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Syntheses and crystal structures of the one-dimensional coordination polymers formed by $[Ni(cyclam)]^{2+}$ cations and 1,3-bis(3-carboxypropyl)tetramethyldisiloxane anions in different degrees of deprotonation

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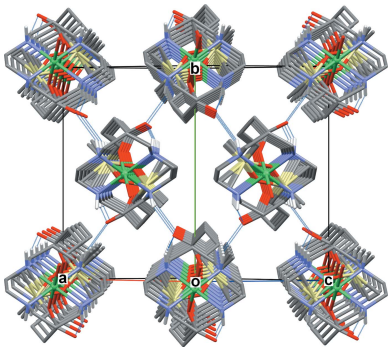
The asymmetric units of the title compounds, namely, *catena*-poly[[(1,4,8,11-tetraazacyclotetradecane-$\kappa^4N^1,N^4,N^8,N^{11}$)nickel(II)]-$\mu$-1,3-bis(3-carboxylatopropyl)tetramethyldisiloxane-$\kappa^2O:O'$], $[Ni(C_{10}H_{24}O_5Si_2)(C_{12}H_{24}N_4)]_n$ (**I**), and *catena*-poly[[[(1,4,8,11-tetraazacyclotetradecane-$\kappa^4N^1,N^4,N^8,N^{11}$)nickel(II)]-$\mu$-4-({[(3-carboxypropyl)dimethylsilyl]oxy}dimethylsilyl)butanoato-$\kappa^2O:O'$] perchlorate], $\{[Ni(C_{10}H_{25}O_5Si_2)(C_{12}H_{24}N_4)]ClO_4\}_n$ (**II**), consist of one (in **I**) or two crystallographically non-equivalent (in **II**) centrosymmetric macrocyclic cations and one centrosymmetric dianion (in **I**) or two centrosymmetric monoanions (in **II**). In each compound, the metal ion is coordinated by the four secondary N atoms of the macrocyclic ligand, which adopts the most energetically stable *trans*-III conformation, and the mutually *trans* O atoms of the carboxylate in a slightly tetragonally distorted *trans*-NiN_4O_2 octahedral coordination geometry. The crystals of both types of compounds are composed of parallel polymeric chains of the macrocyclic cations linked by the anions of the acid running along the [101] and [110] directions in **I** and **II**, respectively. In **I**, each polymeric chain is linked to four neighbouring ones by hydrogen bonding between the NH groups of the macrocycle and the carboxylate O atoms, thus forming a three-dimensional supramolecular network. In **II**, each polymeric chain contacts with only two neighbours, forming hydrogen bonds between the partially protonated carboxylic groups of the bridging ligand. As a result, a lamellar structure is formed with the layers oriented parallel to the $(1\bar{1}1)$ plane.



1. Chemical context

Transition-metal complexes of polyazamacrocyclic ligands, in particular of 1,4,8,11-tetraazacyclotetradecane (cyclam), are characterized by a number of unique properties, such as exceptionally high thermodynamic stability, kinetic inertness and unusual redox characteristics (Melson, 1979; Yatsimirskii & Lampeka, 1985), which have stimulated continuing interest in such systems for a number of decades. In conjunction with polycarboxylate ligands as spacers, macrocyclic complexes have been employed successfully for the construction of metal–organic frameworks (MOFs) (Lampeka & Tsymbal, 2004; Suh & Moon, 2007; Suh *et al.*, 2012; Stackhouse & Ma, 2018), which are considered to be promising materials for applications in gas storage, separation, catalysis, *etc.* (Farrusseng, 2011; MacGillivray & Lukehart, 2014; Kaskel, 2016).

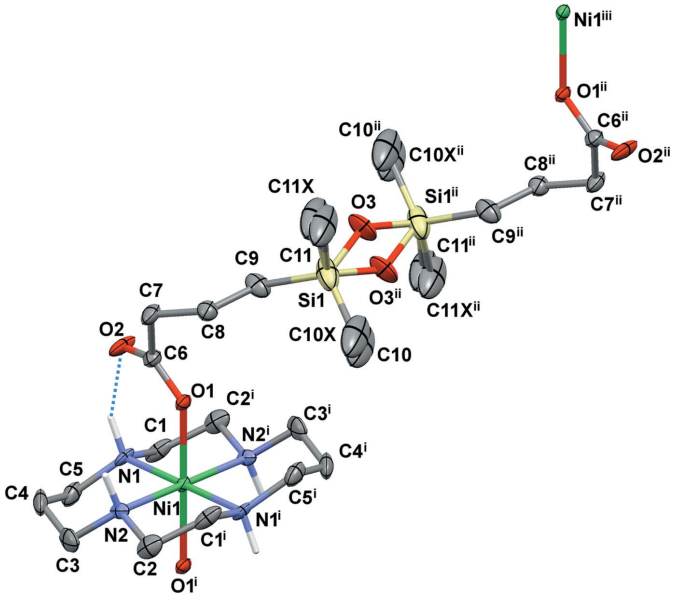
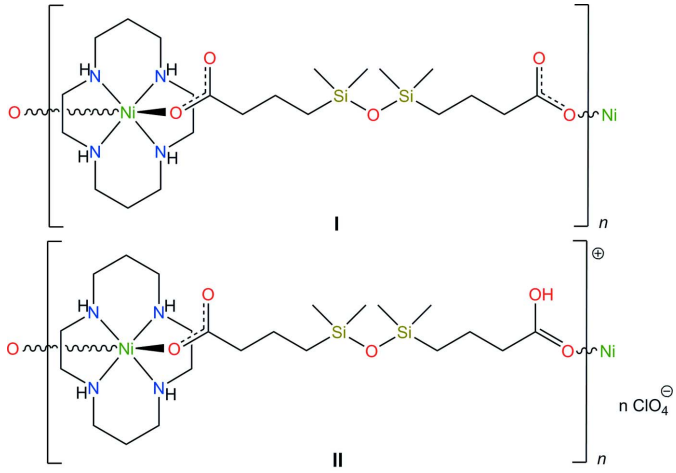


Figure 1
View of the molecular structure of **I** showing atom-labelling scheme with displacement ellipsoids drawn at the 30% probability level. C-bound H atoms are omitted for clarity. Hydrogen-bonding interactions are shown as dotted lines. [Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x+1, -y+1, -z$); (iii) $x-1, y, z-1$].

In contrast to the widespread rigid aromatic carboxylates, flexible spacers incorporating polymethylene chains have rarely been used for the design of MOFs, although this could potentially lead to frameworks possessing unusual properties, the most intriguing of which is a 'breathing' phenomenon (Elsaidi *et al.*, 2018; Lee *et al.*, 2019). A representative example of such a highly flexible ligand is 1,3-bis(3-carboxypropyl)tetramethyldisiloxane – a member of a rather restricted family of silicon-containing carboxylic acids. However, no attempt has been made so far to combine this ligand with macrocyclic complexes in MOF synthesis.

Here, we report the syntheses and crystal structures of the two coordination polymers built of the nickel(II) complex of the 14-membered macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane (L) and the di- or monoanion of 1,3-bis(3-carboxypropyl)tetramethyldisiloxane (H_2Cx), namely, *catena*-poly[[(1,4,8,11-tetraazacyclotetradecane-$\kappa^4N^1,N^4,N^8,N^{11}$)nickel(II)]-$\mu$-1,3-bis(3-carboxylatopropyl)tetramethyldisiloxane-$\kappa^2O{:}O'$], $[Ni(L)(Cx)]_n$, (**I**) and *catena*-poly[[[(1,4,8,11-tetraazacyclotetradecane-$\kappa^4N^1,N^4,N^8,N^{11}$)nickel(II)]-$\mu$-4-({[(3-carboxypropyl)dimethylsilyl]oxy}dimethylsilyl)butanoato-$\kappa^2O{:}O'$] perchlorate], $\{[Ni(L)(HCx)]ClO_4\}_n$ (**II**).



2. Structural commentary

The molecular structures of the title compounds are shown in Figs. 1 and 2. Both complexes are one-dimensional coordina-

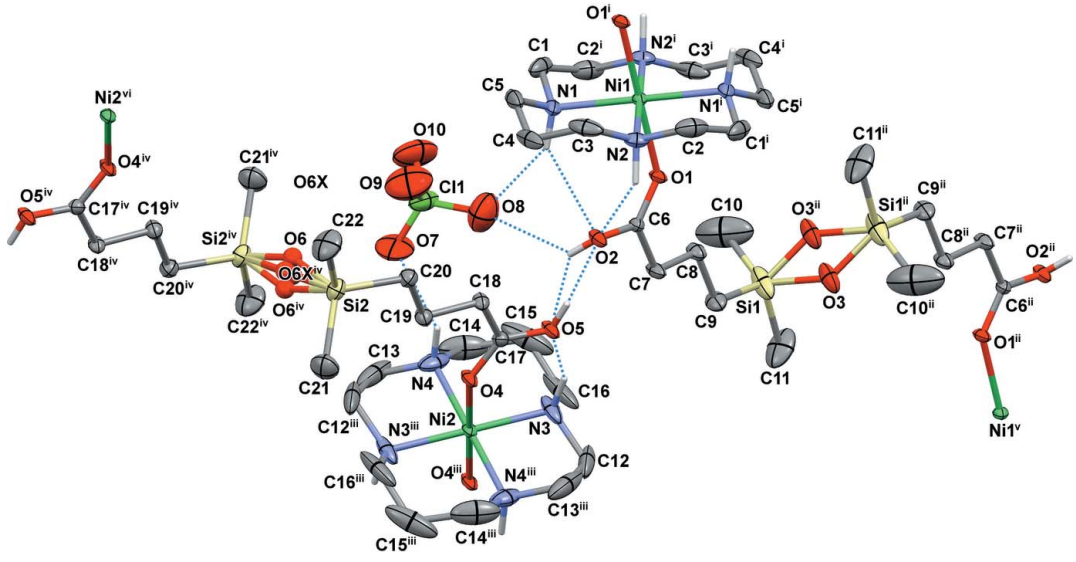


Figure 2
View of the molecular structure of **II** showing atom-labelling scheme with displacement ellipsoids drawn at the 30% probability level. C-bound H atoms are omitted for clarity. Hydrogen-bonding interactions are shown as dotted lines. [Symmetry codes: (i) $-x, -y, -z$; (ii) $-x-1, -y-1, -z$; (iii) $-x, -y-1, -z-1$; (iv) $-x+1, -y, -z-1$; (v) $x-1, y-1, z$; (vi) $x+1, y+1, z$.]

Table 1
Selected geometrical parameters of the complex cations (Å, °).

I		**II**			
Ni1—N1	2.071 (4)	Ni1—N1	2.058 (3)	Ni2—N3	2.043 (4)
Ni1—N2	2.060 (4)	Ni1—N2	2.060 (4)	Ni2—N4	2.054 (4)
Ni1—O1	2.113 (4)	Ni1—O1	2.125 (2)	Ni2—O4	2.131 (2)
N1—Ni1—N2^{i}	85.21 (19)	N1—Ni1—N2^{ii}	85.82 (17)	N3—Ni2—N4^{iii}	85.7 (2)
N1—Ni1—N2	94.79 (19)	N1—Ni1—N2	94.18 (17)	N3—Ni2—N4	94.3 (2)

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

Table 2
Hydrogen-bond geometry (Å, °) for **I**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.98	1.96	2.845 (6)	150
N2—H2···O2^{i}	0.98	2.07	2.883 (6)	139

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

Table 3
Hydrogen-bond geometry (Å, °) for **II**.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.98	2.51	3.225 (5)	130
N1—H1···O8	0.98	2.45	3.315 (6)	147
N2—H2···O2	0.98	2.38	3.143 (4)	134
N3—H3···O5	0.98	2.01	2.901 (5)	150
N4—H4···O7	0.98	2.18	3.012 (6)	142
O2—H2*C*···O5	0.82	1.84	2.456 (4)	131
O2—H2*C*···O8	0.82	2.65	3.260 (5)	133
O5—H5*C*···O2	0.82	1.70	2.456 (4)	151

tion polymers consisting of centrosymmetric macrocyclic $[Ni(L)]^{2+}$ cations coordinated by the oxygen atoms of the carboxylic groups of the centrosymmetric acid, completely deprotonated (in **I**) and monoprotonated (in **II**), in the axial positions. In the latter case, there are two crystallographically independent cations and anions and the H2*C* and H5*C* acidic H atoms are distributed over two carboxylic groups with site occupancies of 50%.

The macrocyclic ligands in the complex cations adopt the most energetically favourable *trans*-III (*R,R,S,S*) conformation (Bosnich *et al.*, 1965) with five-membered chelate rings in *gauche* and six-membered chelate rings in *chair* conformations. As a result of the presence of the inversion centres, all $Ni(N_4)$ fragments are strictly planar. The equatorial Ni—N bond lengths and bite angles fall in a range typical of high-spin $3d^8$ nickel(II) complexes with 14-membered tetraamine ligands (Table 1). The axial Ni—O bond lengths are slightly longer than the Ni—N ones, and the geometry of the nickel(II) polyhedra can be described as tetragonally distorted *trans*-N_4O_2 octahedra.

In two cases (Ni1 in **I** and Ni2 in **II**), a monodentate coordination of the carboxylate to the complex cation is complemented by strong hydrogen bonding between the non-coordinated O atom of the carboxylic group and the NH group of the macrocycle, which is often observed in complexes of cyclam-like ligands. For the $[Ni1(L)]^{2+}$ cation in **II**, the non-coordinated O2 atom is almost equidistant from the N1 and N2 centres [3.225 (5) and 3.143 (4) Å, respectively], so that two weak hydrogen bonds are formed in this case (Figs. 1 and 2, Tables 2 and 3).

The C—O bond lengths in the carboxylic group of the bridging ligand Cx^{2-} in **I** are nearly identical [C6—O1 = 1.245 (7) and C6—O2 = 1.242 (7) Å], thus indicating essential electronic delocalization. At the same time, they differ significantly in **II** [C6—O1 = 1.232 (4) *versus* C6—O2 = 1.291 (5) Å; C17—O4 = 1.245 (4) *versus* C17—O5 = 1.280 (5) Å], so formally the Ni—O bonding in this compound can be treated as the interaction of the metal ion with the carbonyl oxygen atom of the carboxylic group.

Because of the presence of flexible trimethylene fragments, the dicarboxylate ligand can adopt various conformations, both symmetric and asymmetric. In the present cases the anions possess a transoid conformation of the siloxane linkages with the disordered O3 atoms [site occupancies 50%, Si1—O3—Si1 = 141.2 (7) and 137.4 (4)° in **I** and **II**, respectively], as well as with the 25% occupancy atoms O6 and O6*X* in **II** [the corresponding Si2—O6(6*X*)—Si2 angles are 153.1 (17) and 167 (3)°, respectively] (Figs. 1 and 2). The geometries of the two crystallographically independent anions in complex **II** are actually very similar, but differ from that observed in complex **I** (Fig. 3).

3. Supramolecular features

The crystals of both compounds are composed of parallel polymeric chains of $[Ni(L)]^{2+}$ cations linked by carboxylate bridging ligands. The identical chains in **I** with an intra-chain Ni···Ni separation of 14.325 Å propagate along the [101] direction (Fig. 4). In **II**, two crystallographically independent chains formed by the Ni1 and Ni2 macrocyclic cations

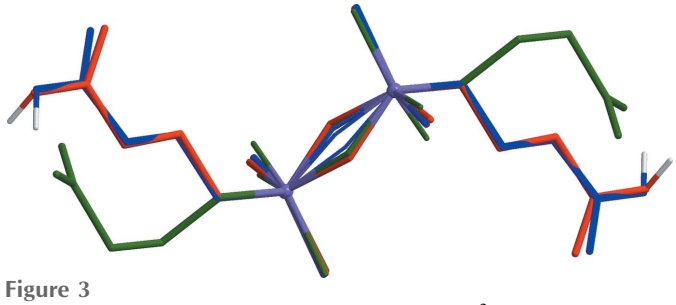


Figure 3
Comparison of the conformations of the dianion Cx^{2-} in **I** (green) and of the monoanions HCx^{-} in **II** (red and blue).

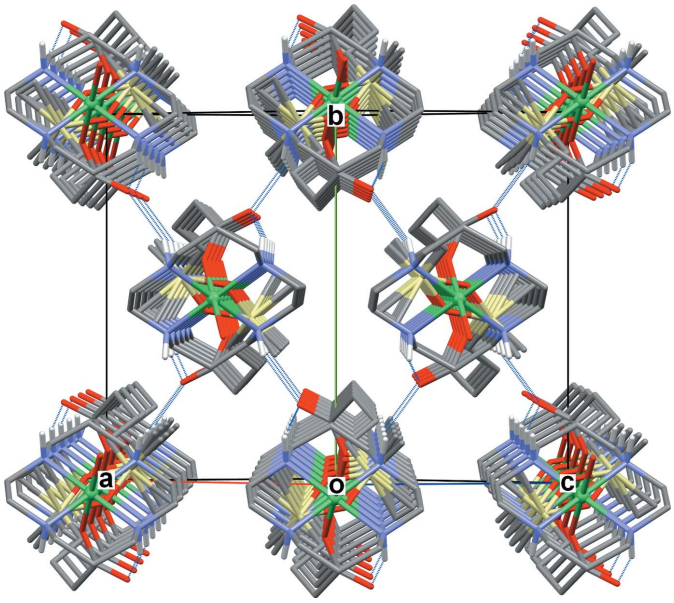


Figure 4
The packing in **I** viewed down the [101] direction with polymeric chains cross-linked by N—H···O hydrogen bonds (dotted lines) to form a three-dimensional supramolecular network. C-bound H atoms are omitted for clarity.

propagate along the [110] direction (Fig. 5) and are characterized by a slightly larger (14.684 Å) intra-chain separation between the Ni^{II} ions.

In the crystals, the interactions between the polymeric chains in **I** and **II** are characterized by markedly different features. In the first case, each chain is linked to four neighbouring ones as a result of hydrogen bonding between the N2—H2 groups of the macrocycles and carboxylate O2 atoms

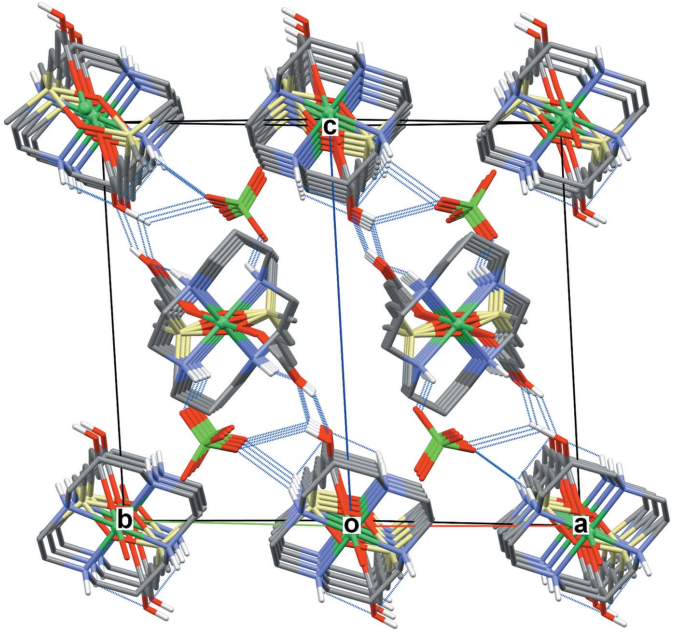


Figure 5
The packing in **II** viewed down the [110] direction with polymeric chains cross-linked by hydrogen bonds (dotted lines).

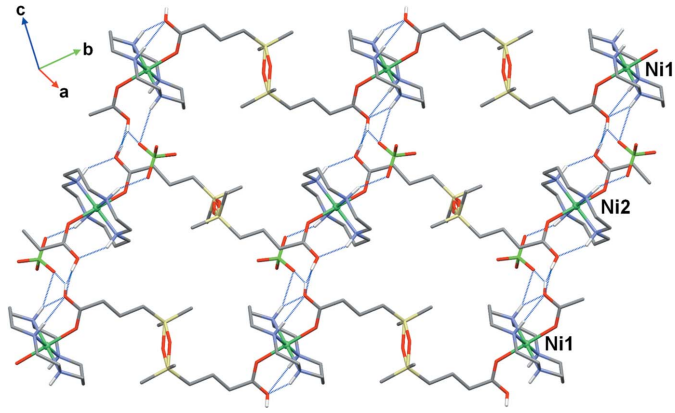


Figure 6
The hydrogen-bonded sheet in **II** parallel to the $(1\bar{1}1)$ plane. C-bound H atoms are omitted for clarity.

(Table 2), resulting in a three-dimensional supramolecular network. On the other hand, in **II** each polymeric chain contacts with only two neighbours *via* paired O2—H2*C*···O5/O2···H5*C*—O5 hydrogen bonds. The bonding is reinforced by the perchlorate anions bridging macrocyclic units: N1—H1···O8—Cl1—O7···H4—N4 (plus an additional very weak O2—H2*C*···O8 contact) (Table 3). As a result, a lamellar structure is formed with the layers lying parallel to the $(1\bar{1}1)$ plane (Fig. 6).

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.40, last update February 2019; Groom *et al.*, 2016) indicated that seven compounds formed by 1,3-bis(3-carboxypropyl)tetramethyldisiloxane itself or its anions have been characterized structurally. Two of them are co-crystals of the acid with organic bases derived from pyridine [refcodes NERTOV (Vlad *et al.*, 2013*a*) and VIPZUR (Racles *et al.*, 2013)]. Other complexes represent one- or two-dimensional coordination polymers formed by Cu^{II} (YIGXOD; Vlad *et al.*, 2013*b*), Co^{II} (NERTIP; Vlad *et al.*, 2013*a*), Zn^{II} [NERTUB (Vlad *et al.*, 2013*a*), GIWSAI (Vlad *et al.*, 2014) and GAPKOA (Zaltariov *et al.*, 2016)]. Except for the last complex, in which the secondary building unit is a hexametal oxocluster bridged by salicylaldoxime ligands, all of the other compounds contain additional heterocyclic co-ligands. No attempt was made to combine this carboxylic acid with macrocyclic cations in MOF synthesis, and thus the title compounds **I** and **II** are the first examples of such compounds described so far.

5. 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 1,3-bis(3-carboxypropyl)tetramethyldisiloxane (H_2Cx) (Mulvaney & Marvel, 1961) were prepared by the reported methods.

Table 4
Experimental details.

	I	II
Crystal data		
Chemical formula	$[Ni(C_{10}H_{24}O_5Si_2)(C_{12}H_{24}N_4)]$	$[Ni(C_{10}H_{25}O_5Si_2)(C_{12}H_{24}N_4)]ClO_4$
M_r	563.53	663.99
Crystal system, space group	Monoclinic, $P2_1/c$	Triclinic, $P\overline{1}$
Temperature (K)	173	200
a, b, c (Å)	13.033 (5), 12.877 (10), 9.028 (3)	9.3815 (7), 12.9009 (8), 14.7604 (10)
α, β, γ (°)	90, 101.31 (3), 90	99.309 (5), 100.343 (6), 99.232 (6)
V (Å^3)	1485.7 (13)	1700.9 (2)
Z	2	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.77	0.77
Crystal size (mm)	0.25 × 0.25 × 0.05	0.45 × 0.35 × 0.30
Data collection		
Diffractometer	Agilent Xcalibur, Eos	Agilent Xcalibur, Eos
Absorption correction	Multi-scan (*CrysAlis PRO*; Agilent, 2014)	Multi-scan (*CrysAlis PRO*; Agilent, 2014)
T_{min}, T_{max}	0.694, 1.000	0.889, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	3957, 3957, 2499	9606, 9606, 5769
R_{int}	0.040	0.063
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.595	0.595
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.065, 0.143, 1.01	0.050, 0.115, 1.01
No. of reflections	3957	9606
No. of parameters	165	367
No. of restraints	6	7
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.56, −0.61	0.51, −0.44

Computer programs: *CrysAlis PRO* (Agilent, 2014), *SIR2008* (Burla *et al.*, 2007), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2018/3* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

{Ni(*L*)(Cx)}$_n$, (I). To a solution of 48 mg (0.24 mmol) of the ligand *L* in 4 ml of water, 30 mg of nickel(II) hydroxide (0.32 mmol) were added and the suspension stirred for 4 d at room temperature to give a yellow-coloured solution. The excess of $Ni(OH)_2$ was filtered off and the filtrate was treated with the solution of 75 mg (0.24 mmol) of H_2Cx in 2 ml of MeOH. This solution was rotary evaporated to give an oily material. The residue was dissolved in 2 ml of MeOH, and the product precipitated with acetonitrile. It was recrystallized in a similar fashion from a MeOH/MeCN (1:15 *v*/*v*) solvent mixture. Yield 54 mg (40%). Analysis calculated for $C_{22}H_{48}N_4NiO_5Si_2$: C, 46.89; H, 8.59; N, 9.94%. Found: C, 46.76; H, 8.64; N, 9.85%.

Single crystals of **I** suitable for X-ray diffraction analysis were obtained analogously, except that precipitation was carried out using a diffusion regime (a methanolic solution of complex was layered with MeCN).

{[Ni(*L*)(HCx)]ClO$_4$}$_n$ (II). A solution of 100 mg (0.26 mmol) of K_2Cx in 1 ml of water was added to a solution of 130 mg (0.28 mmol) of $[Ni(L)](ClO_4)_2$ in 3 ml of water and the mixture was left at room temperature. Potassium perchlorate crystals, which formed after *ca* two weeks, were removed by filtration and the filtrate was allowed to evaporate slowly at room temperature. The crystals of the product formed after about one month. Yield 59 mg (34%). Analysis calculated for $C_{22}H_{49}N_4ClNiO_9Si_2$: C, 39.80; H, 7.44; N, 8.44%. Found: C, 39.67; H, 7.51; N, 8.36%.

Single crystals of **II** suitable for X-ray diffraction analysis were selected from the sample resulting from the synthesis.

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

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. All H atoms in **I** and **II** were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H = 0.97 Å, N—H = 0.98 Å and carboxylate O—H = 0.82 Å, with U_{iso}(H) values of 1.2 or 1.5U_{eq} of the parent atoms.

References

Agilent (2014). *CrysAlis PRO*. Agilent Technologies Ltd, Yarnton, England.

Barefield, E. K., Wagner, F., Herlinger, A. W. & Dahl, A. R. (1976). *Inorg. Synth.* **16**, 220–224.

Bosnich, B., Poon, C. K. & Tobe, M. C. (1965). *Inorg. Chem.* **4**, 1102–1108.

Burla, M. C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G. L., De Caro, L., Giacovazzo, C., Polidori, G., Siliqi, D. & Spagna, R. (2007). *J. Appl. Cryst.* **40**, 609–613.

Elsaidi, S. K., Mohamed, M. H., Banerjee, D. & Thallapally, P. K. (2018). *Coord. Chem. Rev.* **358**, 125–152.

Farrusseng, D. (2011). Editor. *Metal-Organic Frameworks Applications from Catalysis to Gas Storage*, Weinheim: Wiley-VCH.

Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Kaskel, S. (2016). Editor. *The Chemistry of Metal–Organic Frameworks: Synthesis, Characterization, and Applications*. Weinheim: Wiley-VCH.
Lampeka, Ya. D. & Tsymbal, L. V. (2004). *Theor. Exp. Chem.* **40**, 345–371.
Lee, J. H., Jeoung, S., Chung, Y. G. & Moon, H. R. (2019). *Coord. Chem. Rev.* **389**, 161–188.
MacGillivray, L. R. & Lukehart, C. M. (2014). Editors. *Metal–Organic Framework Materials*, Hoboken: John Wiley and Sons.
Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
Melson, G. A. (1979). Editor. *Coordination Chemistry of Macrocyclic Compounds*. New York: Plenum Press.
Mulvaney, J. E. & Marvel, C. S. (1961). *J. Polym. Sci.* **50**, 541–547.
Racles, C., Shova, S., Cazacu, M. & Timpu, D. (2013). *Polymer*, **54**, 6096–6104.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Stackhouse, C. A. & Ma, S. (2018). *Polyhedron*, **145**, 154–165.
Suh, M. P. & Moon, H. R. (2007). *Advances in Inorganic Chemistry*, Vol. 59, edited by R. van Eldik & K. Bowman-James, pp. 39–79. San Diego: Academic Press.
Suh, M. P., Park, H. J., Prasad, T. K. & Lim, D.-W. (2012). *Chem. Rev.* **112**, 782–835.
Vlad, A., Cazacu, M., Zaltariov, M.-F., Bargan, A., Shova, S. & Turta, C. (2014). *J. Mol. Struct.* **1060**, 94–101.
Vlad, A., Cazacu, M., Zaltariov, M.-F., Shova, S., Turta, C. & Airinei, A. (2013*a*). *Polymer*, **54**, 43–53.
Vlad, A., Zaltariov, M.-F., Shova, S., Novitchi, G., Varganici, C.-D., Train, C. & Cazacu, M. (2013*b*). *CrystEngComm*, **15**, 5368–5375.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Yatsimirskii, K. B. & Lampeka, Ya. D. (1985). *Physicochemistry of Metal Complexes with Macrocyclic Ligands*, Kiev: Naukova Dumka. (In Russian.)
Zaltariov, M.-F., Cazacu, M., Sacarescu, L., Vlad, A., Novitchi, G., Train, C., Shova, S. & Arion, V. B. (2016). *Macromolecules*, **49**, 6163–6172.

supporting information

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Computing details

For both structures, data collection: *CrysAlis PRO* (Agilent, 2014); cell refinement: *CrysAlis PRO* (Agilent, 2014); data reduction: *CrysAlis PRO* (Agilent, 2014). Program(s) used to solve structure: *SIR2008* (Burla *et al.*, 2007) for (I); SHELXT (Sheldrick, 2015a) for (II). For both structures, program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

***catena*-Poly[[(1,4,8,11-tetraazacyclotetradecane-$\kappa^4N^1,N^4,N^8,N^{11}$)nickel(II)]-$\mu$-1,3-bis(3-carboxylatopropyl)tetramethyldisiloxane-$\kappa^2O:O'$] (I)**

Crystal data

$[Ni(C_{10}H_{24}O_5Si_2)(C_{12}H_{24}N_4)]$
M_r = 563.53
Monoclinic, $P2_1/c$
a = 13.033 (5) Å
b = 12.877 (10) Å
c = 9.028 (3) Å
β = 101.31 (3)°
V = 1485.7 (13) Å^3
Z = 2
$F(000)$ = 608
D_x = 1.260 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 468 reflections
θ = 2.2–23.0°
μ = 0.77 mm^{-1}
T = 173 K
Plate, clear light colourless
0.25 × 0.25 × 0.05 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 (CrysAlis PRO; Agilent, 2014)
T_{min} = 0.694, T_{max} = 1.000
3957 measured reflections
3957 independent reflections
2499 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 25.0°, θ_{min} = 2.3°
h = −15→15
k = −15→15
l = −10→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.143$
$S = 1.00$
3957 reflections
165 parameters
6 restraints

Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0618P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.61$ e Å^{-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.

Refinement. Refined as a 2-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ni1	1.000000	0.500000	0.500000	0.0224 (3)	
Si1	0.51530 (16)	0.4465 (2)	0.1590 (4)	0.0810 (8)	
O1	0.8723 (3)	0.4020 (3)	0.4131 (4)	0.0278 (10)	
O2	0.9375 (4)	0.2757 (3)	0.2920 (5)	0.0546 (13)	
O3	0.4991 (12)	0.4662 (10)	−0.0400 (11)	0.090 (4)	0.5
N1	1.1059 (4)	0.4111 (4)	0.4113 (5)	0.0313 (13)	
H1	1.068906	0.348403	0.368383	0.038*	
N2	1.0173 (4)	0.4173 (4)	0.6987 (5)	0.0302 (12)	
H2	0.974805	0.354292	0.677540	0.036*	
C1	1.1301 (5)	0.4718 (5)	0.2850 (7)	0.047 (2)	
H1A	1.161336	0.427243	0.219319	0.057*	
H1B	1.179620	0.526309	0.323016	0.057*	
C2	0.9705 (5)	0.4810 (5)	0.8028 (7)	0.050 (2)	
H2A	1.018601	0.535473	0.845711	0.060*	
H2B	0.955552	0.438364	0.884604	0.060*	
C3	1.1239 (5)	0.3849 (5)	0.7630 (7)	0.051 (2)	
H3A	1.123929	0.344748	0.853931	0.061*	
H3B	1.167199	0.445811	0.790758	0.061*	
C4	1.1691 (6)	0.3211 (6)	0.6537 (9)	0.056 (2)	
H4A	1.118692	0.267578	0.614158	0.067*	
H4B	1.230881	0.286356	0.709093	0.067*	
C5	1.1991 (5)	0.3767 (5)	0.5216 (8)	0.050 (2)	
H5A	1.241788	0.436626	0.557967	0.061*	
H5B	1.240623	0.330662	0.471842	0.061*	
C6	0.8685 (5)	0.3154 (5)	0.3510 (7)	0.0354 (16)	
C7	0.7696 (5)	0.2514 (5)	0.3470 (8)	0.0449 (18)	
H7A	0.778986	0.208718	0.437187	0.054*	
H7B	0.760544	0.205156	0.260604	0.054*	

C8	0.6702 (5)	0.3156 (5)	0.3376 (7)	0.0403 (18)	
H8A	0.613522	0.269978	0.350886	0.048*	
H8B	0.680861	0.365496	0.419680	0.048*	
C9	0.6386 (4)	0.3731 (5)	0.1896 (8)	0.0517 (19)	
H9A	0.634154	0.323019	0.108349	0.062*	
H9B	0.694402	0.421166	0.180578	0.062*	
C10X	0.4972 (14)	0.5342 (14)	0.313 (2)	0.139 (5)	0.5
H10A	0.504595	0.495602	0.405513	0.209*	0.5
H10B	0.428590	0.564443	0.289455	0.209*	0.5
H10C	0.548903	0.588187	0.324362	0.209*	0.5
C11	0.3986 (16)	0.369 (2)	0.171 (7)	0.139 (5)	0.5
H11A	0.340588	0.414111	0.173486	0.209*	0.5
H11B	0.412287	0.327371	0.261206	0.209*	0.5
H11C	0.382182	0.324019	0.084404	0.209*	0.5
C10	0.5355 (15)	0.5612 (13)	0.283 (2)	0.139 (5)	0.5
H10D	0.581626	0.609001	0.247371	0.209*	0.5
H10E	0.565898	0.539997	0.384236	0.209*	0.5
H10F	0.469460	0.594367	0.282739	0.209*	0.5
C11X	0.4087 (17)	0.3521 (18)	0.156 (7)	0.139 (5)	0.5
H11D	0.342613	0.385730	0.121176	0.209*	0.5
H11E	0.411408	0.325433	0.255871	0.209*	0.5
H11F	0.416537	0.296006	0.088976	0.209*	0.5

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0285 (5)	0.0157 (5)	0.0236 (5)	0.0026 (6)	0.0068 (5)	0.0002 (6)
Si1	0.0406 (13)	0.0755 (19)	0.119 (2)	−0.0021 (12)	−0.0034 (15)	0.0400 (17)
O1	0.029 (2)	0.019 (3)	0.035 (3)	0.003 (2)	0.0052 (18)	−0.0074 (19)
O2	0.046 (3)	0.031 (3)	0.091 (4)	−0.006 (2)	0.023 (3)	−0.033 (3)
O3	0.103 (8)	0.105 (14)	0.043 (9)	0.010 (10)	−0.031 (9)	0.010 (6)
N1	0.037 (3)	0.014 (3)	0.046 (3)	−0.002 (3)	0.017 (3)	−0.012 (2)
N2	0.045 (3)	0.025 (3)	0.019 (3)	−0.013 (3)	0.001 (2)	0.005 (2)
C1	0.070 (5)	0.028 (5)	0.056 (5)	−0.014 (4)	0.042 (4)	−0.013 (3)
C2	0.077 (6)	0.039 (6)	0.040 (4)	−0.013 (4)	0.026 (4)	0.003 (4)
C3	0.060 (5)	0.046 (5)	0.040 (4)	−0.002 (4)	−0.007 (4)	0.023 (4)
C4	0.041 (4)	0.029 (5)	0.089 (6)	0.009 (4)	−0.009 (4)	0.018 (4)
C5	0.038 (4)	0.029 (5)	0.085 (6)	0.006 (4)	0.016 (4)	−0.008 (4)
C6	0.034 (4)	0.025 (5)	0.046 (4)	−0.002 (3)	0.003 (3)	−0.003 (3)
C7	0.038 (4)	0.022 (5)	0.074 (5)	−0.001 (3)	0.009 (3)	−0.008 (4)
C8	0.032 (4)	0.039 (5)	0.050 (4)	−0.002 (3)	0.007 (3)	−0.001 (3)
C9	0.034 (4)	0.067 (5)	0.053 (4)	−0.009 (4)	0.006 (4)	0.011 (4)
C10X	0.039 (6)	0.077 (7)	0.295 (14)	0.005 (5)	0.016 (7)	0.004 (9)
C11	0.039 (6)	0.077 (7)	0.295 (14)	0.005 (5)	0.016 (7)	0.004 (9)
C10	0.039 (6)	0.077 (7)	0.295 (14)	0.005 (5)	0.016 (7)	0.004 (9)
C11X	0.039 (6)	0.077 (7)	0.295 (14)	0.005 (5)	0.016 (7)	0.004 (9)

Geometric parameters (Å, º)

Ni1—O1	2.113 (4)	C3—H3B	0.9700
Ni1—O1^{i}	2.113 (4)	C3—C4	1.491 (9)
Ni1—N1	2.071 (4)	C4—H4A	0.9700
Ni1—N1^{i}	2.071 (4)	C4—H4B	0.9700
Ni1—N2	2.060 (4)	C4—C5	1.508 (9)
Ni1—N2^{i}	2.060 (4)	C5—H5A	0.9700
Si1—O3	1.785 (11)	C5—H5B	0.9700
Si1—O3^{ii}	1.541 (13)	C6—C7	1.524 (9)
Si1—C9	1.838 (6)	C7—H7A	0.9700
Si1—C10X	1.842 (7)	C7—H7B	0.9700
Si1—C11	1.842 (7)	C7—C8	1.525 (8)
Si1—C10	1.842 (7)	C8—H8A	0.9700
Si1—C11X	1.842 (7)	C8—H8B	0.9700
O1—C6	1.245 (7)	C8—C9	1.512 (8)
O2—C6	1.242 (7)	C9—H9A	0.9700
O3—O3^{ii}	1.13 (2)	C9—H9B	0.9700
N1—H1	0.9800	C10X—H10A	0.9600
N1—C1	1.467 (7)	C10X—H10B	0.9600
N1—C5	1.479 (7)	C10X—H10C	0.9600
N2—H2	0.9800	C11—H11A	0.9600
N2—C2	1.467 (7)	C11—H11B	0.9600
N2—C3	1.459 (7)	C11—H11C	0.9600
C1—H1A	0.9700	C10—H10D	0.9600
C1—H1B	0.9700	C10—H10E	0.9600
C1—C2^{i}	1.519 (8)	C10—H10F	0.9600
C2—H2A	0.9700	C11X—H11D	0.9600
C2—H2B	0.9700	C11X—H11E	0.9600
C3—H3A	0.9700	C11X—H11F	0.9600

O1^{i}—Ni1—O1	180.0	N2—C3—C4	111.3 (5)
N1—Ni1—O1	93.58 (17)	H3A—C3—H3B	108.0
N1^{i}—Ni1—O1	86.42 (17)	C4—C3—H3A	109.4
N1—Ni1—O1^{i}	86.42 (17)	C4—C3—H3B	109.4
N1^{i}—Ni1—O1^{i}	93.58 (17)	C3—C4—H4A	108.0
N1—Ni1—N1^{i}	180.0	C3—C4—H4B	108.0
N2^{i}—Ni1—O1	92.40 (16)	C3—C4—C5	117.3 (6)
N2—Ni1—O1^{i}	92.40 (16)	H4A—C4—H4B	107.2
N2—Ni1—O1	87.60 (16)	C5—C4—H4A	108.0
N2^{i}—Ni1—O1^{i}	87.60 (16)	C5—C4—H4B	108.0
N2—Ni1—N1^{i}	85.21 (19)	N1—C5—C4	111.6 (5)
N2^{i}—Ni1—N1^{i}	94.79 (19)	N1—C5—H5A	109.3
N2—Ni1—N1	94.79 (19)	N1—C5—H5B	109.3
N2^{i}—Ni1—N1	85.21 (19)	C4—C5—H5A	109.3
N2^{i}—Ni1—N2	180.0 (2)	C4—C5—H5B	109.3
O3^{ii}—Si1—O3	38.8 (7)	H5A—C5—H5B	108.0
O3—Si1—C9	98.7 (5)	O1—C6—C7	117.0 (6)

O3^{ii}—Si1—C9	117.6 (6)	O2—C6—O1	126.5 (6)
O3^{ii}—Si1—C10X	93.6 (8)	O2—C6—C7	116.5 (6)
O3—Si1—C10X	131.7 (9)	C6—C7—H7A	108.7
O3—Si1—C11	102 (2)	C6—C7—H7B	108.7
O3^{ii}—Si1—C11	116.7 (16)	C6—C7—C8	114.4 (5)
O3—Si1—C10	118.2 (9)	H7A—C7—H7B	107.6
O3^{ii}—Si1—C10	79.8 (9)	C8—C7—H7A	108.7
O3—Si1—C11X	98 (2)	C8—C7—H7B	108.7
O3^{ii}—Si1—C11X	118.8 (18)	C7—C8—H8A	108.9
C9—Si1—C10X	116.1 (7)	C7—C8—H8B	108.9
C9—Si1—C11	114.8 (10)	H8A—C8—H8B	107.7
C9—Si1—C10	107.7 (7)	C9—C8—C7	113.3 (5)
C9—Si1—C11X	107.3 (9)	C9—C8—H8A	108.9
C11—Si1—C10X	93.4 (18)	C9—C8—H8B	108.9
C11X—Si1—C10	123.8 (18)	Si1—C9—H9A	107.9
C6—O1—Ni1	131.4 (4)	Si1—C9—H9B	107.9
Si1^{ii}—O3—Si1	141.2 (7)	C8—C9—Si1	117.6 (4)
O3^{ii}—O3—Si1	58.8 (11)	C8—C9—H9A	107.9
O3^{ii}—O3—Si1^{ii}	82.4 (14)	C8—C9—H9B	107.9
Ni1—N1—H1	107.2	H9A—C9—H9B	107.2
C1—N1—Ni1	105.5 (4)	Si1—C10X—H10A	109.5
C1—N1—H1	107.2	Si1—C10X—H10B	109.5
C1—N1—C5	114.1 (5)	Si1—C10X—H10C	109.5
C5—N1—Ni1	115.3 (4)	H10A—C10X—H10B	109.5
C5—N1—H1	107.2	H10A—C10X—H10C	109.5
Ni1—N2—H2	107.3	H10B—C10X—H10C	109.5
C2—N2—Ni1	106.3 (4)	Si1—C11—H11A	109.5
C2—N2—H2	107.3	Si1—C11—H11B	109.5
C3—N2—Ni1	115.3 (4)	Si1—C11—H11C	109.5
C3—N2—H2	107.3	H11A—C11—H11B	109.5
C3—N2—C2	112.9 (5)	H11A—C11—H11C	109.5
N1—C1—H1A	109.9	H11B—C11—H11C	109.5
N1—C1—H1B	109.9	Si1—C10—H10D	109.5
N1—C1—C2^{i}	108.9 (5)	Si1—C10—H10E	109.5
H1A—C1—H1B	108.3	Si1—C10—H10F	109.5
C2^{i}—C1—H1A	109.9	H10D—C10—H10E	109.5
C2^{i}—C1—H1B	109.9	H10D—C10—H10F	109.5
N2—C2—C1^{i}	108.3 (5)	H10E—C10—H10F	109.5
N2—C2—H2A	110.0	Si1—C11X—H11D	109.5
N2—C2—H2B	110.0	Si1—C11X—H11E	109.5
C1^{i}—C2—H2A	110.0	Si1—C11X—H11F	109.5
C1^{i}—C2—H2B	110.0	H11D—C11X—H11E	109.5
H2A—C2—H2B	108.4	H11D—C11X—H11F	109.5
N2—C3—H3A	109.4	H11E—C11X—H11F	109.5
N2—C3—H3B	109.4		

Ni1—O1—C6—O2	−18.8 (10)	C6—C7—C8—C9	67.1 (7)
Ni1—O1—C6—C7	161.1 (4)	C7—C8—C9—Si1	176.0 (4)

Ni1—N1—C1—C2^{i}	−41.9 (5)	C9—Si1—O3—Si1^{ii}	−123.8 (15)
Ni1—N1—C5—C4	53.8 (7)	C9—Si1—O3—O3^{ii}	−123.8 (15)
Ni1—N2—C2—C1^{i}	41.2 (5)	C10X—Si1—O3—Si1^{ii}	13 (2)
Ni1—N2—C3—C4	−57.1 (7)	C10X—Si1—O3—O3^{ii}	13 (2)
O1—C6—C7—C8	31.8 (8)	C10X—Si1—C9—C8	49.5 (9)
O2—C6—C7—C8	−148.4 (6)	C11—Si1—O3—Si1^{ii}	118.5 (18)
O3^{ii}—Si1—O3—Si1^{ii}	0.003 (1)	C11—Si1—O3—O3^{ii}	118.5 (18)
O3—Si1—C9—C8	−165.0 (7)	C11—Si1—C9—C8	−58 (2)
O3^{ii}—Si1—C9—C8	159.0 (6)	C10—Si1—O3—Si1^{ii}	−8.3 (19)
N2—C3—C4—C5	72.9 (8)	C10—Si1—O3—O3^{ii}	−8.3 (19)
C1—N1—C5—C4	176.2 (5)	C10—Si1—C9—C8	71.5 (10)
C2—N2—C3—C4	−179.6 (5)	C11X—Si1—O3—Si1^{ii}	127.1 (18)
C3—N2—C2—C1^{i}	168.6 (5)	C11X—Si1—O3—O3^{ii}	127.1 (18)
C3—C4—C5—N1	−71.1 (8)	C11X—Si1—C9—C8	−64 (2)
C5—N1—C1—C2^{i}	−169.5 (5)		

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+1, −*y*+1, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.98	1.96	2.845 (6)	150
N2—H2···O2^{iii}	0.98	2.07	2.883 (6)	139

Symmetry code: (iii) *x*, −*y*+1/2, *z*+1/2.

catena-Poly[[[(1,4,8,11-tetraazacyclotetradecane-$\kappa^4N^1,N^4,N^8,N^{11}$)nickel(II)]-$\mu$-4-({[(3-carboxypropyl)dimethylsilyl]oxy}dimethylsilyl)butanoato-$\kappa^2O:O'$] perchlorate] (II)

Crystal data

$[Ni(C_{10}H_{25}O_5Si_2)(C_{12}H_{24}N_4)]ClO_4$
M_r = 663.99
Triclinic, $P\overline{1}$
a = 9.3815 (7) Å
b = 12.9009 (8) Å
c = 14.7604 (10) Å
α = 99.309 (5)°
β = 100.343 (6)°
γ = 99.232 (6)°
V = 1700.9 (2) Å^3
Z = 2
$F(000)$ = 708
D_x = 1.296 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2033 reflections
θ = 1.7–24.6°
μ = 0.77 mm^{-1}
T = 200 K
Block, clear light colourless
0.45 × 0.35 × 0.30 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 (CrysAlis PRO; Agilent, 2014)
T_{min} = 0.889, T_{max} = 1.000
9606 measured reflections
9606 independent reflections
5769 reflections with $I > 2\sigma(I)$
R_{int} = 0.063
θ_{max} = 25.0°, θ_{min} = 2.0°
h = −11→11
k = −15→15
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.115$
$S = 1.01$
9606 reflections
367 parameters
7 restraints

Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0451P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.51$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-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.

Refinement. Refined as a 2-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ni1	0.000000	0.000000	0.000000	0.0241 (2)	
Si1	−0.3977 (2)	−0.55987 (11)	−0.05469 (15)	0.0729 (6)	
O1	−0.1184 (3)	−0.1542 (2)	−0.0727 (2)	0.0310 (8)	
O2	−0.0826 (3)	−0.1583 (2)	−0.2165 (2)	0.0339 (8)	
H2C	−0.034950	−0.196653	−0.243367	0.051*	0.5
O3	−0.5535 (8)	−0.5084 (6)	−0.0332 (5)	0.061 (3)	0.5
N1	0.1859 (4)	−0.0236 (3)	−0.0499 (3)	0.0408 (11)	
H1	0.157126	−0.087684	−0.099864	0.049*	
N2	−0.0809 (4)	0.0725 (3)	−0.1075 (3)	0.0390 (11)	
H2	−0.128011	0.014955	−0.161639	0.047*	
C1	0.2858 (6)	−0.0494 (5)	0.0295 (4)	0.065 (2)	
H1A	0.335337	0.015969	0.073702	0.078*	
H1B	0.360480	−0.083840	0.006336	0.078*	
C2	−0.1992 (7)	0.1219 (4)	−0.0773 (4)	0.0649 (19)	
H2A	−0.156944	0.189771	−0.034619	0.078*	
H2B	−0.263674	0.135605	−0.131369	0.078*	
C3	0.0282 (7)	0.1448 (4)	−0.1388 (4)	0.0634 (18)	
H3A	0.071451	0.206181	−0.088446	0.076*	
H3B	−0.020855	0.170724	−0.191801	0.076*	
C4	0.1501 (7)	0.0909 (4)	−0.1671 (4)	0.068 (2)	
H4A	0.104405	0.025115	−0.211911	0.081*	
H4B	0.205970	0.137198	−0.199462	0.081*	
C5	0.2570 (6)	0.0641 (4)	−0.0893 (4)	0.0608 (18)	
H5A	0.339987	0.043288	−0.113487	0.073*	
H5B	0.294711	0.127196	−0.039965	0.073*	
C6	−0.1332 (4)	−0.2035 (3)	−0.1537 (3)	0.0254 (11)	
C7	−0.2146 (5)	−0.3171 (3)	−0.1832 (3)	0.0378 (13)	
H7A	−0.303379	−0.319448	−0.229384	0.045*	
H7B	−0.153320	−0.358866	−0.214036	0.045*	

C8	−0.2580 (5)	−0.3700 (3)	−0.1066 (3)	0.0363 (12)	
H8A	−0.316658	−0.327704	−0.073869	0.044*	
H8B	−0.169508	−0.371782	−0.061703	0.044*	
C9	−0.3463 (5)	−0.4842 (3)	−0.1431 (3)	0.0477 (14)	
H9A	−0.289182	−0.524186	−0.179202	0.057*	
H9B	−0.436249	−0.480898	−0.185840	0.057*	
C10	−0.2275 (11)	−0.5710 (6)	0.0258 (5)	0.168 (4)	
H10A	−0.191865	−0.505635	0.071407	0.252*	
H10B	−0.153386	−0.583786	−0.009580	0.252*	
H10C	−0.248872	−0.629417	0.057238	0.252*	
C11	−0.5003 (7)	−0.6957 (4)	−0.1124 (5)	0.102 (3)	
H11A	−0.442542	−0.730299	−0.150911	0.153*	
H11B	−0.592187	−0.690955	−0.150829	0.153*	
H11C	−0.519460	−0.736539	−0.065495	0.153*	
Ni2	0.000000	−0.500000	−0.500000	0.0281 (2)	
Si2	0.35316 (15)	0.04647 (10)	−0.52679 (11)	0.0404 (4)	
O4	0.0305 (3)	−0.3297 (2)	−0.47284 (19)	0.0333 (8)	
O5	−0.0840 (3)	−0.2890 (2)	−0.3576 (2)	0.0376 (9)	
H5C	−0.095950	−0.235276	−0.324118	0.056*	0.5
N3	−0.1442 (6)	−0.5206 (3)	−0.4129 (4)	0.0621 (15)	
H3	−0.143842	−0.449452	−0.377416	0.075*	
N4	0.1844 (5)	−0.4870 (3)	−0.3968 (4)	0.0675 (16)	
H4	0.207815	−0.412879	−0.361974	0.081*	
C12	−0.2937 (7)	−0.5585 (5)	−0.4771 (6)	0.094 (3)	
H12A	−0.370162	−0.545605	−0.442664	0.113*	
H12B	−0.309077	−0.634809	−0.501474	0.113*	
C13	0.3020 (7)	−0.5012 (5)	−0.4435 (7)	0.111 (4)	
H13A	0.295115	−0.576820	−0.467592	0.133*	
H13B	0.395995	−0.474737	−0.399517	0.133*	
C14	0.1635 (10)	−0.5587 (5)	−0.3256 (6)	0.112 (3)	
H14A	0.151266	−0.632881	−0.356424	0.134*	
H14B	0.251865	−0.542354	−0.276130	0.134*	
C15	0.0318 (15)	−0.5454 (6)	−0.2821 (5)	0.136 (4)	
H15A	0.035328	−0.582999	−0.230129	0.163*	
H15B	0.040102	−0.470013	−0.256570	0.163*	
C16	−0.1145 (11)	−0.5851 (5)	−0.3474 (6)	0.116 (4)	
H16A	−0.117774	−0.657098	−0.380421	0.139*	
H16B	−0.191132	−0.588632	−0.311103	0.139*	
C17	0.0036 (5)	−0.2625 (3)	−0.4108 (3)	0.0278 (11)	
C18	0.0724 (5)	−0.1463 (3)	−0.3978 (3)	0.0287 (12)	
H18A	0.132997	−0.123812	−0.334828	0.034*	
H18B	−0.006193	−0.105610	−0.401545	0.034*	
C19	0.1664 (5)	−0.1164 (3)	−0.4662 (3)	0.0359 (12)	
H19A	0.108087	−0.140813	−0.529665	0.043*	
H19B	0.249045	−0.153188	−0.460348	0.043*	
C20	0.2255 (5)	0.0035 (3)	−0.4507 (3)	0.0373 (13)	
H20A	0.276718	0.028112	−0.385648	0.045*	
H20B	0.142064	0.039091	−0.460546	0.045*	

C21	0.2725 (6)	−0.0094 (4)	−0.6529 (4)	0.0706 (18)	
H21A	0.180766	0.013540	−0.670484	0.106*	
H21B	0.255162	−0.086153	−0.663382	0.106*	
H21C	0.339876	0.015653	−0.690111	0.106*	
C22	0.3997 (6)	0.1939 (4)	−0.5079 (5)	0.084 (2)	
H22A	0.445438	0.222461	−0.443122	0.126*	
H22B	0.311213	0.221370	−0.523912	0.126*	
H22C	0.466709	0.214650	−0.546789	0.126*	
O6X	0.493 (3)	−0.013 (5)	−0.497 (6)	0.037 (3)*	0.25
O6	0.510 (3)	0.021 (4)	−0.4772 (12)	0.037 (3)*	0.25
Cl1	0.38292 (17)	−0.21590 (12)	−0.21055 (12)	0.0683 (5)	
O7	0.3941 (6)	−0.2883 (5)	−0.2826 (4)	0.194 (3)	
O8	0.2362 (5)	−0.2323 (4)	−0.1955 (4)	0.1227 (19)	
O9	0.4112 (6)	−0.1102 (4)	−0.2279 (4)	0.147 (2)	
O10	0.4768 (6)	−0.2161 (4)	−0.1271 (4)	0.137 (2)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0254 (4)	0.0202 (4)	0.0226 (5)	−0.0021 (4)	0.0072 (4)	−0.0040 (3)
Si1	0.1134 (15)	0.0274 (8)	0.0967 (15)	0.0056 (9)	0.0774 (14)	0.0135 (8)
O1	0.0404 (19)	0.0256 (16)	0.0206 (19)	−0.0064 (14)	0.0113 (15)	−0.0065 (14)
O2	0.051 (2)	0.0206 (16)	0.030 (2)	−0.0038 (14)	0.0228 (17)	−0.0013 (14)
O3	0.085 (7)	0.051 (4)	0.069 (8)	0.020 (5)	0.056 (5)	0.020 (5)
N1	0.033 (2)	0.038 (2)	0.041 (3)	−0.005 (2)	0.016 (2)	−0.017 (2)
N2	0.052 (3)	0.026 (2)	0.031 (3)	0.006 (2)	−0.001 (2)	−0.0044 (18)
C1	0.028 (3)	0.065 (4)	0.081 (5)	0.019 (3)	−0.006 (3)	−0.032 (4)
C2	0.072 (4)	0.048 (3)	0.058 (4)	0.024 (3)	−0.022 (4)	−0.009 (3)
C3	0.119 (5)	0.027 (3)	0.032 (3)	−0.010 (3)	0.006 (4)	0.003 (2)
C4	0.106 (5)	0.045 (3)	0.036 (4)	−0.041 (3)	0.039 (4)	−0.009 (3)
C5	0.059 (4)	0.060 (4)	0.051 (4)	−0.023 (3)	0.036 (3)	−0.018 (3)
C6	0.026 (3)	0.025 (2)	0.023 (3)	0.000 (2)	0.008 (2)	−0.002 (2)
C7	0.053 (3)	0.027 (3)	0.027 (3)	−0.010 (2)	0.018 (3)	−0.004 (2)
C8	0.048 (3)	0.025 (2)	0.033 (3)	−0.001 (2)	0.016 (3)	−0.002 (2)
C9	0.056 (3)	0.028 (3)	0.053 (4)	−0.010 (2)	0.022 (3)	−0.004 (2)
C10	0.274 (12)	0.096 (6)	0.091 (7)	−0.042 (7)	−0.030 (7)	0.047 (5)
C11	0.075 (5)	0.042 (4)	0.192 (8)	−0.006 (3)	0.039 (5)	0.034 (4)
Ni2	0.0285 (5)	0.0228 (4)	0.0292 (5)	−0.0009 (4)	0.0125 (4)	−0.0067 (4)
Si2	0.0330 (8)	0.0396 (8)	0.0503 (10)	0.0047 (7)	0.0090 (7)	0.0156 (7)
O4	0.0421 (19)	0.0242 (16)	0.0334 (19)	0.0031 (14)	0.0212 (16)	−0.0061 (14)
O5	0.053 (2)	0.0263 (17)	0.033 (2)	−0.0013 (15)	0.0258 (18)	−0.0061 (14)
N3	0.099 (4)	0.026 (2)	0.073 (4)	0.007 (3)	0.064 (3)	−0.002 (3)
N4	0.056 (3)	0.043 (3)	0.080 (4)	0.016 (3)	−0.019 (3)	−0.027 (3)
C12	0.049 (4)	0.056 (4)	0.167 (7)	−0.010 (3)	0.066 (5)	−0.033 (4)
C13	0.039 (4)	0.062 (5)	0.188 (10)	0.014 (4)	−0.027 (5)	−0.048 (5)
C14	0.164 (8)	0.055 (4)	0.088 (6)	0.040 (5)	−0.055 (6)	0.004 (4)
C15	0.313 (15)	0.067 (5)	0.049 (5)	0.084 (8)	0.047 (8)	0.019 (4)
C16	0.238 (11)	0.045 (4)	0.088 (7)	0.012 (6)	0.122 (7)	0.001 (4)

C17	0.028 (3)	0.028 (2)	0.024 (3)	0.005 (2)	0.003 (2)	0.000 (2)
C18	0.033 (3)	0.018 (2)	0.036 (3)	0.003 (2)	0.014 (2)	0.001 (2)
C19	0.038 (3)	0.031 (3)	0.041 (3)	0.004 (2)	0.017 (3)	0.003 (2)
C20	0.034 (3)	0.035 (3)	0.041 (3)	0.003 (2)	0.011 (3)	0.002 (2)
C21	0.079 (4)	0.088 (4)	0.045 (4)	0.017 (4)	0.011 (3)	0.017 (3)
C22	0.082 (5)	0.048 (3)	0.116 (6)	−0.012 (3)	0.023 (4)	0.021 (4)
Cl1	0.0571 (10)	0.0599 (10)	0.0695 (12)	0.0139 (8)	−0.0151 (10)	−0.0111 (9)
O7	0.137 (5)	0.163 (5)	0.202 (6)	−0.019 (4)	0.037 (4)	−0.146 (5)
O8	0.077 (3)	0.154 (5)	0.144 (5)	0.026 (3)	0.017 (3)	0.050 (4)
O9	0.176 (6)	0.079 (4)	0.158 (5)	−0.006 (4)	−0.005 (5)	0.016 (3)
O10	0.117 (4)	0.143 (4)	0.115 (4)	0.037 (3)	−0.050 (4)	−0.006 (4)

Geometric parameters (Å, º)

Ni1—O1	2.125 (2)	Ni2—N4	2.054 (4)
Ni1—O1^{i}	2.125 (2)	Ni2—N4^{iii}	2.054 (4)
Ni1—N1^{i}	2.058 (3)	Si2—C20	1.864 (5)
Ni1—N1	2.058 (3)	Si2—C21	1.855 (5)
Ni1—N2^{i}	2.060 (4)	Si2—C22	1.845 (5)
Ni1—N2	2.060 (4)	Si2—O6X^{iv}	1.570 (19)
Si1—O3	1.757 (8)	Si2—O6X	1.651 (19)
Si1—O3^{ii}	1.626 (7)	Si2—O6^{iv}	1.66 (2)
Si1—C9	1.837 (5)	Si2—O6	1.632 (16)
Si1—C10	1.852 (9)	O4—C17	1.245 (4)
Si1—C11	1.845 (5)	O5—H5C	0.8199
O1—C6	1.232 (4)	O5—C17	1.280 (5)
O2—H2C	0.8200	N3—H3	0.9800
O2—C6	1.291 (5)	N3—C12	1.502 (8)
O3—O3^{ii}	1.234 (13)	N3—C16	1.393 (9)
N1—H1	0.9800	N4—H4	0.9800
N1—C1	1.481 (6)	N4—C13	1.422 (8)
N1—C5	1.475 (6)	N4—C14	1.527 (9)
N2—H2	0.9800	C12—H12A	0.9700
N2—C2	1.467 (6)	C12—H12B	0.9700
N2—C3	1.461 (6)	C12—C13^{iii}	1.502 (10)
C1—H1A	0.9700	C13—H13A	0.9700
C1—H1B	0.9700	C13—H13B	0.9700
C1—C2^{i}	1.486 (7)	C14—H14A	0.9700
C2—H2B	0.9700	C14—H14B	0.9700
C2—H2A	0.9700	C14—C15	1.512 (11)
C3—H3A	0.9700	C15—H15A	0.9700
C3—H3B	0.9700	C15—H15B	0.9700
C3—C4	1.516 (7)	C15—C16	1.488 (11)
C4—H4A	0.9700	C16—H16A	0.9700
C4—H4B	0.9700	C16—H16B	0.9700
C4—C5	1.507 (7)	C20—H20A	0.9700
C5—H5A	0.9700	C20—H20B	0.9700
C5—H5B	0.9700	C20—C19	1.521 (5)

C6—C7	1.496 (5)	C19—H19A	0.9700
C7—H7A	0.9700	C19—H19B	0.9700
C7—H7B	0.9700	C19—C18	1.512 (6)
C7—C8	1.496 (6)	C18—H18A	0.9700
C8—H8A	0.9700	C18—H18B	0.9700
C8—H8B	0.9700	C18—C17	1.501 (5)
C8—C9	1.529 (5)	C21—H21A	0.9600
C9—H9A	0.9700	C21—H21B	0.9600
C9—H9B	0.9700	C21—H21C	0.9600
C10—H10A	0.9600	C22—H22A	0.9600
C10—H10B	0.9600	C22—H22B	0.9600
C10—H10C	0.9600	C22—H22C	0.9600
C11—H11A	0.9600	O6X—O6X^{iv}	0.38 (7)
C11—H11B	0.9600	O6—O6^{iv}	0.77 (5)
C11—H11C	0.9600	Cl1—O7	1.329 (4)
Ni2—O4^{iii}	2.131 (2)	Cl1—O8	1.421 (5)
Ni2—O4	2.131 (2)	Cl1—O9	1.420 (5)
Ni2—N3^{iii}	2.043 (4)	Cl1—O10	1.380 (5)
Ni2—N3	2.043 (4)		

O1—Ni1—O1^{i}	180.0	N3^{iii}—Ni2—N4	85.7 (2)
N1^{i}—Ni1—O1	88.17 (12)	N4—Ni2—O4^{iii}	91.33 (14)
N1^{i}—Ni1—O1^{i}	91.83 (12)	N4—Ni2—O4	88.67 (14)
N1—Ni1—O1^{i}	88.17 (12)	N4^{iii}—Ni2—O4	91.33 (14)
N1—Ni1—O1	91.83 (12)	N4^{iii}—Ni2—O4^{iii}	88.67 (14)
N1^{i}—Ni1—N1	180.0	N4—Ni2—N4^{iii}	180.0
N1^{i}—Ni1—N2	85.82 (17)	C21—Si2—C20	111.6 (2)
N1—Ni1—N2^{i}	85.82 (17)	C22—Si2—C20	110.6 (2)
N1^{i}—Ni1—N2^{i}	94.18 (17)	C22—Si2—C21	109.6 (3)
N1—Ni1—N2	94.18 (17)	O6X^{iv}—Si2—C20	113.4 (14)
N2—Ni1—O1^{i}	87.38 (12)	O6X—Si2—C20	102.5 (13)
N2^{i}—Ni1—O1	87.38 (12)	O6X—Si2—C21	107 (3)
N2—Ni1—O1	92.62 (12)	O6X^{iv}—Si2—C21	107 (3)
N2^{i}—Ni1—O1^{i}	92.62 (12)	O6X—Si2—C22	116 (2)
N2—Ni1—N2^{i}	180.0	O6X^{iv}—Si2—C22	104 (2)
O3^{ii}—Si1—O3	42.6 (4)	O6X^{iv}—Si2—O6X	13 (3)
O3^{ii}—Si1—C9	115.6 (3)	O6X—Si2—O6^{iv}	13 (3)
O3—Si1—C9	100.2 (3)	O6X^{iv}—Si2—O6^{iv}	17 (2)
O3—Si1—C10	131.5 (4)	O6^{iv}—Si2—C20	111.2 (17)
O3^{ii}—Si1—C10	89.4 (4)	O6—Si2—C20	103.5 (15)
O3^{ii}—Si1—C11	121.3 (4)	O6—Si2—C21	120.4 (6)
O3—Si1—C11	95.7 (3)	O6^{iv}—Si2—C21	94.3 (5)
C9—Si1—C10	109.0 (3)	O6—Si2—C22	100.3 (19)
C9—Si1—C11	110.1 (3)	O6^{iv}—Si2—C22	118.5 (19)
C11—Si1—C10	108.8 (3)	O6—Si2—O6^{iv}	26.9 (17)
C6—O1—Ni1	132.9 (3)	C17—O4—Ni2	133.8 (3)
C6—O2—H2C	109.8	C17—O5—H5C	109.9
Si1^{ii}—O3—Si1	137.4 (4)	Ni2—N3—H3	106.9

O3^{ii}—O3—Si1	63.0 (6)	C12—N3—Ni2	105.1 (4)
O3^{ii}—O3—Si1^{ii}	74.4 (7)	C12—N3—H3	106.9
Ni1—N1—H1	107.4	C16—N3—Ni2	117.3 (4)
C1—N1—Ni1	105.0 (3)	C16—N3—H3	106.9
C1—N1—H1	107.4	C16—N3—C12	113.2 (6)
C5—N1—Ni1	116.2 (3)	Ni2—N4—H4	106.8
C5—N1—H1	107.4	C13—N4—Ni2	106.5 (4)
C5—N1—C1	113.1 (4)	C13—N4—H4	106.8
Ni1—N2—H2	106.7	C13—N4—C14	115.0 (6)
C2—N2—Ni1	105.7 (3)	C14—N4—Ni2	114.4 (4)
C2—N2—H2	106.7	C14—N4—H4	106.8
C3—N2—Ni1	116.1 (3)	N3—C12—H12A	109.9
C3—N2—H2	106.7	N3—C12—H12B	109.9
C3—N2—C2	114.2 (4)	N3—C12—C13^{iii}	108.8 (5)
N1—C1—H1A	109.7	H12A—C12—H12B	108.3
N1—C1—H1B	109.7	C13^{iii}—C12—H12A	109.9
N1—C1—C2^{i}	109.7 (4)	C13^{iii}—C12—H12B	109.9
H1A—C1—H1B	108.2	N4—C13—C12^{iii}	109.6 (6)
C2^{i}—C1—H1A	109.7	N4—C13—H13A	109.8
C2^{i}—C1—H1B	109.7	N4—C13—H13B	109.8
N2—C2—C1^{i}	109.8 (4)	C12^{iii}—C13—H13A	109.8
N2—C2—H2B	109.7	C12^{iii}—C13—H13B	109.8
N2—C2—H2A	109.7	H13A—C13—H13B	108.2
C1^{i}—C2—H2B	109.7	N4—C14—H14A	109.0
C1^{i}—C2—H2A	109.7	N4—C14—H14B	109.0
H2B—C2—H2A	108.2	H14A—C14—H14B	107.8
N2—C3—H3A	109.1	C15—C14—N4	113.0 (6)
N2—C3—H3B	109.1	C15—C14—H14A	109.0
N2—C3—C4	112.3 (4)	C15—C14—H14B	109.0
H3A—C3—H3B	107.9	C14—C15—H15A	108.5
C4—C3—H3A	109.1	C14—C15—H15B	108.5
C4—C3—H3B	109.1	H15A—C15—H15B	107.5
C3—C4—H4A	108.1	C16—C15—C14	115.0 (6)
C3—C4—H4B	108.1	C16—C15—H15A	108.5
H4A—C4—H4B	107.3	C16—C15—H15B	108.5
C5—C4—C3	116.7 (4)	N3—C16—C15	113.1 (7)
C5—C4—H4A	108.1	N3—C16—H16A	109.0
C5—C4—H4B	108.1	N3—C16—H16B	109.0
N1—C5—C4	111.4 (4)	C15—C16—H16A	109.0
N1—C5—H5A	109.4	C15—C16—H16B	109.0
N1—C5—H5B	109.4	H16A—C16—H16B	107.8
C4—C5—H5A	109.4	Si2—C20—H20A	108.3
C4—C5—H5B	109.4	Si2—C20—H20B	108.3
H5A—C5—H5B	108.0	H20A—C20—H20B	107.4
O1—C6—O2	121.4 (4)	C19—C20—Si2	115.9 (3)
O1—C6—C7	120.8 (4)	C19—C20—H20A	108.3
O2—C6—C7	117.7 (4)	C19—C20—H20B	108.3
C6—C7—H7A	108.3	C20—C19—H19A	109.0

C6—C7—H7B	108.3	C20—C19—H19B	109.0
H7A—C7—H7B	107.4	H19A—C19—H19B	107.8
C8—C7—C6	116.0 (4)	C18—C19—C20	113.1 (3)
C8—C7—H7A	108.3	C18—C19—H19A	109.0
C8—C7—H7B	108.3	C18—C19—H19B	109.0
C7—C8—H8A	109.0	C19—C18—H18A	108.1
C7—C8—H8B	109.0	C19—C18—H18B	108.1
C7—C8—C9	112.8 (4)	H18A—C18—H18B	107.3
H8A—C8—H8B	107.8	C17—C18—C19	116.7 (3)
C9—C8—H8A	109.0	C17—C18—H18A	108.1
C9—C8—H8B	109.0	C17—C18—H18B	108.1
Si1—C9—H9A	108.1	O4—C17—O5	121.9 (4)
Si1—C9—H9B	108.1	O4—C17—C18	120.1 (4)
C8—C9—Si1	116.8 (3)	O5—C17—C18	118.0 (3)
C8—C9—H9A	108.1	Si2—C21—H21A	109.5
C8—C9—H9B	108.1	Si2—C21—H21B	109.5
H9A—C9—H9B	107.3	Si2—C21—H21C	109.5
Si1—C10—H10A	109.5	H21A—C21—H21B	109.5
Si1—C10—H10B	109.5	H21A—C21—H21C	109.5
Si1—C10—H10C	109.5	H21B—C21—H21C	109.5
H10A—C10—H10B	109.5	Si2—C22—H22A	109.5
H10A—C10—H10C	109.5	Si2—C22—H22B	109.5
H10B—C10—H10C	109.5	Si2—C22—H22C	109.5
Si1—C11—H11A	109.5	H22A—C22—H22B	109.5
Si1—C11—H11B	109.5	H22A—C22—H22C	109.5
Si1—C11—H11C	109.5	H22B—C22—H22C	109.5
H11A—C11—H11B	109.5	Si2^{iv}—O6X—Si2	167 (3)
H11A—C11—H11C	109.5	O6X^{iv}—O6X—Si2^{iv}	96 (6)
H11B—C11—H11C	109.5	O6X^{iv}—O6X—Si2	71 (6)
O4—Ni2—O4^{iii}	180.00 (3)	Si2—O6—Si2^{iv}	153.1 (17)
N3^{iii}—Ni2—O4^{iii}	94.96 (13)	O6^{iv}—O6—Si2	78 (2)
N3—Ni2—O4	94.96 (13)	O7—Cl1—O8	110.3 (3)
N3^{iii}—Ni2—O4	85.04 (13)	O7—Cl1—O9	112.0 (4)
N3—Ni2—O4^{iii}	85.04 (13)	O7—Cl1—O10	114.2 (4)
N3^{iii}—Ni2—N3	180.0	O9—Cl1—O8	105.3 (3)
N3^{iii}—Ni2—N4^{iii}	94.3 (2)	O10—Cl1—O8	107.7 (4)
N3—Ni2—N4	94.3 (2)	O10—Cl1—O9	106.8 (3)
N3—Ni2—N4^{iii}	85.7 (2)		

Ni1—O1—C6—O2	−7.2 (6)	Ni2—N4—C14—C15	−52.9 (7)
Ni1—O1—C6—C7	174.5 (3)	Si2—C20—C19—C18	176.0 (3)
Ni1—N1—C1—C2^{i}	40.9 (4)	N4—C14—C15—C16	68.4 (9)
Ni1—N1—C5—C4	−56.2 (5)	C12—N3—C16—C15	−178.2 (6)
Ni1—N2—C2—C1^{i}	−39.8 (4)	C13—N4—C14—C15	−176.6 (6)
Ni1—N2—C3—C4	55.3 (5)	C14—N4—C13—C12^{iii}	169.9 (5)
O1—C6—C7—C8	−7.7 (6)	C14—C15—C16—N3	−71.7 (8)
O2—C6—C7—C8	174.0 (4)	C16—N3—C12—C13^{iii}	−168.2 (5)
O3^{ii}—Si1—O3—Si1^{ii}	−0.001 (2)	C20—Si2—O6X—Si2^{iv}	−148 (28)

O3—Si1—C9—C8	81.0 (4)	C20—Si2—O6X—O6X^{iv}	−148 (28)
O3^{ii}—Si1—C9—C8	39.0 (5)	C20—Si2—O6—Si2^{iv}	110 (7)
N2—C3—C4—C5	−70.0 (6)	C20—Si2—O6—O6^{iv}	110 (7)
C1—N1—C5—C4	−177.7 (4)	C20—C19—C18—C17	177.2 (4)
C2—N2—C3—C4	178.7 (4)	C19—C18—C17—O4	3.3 (6)
C3—N2—C2—C1^{i}	−168.7 (4)	C19—C18—C17—O5	−175.7 (4)
C3—C4—C5—N1	70.1 (5)	C21—Si2—C20—C19	52.0 (4)
C5—N1—C1—C2^{i}	168.6 (4)	C21—Si2—O6X—Si2^{iv}	95 (29)
C6—C7—C8—C9	177.5 (4)	C21—Si2—O6X—O6X^{iv}	95 (29)
C7—C8—C9—Si1	176.9 (4)	C21—Si2—O6—Si2^{iv}	−15 (9)
C9—Si1—O3—Si1^{ii}	−116.9 (7)	C21—Si2—O6—O6^{iv}	−15 (9)
C9—Si1—O3—O3^{ii}	−116.9 (7)	C22—Si2—C20—C19	174.3 (4)
C10—Si1—O3—Si1^{ii}	10.0 (10)	C22—Si2—O6X—Si2^{iv}	−27 (30)
C10—Si1—O3—O3^{ii}	10.0 (10)	C22—Si2—O6X—O6X^{iv}	−27 (30)
C10—Si1—C9—C8	−59.7 (5)	C22—Si2—O6—Si2^{iv}	−135 (8)
C11—Si1—O3—Si1^{ii}	131.5 (8)	C22—Si2—O6—O6^{iv}	−135 (8)
C11—Si1—O3—O3^{ii}	131.5 (8)	O6X^{iv}—Si2—C20—C19	−70 (4)
C11—Si1—C9—C8	−179.0 (4)	O6X—Si2—C20—C19	−62 (3)
Ni2—O4—C17—O5	−16.3 (6)	O6X^{iv}—Si2—O6X—Si2^{iv}	−0.01 (14)
Ni2—O4—C17—C18	164.8 (3)	O6^{iv}—Si2—C20—C19	−51.9 (12)
Ni2—N3—C12—C13^{iii}	−39.0 (6)	O6—Si2—C20—C19	−79.0 (15)
Ni2—N3—C16—C15	59.1 (7)	O6^{iv}—Si2—O6—Si2^{iv}	0.006 (14)
Ni2—N4—C13—C12^{iii}	42.1 (6)		

Symmetry codes: (i) −*x*, −*y*, −*z*; (ii) −*x*−1, −*y*−1, −*z*; (iii) −*x*, −*y*−1, −*z*−1; (iv) −*x*+1, −*y*, −*z*−1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O2	0.98	2.51	3.225 (5)	130
N1—H1···O8	0.98	2.45	3.315 (6)	147
N2—H2···O2	0.98	2.38	3.143 (4)	134
N3—H3···O5	0.98	2.01	2.901 (5)	150
N4—H4···O7	0.98	2.18	3.012 (6)	142
O2—H2*C*···O5	0.82	1.84	2.456 (4)	131
O2—H2*C*···O8	0.82	2.65	3.260 (5)	133
O5—H5*C*···O2	0.82	1.70	2.456 (4)	151