

Crystal structure of the one-dimensional coordination polymer formed by the macrocyclic $[\text{Ni}(\text{cyclam})]^{2+}$ cation and the dianion of diphenylsilanediylbis(4-benzoic acid)

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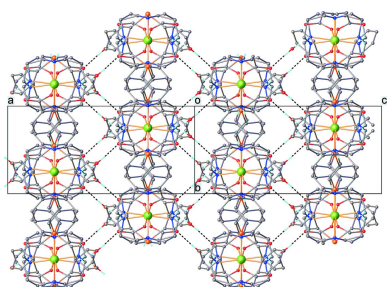
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The asymmetric unit of the title compound, *catena*-poly[[[(1,4,8,11-tetraazacyclotetradecane- $\kappa^4\text{N}^1, \text{N}^4, \text{N}^8, \text{N}^{11}$)nickel(II)]- μ -4,4'-(diphenylsilanediyl)dibenzoato- $\kappa^2\text{O}:\text{O}'$] sesquihydrate], $\{[\text{Ni}(\text{C}_{26}\text{H}_{18}\text{O}_4\text{Si})(\text{C}_{10}\text{H}_{24}\text{N}_4)] \cdot 1.5\text{H}_2\text{O}\}_n$, consists of the halves of the centrosymmetric macrocyclic cation and the C_2 -symmetric dicarboxylate dianion and of the water molecule of crystallization. The Ni^{2+} ion is coordinated by the four secondary N atoms of the macrocyclic ligand characterized by the most energetically favourable *trans*-III conformation and two mutually *trans* O atoms of the carboxylate, forming a slightly tetragonally elongated *trans*- N_4O_2 octahedron. The crystals are composed of parallel polymeric chains of the macrocyclic cations linked by the anions of the acid running along the [101] direction. Each polymeric chain is bonded to four neighbouring ones *via* water molecules providing $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds to the non-coordinated carboxyl O atoms to form a three-dimensional supra-molecular network.

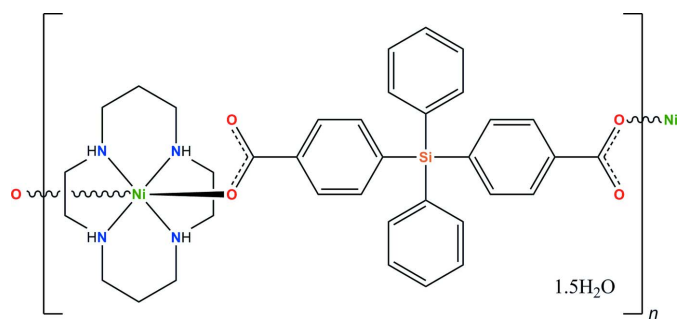
1. Chemical context

Aromatic carboxylates are the most popular ligands employed as linkers joining metal-containing fragments (secondary building units, SBUs) in the construction of coordination polymers (Rao *et al.*, 2004). This class of hybrid organic–inorganic materials possesses great potential for applications in gas storage, separation, catalysis, *etc.* (MacGillivray & Lukehart, 2014; Kaskel, 2016). At the same time, carboxylate linkers containing a silicon core are still rare objects of investigation, although it is assumed that the presence of these heteroatoms may affect the topology and properties of the resulting coordination polymers, which are known to be rather sensitive to tiny structural variations in the constituting parts. Besides these structural aspects, carboxylate ligands containing heteroatoms are of current interest as precursors for the preparation of structured heteroatom-doped carbonaceous materials possessing excellent electron conductivity, high porosity and diverse applications, including electrocatalysis and energy storage and conversion (Yang *et al.*, 2019; Zhong *et al.*, 2019).

Diphenylsilanediylbis(4-benzoic acid), a dicarboxylate possessing a characteristic bent shape, has been already utilized for the synthesis of coordination polymers with tetranuclear Zn^{II} (Liu *et al.*, 2009) and dinuclear Zn^{II} and Mn^{II} (Turcan-Trofin *et al.*, 2018) SBUs, as well as a copper(II)



complex with 1,10-phenanthroline as co-ligand (Cazacu *et al.*, 2014). However, no attempt has been made thus far to combine this linker with macrocyclic complexes, which provide pre-formed SBUs of another type (two vacant *trans* axial positions in the coordination sphere of the metal ion) with an additional benefit of extremely high thermodynamic stability and kinetic inertness (Melson, 1979; Yatsimirskii & Lampeka, 1985). At the same time, such SBUs have been used successfully for the assembly of a number of coordination polymers (Lampeka & Tsymbal, 2004; Suh & Moon, 2007; Suh *et al.*, 2012; Stackhouse & Ma, 2018), including those with some other Si-containing carboxylates (Gavriš *et al.*, 2020a; Gavriš *et al.*, 2020b).



As part of our research on such compounds, we report herein the synthesis and crystal structure of the coordination polymer built up from the nickel(II) complex of the 14-membered macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane (cyclam, *L*), and the dianion of diphenylsilane-diybis(4-benzoic acid) (H_2A), *viz.*, *catena*-poly[[[(1,4,8,11-tetraazacyclotetradecane- $\kappa^4N^1N^4N^8N^{11}$)nickel(II)]- μ -diphenylsilane-diybis(4-benzoato)- $\kappa^2O:O'$] sesquihydrate], $[Ni(L)(A)\cdot 1.5H_2O]_n$, (**I**).

2. Structural commentary

The molecular structure of the title compound **I** is shown in Fig. 1. It represents a one-dimensional coordination polymer built of the centrosymmetric macrocyclic $[Ni(L)]^{2+}$ cations coordinated in axial positions by the oxygen atoms of the carboxyl groups of the acid.

The macrocyclic ligand in the complex cation adopts the most abundant energetically favourable *trans*-III (*R,R,S,S*) conformation (Bosnich *et al.*, 1965) with almost equal Ni–N bond lengths (Table 1). The five-membered chelate rings are present in *gauche* and the six-membered in *chair* conformations. The geometric parameters observed are characteristic of high-spin nickel(II) complexes with 14-membered tetraamine ligands (Lampeka & Tsymbal, 2004). The axial Ni–O bond lengths are somewhat longer than the Ni–N ones resulting in a slight tetragonal distortion of the *trans*- N_4O_2 nickel(II) coordination polyhedron. The location of the metal ion on the inversion centre enforces strict planarity of the equatorial N_4 fragment.

The dianion of the acid in complex **I** possesses intrinsic twofold axial symmetry, with the Si atom lying on the rotation axis. An analogous C_2 -symmetric conformation was found

Table 1
Selected bond lengths and angles (Å, °).

| Distances | | Bite angles | |
|-----------|-----------|------------------------|------------|
| Ni1–N1 | 2.066 (3) | N1–Ni1–N2 | 86.05 (13) |
| Ni1–N2 | 2.068 (3) | N1–Ni1–N2 ⁱ | 93.95 (13) |
| Ni1–O1 | 2.128 (2) | | |

Symmetry code: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$.

[Cambridge Structural Database (CSD, Version 5.40, last update February 2019; Groom *et al.*, 2016)] for the molecules/anions of the acid in the structures XOZVIT (Cazacu *et al.*, 2014) and ZIGXEV (Turcan-Trofin *et al.*, 2018). In two cases [XOZWAM (Cazacu *et al.*, 2014) and ZIGXIZ (Turcan-Trofin *et al.*, 2018)], the carboxylate is present in an asymmetric conformation. At the same time, the coordination polymer XOQXIL (Liu *et al.*, 2009) includes dianions of the acid in both C_2 -symmetric and asymmetric conformations. All these data are summarized in Fig. 2, which clearly illustrates the capability of rotation of aromatic rings in the tetraphenylsilane moiety around the Si–C_{aryl} bonds by a wide range of angles. Another feature worth noting is that the symmetric and asymmetric species in fact refer to essentially different types with minor structural variations within each group, with the exception of anion XOQXIL-1.

The carboxyl groups in **I** are coordinated in a monodentate fashion *via* the O1 atom. The non-coordinated O2 atom is involved as proton acceptor in strong hydrogen bonding with the NH group of the macrocycle (Fig. 1, Table 2), a situation that is frequently observed in carboxylate complexes of cyclam-like ligands. Almost identical C–O bond lengths [C6–O1 = 1.254 (4) and C6–O2 = 1.260 (4) Å] support the model of essential electronic delocalization in the carboxylate group. The carboxyl group is tilted with respect to the plane of benzene ring by 23.6 (2)°. In general, this angle is prone to large variations, *e.g.* for the structures presented in Fig. 2 it spans the range 4.1–30.1°.

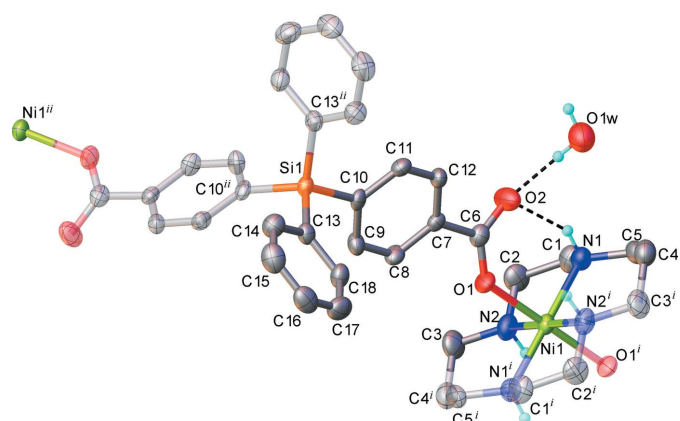


Figure 1

The extended asymmetric unit in **I** showing the coordination environment of the Ni atoms and the atom-labelling scheme (displacement ellipsoids are drawn at the 40% probability level). The atoms obtained by symmetry transformations are shown with 50% transparency. C-bound H atoms are omitted for clarity. Dashed lines represent hydrogen-bonding interactions. [Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (ii) $-x + 1, y, -z + \frac{1}{2}$].

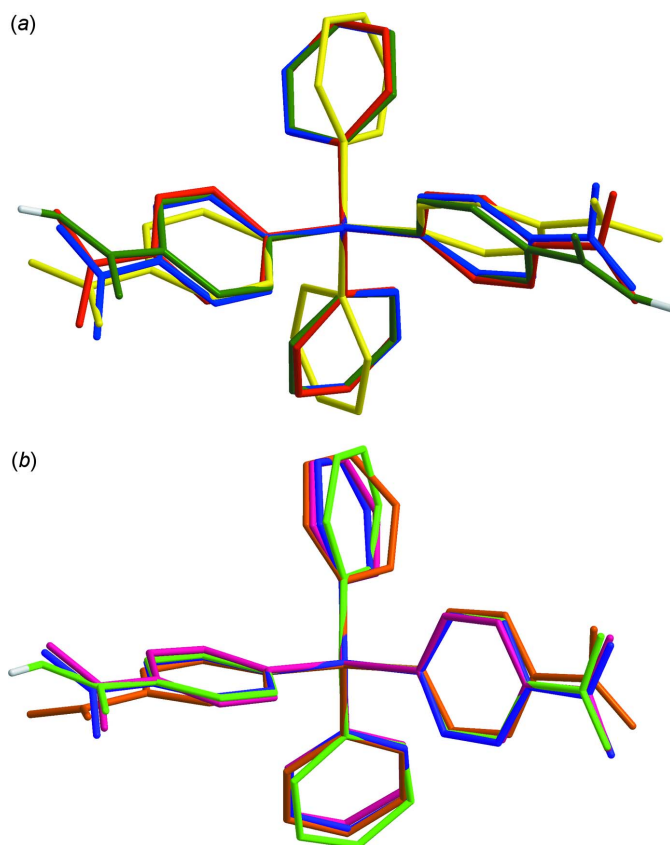


Figure 2
Comparison of the conformations of diphenylsilanediylbis(4-benzoic acid) and its anions. (a) C_2 -symmetric structures. H_2A : dark-green – XOZVIT; A^{2-} : red – **I** (current work), blue – ZIGXEV-1, yellow – XOQXIL-1. (b) Asymmetric structures. HA^- : light-green – XOZWAM; A^{2-} : lilac – ZIGXIZ-1, pink – ZIGXIZ-2, orange – XOQXIL-2. Numbers accompanying refcodes refer to two structurally non-equivalent anions in a given compound. The disordered symmetric anion in ZIGXEV-2 is not shown.

3. Supramolecular features

The crystals of **I** are composed of polymeric chains of $[Ni(L)]^{2+}$ cations bridged by the carboxylate ligands, which propagate along the [101] direction. These chains have a distinctive zigzag shape with a chain link length (Si \cdots Si distance) of 17.854 (3) Å and an almost ideal tetrahedral angle (Si \cdots Si \cdots Si) of 109.09 (2) $^\circ$ (Fig. 3). The nickel(II) cations in a

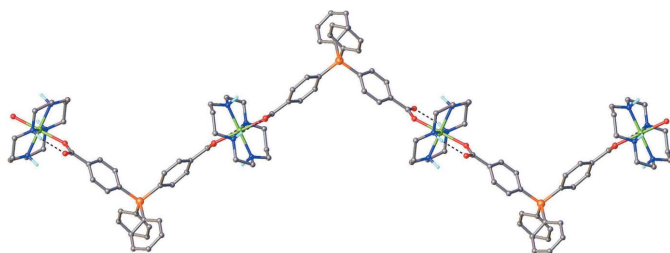


Figure 3
The structure of the polymeric chain in **I**. C-bound H atoms are omitted for clarity.

Table 2
Hydrogen-bond geometry (Å, $^\circ$).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|-------|-------------|-------------|---------------|
| N1–H1 \cdots O2 | 0.98 | 2.02 | 2.916 (4) | 151 |
| O1W–H1WA \cdots O2 ⁱ | 0.85 | 2.05 | 2.850 (5) | 156 |
| O1W–H1WB \cdots O2 | 0.85 | 1.89 | 2.744 (5) | 177 |

Symmetry code: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

chain are arranged in line with an Ni \cdots Ni separation of 14.543 (2) Å.

In the crystal, each such chain is linked to four neighbouring ones due to formation of water-mediated hydrogen bonds between the non-coordinated O2 atoms of the carboxyl group: O2 \cdots HO1W–H \cdots O2 (Table 2). In turn, each O2 atom is involved in hydrogen bonding with two H₂O molecules [symmetry codes: x, y, z ; $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$], which in conjunction with the N1–H \cdots O2 hydrogen bond makes it a triple proton acceptor, while the water molecule serves as a proton donor only. Thus, the water molecules of crystallization play a key role in assembling the one-dimensional polymeric chains into a three-dimensional supramolecular network (Fig. 4).

4. Synthesis and crystallization

All chemicals and solvents used in this work were purchased from Sigma–Aldrich and were used without further purification. The macrocyclic nickel(II) complex $Ni(L)(ClO_4)_2$ (Barefield *et al.*, 1976) and diphenylsilanediylbis(4-benzoic acid) (Cazacu *et al.*, 2014) were prepared according to procedures described previously.

[Ni(L)(A)·1.5H₂O]_n (I). A solution of 100 mg (0.236 mmol) of the acid (H_2A) in 24.5 ml of DMF containing 0.3 ml of triethylamine was thoroughly layered on top of the solution of

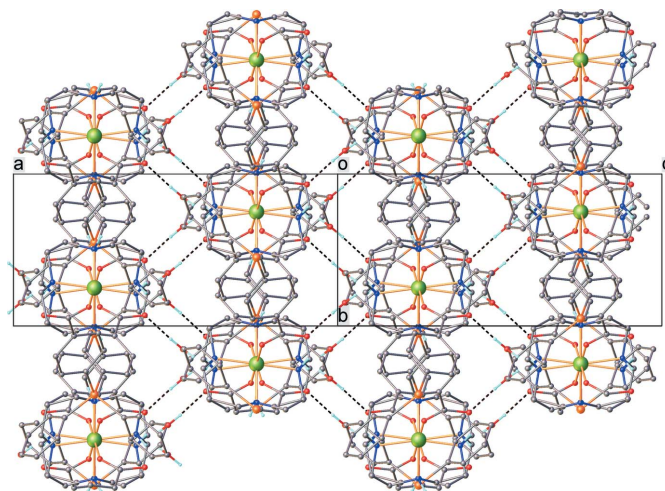


Figure 4
The packing in **I** viewed down the [101] direction with polymeric chains cross-linked by O2 \cdots H–O1W–H \cdots O2 hydrogen bonds (dotted lines) to form a three-dimensional supramolecular network. C-bound H atoms are omitted for clarity.

Table 3
Experimental details.

| | |
|--|--|
| Crystal data | |
| Chemical formula | [Ni(C ₂₆ H ₁₈ O ₄ Si)(C ₁₀ H ₂₄ N ₄)]·1.5H ₂ O |
| <i>M_r</i> | 1417.11 |
| Crystal system, space group | Monoclinic, C2/c |
| Temperature (K) | 200 |
| <i>a</i> , <i>b</i> , <i>c</i> (Å) | 25.390 (4), 7.3865 (10), 18.2424 (16) |
| β (°) | 98.161 (10) |
| <i>V</i> (Å ³) | 3386.6 (8) |
| <i>Z</i> | 2 |
| Radiation type | Mo Kα |
| μ (mm ⁻¹) | 0.66 |
| Crystal size (mm) | 0.35 × 0.10 × 0.10 |
| Data collection | |
| Diffractometer | Agilent Xcalibur, Eos |
| Absorption correction | Multi-scan (CrysAlis PRO; Agilent, 2014), |
| <i>T_{min}</i> , <i>T_{max}</i> | 0.964, 1.000 |
| No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections | 7999, 3926, 2512 |
| <i>R_{int}</i> | 0.052 |
| (sin θ/λ) _{max} (Å ⁻¹) | 0.693 |
| Refinement | |
| <i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i> | 0.066, 0.147, 1.03 |
| No. of reflections | 3926 |
| No. of parameters | 219 |
| H-atom treatment | H-atom parameters constrained |
| Δρ _{max} , Δρ _{min} (e Å ⁻³) | 0.51, -0.51 |

Computer programs: CrysAlis PRO (Agilent, 2014), SHELXT (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b), OLEX2 (Dolomanov *et al.*, 2009) and publCIF (Westrip, 2010).

120 mg (0.262 mmol) of [Ni(L)](ClO₄)₂ in 7.5 ml of water and the tightly closed system was left for two weeks at room temperature. The crystalline precipitate formed was filtered off, washed with DMF, methanol and dried in air. Yield 157 mg (94%). Analysis calculated for C₇₂H₉₀N₈Ni₂O₁₁Si₂: C, 61.03; H, 6.40; N, 7.91%. Found: C, 61.16; H, 6.36; N, 8.09%.

Single crystals of **I** in the form of light-yellow prisms suitable for X-ray diffraction analysis were obtained analogously using *ca* 10 times lower concentration of reagents.

Safety note: Perchlorate salts of metal complexes are potentially explosive and should be handled with care.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.93 (ring H atoms) or 0.97 Å (open-chain H atoms), an N—H distance of 0.98 Å and an aqua O—H distance of 0.85 Å with *U*_{iso}(H) values of 1.2 or 1.5*U*_{eq} times that of the parent atoms. Since the water molecule of crystallization at full occupancy exhibited unrea-

sonably high displacement ellipsoids, its occupancy parameter was reduced to 75%.

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supporting information

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Computing details

Data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014); program(s) used to solve structure: SHELXT (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

catena-Poly[[[(1,4,8,11-tetraazacyclotetradecane- κ^4 N¹,N⁴,N⁸,N¹¹)nickel(II)]- μ -4,4'-(diphenylsilanediyl)dibenzoato- κ^2 O:O'] sesquihydrate]

Crystal data

[Ni(C₂₆H₁₈O₄Si)(C₁₀H₂₄N₄)]·1.5H₂O
M_r = 1417.11
 Monoclinic, *C2/c*
a = 25.390 (4) Å
b = 7.3865 (10) Å
c = 18.2424 (16) Å
 β = 98.161 (10)°
V = 3386.6 (8) Å³
Z = 2

F(000) = 1500
D_x = 1.390 Mg m⁻³
 Mo *K* α radiation, λ = 0.71073 Å
 Cell parameters from 1577 reflections
 θ = 2.6–29.5°
 μ = 0.66 mm⁻¹
T = 200 K
 Prism, clear light yellow
 0.35 × 0.10 × 0.10 mm

Data collection

Agilent Xcalibur, Eos
 diffractometer
 Radiation source: Enhance (Mo) X-ray Source
 Graphite monochromator
 Detector resolution: 16.1593 pixels mm⁻¹
 ω scans
 Absorption correction: multi-scan
 (CrysAlisPro; Agilent, 2014),
T_{min} = 0.964, *T_{max}* = 1.000

7999 measured reflections
 3926 independent reflections
 2512 reflections with *I* > 2 σ (*I*)
R_{int} = 0.052
 θ_{\max} = 29.5°, θ_{\min} = 2.6°
h = -31→21
k = -10→9
l = -21→23

Refinement

Refinement on *F*²
 Least-squares matrix: full
R [*F*² > 2 σ (*F*²)] = 0.066
wR(*F*²) = 0.147
S = 1.03
 3926 reflections

219 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods
 Hydrogen site location: mixed
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0427P)^2 + 4.2041P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$

$$\Delta\rho_{\max} = 0.51 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.51 \text{ e } \text{\AA}^{-3}$$

Special details

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

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|-----|--------------|--------------|--------------|----------------------------------|-----------|
| Ni1 | 0.250000 | 0.250000 | 0.000000 | 0.0273 (2) | |
| Si1 | 0.500000 | 0.95105 (19) | 0.250000 | 0.0256 (3) | |
| O1 | 0.30989 (10) | 0.3756 (4) | 0.07669 (14) | 0.0372 (7) | |
| O2 | 0.27252 (11) | 0.4301 (4) | 0.17836 (15) | 0.0514 (8) | |
| N1 | 0.19897 (12) | 0.2120 (5) | 0.07732 (17) | 0.0377 (8) | |
| H1 | 0.214580 | 0.275668 | 0.122344 | 0.045* | |
| N2 | 0.27921 (12) | -0.0047 (4) | 0.03013 (18) | 0.0381 (8) | |
| H2 | 0.262042 | -0.087426 | -0.007954 | 0.046* | |
| C1 | 0.20090 (17) | 0.0146 (6) | 0.0952 (2) | 0.0464 (11) | |
| H1A | 0.177654 | -0.051687 | 0.057721 | 0.056* | |
| H1B | 0.188941 | -0.005714 | 0.142697 | 0.056* | |
| C2 | 0.25790 (17) | -0.0508 (6) | 0.0976 (2) | 0.0480 (11) | |
| H2A | 0.279912 | 0.003615 | 0.139702 | 0.058* | |
| H2B | 0.259044 | -0.181115 | 0.104319 | 0.058* | |
| C3 | 0.33655 (17) | -0.0306 (6) | 0.0316 (2) | 0.0490 (12) | |
| H3A | 0.345186 | -0.156556 | 0.042523 | 0.059* | |
| H3B | 0.355364 | 0.042076 | 0.071235 | 0.059* | |
| C4 | 0.14439 (17) | 0.4804 (6) | 0.0397 (2) | 0.0477 (11) | |
| H4A | 0.108246 | 0.524309 | 0.038067 | 0.057* | |
| H4B | 0.166204 | 0.543620 | 0.079585 | 0.057* | |
| C5 | 0.14505 (15) | 0.2795 (6) | 0.0585 (2) | 0.0435 (11) | |
| H5A | 0.125675 | 0.260021 | 0.100024 | 0.052* | |
| H5B | 0.127171 | 0.212343 | 0.016526 | 0.052* | |
| C6 | 0.30912 (15) | 0.4468 (5) | 0.1389 (2) | 0.0319 (9) | |
| C7 | 0.35609 (14) | 0.5657 (5) | 0.16868 (18) | 0.0247 (8) | |
| C8 | 0.40442 (14) | 0.5475 (5) | 0.14241 (19) | 0.0312 (9) | |
| H8 | 0.408530 | 0.458487 | 0.107630 | 0.037* | |
| C9 | 0.44678 (14) | 0.6610 (5) | 0.1675 (2) | 0.0329 (9) | |
| H9 | 0.479200 | 0.644164 | 0.150332 | 0.039* | |
| C10 | 0.44174 (14) | 0.8002 (5) | 0.21810 (18) | 0.0264 (8) | |
| C11 | 0.39244 (14) | 0.8183 (5) | 0.24315 (18) | 0.0296 (8) | |
| H11 | 0.387380 | 0.911020 | 0.275947 | 0.035* | |
| C12 | 0.35091 (14) | 0.7001 (5) | 0.21976 (19) | 0.0309 (9) | |
| H12 | 0.319013 | 0.711608 | 0.238874 | 0.037* | |
| C13 | 0.51508 (14) | 1.1037 (5) | 0.1735 (2) | 0.0285 (8) | |
| C14 | 0.55319 (15) | 1.2399 (5) | 0.1896 (2) | 0.0371 (9) | |

| | | | | | |
|------|--------------|------------|------------|-------------|------|
| H14 | 0.571043 | 1.249604 | 0.237641 | 0.044* | |
| C15 | 0.56512 (17) | 1.3597 (6) | 0.1370 (2) | 0.0466 (11) | |
| H15 | 0.590586 | 1.449113 | 0.149517 | 0.056* | |
| C16 | 0.53943 (17) | 1.3472 (6) | 0.0658 (2) | 0.0458 (11) | |
| H16 | 0.547953 | 1.426763 | 0.029713 | 0.055* | |
| C17 | 0.50098 (17) | 1.2169 (6) | 0.0477 (2) | 0.0464 (11) | |
| H17 | 0.483033 | 1.210014 | -0.000366 | 0.056* | |
| C18 | 0.48907 (15) | 1.0964 (5) | 0.1009 (2) | 0.0361 (9) | |
| H18 | 0.463175 | 1.008505 | 0.088027 | 0.043* | |
| O1W | 0.19429 (16) | 0.6528 (6) | 0.2165 (2) | 0.0640 (12) | 0.75 |
| H1WA | 0.205149 | 0.708674 | 0.256534 | 0.096* | 0.75 |
| H1WB | 0.218579 | 0.582004 | 0.206074 | 0.096* | 0.75 |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| Ni1 | 0.0236 (4) | 0.0255 (4) | 0.0312 (4) | -0.0020 (3) | -0.0015 (3) | -0.0022 (3) |
| Si1 | 0.0214 (7) | 0.0242 (7) | 0.0295 (7) | 0.000 | -0.0019 (6) | 0.000 |
| O1 | 0.0313 (15) | 0.0442 (17) | 0.0345 (14) | -0.0102 (13) | -0.0009 (11) | -0.0133 (14) |
| O2 | 0.0425 (19) | 0.065 (2) | 0.0492 (17) | -0.0234 (16) | 0.0151 (14) | -0.0184 (16) |
| N1 | 0.0339 (19) | 0.043 (2) | 0.0352 (18) | -0.0042 (16) | 0.0013 (14) | -0.0049 (16) |
| N2 | 0.035 (2) | 0.0298 (18) | 0.047 (2) | 0.0013 (15) | -0.0039 (15) | 0.0018 (17) |
| C1 | 0.046 (3) | 0.039 (2) | 0.054 (3) | -0.011 (2) | 0.005 (2) | 0.004 (2) |
| C2 | 0.052 (3) | 0.041 (3) | 0.051 (3) | 0.008 (2) | 0.006 (2) | 0.016 (2) |
| C3 | 0.040 (3) | 0.046 (3) | 0.060 (3) | 0.016 (2) | 0.003 (2) | 0.002 (2) |
| C4 | 0.037 (3) | 0.050 (3) | 0.053 (3) | 0.004 (2) | -0.001 (2) | -0.004 (2) |
| C5 | 0.028 (2) | 0.059 (3) | 0.044 (2) | -0.002 (2) | 0.0067 (18) | -0.009 (2) |
| C6 | 0.032 (2) | 0.025 (2) | 0.036 (2) | -0.0021 (17) | -0.0012 (17) | 0.0018 (18) |
| C7 | 0.0252 (19) | 0.0228 (18) | 0.0245 (18) | -0.0011 (15) | -0.0023 (14) | 0.0033 (16) |
| C8 | 0.033 (2) | 0.028 (2) | 0.031 (2) | 0.0018 (17) | -0.0005 (16) | -0.0102 (17) |
| C9 | 0.021 (2) | 0.033 (2) | 0.043 (2) | -0.0005 (17) | 0.0023 (16) | -0.0034 (19) |
| C10 | 0.0216 (19) | 0.0271 (19) | 0.0277 (18) | 0.0005 (15) | -0.0060 (14) | 0.0048 (16) |
| C11 | 0.030 (2) | 0.034 (2) | 0.0238 (18) | -0.0023 (17) | -0.0003 (15) | -0.0045 (17) |
| C12 | 0.0223 (19) | 0.039 (2) | 0.0311 (19) | -0.0028 (17) | 0.0026 (15) | -0.0015 (18) |
| C13 | 0.024 (2) | 0.0255 (19) | 0.036 (2) | 0.0017 (16) | 0.0037 (15) | 0.0035 (18) |
| C14 | 0.038 (2) | 0.032 (2) | 0.040 (2) | -0.0025 (19) | 0.0004 (17) | 0.002 (2) |
| C15 | 0.041 (3) | 0.032 (2) | 0.067 (3) | -0.005 (2) | 0.008 (2) | 0.004 (2) |
| C16 | 0.046 (3) | 0.039 (3) | 0.054 (3) | 0.011 (2) | 0.015 (2) | 0.017 (2) |
| C17 | 0.049 (3) | 0.053 (3) | 0.036 (2) | 0.010 (2) | 0.0020 (19) | 0.008 (2) |
| C18 | 0.028 (2) | 0.038 (2) | 0.040 (2) | -0.0006 (18) | -0.0031 (17) | 0.003 (2) |
| O1W | 0.050 (3) | 0.070 (3) | 0.072 (3) | 0.000 (2) | 0.009 (2) | -0.012 (3) |

Geometric parameters (Å, °)

| | | | |
|---------------------|-----------|--------|-----------|
| Ni1—O1 ⁱ | 2.128 (2) | C4—C5 | 1.523 (6) |
| Ni1—O1 | 2.128 (2) | C5—H5A | 0.9700 |
| Ni1—N1 | 2.066 (3) | C5—H5B | 0.9700 |
| Ni1—N1 ⁱ | 2.065 (3) | C6—C7 | 1.518 (5) |

| | | | |
|--|-------------|-------------------------|-----------|
| Ni1—N2 ⁱ | 2.068 (3) | C7—C8 | 1.386 (5) |
| Ni1—N2 | 2.068 (3) | C7—C12 | 1.381 (5) |
| Si1—C10 ⁱⁱ | 1.878 (4) | C8—H8 | 0.9300 |
| Si1—C10 | 1.878 (4) | C8—C9 | 1.389 (5) |
| Si1—C13 ⁱⁱ | 1.875 (4) | C9—H9 | 0.9300 |
| Si1—C13 | 1.875 (4) | C9—C10 | 1.399 (5) |
| O1—C6 | 1.254 (4) | C10—C11 | 1.399 (5) |
| O2—C6 | 1.260 (4) | C11—H11 | 0.9300 |
| N1—H1 | 0.9800 | C11—C12 | 1.389 (5) |
| N1—C1 | 1.493 (5) | C12—H12 | 0.9300 |
| N1—C5 | 1.452 (5) | C13—C14 | 1.398 (5) |
| N2—H2 | 0.9800 | C13—C18 | 1.395 (5) |
| N2—C2 | 1.455 (5) | C14—H14 | 0.9300 |
| N2—C3 | 1.465 (5) | C14—C15 | 1.371 (5) |
| C1—H1A | 0.9700 | C15—H15 | 0.9300 |
| C1—H1B | 0.9700 | C15—C16 | 1.372 (6) |
| C1—C2 | 1.520 (5) | C16—H16 | 0.9300 |
| C2—H2A | 0.9700 | C16—C17 | 1.377 (6) |
| C2—H2B | 0.9700 | C17—H17 | 0.9300 |
| C3—H3A | 0.9700 | C17—C18 | 1.382 (5) |
| C3—H3B | 0.9700 | C18—H18 | 0.9300 |
| C3—C4 ⁱ | 1.497 (6) | O1W—H1WA | 0.8499 |
| C4—H4A | 0.9700 | O1W—H1WB | 0.8504 |
| C4—H4B | 0.9700 | | |
| O1—Ni1—O1 ⁱ | 180.0 | C3 ⁱ —C4—H4A | 108.2 |
| N1 ⁱ —Ni1—O1 ⁱ | 93.98 (11) | C3 ⁱ —C4—H4B | 108.2 |
| N1 ⁱ —Ni1—O1 | 86.02 (11) | C3 ⁱ —C4—C5 | 116.3 (4) |
| N1—Ni1—O1 | 93.98 (11) | H4A—C4—H4B | 107.4 |
| N1—Ni1—O1 ⁱ | 86.02 (11) | C5—C4—H4A | 108.2 |
| N1 ⁱ —Ni1—N1 | 180.0 | C5—C4—H4B | 108.2 |
| N1—Ni1—N2 | 93.95 (13) | N1—C5—C4 | 111.6 (3) |
| N1—Ni1—N2 | 86.05 (13) | N1—C5—H5A | 109.3 |
| N1 ⁱ —Ni1—N2 | 93.95 (13) | N1—C5—H5B | 109.3 |
| N1 ⁱ —Ni1—N2 ⁱ | 86.05 (13) | C4—C5—H5A | 109.3 |
| N2—Ni1—O1 ⁱ | 88.51 (11) | C4—C5—H5B | 109.3 |
| N2—Ni1—O1 | 91.49 (11) | H5A—C5—H5B | 108.0 |
| N2 ⁱ —Ni1—O1 | 88.51 (11) | O1—C6—O2 | 125.7 (3) |
| N2 ⁱ —Ni1—O1 ⁱ | 91.49 (11) | O1—C6—C7 | 117.0 (3) |
| N2—Ni1—N2 ⁱ | 180.0 | O2—C6—C7 | 117.3 (3) |
| C10—Si1—C10 ⁱⁱ | 107.2 (2) | C8—C7—C6 | 120.6 (3) |
| C13 ⁱⁱ —Si1—C10 ⁱⁱ | 111.20 (15) | C12—C7—C6 | 120.8 (3) |
| C13—Si1—C10 | 111.20 (15) | C12—C7—C8 | 118.5 (3) |
| C13 ⁱⁱ —Si1—C10 | 110.63 (16) | C7—C8—H8 | 119.7 |
| C13—Si1—C10 ⁱⁱ | 110.63 (16) | C7—C8—C9 | 120.7 (3) |
| C13—Si1—C13 ⁱⁱ | 106.1 (2) | C9—C8—H8 | 119.7 |
| C6—O1—Ni1 | 132.6 (2) | C8—C9—H9 | 119.3 |
| Ni1—N1—H1 | 106.8 | C8—C9—C10 | 121.4 (3) |

| | | | |
|---------------------------|------------|--------------------------------|------------|
| C1—N1—Ni1 | 106.1 (2) | C10—C9—H9 | 119.3 |
| C1—N1—H1 | 106.8 | C9—C10—Si1 | 119.9 (3) |
| C5—N1—Ni1 | 117.0 (3) | C11—C10—Si1 | 123.0 (3) |
| C5—N1—H1 | 106.8 | C11—C10—C9 | 117.1 (3) |
| C5—N1—C1 | 112.8 (3) | C10—C11—H11 | 119.5 |
| Ni1—N2—H2 | 105.8 | C12—C11—C10 | 121.0 (3) |
| C2—N2—Ni1 | 106.0 (2) | C12—C11—H11 | 119.5 |
| C2—N2—H2 | 105.8 | C7—C12—C11 | 121.2 (3) |
| C2—N2—C3 | 116.2 (3) | C7—C12—H12 | 119.4 |
| C3—N2—Ni1 | 116.2 (3) | C11—C12—H12 | 119.4 |
| C3—N2—H2 | 105.8 | C14—C13—Si1 | 119.0 (3) |
| N1—C1—H1A | 110.0 | C18—C13—Si1 | 124.3 (3) |
| N1—C1—H1B | 110.0 | C18—C13—C14 | 116.6 (3) |
| N1—C1—C2 | 108.6 (3) | C13—C14—H14 | 118.9 |
| H1A—C1—H1B | 108.4 | C15—C14—C13 | 122.2 (4) |
| C2—C1—H1A | 110.0 | C15—C14—H14 | 118.9 |
| C2—C1—H1B | 110.0 | C14—C15—H15 | 120.1 |
| N2—C2—C1 | 111.6 (3) | C14—C15—C16 | 119.8 (4) |
| N2—C2—H2A | 109.3 | C16—C15—H15 | 120.1 |
| N2—C2—H2B | 109.3 | C15—C16—H16 | 120.0 |
| C1—C2—H2A | 109.3 | C15—C16—C17 | 120.0 (4) |
| C1—C2—H2B | 109.3 | C17—C16—H16 | 120.0 |
| H2A—C2—H2B | 108.0 | C16—C17—H17 | 120.0 |
| N2—C3—H3A | 108.9 | C16—C17—C18 | 120.0 (4) |
| N2—C3—H3B | 108.9 | C18—C17—H17 | 120.0 |
| N2—C3—C4 ⁱ | 113.2 (3) | C13—C18—H18 | 119.3 |
| H3A—C3—H3B | 107.7 | C17—C18—C13 | 121.4 (4) |
| C4 ⁱ —C3—H3A | 108.9 | C17—C18—H18 | 119.3 |
| C4 ⁱ —C3—H3B | 108.9 | H1WA—O1W—H1WB | 109.5 |
| | | | |
| Ni1—O1—C6—O2 | 14.6 (6) | C8—C9—C10—Si1 | -179.6 (3) |
| Ni1—O1—C6—C7 | -164.5 (2) | C8—C9—C10—C11 | 0.9 (5) |
| Ni1—N1—C1—C2 | 38.6 (4) | C9—C10—C11—C12 | 1.4 (5) |
| Ni1—N1—C5—C4 | -55.8 (4) | C10 ⁱⁱ —Si1—C10—C9 | -51.0 (3) |
| Ni1—N2—C2—C1 | 38.2 (4) | C10 ⁱⁱ —Si1—C10—C11 | 128.4 (3) |
| Ni1—N2—C3—C4 ⁱ | -54.2 (4) | C10 ⁱⁱ —Si1—C13—C14 | -68.5 (3) |
| Si1—C10—C11—C12 | -178.0 (3) | C10—Si1—C13—C14 | 172.6 (3) |
| Si1—C13—C14—C15 | -178.1 (3) | C10 ⁱⁱ —Si1—C13—C18 | 114.3 (3) |
| Si1—C13—C18—C17 | 177.9 (3) | C10—Si1—C13—C18 | -4.6 (4) |
| O1—C6—C7—C8 | -21.4 (5) | C10—C11—C12—C7 | -2.8 (5) |
| O1—C6—C7—C12 | 155.4 (3) | C12—C7—C8—C9 | 0.6 (5) |
| O2—C6—C7—C8 | 159.4 (4) | C13 ⁱⁱ —Si1—C10—C9 | -172.4 (3) |
| O2—C6—C7—C12 | -23.9 (5) | C13—Si1—C10—C9 | 70.0 (3) |
| N1—C1—C2—N2 | -53.4 (4) | C13 ⁱⁱ —Si1—C10—C11 | 7.0 (3) |
| C1—N1—C5—C4 | -179.3 (3) | C13—Si1—C10—C11 | -110.6 (3) |
| C2—N2—C3—C4 ⁱ | 180.0 (4) | C13 ⁱⁱ —Si1—C13—C14 | 52.2 (3) |
| C3—N2—C2—C1 | 169.0 (3) | C13 ⁱⁱ —Si1—C13—C18 | -125.0 (4) |
| C3 ⁱ —C4—C5—N1 | 70.1 (5) | C13—C14—C15—C16 | -0.3 (6) |

| | | | |
|---------------|------------|-----------------|----------|
| C5—N1—C1—C2 | 168.0 (3) | C14—C13—C18—C17 | 0.6 (6) |
| C6—C7—C8—C9 | 177.4 (3) | C14—C15—C16—C17 | 1.3 (6) |
| C6—C7—C12—C11 | -175.1 (3) | C15—C16—C17—C18 | -1.3 (6) |
| C7—C8—C9—C10 | -2.0 (5) | C16—C17—C18—C13 | 0.3 (6) |
| C8—C7—C12—C11 | 1.8 (5) | C18—C13—C14—C15 | -0.7 (6) |

Symmetry codes: (i) $-x+1/2, -y+1/2, -z$; (ii) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry (Å, °)

| <i>D—H...A</i> | <i>D—H</i> | <i>H...A</i> | <i>D...A</i> | <i>D—H...A</i> |
|--|------------|--------------|--------------|----------------|
| N1—H1...O2 | 0.98 | 2.02 | 2.916 (4) | 151 |
| O1 <i>W</i> —H1 <i>WA</i> ...O2 ⁱⁱⁱ | 0.85 | 2.05 | 2.850 (5) | 156 |
| O1 <i>W</i> —H1 <i>WB</i> ...O2 | 0.85 | 1.89 | 2.744 (5) | 177 |

Symmetry code: (iii) $-x+1/2, y+1/2, -z+1/2$.