

and Al—Ge bonds, respectively. However, as mentioned above, in the other structure-type branch, characterized by the Hf<sub>2</sub>Ni<sub>3</sub>Si<sub>4</sub> structure, there are Si—Si chains along the [100] direction.

As can be seen from Table 3 the unit-cell parameters and cell volumes of the isotypic R<sub>2</sub>Al<sub>3</sub>Ge<sub>4</sub> compounds decrease smoothly with increasing atomic number of the lanthanide elements. This is to be expected from the lanthanide contraction.

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## Structure of 1,3,5,7-Tetrafluorocyclotetraazathiene at 103 K

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**Abstract.** N<sub>4</sub>F<sub>4</sub>S<sub>4</sub>, *M<sub>r</sub>* = 260.26, tetragonal, *P* $\bar{4}$ 2<sub>1</sub>*c*, *a* = 9.090 (3), *c* = 4.199 (3) Å, *V* = 346.9 (5) Å<sup>3</sup>, *Z* = 2, *D<sub>x</sub>* = 2.49 Mg m<sup>-3</sup>, λ(Mo *K*α) = 0.71069 Å, μ = 1.34 mm<sup>-1</sup>, *F*(000) = 256, *T* = 103 (3) K, *R* = 0.0385, *wR* = 0.0384 (inverted direction *R* = 0.052 and *wR* = 0.038) based on 1384 unique reflections with *F* ≥ 3σ(*F*). The extended low-temperature data set yielded precise positional and thermal parameters. The bond lengths for N—S are 1.655 (2) and 1.544 (2) Å, the S—F distance is 1.616 (1) Å. The angles are: S—N—S 123.3 (1), N—S—N 111.7 (1), F—S—N 91.6 (1) and F—S=N 106.2 (1)°.

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**Introduction.** The present structure investigation was performed as part of a detailed study of S—N bonding. An electron density study of S<sub>4</sub>N<sub>4</sub>H<sub>4</sub> (Gregson, Klebe & Fuess, 1988) revealed the distribution of density between the atoms and in the lone-pair regions. Furthermore, the influence of hydrogen bonds on the electron density was stated. Whereas the S—N bonds in S<sub>4</sub>N<sub>4</sub>H<sub>4</sub> are almost equal in length, considerable differences were reported for S<sub>4</sub>N<sub>4</sub>F<sub>4</sub> which, therefore, seemed to be a good candidate for a comparative study. The electron densities were, however, not conclusive and we therefore report here the results of a precise low-temperature X-ray structure refinement.

**Experimental.** The title compound has been prepared by fluorination of S<sub>4</sub>N<sub>4</sub> by AgF<sub>2</sub> in CCl<sub>4</sub> as solvent as described by Glemser, Schröder & Haeseler

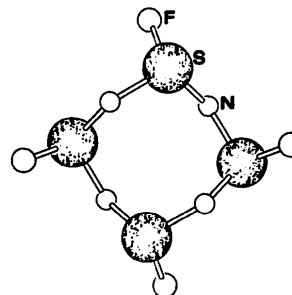
Table 1. Atomic fractional positional coordinates and anisotropic displacement parameters for  $S_4N_4F_4$ 

Temperature factors are given as  $\exp(-2\pi^2\sum_{ij}U_{ij}h_ih_ja_i^*a_j^*)$ .

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
S	0.02657 (3)	0.79006 (3)	0.9135 (9)	0.0094 (1)	0.0078 (1)	0.0090 (1)	0.0008 (1)	-0.0001 (1)	0.0002 (1)
N	0.1275 (1)	0.8834 (1)	0.1717 (3)	0.0100 (4)	0.0100 (4)	0.0106 (4)	-0.0017 (3)	-0.0014 (3)	0.0012 (4)
F	0.3279 (1)	0.9823 (1)	0.8185 (2)	0.0099 (3)	0.0146 (4)	0.0152 (4)	0.0020 (3)	0.0045 (3)	0.0016 (3)

Table 2. Bond lengths (Å) and angles (°) at 103 K and room temperature (Wiegiers &amp; Vos, 1963) (e.s.d.'s in parentheses)

	103 K	Room temperature
N—S	1.655 (2)	1.66 (1)
N=S	1.544 (2)	1.54 (1)
S—F	1.616 (1)	1.602 (6)
S—N—S	123.3 (1)	123.9 (6)
N—S—N	111.7 (1)	111.7 (6)
F—S—N	91.6 (1)	91.5 (4)
F—S=N	106.2 (1)	106.2 (4)

Fig. 1. The molecular geometry of  $S_4N_4F_4$  viewed down [001].

(1955). The material was recrystallized from  $CCl_4$ . The crystal used for intensity measurement was of dimensions  $0.10 \times 0.18 \times 0.40$  mm.  $\omega$ - $2\theta$  scan. The value of the measured density was taken from Wiegiers & Vos (1961). Cell parameters were determined by refinement against 25 centered reflections in the range  $20 < \theta < 30^\circ$ . Correction for absorption was carried out using the program of Alcock (1970) which gave maximum and minimum transmission coefficients of 99.9 and 95.1, respectively. 6047 reflections were measured ( $h$  0 to 24;  $k$  0 to 17;  $l$  -9 to 11) at 103 K on a Nonius CAD-4 diffractometer up to  $(\sin\theta_{\max})/\lambda = 1.361 \text{ \AA}^{-1}$ . After merging ( $R_{\text{int}} = 0.030$ ), there were 1686 unique reflections of which 1669 were greater than zero. 1384 unique reflections with  $F \geq 3\sigma(F)$ . The check reflections (501, 360, 023) showed a decrease of 15.4% by the end of the measurement; the decay was approximately linear and the intensities were adjusted by scaling. The coordinates published by Wiegiers & Vos (1963) were used as the starting model. Refinements were carried out against  $|F_{\text{obs}}|$ ; conventional, high-order and multipole refinements were attempted using the program *MOLLY* (Hansen & Coppens, 1978). The latter two refinements were not successful. We therefore concluded that the high-angle data are not of the desired quality for electron density work due to the decay of the crystal. In the case of the conventional refinement, the parameters refined were scale factor, isotropic extinction parameter and atomic positional and anisotropic displacement parameters for all atoms. After three full-matrix least-squares cycles the maximum shift to e.s.d. ratio was 0.001 with  $\Delta\rho_{\max}$  and  $\Delta\rho_{\min}$  equal to 0.2 and  $-0.5 \text{ e \AA}^{-3}$ , respectively. X-ray scattering factors were taken from Fukamachi (1970) and anomalous-dispersion corrections for S, N and F

from *International Tables for X-ray Crystallography* (1974, Vol. IV). The refinement based on the coordinates of Wiegiers & Vos (1963) converged to  $R = 0.052$ ,  $wR = 0.038$  and  $S = 1.25$ . Inversion of the polar direction reduced the reliability factor considerably ( $R = 0.038$ ,  $wR = 0.0384$  and  $S = 1.17$ ).  $w = 1/\sigma^2(F)$ .

**Discussion.** This study was originally undertaken as part of a charge density determination in sulfur-nitrogen compounds together with  $(SNH)_4$  (Gregson, Klebe & Fuess, 1988). The data for the title compound unfortunately proved to be of insufficient quality successfully to conclude multipole refinements and the high-angle data in particular ( $\sin\theta/\lambda > 0.7 \text{ \AA}^{-1}$ ) were not good enough. Thus, the original idea was abandoned; nonetheless, the data form the most complete and only low-temperature set available and a conventional refinement yields precise values for the atomic coordinates and thus the bond lengths and angles. Table 1\* lists the atomic fractional coordinates [inverted as compared to the previous study of Wiegiers & Vos (1963)]. The absolute structure was established by the use of Roger's  $\eta$ -parameter refinement as implemented in the *SHELXTL* program package (Sheldrick, 1983); the orientation chosen was indicated by  $\eta = 0.97$  (24). Table 2 gives the bond lengths and angles and compares them with the values obtained from the room-temperature study (Wiegiers & Vos, 1963); bond lengths and angles were calculated using the

\* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53631 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

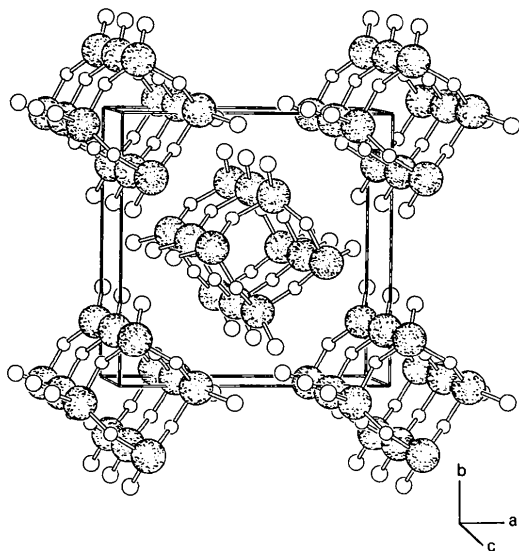


Fig. 2. The packing diagram for  $S_4N_4F_4$ . There are three unit cells along  $z$ .

**BONDLA** link of the **XRAY** suite of programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and include the error contribution from the uncertainties in the unit-cell dimensions. Fig. 1 shows the molecular geometry and Fig. 2 the packing of the molecules in the unit cell; these figures were drawn using the program **SCHAKAL86** (Keller, 1986). Structural information has already been published (Wieggers & Vos, 1961, 1963) and reference to Table 2 shows that within the errors of the

room-temperature study none of the bond angles change on cooling and none of the bonds are more than twice the e.s.d. removed from the room-temperature value. The low-temperature cell dimensions are reduced with respect to their room-temperature values by 0.1 Å in  $a$  (1.1%) and 0.1 Å in  $c$  (2.4%).

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## Structure of Hexaaquanickel(II) Bromate

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**Abstract.**  $[Ni(H_2O)_6](BrO_3)_2$ ,  $M_r = 422.60$ , cubic,  $Pa\bar{3}$ ,  $a = 10.2987(6)$  Å,  $V = 1092.3(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $F(000) = 824$ ,  $D_x = 2.57$  g cm<sup>-3</sup>,  $\lambda(Mo K\alpha) = 0.71073$  Å,  $\mu = 90.79$  cm<sup>-1</sup>,  $T = 296$  K,  $R = 0.024$  for 360 unique reflections having  $I > \sigma_I$ . The single type of nickel ion is coordinated by six water-molecule O atoms, each at an observed distance of 2.061(2) Å, in an almost regular octahedral array.

The single type of bromate ion has an observed Br—O bond length of 1.655(2) Å and O—Br—O bond angle 104.25(9)°. Both the nickel—oxygen complex and the bromate ion were found to manifest rigid-body behavior. The Ni—O distance corrected for rigid-body motion is 2.065 Å, while the corrected Br—O bond length is 1.663 Å. Location and refinement of the two inequivalent H atoms permitted a detailed analysis of the hydrogen bonding, which occurs principally between the oxygen octa-

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