contacts are > 3 Å). In the $AsF_6^-$ salt the closest S···F contacts are ≥ 2·91 Å in length.

(2) $S_8(Sb_3F_{14})(SbF_6)$. The $S_8^{2+}$ cation in this compound has been previously identified as a hexafluoroarsenate salt (Davies *et al.*, 1971) and the isostructural $Se_8^{2+}$ cation is known in the compounds $Se_8(AlCl_4)_2$ and $(Te_6)(Se_8)(AsF_6)_6(SO_2)$ (McMullan, Prince & Corbett, 1971; Collins, Gillespie & Sawyer, 1988*a*). The most significant feature of the structure of this cation is the drastic change in conformation from the *exo-exo* crown-shaped ring of neutral $S_8$ to the observed *exo-endo* conformation (Fig. 3) in which a transannular S···S contact [S(3)···S(7) = 2·906 (6) Å] is appreciably less than van der Waals distances (3·8 Å) but comparable in length to the analogous contacts in the two independent cations in the $AsF_6^-$ salt [2·889 (12) and 2·832 (10) Å (Davies *et al.*, 1971)] (Fig. 4), and significantly shorter than all the other next-neighbor contacts ( > 2·96 Å). In the isostructural $Se_8^{2+}$ cations the analogous transannular contacts are even stronger with Se···Se distances of 2·902 (4) Å in $(Te_6)(Se_8)(AsF_6)_6(SO_2)$ and 2·84 (1) Å in $Se_8(AlCl_4)_2$. Interestingly, the compounds 1-acetonyl-1-thionia-5-thiacyclooctane, 2-chloro-1,3,6,2-trithiaarsaocane and its Sb analogue also contain eight-membered rings whose conformations are determined by transannular S···S, As···S and Sb···S weak bonds (Johnson, Maier & Paul, 1970; Draeger, 1974, 1977). In the sulfur compound the transannular contact has a length of 3·121 (5) Å.

In the present cation S—S bond lengths around the ring [2·001–2·054 (6) Å; Fig. 3] do not deviate very significantly from the average (2·031 Å) distance which is notably shorter than the ⟨S—S⟩ distance in monoclinic $S_8$. Similarly, bond angles [93·1–104·5 (2)°] are all smaller than the tetrahedral value and the largest include the atoms involved in the transannular bond: the smallest angles are at S(3) and S(7), the *exo* and *endo* atoms. Similar trends are observed for the cations in $S_8(AsF_6)_2$.

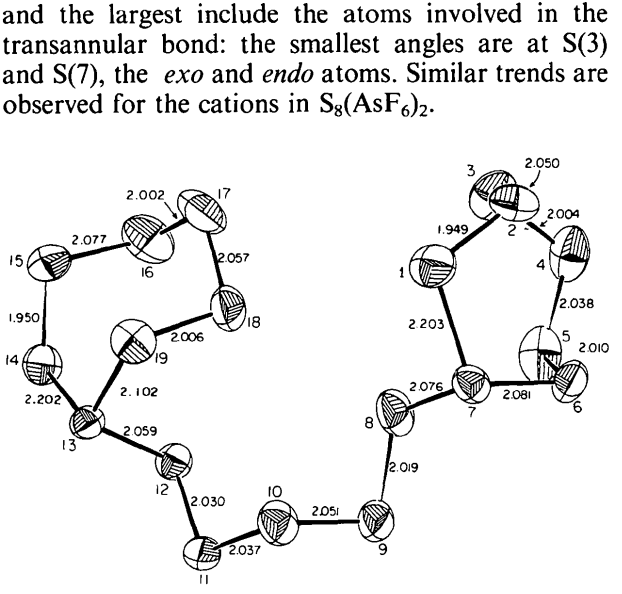

Fig. 1. *ORTEP* view (Johnson, 1976) of the $S_{19}^{2+}$ cation showing the atomic numbering scheme used and S—S bond distances (Å). E.s.d.'s are 0·005–0·006 Å. Thermal ellipsoids are drawn at the 50% probability level.

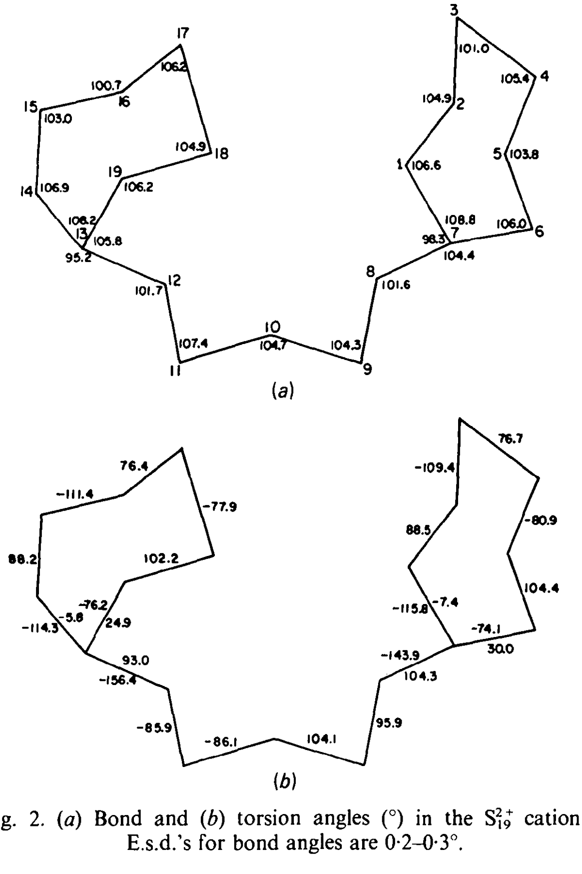

Fig. 2. (*a*) Bond and (*b*) torsion angles (°) in the $S_{19}^{2+}$ cation. E.s.d.'s for bond angles are 0·2–0·3°.

The geometry of the $Sb_3F_{14}^-$ anion is very similar to that found in other compounds containing this anion, although there are significant differences in the way these anions pack in the crystal lattice and in the secondary $Sb^{III}\cdots F$ bonds that surround the equatorial lone pair on $Sb^{III}$ (Boldrini, Brown, Collins, Gillespie, Maharajh, Slim & Sawyer, 1985). In the present case there are four face-capping and two edge-bridging $Sb^{III}\cdots F$ contacts, two of which involve the F atoms on $Sb^VF_6^-$ anions which are *trans* to the bridging atoms F(12) and F(32) in two other $Sb_3F_{14}^-$ anions (Fig. 5). A bond-valence calculation (Brown, 1974) summing individual valences for all $Sb^{III}$—F interactions less than van der Waals limits gives a value of 3·15 (3·0 expected). Some of the $Sb^V$—F bond lengths in the anions have been slightly lengthened by these interactions. Bond angles around Sb(1) and Sb(3) indicate that the 'equatorial' F atoms bend by up to 5° towards the bridging atoms F(12) and F(23) [F—Sb—F angles are in the range 85·0–88·4 (4)°].

The crystal packing (supplementary figure) is very similar to that of the compound $(Te_2Se_4)(Sb_3F_{14})(SbF_6)$ (Collins, Gillespie & Sawyer, 1988*b*). Both compounds crystallize with similar cell dimensions in the space group *Pbca* and the cations $S_8^{2+}$ and $Te_2Se_4^{2+}$ are located in cavities formed by layers of interacting $Sb_3F_{14}^-$ anions which are cross-linked by the $Sb^{III}\cdots F$ interactions involving $SbF_6^-$ anions.

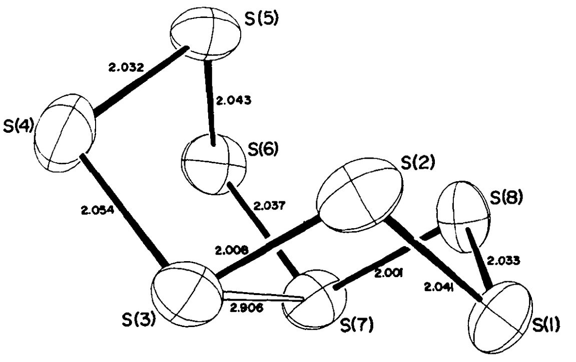

Fig. 3. *ORTEP* view of the $S_8^{2+}$ cation showing the atomic numbering scheme used and S—S bond distances (Å). E.s.d.'s are 0·005–0·006 Å.

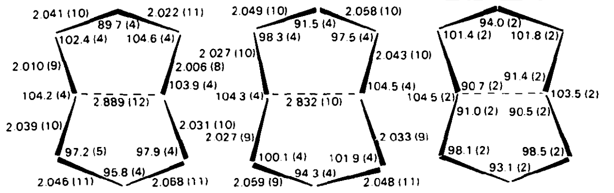

Fig. 4. Bond distances (Å) and bond angles (°) in $S_8(AsF_6)_2$ (Davies, Gillespie, Park & Passmore, 1971) and $S_8(Sb_3F_{14})(SbF_6)$ (this work).

In (2), some S···F contacts between the ions are as short as 2·916 (11) Å. Similar contacts are observed in $S_8(AsF_6)_2$ and these nucleophilic contacts presumably form in directions which are minima in the bonding and non-bonding electron density around each S, *i.e.* they tend to be approximately collinear to S—S bonds in the SSS plane or to be approximately *trans* to lone pairs (*i.e.* *ca* 70–80° to the SSS plane).

(3) $S_4(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$. This compound is isomorphous with a tetraselenium analogue* and the asymmetric unit contains $S_4^{2+}$ cations about the centers of symmetry at $(0, \frac{1}{2}, \frac{1}{2})$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and $Sb_2F_4^{2+}$ cations about centers of symmetry at $(0, \frac{1}{2}, 0)$ and $(\frac{1}{2}, \frac{1}{2}, 0)$. As discussed previously, the above formulation of the compound depends on the limitation of the $Sb^{III}$—F primary bond lengths to *ca* 2·4 Å since the lattice also contains many other $Sb^{III}$···F distances between the $Sb^{III}$ cations and the $SbF_6^-$ anions. These latter distances vary in length up to the van der Waals limit and their stereochemistry is determined by the positions of the lone pair on each $Sb^{III}$. A comparison of selected Sb/F distances in the sulfur and selenium compounds is given in Table 3. The max. differences between comparable distances are for Sb(3)···F(85), Sb(4)···F(62) and Sb(4)···F(72) for which deviations of 0·08–0·10 Å are observed; corresponding differences among the bond angles between the strongest bonds are ≤ 2·5°.

In the $S_4^{2+}$ cations bond lengths are 1·985 (5) and 1·996 (5) Å for the cation at $(0, \frac{1}{2}, \frac{1}{2})$ and 1·994 (5) and 1·975 (5) Å for the cation at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, while the SSS bond angles are 90·2, 89·8, 89·5 and 90·5 (2)° at S(1)–S(4) respectively. These distances are comparable to those observed for the cations in the compounds $S_4(AsF_6)_2.0{\cdot}6SO_2$ [2·013 and 2·015 (2) Å] and $S_4^{2+}(S_7I^+)_4\,(AsF_6)_6$ [1·98 (1) Å] (Passmore *et al.*, 1980). As with the Se compound, the present cations are involved in several S···F contacts significantly less than van der Waals limits which bridge edges and are approximately collinear with the extensions of the diagonals of the square cations (Fig. 6). These distances are as short as 2·504 (19) Å [S(4)···F(96)], that is, *ca* 0·70 Å less than the sum of the neutral-atom van der Waals radii for S + F. In general, the shorter of the present contacts are slightly stronger than analogous contacts in the other $S_4^{2+}$ cations [see Table 4 in Cardinal *et al.* (1982)] and, when the differences in radii are taken into consideration, are comparable to the strengths of the Se···F interactions in the isomorphous $Se_4^{2+}$ cations.

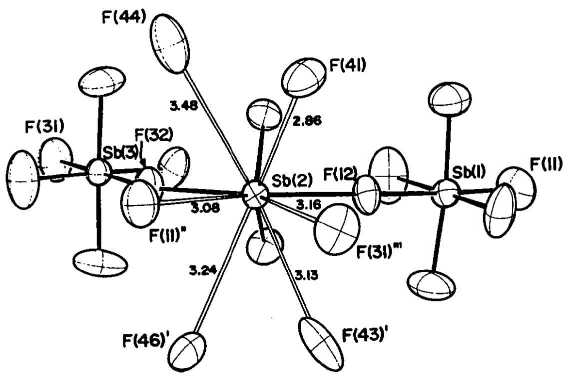

Fig. 5. *ORTEP* view of the $Sb_3F_{14}^-$ anion including the weaker $Sb^{III}$···F secondary contacts out to the van der Waals limit (3·55 Å) as the unfilled bonds.

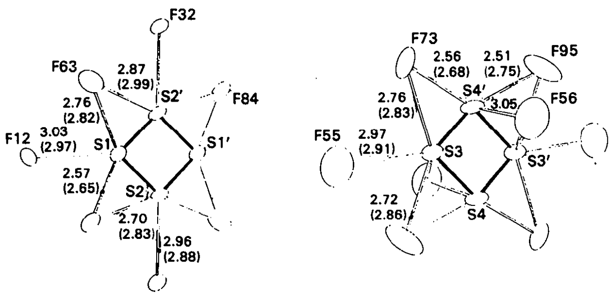

Fig. 6. *ORTEP* view of the $S_4^{2+}$ cations in $S_4(Sb_2F_4)(Sb_2F_5)(SbF_6)_5$ including all S···F interactions out to 3·2 Å as unfilled bonds.

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* $Se_4Sb_9F_{39}$ is monoclinic, $P2_1/c$, with $a = 15{\cdot}739$ (3), $b = 13{\cdot}498$ (2), $c = 17{\cdot}040$ (4) Å, $\beta = 92{\cdot}26$ (2)°, $V = 3617$ (1) Å$^3$, $D_x = 4{\cdot}0$ g cm$^{-3}$ (Cardinal *et al.*, 1982).

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# $Sc_3Ni_2Si_3$ with $Hf_3Ni_2Si_3$-Type Structure, an Intergrowth of CrB-, $ThCr_2Si_2$- and W-Type Slabs

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**Abstract.** $Sc_3Ni_2Si_3$, $M_r = 336{\cdot}55$, orthorhombic, $oS32$, $Cmcm - f^3c^2$, $a = 3{\cdot}9812\ (7)$, $b = 9{\cdot}688\ (2)$, $c = 13{\cdot}111\ (2)$ Å, $V = 505{\cdot}7\ (1)$ Å$^3$, $Z = 4$, $D_x = 4{\cdot}420$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·71073 Å, $\mu = 11{\cdot}62$ mm$^{-1}$, $F(000) = 644$, $T = 293$ K, $wR = 0{\cdot}041$ for 431 unique reflections. The $Sc_3Ni_2Si_3$ structure with $Hf_3Ni_2Si_3$ type is a member of the structure series with general formula $R_{2+n}T_2M_{2+n}$, in which the structures can be interpreted as an intergrowth of slabs cut from the CrB, $ThCr_2Si_2$ and W types.

**Introduction.** The Sc–Ni–Si phase diagram has been investigated by Bodak, Kotur & Gladyshevskii (1976) and 15 ternary compounds were reported. Among the known structures, many, including the recently determined $Sc_3Ni_2Si_4$ structure (Zhao & Parthé, 1989), can be interpreted as an intergrowth of segments cut from simple parent structures. It was found of interest to study unknown structures and to find out how far this concept is applicable.

**Experimental.** The sample of nominal composition $Sc_2NiSi_2$, reported as a phase of unknown structure in the Sc–Ni–Si phase diagram, was prepared by arc melting under argon atmosphere (Sc 99·99, Ni 99·99 and Si 99·999%). The weight loss was 0·6%. The sample was annealed at 1073 K for 12 d in a silica tube under 300 mm Hg argon atmosphere. A single crystal with regular shape [±(100): 0·032 mm, ±(010): 0·016 mm, ±(001): 0·080 mm] obtained from the annealed sample was mounted on a Philips PW 1100 automatic four-circle diffractometer, Mo $K\alpha$ radiation with graphite monochromator. The cell parameters were refined from $2\theta$ values of 29 reflections (Mo $K\alpha$, $\lambda = 0{\cdot}71073$ Å, $20 < 2\theta < 42°$) using the program *LATCON*. 1830 reflections were collected to $(\sin\theta)/\lambda = 0{\cdot}70$ Å$^{-1}$ ($0 \le h \le 5$, $0 \le k \le 13$, $0 \le l \le 18$ and the anti-reflections) in the $\omega$–$2\theta$ scan mode, yielding 437 unique reflections. Two standard reflections ($33\bar{1}$ and 141) were measured with maximum intensity variations 0·5 and 0·7% respectively. Absorption corrections were made using the program *ABSORB* with max. and min. transmission factors of 0·68871 and 0·48638. The atomic

Table 1. *Atomic positional and displacement parameters for* $Sc_3Ni_2Si_3$ *with* $Hf_3Ni_2Si_3$*-type structure (space group Cmcm)*

The isotropic atomic displacement factors are expressed as $T = \exp[-2\pi^2U(\sin\theta/\lambda)^2]$. E.s.d.'s are given in parentheses.

| | Wyckoff position | $x$ | $y$ | $z$ | $U$(Å$^2$ × 100) |
|---|---|---|---|---|---|
| Sc(1) | 8($f$) | 0 | 0·0834 (2) | 0·1117 (1) | 0·50 (4) |
| Ni(1) | 8($f$) | 0 | 0·2077 (1) | 0·59583 (9) | 0·62 (3) |
| Si(1) | 8($f$) | 0 | 0·3845 (2) | 0·0389 (2) | 0·57 (5) |
| Sc(2) | 4($c$) | 0 | 0·3625 (2) | $\frac{1}{4}$ | 0·49 (5) |
| Si(2) | 4($c$) | 0 | 0·6598 (4) | $\frac{1}{4}$ | 0·56 (8) |

Table 2. *Interatomic distances up to* 3·5 Å *in* $Sc_3Ni_2Si_3$

| | | | |
|---|---|---|---|
| Sc(1)—2Si(2) | 2·792 (2) | Ni(1)—2Sc(1) | 2·847 (1) |
| 2Si(1) | 2·821 (2) | 2Sc(2) | 2·917 (1) |
| Ni(1) | 2·828 (2) | Sc(1) | 2·976 (2) |
| 2Ni(1) | 2·847 (1) | 2Ni(1) | 3·309 (1) |
| 2Si(1) | 2·930 (2) | | |
| Ni(1) | 2·976 (2) | Si(1)—2Ni(1) | 2·306 (1) |
| Si(1) | 3·070 (3) | Si(1) | 2·459 (3) |
| Sc(2) | 3·256 (3) | Ni(1) | 2·461 (3) |
| Sc(1) | 3·346 (2) | Sc(2) | 2·776 (3) |
| 2Sc(2) | 3·439 (2) | 2Sc(1) | 2·821 (2) |
| | | 2Sc(1) | 2·930 (2) |
| Sc(2)—2Si(1) | 2·776 (3) | Sc(1) | 3·070 (3) |
| 2Si(2) | 2·797 (3) | 2Si(1) | 3·435 (3) |
| Si(2) | 2·880 (4) | | |
| 4Ni(1) | 2·917 (1) | Si(2)—2Ni(1) | 2·395 (2) |
| 2Sc(1) | 3·256 (3) | 4Sc(1) | 2·792 (2) |
| 4Sc(1) | 3·439 (2) | 2Sc(2) | 2·797 (3) |
| | | Sc(2) | 2·880 (4) |
| Ni(1)—2Si(1) | 2·306 (1) | | |
| Si(2) | 2·395 (2) | | |
| Si(1) | 2·461 (3) | | |
| Sc(1) | 2·828 (2) | | |

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