Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

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

Jaroslava Haníková,[a]* Juraj Kuchár,[a] Juraj Černák[a] and Giorgio Pelosi[b]

[a]Department of Inorganic Chemistry, Institute of Chemistry, P. J. Šafárik University, Moyzesova 11, 041 54 Košice, Slovakia, and [b]Dipartimento di Chimica Generale ed Inorganica, Universitá di Parma, Viale della Scienze, 43124 Parma, Italy
Correspondence e-mail: jaroslava.hanikova@student.upjs.sk

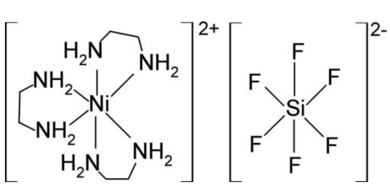
Received 9 September 2010; accepted 14 October 2010

Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.003 Å; R factor = 0.027; wR factor = 0.064; data-to-parameter ratio = 16.8.

The ionic title complex, $[Ni(C_2H_8N_2)_3](SiF_6)$, is built up of $[Ni(en)_3]^{2+}$ complex cations (en = 1,2-diaminoethane) and hexafluoridosilicate anions. Single crystals of the title complex were isolated from an aqueous–ethanolic Ni^{2+}–en–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 counter-ion, 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 $[Ni(en)_3]^{2+}$ 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

$[Ni(C_2H_8N_2)_3](SiF_6)$
M_r = 381.11
Hexagonal, $P6_322$
a = 9.1670 (9) Å
c = 9.763 (1) Å
V = 710.51 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.52 mm^{-1}
T = 291 K
0.42 × 0.21 × 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_{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^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}
Absolute structure: Flack (1983), 89 Friedel pairs
Flack parameter: 0.49 (3)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···F1^{i}	0.90	2.30	3.137 (2)	154
N1—H1···F1^{ii}	0.90	2.48	3.235 (2)	142
N1—H2···F1^{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).

References

Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A**51**, 887–897.
Contakes, S. M., Klausmeyer, K. K. & Rauchfuss, T. B. (2000). *Inorg. Chem.* **39**, 2069–2075.
Crystal Impact (2007). *DIAMOND*. Crystal Impact, Bonn, Germany.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
James, M., Kawaguchi, H. & Tatsumi, K. (1998). *Polyhedron*, **17**, 1571–1577.
Li, Y., Shi, Q., Slawin, A. M. Z., Woollins, J. D. & Dong, J. (2009). *Acta Cryst.* E**65**, m1522.
Oxford Diffraction (2009). *CrysAlis PRO*. Oxford Diffraction Ltd, Abingdon, England.

Pan, Q.-H., Li, J.-Y., Yu, J.-H., Wang, Y., Fang, Q.-R. & Xu, R.-R. (2005). *Gaodeng Xuexiao Huaxue Xuebao*, **26**, 2199–2200.
Ribas, J., Monfort, M., Resino, I., Ghosh, B. K., Solans, X. & Font-Bardia, M. (1998). *Polyhedron*, **17**, 1735–1739.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L., Duisenberg, A. J. M., Bouwman, E., Driessen, W. L. & Reedijk, J. (1988). *Acta Cryst.* C**44**, 1569–1572.
Wu, L.-P., Zhao, S.-M., Zhang, G.-F. & Ng, S. W. (2008). *Acta Cryst.* E**64**, m802.

supplementary materials

Acta Cryst. (2010). E**66**, m1451-m1452 [**doi:10.1107/S1600536810041553**]

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

J. Haníková, J. Kuchár, J. Cernák and G. Pelosi

Comment

The crystal structure of the title complex is ionic and is built up of $[Ni(en)_3]^{2+}$ complex cations and SiF_6^{2-} anions, as shown in Fig. 1. The Ni^{II} atom (site symmetry 32) in the $[Ni(en)_3]^{2+}$ 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 Λδδδ and Δλλλ configurations were present in the crystal. In the isostructural $[Zn(en))_3]SiF_6$ complex the cations exhibit Λδδδ 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 $[Ni(en)_3]GeF_6$ (Pan *et al.*, 2005). The positive charge of the complex cation is compensated for by the non-coordinated 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 $[Zn(en)_3]SiF_6$ (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 fluorido acceptors. The observed geometric parameters associated with the hydrogen bonds correspond to those in $Zn(en))_3]SiF_6$ (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_3 screw axis (Fig. 4a and 4 b), as was already observed in the GeF_6 analog (Pan *et al.*, 2005).

Experimental

To a solution of 0.24 g of $NiCl_2.6H_2O$ (1 mmol) in 10 cm^3 of water:ethanol mixture (1:1 in vol) wre added successively 0.27 cm^3 of 1,2-diaminoethane (en) (4 mmol) and 0.18 g of $(NH_4)SiF_6$ (1 mmol), dissolved in 10 cm^3 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 $Ni_1C_6N_6H_{24}Si_1F_6$: 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^{-1}): 3300*m*; 3170*m*; 2954*m*; 2925*m*; 2887*m*; 1598 s; 1456 s; 1385w; 1370w; 1125 s; 1064 s, 717 s; 500 s; 478*m*. 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.

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_{iso}(H) = 1.2U_{eq}(parent N– or C-atom).

Figures

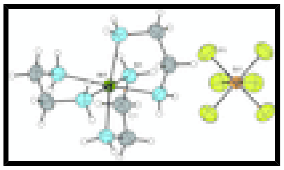


Fig. 1. Molecular structure of the title ionic complex along with the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

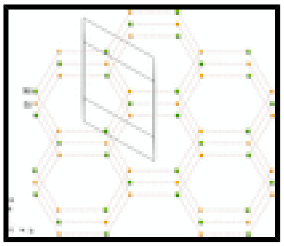


Fig. 2. Packing of the ions in the title complex leading to the hexagonal BN structure type.

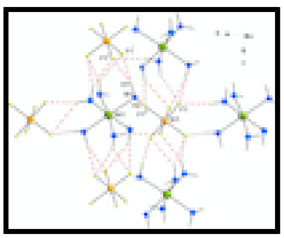


Fig. 3. Detailed view of the hydrogen bonding scheme (dashed lines) in the title complex. For the sake of clarity only the NH_2 groups of the *en* ligands are shown. Symmetry codes: (i) = *y*, *x*, -*z*; (ii) = 1 - *x*, 1 - *x* + *y*, *z*; (iii) = 1 - *x* + *y*, 1 - *x*, *z*.

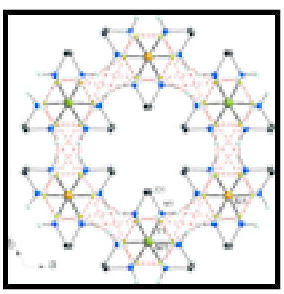


Fig. 4. Formation of hydrophobic pseudo-channels inside the hydrogen bonded complex cations and anions running along the 6_3 screw axis: view of one channel. Hydrogen atoms bonded to the carbon atoms are omitted for the sake of clarity.

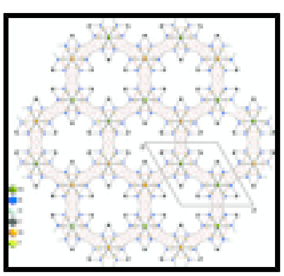


Fig. 5. Formation of hydrophobic pseudo-channels inside the hydrogen bonded complex cations and anions running along the 6_3 screw axis: arrangement of the neighbouring channels. Hydrogen atoms bonded to the carbon atoms are omitted for the sake of clarity.

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

Crystal data

$[Ni(C_2H_8N_2)_3](SiF_6)$	D_x = 1.781 Mg m^{-3}
M_r = 381.11	Mo $K\alpha$ radiation, λ = 0.71069 Å
Hexagonal, $P6_322$	Cell parameters from 8628 reflections
Hall symbol: P 6c 2c	θ = 2.6–27.4°
a = 9.1670 (9) Å	μ = 1.52 mm^{-1}
c = 9.763 (1) Å	T = 291 K
V = 710.51 (12) Å^3	Prism, pink
Z = 2	0.42 × 0.21 × 0.15 mm
F(000) = 396	

Data collection

Oxford Diffraction Xcalibur diffractometer with Sapphire2 detector	554 independent reflections
Radiation source: fine-focus sealed tube	489 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.050
Detector resolution: 8.3438 pixels mm^{-1}	θ_{max} = 27.4°, θ_{min} = 2.6°
ω scans	$h = -11 \rightarrow 11$
Absorption correction: numerical [Clark & Reid (1995) in *CrysAlis PRO* (Oxford Diffraction, 2009)]	$k = -11 \rightarrow 11$
T_{min} = 0.834, T_{max} = 0.859	$l = -12 \rightarrow 12$
8628 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.027	H-atom parameters constrained
$wR(F^2)$ = 0.064	$w = 1/[\sigma^2(F_o^2) + (0.0413P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.07	$(\Delta/\sigma)_{max}$ < 0.001
554 reflections	$\Delta\rho_{max}$ = 0.68 e Å^{-3}
33 parameters	$\Delta\rho_{min}$ = −0.19 e Å^{-3}
0 restraints	Absolute structure: Flack (1983), 89 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack 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 (Å^2)

	x	y	z	U_{iso}*/U_{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 (Å^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 (Å, °)

Ni1—N1^{i}	2.1233 (18)	C1—C1^{iv}	1.515 (4)
Ni1—N1^{ii}	2.1233 (18)	C1—H5	0.9700
Ni1—N1^{iii}	2.1233 (18)	C1—H6	0.9700
Ni1—N1^{iv}	2.1233 (18)	Si1—F1^{vi}	1.6812 (14)
Ni1—N1	2.1233 (18)	Si1—F1^{vii}	1.6812 (14)
Ni1—N1^{v}	2.1233 (18)	Si1—F1	1.6812 (14)
N1—C1	1.475 (2)	Si1—F1^{v}	1.6812 (14)
N1—H1	0.9000	Si1—F1^{viii}	1.6812 (14)
N1—H2	0.9000	Si1—F1^{ix}	1.6812 (14)

$N1^{i}$—Ni1—$N1^{ii}$	81.62 (9)	N1—C1—$C1^{iv}$	109.08 (16)
$N1^{i}$—Ni1—$N1^{iii}$	93.12 (7)	N1—C1—H5	109.9
$N1^{ii}$—Ni1—$N1^{iii}$	92.62 (10)	$C1^{iv}$—C1—H5	109.9
$N1^{i}$—Ni1—$N1^{iv}$	92.62 (10)	N1—C1—H6	109.9
$N1^{ii}$—Ni1—$N1^{iv}$	93.12 (7)	$C1^{iv}$—C1—H6	109.9
$N1^{iii}$—Ni1—$N1^{iv}$	172.42 (9)	H5—C1—H6	108.3
$N1^{i}$—Ni1—N1	93.12 (7)	$F1^{vi}$—Si1—$F1^{vii}$	90.75 (10)
$N1^{ii}$—Ni1—N1	172.42 (9)	$F1^{vi}$—Si1—F1	90.12 (10)
$N1^{iii}$—Ni1—N1	93.12 (6)	$F1^{vii}$—Si1—F1	89.57 (7)
$N1^{iv}$—Ni1—N1	81.62 (9)	$F1^{vi}$—Si1—$F1^{v}$	89.57 (7)
$N1^{i}$—Ni1—$N1^{v}$	172.42 (9)	$F1^{vii}$—Si1—$F1^{v}$	90.12 (10)
$N1^{ii}$—Ni1—$N1^{v}$	93.12 (7)	F1—Si1—$F1^{v}$	179.56 (10)
$N1^{iii}$—Ni1—$N1^{v}$	81.62 (9)	$F1^{vi}$—Si1—$F1^{viii}$	89.57 (7)
$N1^{iv}$—Ni1—$N1^{v}$	93.12 (6)	$F1^{vii}$—Si1—$F1^{viii}$	179.56 (10)
N1—Ni1—$N1^{v}$	92.62 (10)	F1—Si1—$F1^{viii}$	90.75 (10)
C1—N1—Ni1	108.97 (13)	$F1^{v}$—Si1—$F1^{viii}$	89.57 (7)
C1—N1—H1	109.9	$F1^{vi}$—Si1—$F1^{ix}$	179.56 (10)
Ni1—N1—H1	109.9	$F1^{vii}$—Si1—$F1^{ix}$	89.57 (7)
C1—N1—H2	109.9	F1—Si1—$F1^{ix}$	89.57 (7)
Ni1—N1—H2	109.9	$F1^{v}$—Si1—$F1^{ix}$	90.75 (10)
H1—N1—H2	108.3	$F1^{viii}$—Si1—$F1^{ix}$	90.12 (10)
$N1^{i}$—Ni1—N1—C1	−78.08 (18)	$N1^{v}$—Ni1—N1—C1	106.88 (16)
$N1^{iii}$—Ni1—N1—C1	−171.38 (15)	Ni1—N1—C1—$C1^{iv}$	−39.4 (3)
$N1^{iv}$—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 (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···$F1^{x}$	0.90	2.30	3.137 (2)	154
N1—H1···$F1^{xi}$	0.90	2.48	3.235 (2)	142
N1—H2···$F1^{ix}$	0.90	2.25	3.137 (2)	167

Symmetry codes: (x) *y*, *x*, −*z*; (xi) −*x*+1, −*x*+*y*+1, −*z*; (ix) −*x*+*y*+1, −*x*+1, *z*.

Fig. 1

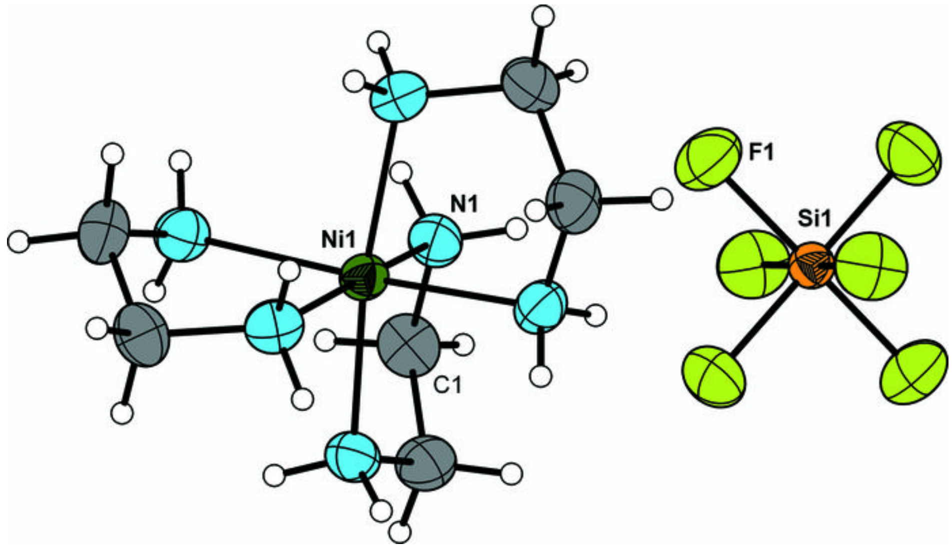


Fig. 2

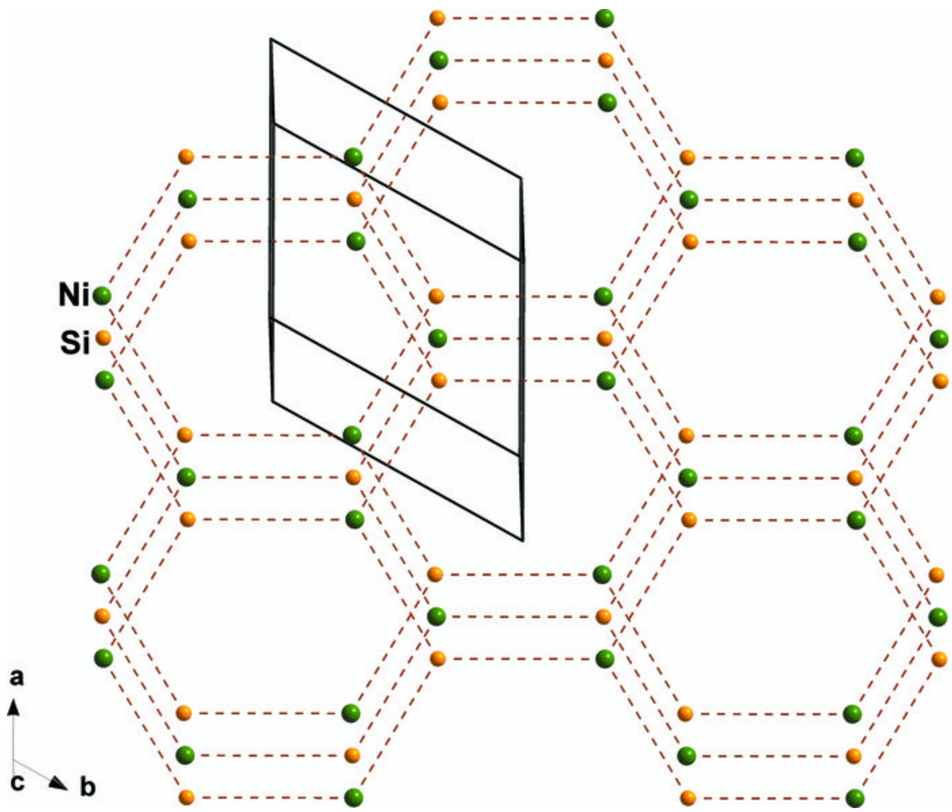


Fig. 3

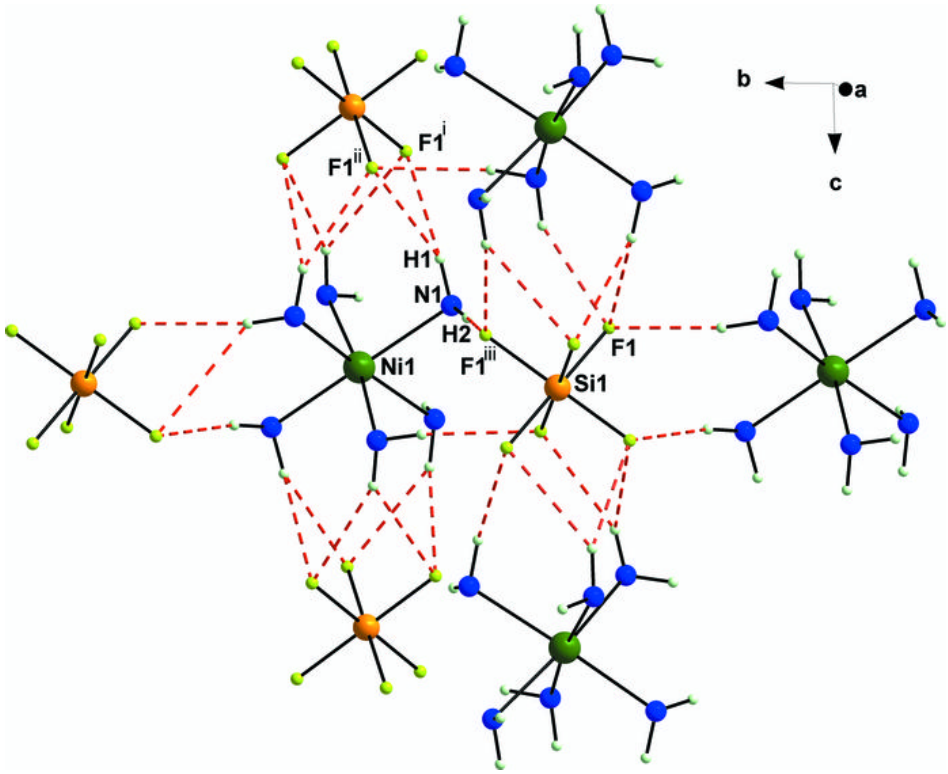


Fig. 4

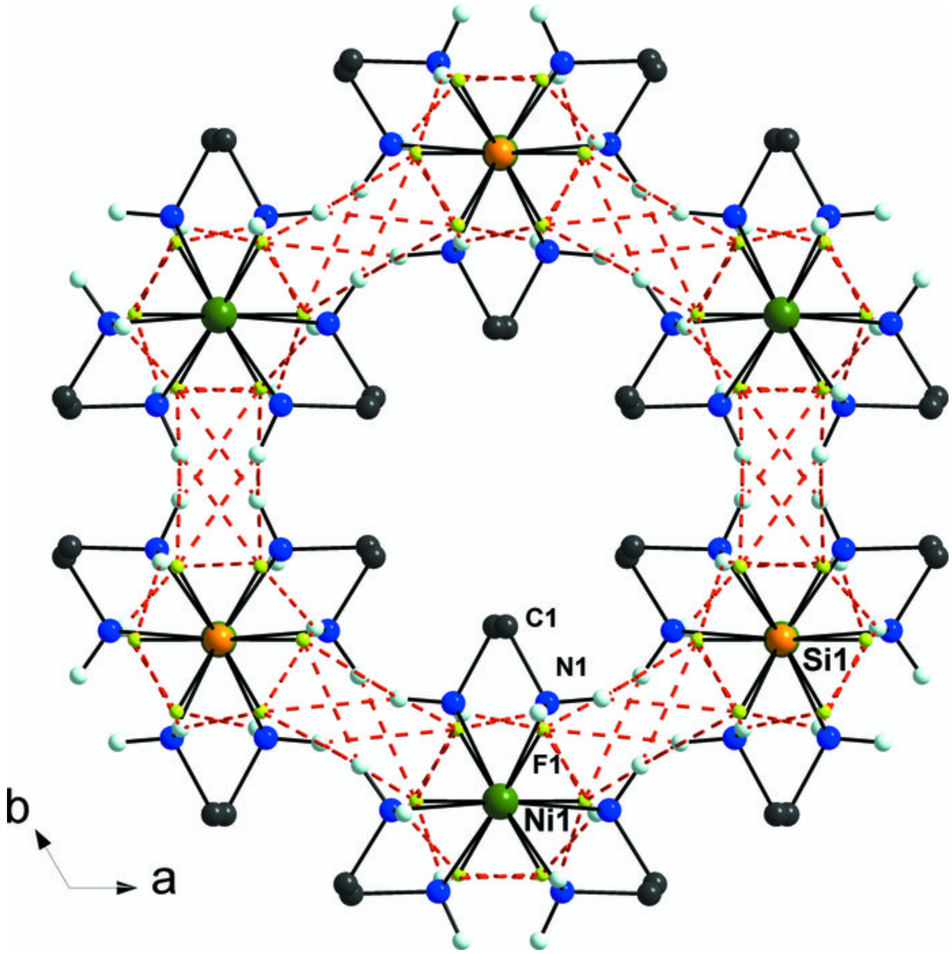


Fig. 5