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## Structure Reports

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# Tris(1,2-diaminoethane)nickel(II) hexafluoridosilicate

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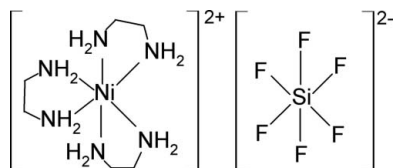
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 Key indicators: single-crystal X-ray study;  $T = 291$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.027;  $wR$  factor = 0.064; data-to-parameter ratio = 16.8.

The ionic title complex,  $[\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_3](\text{SiF}_6)$ , is built up of  $[\text{Ni}(\text{en})_3]^{2+}$  complex cations ( $\text{en} = 1,2$ -diaminoethane) and hexafluoridosilicate anions. Single crystals of the title complex were isolated from an aqueous–ethanolic  $\text{Ni}^{2+}$ – $\text{en}$ – $\text{SiF}_6^{2-}$  system. The Ni(II) and Si atoms are each located on a special position with site symmetry 3.2. The Ni(II) atom coordination sphere is octahedrally deformed, being coordinated by three chelating diamine ligands with an Ni–N distance of 2.1233 (18) Å. The crystal packing of the respective ions corresponds to the structure type of the hexagonal form of BN. Beside ionic forces, the packing is governed by N–H...F hydrogen bonds, which lead to the formation of hydrophobic channels running along the  $6_3$  screw axis. The structure was refined as an inversion twin [0.49 (3): 0.51 (3)].

## Related literature

For the hexafluoridosilicate anion acting as simple counterion, see: Li *et al.* (2009). For two nickel(II) complexes containing the hexafluoridosilicate anion as counter-ion, see: Spek *et al.* (1988); Wu *et al.* (2008). For complexes containing the  $[\text{Ni}(\text{en})_3]^{2+}$  complex cation and hexafluorido-type anions, see: Pan *et al.* (2005); Ribas *et al.* (1998); James *et al.* (1998); Contakes *et al.* (2000).



## Experimental

### Crystal data

 $[\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_3](\text{SiF}_6)$   
 $M_r = 381.11$   
 Hexagonal,  $P6_322$   
 $a = 9.1670$  (9) Å  
 $c = 9.763$  (1) Å  
 $V = 710.51$  (12) Å<sup>3</sup>
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 1.52$  mm<sup>-1</sup>  
 $T = 291$  K  
 $0.42 \times 0.21 \times 0.15$  mm

### Data collection

 Oxford Diffraction Xcalibur diffractometer with Sapphire2 detector  
 Absorption correction: numerical [Clark & Reid (1995) in *CrysAlis*
 $PRO$  (Oxford Diffraction, 2009)  
 $T_{\min} = 0.834$ ,  $T_{\max} = 0.859$   
 8628 measured reflections  
 554 independent reflections  
 489 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.050$ 

### Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.027$   
 $wR(F^2) = 0.064$   
 $S = 1.07$   
 554 reflections  
 33 parameters  
 H-atom parameters constrained

 $\Delta\rho_{\max} = 0.68$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.19$  e Å<sup>-3</sup>  
 Absolute structure: Flack (1983), 89  
 Friedel pairs  
 Flack parameter: 0.49 (3)

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{F1}^{\text{i}}$	0.90	2.30	3.137 (2)	154
$\text{N1}-\text{H1}\cdots\text{F1}^{\text{ii}}$	0.90	2.48	3.235 (2)	142
$\text{N1}-\text{H2}\cdots\text{F1}^{\text{iii}}$	0.90	2.25	3.137 (2)	167

 Symmetry codes: (i)  $y, x, -z$ ; (ii)  $-x + 1, -x + y + 1, -z$ ; (iii)  $-x + y + 1, -x + 1, z$ .

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Crystal Impact, 2007); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Slovak grant agencies VEGA (grant 1/0089/09) and APVV (contract Nos. APVV-VVCE-0058–07 and APVV-0006–07). Support from P. J. Šafárik University (VVGs PF 19/2010/CH) is also gratefully acknowledged. We thank student M. Adam for help with the experimental work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2212).

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## supporting information

*Acta Cryst.* (2010). E66, m1451–m1452 [https://doi.org/10.1107/S1600536810041553]

**Tris(1,2-diaminoethane)nickel(II) hexafluorosilicate****Jaroslava Haníková, Juraj Kuchár, Juraj Černák and Giorgio Pelosi****S1. Comment**

The crystal structure of the title complex is ionic and is built up of  $[\text{Ni}(\text{en})_3]^{2+}$  complex cations and  $\text{SiF}_6^{2-}$  anions, as shown in Fig. 1. The Ni<sup>II</sup> atom (site symmetry 32) in the  $[\text{Ni}(\text{en})_3]^{2+}$  complex cation has a slightly deformed octahedral coordination sphere, being coordinated by six nitrogen atoms from three chelate bonded *en* ligands.

As the studied single-crystal was an inversion twin [ratio of the two domains was 0.49 (3):0.51 (3)] both  $\Lambda\delta\delta\delta$  and  $\Delta\lambda\lambda\lambda$  configurations were present in the crystal. In the isostructural  $[\text{Zn}(\text{en})_3]\text{SiF}_6$  complex the cations exhibit  $\Lambda\delta\delta\delta$  absolute configuration (Li *et al.*, 2009). The Ni—N bond lengths of 2.1234 (18) Å (6 ×) corresponds well to the value of 2.1318 (2) Å found in the analogous hexafluoridogermanate complex  $[\text{Ni}(\text{en})_3]\text{GeF}_6$  (Pan *et al.*, 2005). The positive charge of the complex cation is compensated for by the non-coordinated  $\text{SiF}_6^{2-}$  anion, that exhibits almost ideal octahedral symmetry. The Si atom is located on the 3-fold axis (site symmetry 32). The Si—F bond length of 1.681 (2) Å (6 ×) is in line with the value of 1.6942 (15) Å found in  $[\text{Zn}(\text{en})_3]\text{SiF}_6$  (Li *et al.*, 2009).

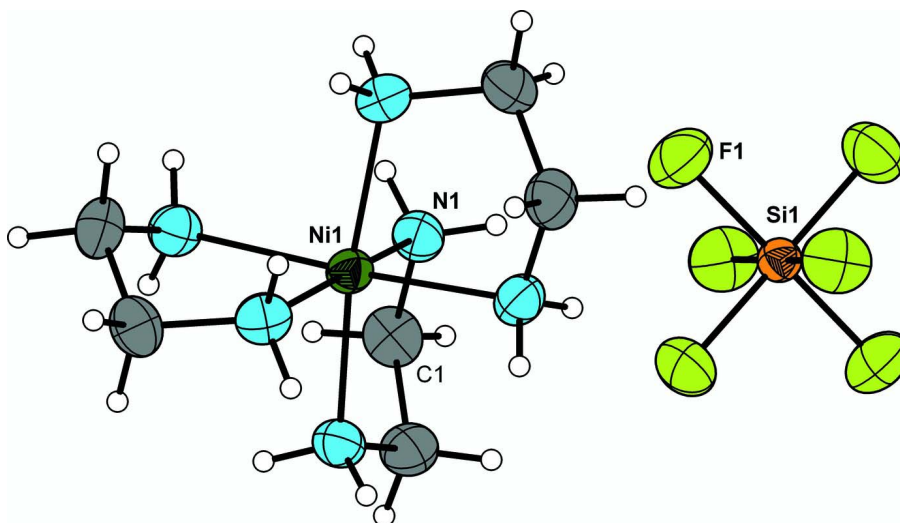
In the crystal the packing of the respective ions corresponds to the hexagonal structure of BN, with a Ni⋯Si distance of 5.2927 (4) Å within the hexagonal plane and a Ni⋯Si distance of 4.8815 (5) Å between the planes (Fig. 2). To the packing forces contribute also N—H⋯F type hydrogen bonds with N⋯F distances in the range 3.137 (2) - 3.235 (2) Å (Table 1, Fig. 3). Some of the hydrogen bonds are three-centered with two fluoro acceptors. The observed geometric parameters associated with the hydrogen bonds correspond to those in  $[\text{Zn}(\text{en})_3]\text{SiF}_6$  (Li *et al.*, 2009) where the N⋯F distances range from 3.113 (3) - 3.239 (3) Å. The hydrogen bonding leads to the formation of hydrophobic channels running along the 6<sub>3</sub> screw axis (Fig. 4a and 4 b), as was already observed in the  $\text{GeF}_6$  analog (Pan *et al.*, 2005).

**S2. Experimental**

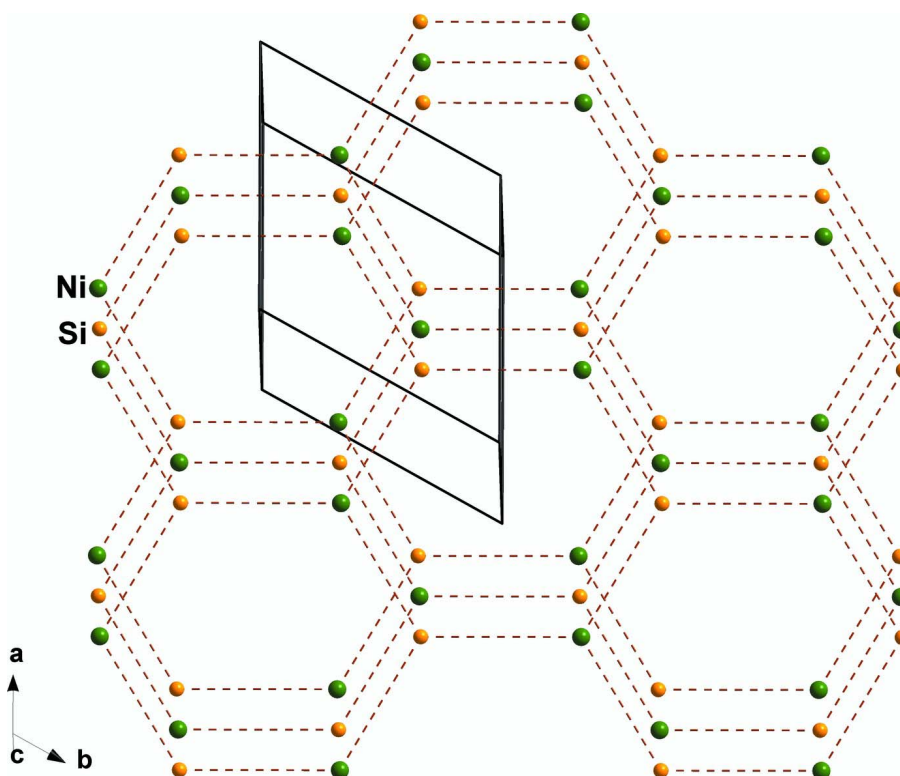
To a solution of 0.24 g of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (1 mmol) in 10 cm<sup>3</sup> of water:ethanol mixture (1:1 in vol) we added successively 0.27 cm<sup>3</sup> of 1,2-diaminoethane (*en*) (4 mmol) and 0.18 g of  $(\text{NH}_4)\text{SiF}_6$  (1 mmol), dissolved in 10 cm<sup>3</sup> of water:ethanol mixture (1:1 / v:v), under constant stirring. The dark pink solution that formed was filtered and left aside for crystallization at RT. Within a few days light-pink prisms were formed. They were collected by filtration and subsequently recrystallized from a water:ethanol mixture to give crystals suitable for X-ray diffraction analysis. Anal. [%], calculated for  $\text{Ni}_1\text{C}_6\text{N}_6\text{H}_{24}\text{Si}_1\text{F}_6$ : C, 18.92; H, 6.35; N, 22.05. Found: C, 18.97; H, 5.76; N, 14.55. IR (KBr pellets, FT—IR Avatar 330 (ThermoNicolet), cm<sup>-1</sup>): 3300m; 3170m; 2954m; 2925m; 2887m; 1598 s; 1456 s; 1385w; 1370w; 1125 s; 1064 s; 717 s; 500 s; 478m. Thermal Analysis (TA Instrument, air atmosphere): the complex was thermally stable up to 501 K and decomposed in one step in the temperature range 501 - 693 K.

**S3. Refinement**

The structure was refined as an inversion twin [0.49 (3): 0.51 (3)]. All the H atoms were included in calculated positions and treated as riding atoms: N—H = 0.90 Å, C—H = 0.97 Å, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent N- or C-atom})$ .

**Figure 1**

Molecular structure of the title ionic complex along with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

**Figure 2**

Packing of the ions in the title complex leading to the hexagonal BN structure type.

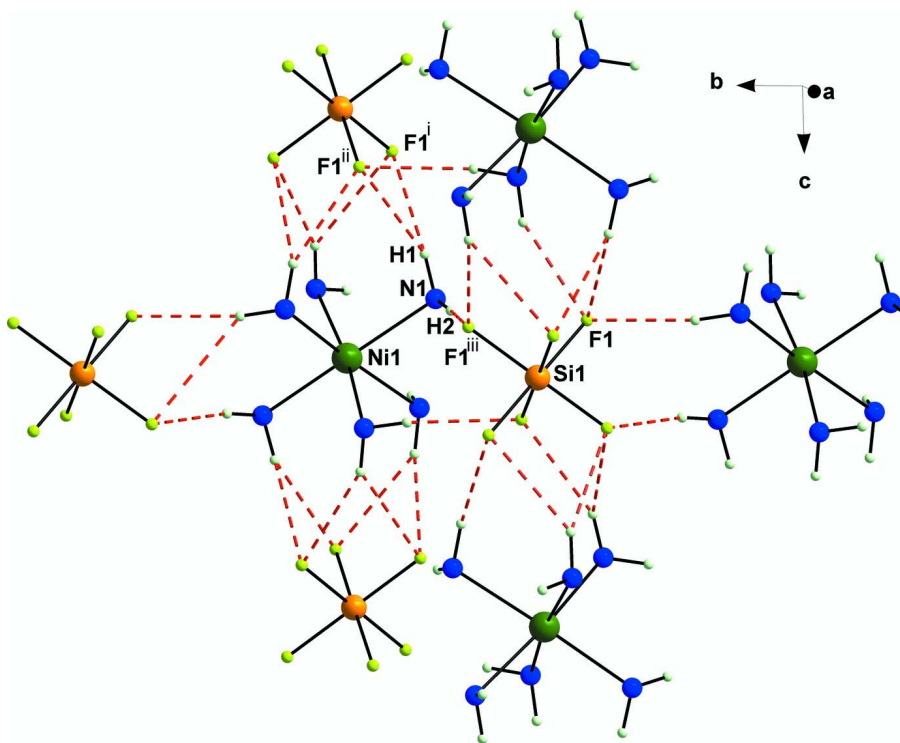
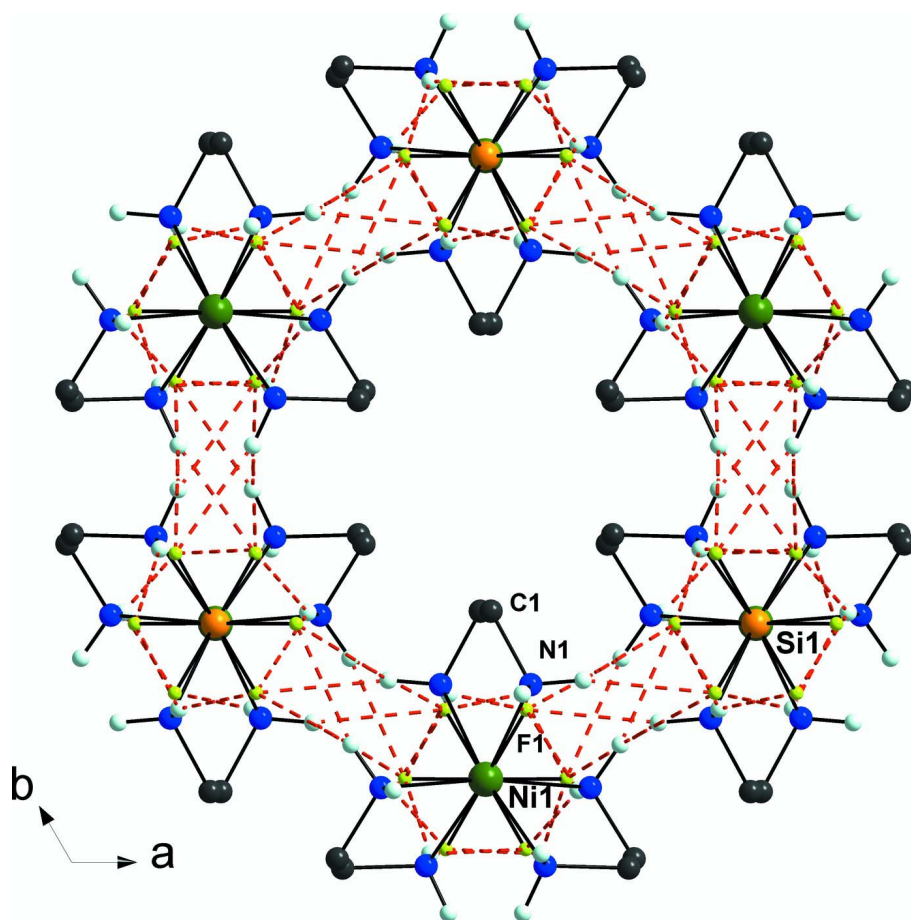


Figure 3

Detailed view of the hydrogen bonding scheme (dashed lines) in the title complex. For the sake of clarity only the  $\text{NH}_2$  groups of the *en* ligands are shown. Symmetry codes: (i) =  $y, x, -z$ ; (ii) =  $1 - x, 1 - x + y, z$ ; (iii) =  $1 - x + y, 1 - x, z$ .



**Figure 4**

Formation of hydrophobic pseudo-channels inside the hydrogen bonded complex cations and anions running along the  $6_3$  screw axis: view of one channel. Hydrogen atoms bonded to the carbon atoms are omitted for the sake of clarity.



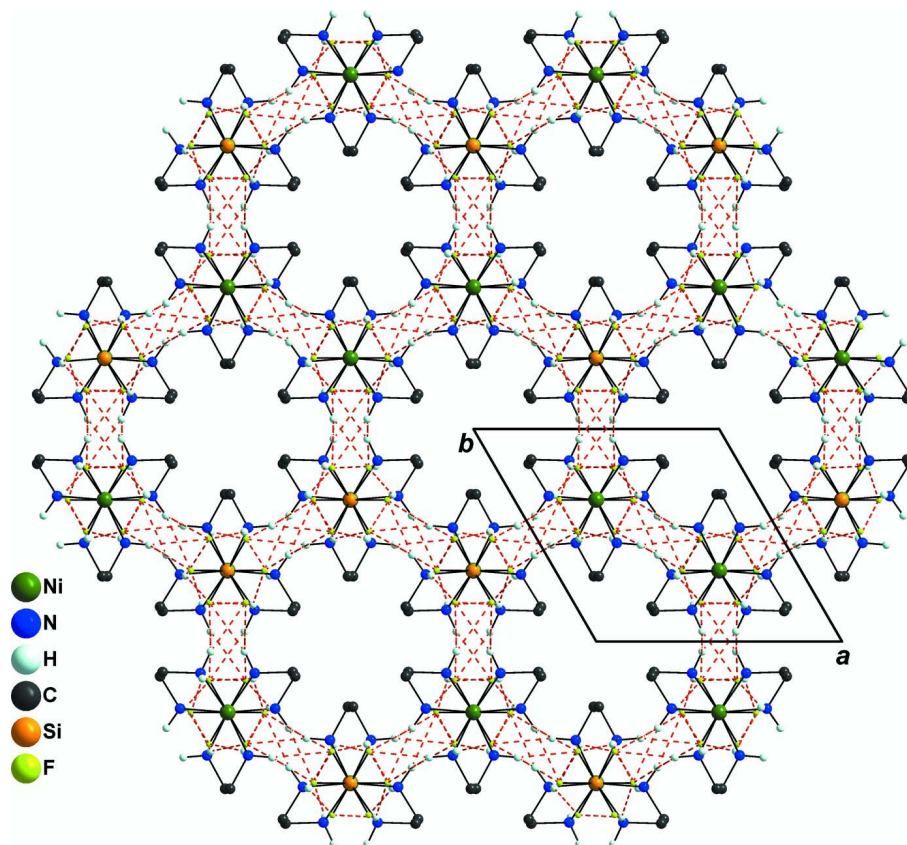


Figure 5

Formation of hydrophobic pseudo-channels inside the hydrogen bonded complex cations and anions running along the  $6_3$  screw axis: arrangement of the neighbouring channels. Hydrogen atoms bonded to the carbon atoms are omitted for the sake of clarity.

### Tris(1,2-diaminoethane)nickel(II) hexafluorosilicate

#### Crystal data

$[\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_3](\text{SiF}_6)$

$M_r = 381.11$

Hexagonal,  $P6_322$

Hall symbol: P 6c 2c

$a = 9.1670$  (9) Å

$c = 9.763$  (1) Å

$V = 710.51$  (12) Å<sup>3</sup>

$Z = 2$

$F(000) = 396$

$D_x = 1.781$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71069$  Å

Cell parameters from 8628 reflections

$\theta = 2.6\text{--}27.4^\circ$

$\mu = 1.52$  mm<sup>-1</sup>

$T = 291$  K

Prism, pink

$0.42 \times 0.21 \times 0.15$  mm

#### Data collection

Oxford Diffraction Xcalibur

diffractometer with Sapphire2 detector

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 8.3438 pixels mm<sup>-1</sup>

$\omega$  scans

Absorption correction: numerical

[Clark & Reid (1995) in *CrysAlis PRO* (Oxford Diffraction, 2009)]

$T_{\min} = 0.834$ ,  $T_{\max} = 0.859$

8628 measured reflections

554 independent reflections

489 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.050$   
 $\theta_{\text{max}} = 27.4^\circ$ ,  $\theta_{\text{min}} = 2.6^\circ$   
 $h = -11 \rightarrow 11$

$k = -11 \rightarrow 11$   
 $l = -12 \rightarrow 12$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.027$   
 $wR(F^2) = 0.064$   
 $S = 1.07$   
 554 reflections  
 33 parameters  
 0 restraints  
 Primary atom site location: structure-invariant  
 direct methods  
 Secondary atom site location: difference Fourier  
 map

Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0413P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.68 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.19 \text{ e } \text{\AA}^{-3}$   
 Absolute structure: Flack (1983), 89 Friedel  
 pairs  
 Absolute structure parameter: 0.49 (3)

*Special details*

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) etc. and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.3333	0.6667	0.2500	0.02783 (19)
N1	0.3156 (2)	0.4642 (2)	0.13146 (17)	0.0368 (4)
H1	0.3098	0.4839	0.0419	0.044*
H2	0.4076	0.4547	0.1449	0.044*
C1	0.1634 (3)	0.3071 (2)	0.1729 (2)	0.0432 (5)
H5	0.1732	0.2107	0.1455	0.052*
H6	0.0651	0.2992	0.1284	0.052*
Si1	0.6667	0.3333	0.2500	0.0267 (3)
F1	0.51790 (19)	0.18375 (19)	0.14983 (14)	0.0550 (4)

*Atomic displacement parameters ( $\text{\AA}^2$ )*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ni1	0.0286 (2)	0.0286 (2)	0.0262 (3)	0.01432 (11)	0.000	0.000
N1	0.0401 (10)	0.0429 (11)	0.0319 (9)	0.0241 (9)	0.0020 (8)	-0.0013 (8)
C1	0.0428 (16)	0.0339 (10)	0.0489 (12)	0.0162 (13)	-0.0016 (11)	-0.0079 (8)
Si1	0.0270 (3)	0.0270 (3)	0.0262 (5)	0.01349 (17)	0.000	0.000
F1	0.0521 (8)	0.0495 (8)	0.0489 (8)	0.0145 (6)	-0.0110 (7)	-0.0086 (7)



Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Ni1—Ni1 <sup>i</sup>	2.1233 (18)	C1—C1 <sup>iv</sup>	1.515 (4)
Ni1—Ni1 <sup>ii</sup>	2.1233 (18)	C1—H5	0.9700
Ni1—Ni1 <sup>iii</sup>	2.1233 (18)	C1—H6	0.9700
Ni1—Ni1 <sup>iv</sup>	2.1233 (18)	Si1—F1 <sup>vi</sup>	1.6812 (14)
Ni1—N1	2.1233 (18)	Si1—F1 <sup>vii</sup>	1.6812 (14)
Ni1—N1 <sup>v</sup>	2.1233 (18)	Si1—F1	1.6812 (14)
N1—C1	1.475 (2)	Si1—F1 <sup>v</sup>	1.6812 (14)
N1—H1	0.9000	Si1—F1 <sup>viii</sup>	1.6812 (14)
N1—H2	0.9000	Si1—F1 <sup>ix</sup>	1.6812 (14)
N1 <sup>i</sup> —Ni1—N1 <sup>ii</sup>	81.62 (9)	N1—C1—C1 <sup>iv</sup>	109.08 (16)
N1 <sup>i</sup> —Ni1—N1 <sup>iii</sup>	93.12 (7)	N1—C1—H5	109.9
N1 <sup>ii</sup> —Ni1—N1 <sup>iii</sup>	92.62 (10)	C1 <sup>iv</sup> —C1—H5	109.9
N1 <sup>i</sup> —Ni1—N1 <sup>iv</sup>	92.62 (10)	N1—C1—H6	109.9
N1 <sup>ii</sup> —Ni1—N1 <sup>iv</sup>	93.12 (7)	C1 <sup>iv</sup> —C1—H6	109.9
N1 <sup>iii</sup> —Ni1—N1 <sup>iv</sup>	172.42 (9)	H5—C1—H6	108.3
N1 <sup>i</sup> —Ni1—N1	93.12 (7)	F1 <sup>vi</sup> —Si1—F1 <sup>vii</sup>	90.75 (10)
N1 <sup>ii</sup> —Ni1—N1	172.42 (9)	F1 <sup>vi</sup> —Si1—F1	90.12 (10)
N1 <sup>iii</sup> —Ni1—N1	93.12 (6)	F1 <sup>vii</sup> —Si1—F1	89.57 (7)
N1 <sup>iv</sup> —Ni1—N1	81.62 (9)	F1 <sup>vi</sup> —Si1—F1 <sup>v</sup>	89.57 (7)
N1 <sup>i</sup> —Ni1—N1 <sup>v</sup>	172.42 (9)	F1 <sup>vii</sup> —Si1—F1 <sup>v</sup>	90.12 (10)
N1 <sup>ii</sup> —Ni1—N1 <sup>v</sup>	93.12 (7)	F1—Si1—F1 <sup>v</sup>	179.56 (10)
N1 <sup>iii</sup> —Ni1—N1 <sup>v</sup>	81.62 (9)	F1 <sup>vi</sup> —Si1—F1 <sup>viii</sup>	89.57 (7)
N1 <sup>iv</sup> —Ni1—N1 <sup>v</sup>	93.12 (6)	F1 <sup>vii</sup> —Si1—F1 <sup>viii</sup>	179.56 (10)
N1—Ni1—N1 <sup>v</sup>	92.62 (10)	F1—Si1—F1 <sup>viii</sup>	90.75 (10)
C1—N1—Ni1	108.97 (13)	F1 <sup>v</sup> —Si1—F1 <sup>viii</sup>	89.57 (7)
C1—N1—H1	109.9	F1 <sup>vi</sup> —Si1—F1 <sup>ix</sup>	179.56 (10)
Ni1—N1—H1	109.9	F1 <sup>vii</sup> —Si1—F1 <sup>ix</sup>	89.57 (7)
C1—N1—H2	109.9	F1—Si1—F1 <sup>ix</sup>	89.57 (7)
Ni1—N1—H2	109.9	F1 <sup>v</sup> —Si1—F1 <sup>ix</sup>	90.75 (10)
H1—N1—H2	108.3	F1 <sup>viii</sup> —Si1—F1 <sup>ix</sup>	90.12 (10)
N1 <sup>i</sup> —Ni1—N1—C1	-78.08 (18)	N1 <sup>v</sup> —Ni1—N1—C1	106.88 (16)
N1 <sup>iii</sup> —Ni1—N1—C1	-171.38 (15)	Ni1—N1—C1—C1 <sup>iv</sup>	-39.4 (3)
N1 <sup>iv</sup> —Ni1—N1—C1	14.11 (12)		

Symmetry codes: (i)  $-x+y, -x+1, z$ ; (ii)  $x, x-y+1, -z+1/2$ ; (iii)  $-y+1, x-y+1, z$ ; (iv)  $-x+y, y, -z+1/2$ ; (v)  $-y+1, -x+1, -z+1/2$ ; (vi)  $-x+y+1, y, -z+1/2$ ; (vii)  $-y+1, x-y, z$ ; (viii)  $x, x-y, -z+1/2$ ; (ix)  $-x+y+1, -x+1, z$ .

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ F1 <sup>x</sup>	0.90	2.30	3.137 (2)	154
N1—H1 $\cdots$ F1 <sup>xi</sup>	0.90	2.48	3.235 (2)	142
N1—H2 $\cdots$ F1 <sup>ix</sup>	0.90	2.25	3.137 (2)	167

Symmetry codes: (ix)  $-x+y+1, -x+1, z$ ; (x)  $y, x, -z$ ; (xi)  $-x+1, -x+y+1, -z$ .