Crystal structure of \([\{\text{Ni}(\text{C}_{10}\text{H}_{24}\text{N}_{4})\}\{\text{Ni}(\text{CN})_{4}\}]\cdot 2\text{H}_{2}\text{O}]_{n}\), a one-dimensional coordination polymer formed from the \([\text{Ni}(\text{cyclam})]^{2+}\) cation and the \([\text{Ni}(\text{CN})_{4}]^{2-}\) anion

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The asymmetric unit of the title compound, catena-poly[[[1,4,8,11-tetraaza-cycloctatetradecane-κ^{4}\text{N}_{1}\text{N}_{4}\text{N}_{8}\text{N}_{11}}\text{Ni}\{\text{II}\}]\cdot \mu\text{cyanido-κ^{2}\text{C}}\text{-}[\text{bis}(\text{cyanido-κC})\text{Ni}\{\text{II}\}]\cdot \mu\text{-cyanido-κ^{2}\text{C}}\text{-N}]\text{dihydrate}, \{\text{Ni}_{2}(\text{CN})_{4}(\text{C}_{10}\text{H}_{24}\text{N}_{4})\}\cdot 2\text{H}_{2}\text{O}]_{n}\) or \([\{\text{Ni}(\text{C}_{10}\text{H}_{24}\text{N}_{4})\}\{\text{Ni}(\text{CN})_{4}\}]\cdot 2\text{H}_{2}\text{O}]_{n}\), consists of a pair of crystallographically non-equivalent macrocyclic cations and anions. The nickel(II) ions (all with site symmetry 1) are coordinated by the four secondary N atoms of the macrocyclic ligands, which adopt the most energetically stable trans-III conformation, and the mutually trans N atoms of the tetracyanonickelate anion in a slightly tetragonally distorted \text{NiN}_{6} octahedral coordination geometry. The \([\text{Ni}(\text{CN})_{4}]^{2-}\) anion exhibits a bridging function, resulting in the formation of parallel polymeric chains running along the [101] direction. The water molecules of crystallization play a pivotal role in the three-dimensional supramolecular organization of the crystal. Acting as acceptors, they form \text{N—H} \cdot \cdot \cdot \text{O}_{\text{w}} (w = \text{water}) hydrogen bonds with the secondary amino groups of the macrocycles, forming layers oriented parallel to the (001) plane. At the same time, as donors, they interact with the non-coordinated cyano groups of the anion via \text{O}_{\text{w}}—\text{H} \cdot \cdot \cdot \text{N}_{\text{c}} (c = \text{cyanide}) hydrogen bonds, giving two-dimensional layers oriented parallel to the (100) plane and thus generating a three-dimensional network.

1. Chemical context

Transition-metal complexes of tetraazamacroyclic ligands, in particular of 1,4,8,11-tetraazacyclotetradecane (cyclam, \(L\)), have been intensively studied for decades. This is explained by their unique properties, in particular, exceptionally high thermodynamic stability, kinetic inertness and the ability to stabilize uncommon oxidation states of coordinated metals (Melson, 1979; Yatsimirskii & Lampeka, 1985). Because of their conformational rigidity during chemical transformation (preservation of two vacant or labile trans axial positions in the coordination sphere of the metal ion), these complexes are also promising secondary building units for the construction of metal–organic frameworks (MOFs) (Lampeka & Tsymbal, 2004; Suh & Moon, 2007; Suh et al., 2012; Stackhouse & Ma, 2018), which possess great potential for applications in different areas including gas storage, separation, catalysis, sensing, etc (MacGillivray & Lukehart, 2014; Kaskel, 2016).

Cyanometallate anions refer to a type of bridging ligands for the creation of MOFs of different topologies possessing promising magnetic and electronic properties (Ohkoshi et al.,
2019). Among such linkers, the tetracyanonickelate(II) dianion has attracted less attention compared to hexa- and octacyanometallates and only one work describing the structure of the coordination polymer formed by the metal(cyclam) complex and this anion, i.e., $[\text{Cu}(L)_2][\text{Ni(CN)}_4]_2^-$, has been published to date (Cernak et al., 2010). Interestingly, despite the diamagnetic nature of the bridging fragment, this complex displays a weak antiferromagnetic exchange coupling between the paramagnetic copper(II) centres.

We report herein the synthesis and crystal structure of the coordination polymer built up of the nickel(II) complex of $L$ and the tetracyanonickelate(II) dianion, namely, catena-$[\text{bis(}\mu_2\text{-cyano-}\kappa^2\text{C,N})\text{-dicyano-}(1,4,8,11\text{-tetraazacyclotetradecane-}\kappa^3\text{N}^1\text{N}^4\text{N}^6\text{N}^{11})\text{-}\text{dinickel(II) dihydrate}], [[[\text{Ni}(L)]\text{[Ni(CN)}_4]\text{]}_22\text{H}_2\text{O}]]_n$. (I).

2. Structural commentary

The molecular structure of I is shown in Fig. 1. It represents a one-dimensional coordination polymer built up from two crystallographically independent centrosymmetric tetragonal macroyclic $[\text{Ni}(L)]^{2+}$ cations and tetracyanonickelate anions $[\text{Ni(CN)}_4]^{2-}$. The coordination of the trans cyanide groups of the anions in the axial positions of the coordination sphere of the metal ions in cations results in the formation of two structurally non-equivalent parallel polymeric chains (Ni1/Ni3 and Ni2/Ni4) running along the $[1\overline{1}0]$ direction.

The location of the metal ions on inversion centres enforces strict planarity of the Ni(N 4) and Ni(C 4) coordination polyhedron. The Ni—C—N angles in the anion deviate only slightly (less than 4°) from linearity. In I, each tetracyanonickelate unit uses two trans cyanide groups for coordination to two macrocyclic moieties. The macrocyclic ligand in the complex cations adopts the most common and energetically favorable 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 (bite angles $ca 85.5^\circ$) and the six-membered in chair (bite angles $ca 94.5^\circ$) conformations (Table 1). The geometric parameters observed are characteristic of high-spin $d^8$ nickel(II) complexes with macrocyclic 14-membered tetramine ligands (Lampeka & Tsymbal, 2004; Tsymbal et al., 2021). The axial Ni—N(CN) bond lengths are somewhat longer than the Ni—N(amine) ones, resulting in a slight tetragonal distortion of the trans-NiN$_2$ coordination polyhedron.

The Ni—C—N angles in the anion deviate only slightly (less than 4°) from linearity. In I, each tetracyanonickelate unit uses two trans cyanide groups for coordination to two macrocyclic moieties in a bent fashion [Ni—N—C = 166.1 (4)°], giving rise to a linear polymeric chain, whereas the two remaining trans CN$^-$ groups are monodentate. The adjacent Ni···Ni distance in the chain is $5.0558\ (5)$ Å, and the shortest interchain Ni···Ni distance is $6.6159\ (5)$ Å.

3. Supramolecular features

The crystals of I are composed of linear polymeric chains of $[\text{Ni}(L)]^{2+}$ cations bridged by the $[\text{Ni(CN)}_4]^{2-}$ anions, which propagate along the $[1\overline{1}0]$ direction. There are no direct contacts between the chains and the water molecules of

| Selected bond lengths (Å). |
|-----------------------------|
| Ni1—N5 2.100 (4) Ni2—N4 2.079 (4) |
| Ni1—N2 2.070 (4) Ni3—C11 1.874 (6) |
| Ni1—N1 2.082 (4) Ni3—C12 1.857 (6) |
| Ni2—N3 2.069 (4) Ni4—C13 1.966 (6) |
| Ni2—N7 2.095 (4) Ni4—C14 1.863 (6) |

Table 2

| Hydrogen-bond geometry (Å, °). |
|-------------------------------|
| D—H···A  | D—H  | H···A  | D···A  | D—H···A  |
| N1—H1···O1W$^+$  | 0.98  | 2.28  | 3.115 (6) | 143  |
| N2—H2···O1W$^+$  | 0.98  | 2.10  | 3.020 (6) | 156  |
| N3—H3···O2W$^{+\#}$ | 0.98  | 2.15  | 3.083 (7) | 159  |
| N4—H4···O2W$^{+\#}$ | 0.98  | 2.26  | 3.080 (6) | 140  |
| O1W—H1WA···N8  | 0.85  | 2.03  | 2.872 (7) | 173  |
| O1W—H1WB···N6$^{\cdot}$ | 0.85  | 2.27  | 3.112 (7) | 171  |
| O2W—H2WA···N6  | 0.85  | 2.03  | 2.853 (6) | 164  |
| O2W—H2WB···N8$^{\cdot}$ | 0.85  | 2.30  | 3.149 (7) | 175  |

Symmetry codes: (i) $-x, y+1, -z+1$; (ii) $x, y, -z+1$; (iii) $x, y-1, z$; (iv) $-x, y+2, -z+1$. | 143 |
| 156 |
| 159 |
| 140 |
| 173 |
| 171 |
| 164 |
| 175 |
crystallization play a key role in assembling them into a three-dimensional supramolecular network. In particular, serving as the acceptor for N—H· · · O hydrogen bonds arising from the secondary amino groups of different macrocyclic ligands in the crystallographically equivalent chains (O1W for Ni1/Ni3, O2W for Ni2/Ni4), the water molecules link them in two-dimensional layers oriented parallel to the (001) plane (Table 2, Fig. 2a). At the same time, acting as the donors in O—H· · · N hydrogen-bonding interactions with the nitrogen atoms of the non-coordinating cyanide groups of the anions belonging to crystallographically non-equivalent polymeric chains, they form two-dimensional layers oriented parallel to the (100) plane (Table 2, Fig. 2b) thus realizing a three-dimensional system of hydrogen bonds in the crystal.

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.42, last update February 2021; Groom et al., 2016) indicated that several one-dimensional coordination polymers formed by diazacyclam nickel(II) cations (diazacyclam = 1,3,5,8,10,12-hexaaazacyclotetradecane) and the tetracyanonickelate anion have been characterized structurally. They include compounds with monomacrocyclic (refcode MIMJIB; Kou et al., 2002) and macrotricyclic [NADVOE (Zhou et al., 2004), YUBHEK, YUBHIO and YUBHOU (Jiang et al., 2015)] tetradentate ligands. The structures of the polymeric chains in these compounds are very similar. In particular, because of comparable Ni—N(CN) bond lengths and Ni—N—C bond angles, the interchain Ni· · · Ni distances fall in the range 5.07–5.15 Å and are slightly longer than that observed in I. Surprisingly, a similar value for this parameter (5.056 Å) is also observed in the complex of the [Cu(L)]2+ cation with [Ni(CN)4]2− (XABGEO; Černák et al., 2010), despite the substantially longer Cu—N(CN) distance (2.532 Å). This feature is explained by the considerable bending of the Cu—N—C (133.0°) angle as compared the nickel analogues.

5. Synthesis and crystallization

All reagents and solvents used in this work were analytical grade and were used without further purification. The macrocyclic nickel(II) complex Ni(L)(ClO4)2 was prepared according to procedures described previously (Barefield et al., 1976).

\[ [(\text{II})][\text{Ni(CN)}_4] \cdot 2\text{H}_2\text{O}]_n \] (I): A solution of 121 mg (0.50 mmol) of K2[Ni(CN)4] in 15 ml of water was added under stirring to a solution of 290 mg (0.50 mmol) Ni(L)(ClO4)2 in 10 ml of dimethylformamide. Filtration and slow evaporation of the resulting solution gave after several days a light-yellow crystalline precipitate, which was washed with DMF, methanol and dried in air. Yield 160 mg (35%). Analysis calculated for C14H28N8Ni2O2: C, 36.72; H, 6.16; N, 24.47%. Found: C, 36.62; H, 6.26; N, 24.19%. Single crystals 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 3. All H atoms in I 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 water O—H = 0.85 Å, with Uiso(H) values of 1.2 or 1.5Ueq of the parent atoms.

References

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Table 3
Experimental details.

| Crystal data |  |  |
|--------------|---|---|
| Chemical formula | [Ni$_2$(CN)$_4$(C$_{10}$H$_{24}$N$_4$)$_2$]·2H$_2$O |  |
| $M_r$ | 457.86 |  |
| Crystal system, space group | Triclinic, $P$
| Temperature (K) | 180 |  |
| $a$, $b$, $c$ (Å) | 7.7325 (6), 8.8809 (7), 15.7780 (12) |  |
| $\alpha$, $\beta$, $\gamma$ (°) | 88.673 (6), 85.682 (7), 74.623 (7) |  |
| $V$ (Å$^3$) | 1041.74 (15) |  |
| Z | 2 |  |
| Radiation type | Mo Kα |  |
| $\mu$ (mm$^{-1}$) | 1.83 |  |
| Crystal size (mm) | 0.30 × 0.20 × 0.06 |  |

Data collection

| Diffractometer | Rigaku Xcalibur, Eos |  |
| Absorption correction | Multi-scan (CrysAlis PRO; Rigaku OD, 2018) |  |
| $T_{	ext{min}}$, $T_{	ext{max}}$ | 0.852, 1.000 |  |
| No. of measured, independent and observed $|I| > 2\sigma(I)$ reflections | 7144, 3673, 2417 |  |
| $R_{	ext{int}}$ | 0.036 |  |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å$^{-1}$) | 0.595 |  |

Refinement

| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.059, 0.159, 1.07 |  |
| No. of reflections | 3673 |  |
| No. of parameters | 247 |  |
| H-atom treatment | H-atom parameters constrained |  |
| $\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å$^{-3}$) | 1.31, −0.42 |  |

Computer programs: CrysAlis PRO (Rigaku OD, 2018), SHELXT2018/2 (Sheldrick, 2015a), SHELXL2018/3 (Sheldrick, 2015b), Mercury (Macrae et al., 2020) and publCIF (Westrip, 2010).

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Crystal structure of \([[[\text{Ni}(\text{C}_{10}\text{H}_{24}\text{N}_{4})][\text{Ni}(\text{CN})_{4}]]\cdot2\text{H}_{2}\text{O}]]_{n}\), a one-dimensional coordination polymer formed from the \([\text{Ni}(\text{cyclam})]^{2+}\) cation and the \([\text{Ni}(\text{CN})_{4}]^{2-}\) anion

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Computing details

Data collection: *CrysAlis PRO* (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* (Rigaku OD, 2018); data reduction: *CrysAlis PRO* (Rigaku OD, 2018); program(s) used to solve structure: *SHELXT2018/2* (Sheldrick, 2015a); 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-\(\kappa^{4}N_{1},N_{4},N_{8},N_{11}\))nickel(II)]-\(\mu\)-cyanido-\(\kappa^{2}N:C\)-[bis(cyanido-\(\kappa C\))nickel(II)]-\(\mu\)-cyanido-\(\kappa^{2}C:N\)] dihydrate]

**Crystal data**

\([\text{Ni}_{2}(\text{CN})_{4}(\text{C}_{10}\text{H}_{24}\text{N}_{4})]\cdot2\text{H}_{2}\text{O}\)

\(M_r = 457.86\)

Triclinic, \(P\overline{1}\)

\(a = 7.7325 (6)\) Å

\(b = 8.8809 (7)\) Å

\(c = 15.7780 (12)\) Å

\(\alpha = 88.673 (6)\)°

\(\beta = 85.682 (7)\)°

\(\gamma = 74.623 (7)\)°

\(V = 1041.74 (15)\) Å\(^3\)

\(Z = 2\)

\(F(000) = 480\)

\(D_{\text{x}} = 1.460\) Mg m\(^{-3}\)

Mo \(K\alpha\) radiation, \(\lambda = 0.71073\) Å

Cell parameters from 2303 reflections

\(\theta = 2.7–28.8\)°

\(\mu = 1.83\) mm\(^{-1}\)

\(T = 180\) K

Block, colourless

\(0.30 \times 0.20 \times 0.06\) mm

**Data collection**

Rigaku Xcalibur, Eos diffractometer

Radiation source: fine-focus sealed X-ray tube, Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 8.0797 pixels mm\(^{-1}\)

\(\omega\) scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2018)

\(T_{\text{min}} = 0.852, T_{\text{max}} = 1.000\)

7144 measured reflections

3673 independent reflections

2417 reflections with \(I > 2\sigma(I)\)

\(R_{\text{int}} = 0.036\)

\(\theta_{\text{max}} = 25.0\)°, \(\theta_{\text{min}} = 2.4\)°

\(h = -9\rightarrow 9\)

\(k = -9\rightarrow 10\)

\(l = -17\rightarrow 18\)

**Refinement**

Refinement on \(F^2\)

Least-squares matrix: full

\(R(F^2 > 2\sigma(F^2)) = 0.059\)

\(wR(F^2) = 0.159\)

\(S = 1.07\)

3673 reflections

247 parameters

0 restraints
Primary atom site location: dual
Hydrogen site location: mixed
H-atom parameters constrained

\[ w = \frac{1}{[\sigma^2(F_o^2) + (0.064P)^2 + 1.1599P]} \]

where \( P = (F_o^2 + 2F_c^2)/3 \)

\[ (\Delta/\sigma)_{\text{max}} < 0.001 \]
\[ \Delta\rho_{\text{max}} = 1.31 \text{ e Å}^{-3} \]
\[ \Delta\rho_{\text{min}} = -0.42 \text{ e Å}^{-3} \]

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.

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

| Atom  | x     | y     | z     | U_iso* / U_eq |
|-------|-------|-------|-------|---------------|
| Ni4   | 0.000000 | 0.000000 | 0.500000 | 0.0201 (3)   |
| Ni3   | 0.000000 | 1.000000 | 0.000000 | 0.0195 (3)   |
| Ni1   | 0.500000 | 0.500000 | 0.000000 | 0.0172 (3)   |
| Ni2   | 0.500000 | 0.000000 | 0.500000 | 0.0177 (3)   |
| C13   | 0.1682 (7) | 0.3061 (6) | 0.4882 (3) | 0.0190 (11)  |
| N5    | 0.2721 (5) | 0.6907 (5) | 0.0165 (3) | 0.0232 (10)  |
| C8    | 0.3761 (7) | −0.2867 (6) | 0.4659 (4) | 0.0312 (14)  |
| H8A   | 0.496131 | −0.353457 | 0.472014 | 0.037*       |
| H8B   | 0.316556 | −0.338924 | 0.428528 | 0.037*       |
| N8    | −0.0359 (7) | 0.4416 (6) | 0.6889 (3) | 0.0424 (14)  |
| N3    | 0.3772 (6) | −0.0524 (5) | 0.6138 (3) | 0.0259 (11)  |
| H3    | 0.254063 | 0.015213 | 0.617490 | 0.031*       |
| N6    | −0.0089 (7) | 1.0667 (7) | 0.1866 (3) | 0.0459 (14)  |
| N2    | 0.4008 (6) | 0.4404 (5) | −0.1091 (3) | 0.0247 (11)  |
| H2    | 0.278118 | 0.507374 | −0.111458 | 0.030*       |
| C11   | 0.1664 (7) | 0.8059 (7) | 0.0125 (3) | 0.0205 (12)  |
| O2W   | 0.0288 (6) | 0.9077 (5) | 0.3461 (2) | 0.0374 (10)  |
| H2WA  | 0.036923 | 0.959680 | 0.300850 | 0.056*       |
| H2WB  | 0.032480 | 0.814393 | 0.333553 | 0.056*       |
| C14   | −0.0241 (7) | 0.4667 (6) | 0.6168 (4) | 0.0273 (13)  |
| C10   | 0.5288 (8) | 0.0021 (7) | 0.3194 (4) | 0.0322 (14)  |
| H10A  | 0.601399 | −0.007329 | 0.265908 | 0.039*       |
| H10B  | 0.415596 | 0.079153 | 0.312246 | 0.039*       |
| N1    | 0.3727 (5) | 0.3666 (5) | 0.0802 (3) | 0.0224 (10)  |
| H1    | 0.247298 | 0.427127 | 0.090795 | 0.027*       |
| C3    | 0.3903 (7) | 0.2784 (7) | −0.1143 (4) | 0.0336 (14)  |
| H3A   | 0.510949 | 0.209177 | −0.117835 | 0.040*       |
| H3B   | 0.334252 | 0.265566 | −0.165612 | 0.040*       |
| N7    | 0.2769 (5) | 0.1898 (5) | 0.4838 (3) | 0.0231 (10)  |
| C4    | 0.5107 (7) | 0.4876 (7) | −0.1807 (3) | 0.0289 (14)  |
| H4A   | 0.448916 | 0.495059 | −0.232483 | 0.035*       |
| H4B   | 0.625088 | 0.409578 | −0.189027 | 0.035*       |
| C12   | −0.0032 (7) | 1.0368 (6) | 0.1155 (4) | 0.0273 (13)  |
| O1W   | 0.0212 (6) | 0.5830 (5) | 0.8426 (3) | 0.0383 (11)  |
| Atomic displacement parameters ($\overline{A}^2$) |
|-----------------------------------------------|

|         | $U^{11}$  | $U^{22}$  | $U^{33}$  | $U^{12}$  | $U^{13}$  | $U^{23}$  |
|---------|------------|------------|------------|------------|------------|------------|
| Ni4     | 0.0180 (5) | 0.0115 (5) | 0.0275 (6) | 0.0020 (4) | −0.0016 (4) | −0.0006 (4) |
| Ni3     | 0.0170 (5) | 0.0117 (5) | 0.0265 (6) | 0.0015 (4) | −0.0005 (4) | −0.0005 (4) |
| Ni1     | 0.0152 (5) | 0.0111 (5) | 0.0234 (6) | −0.0001 (4) | −0.0012 (4) | −0.0006 (4) |
| Ni2     | 0.0177 (5) | 0.0099 (5) | 0.0228 (6) | 0.0010 (4) | −0.0005 (4) | −0.0019 (4) |
| C13     | 0.017 (3)  | 0.020 (3)  | 0.020 (3)  | −0.006 (2)  | 0.002 (2)   | −0.001 (2)  |
| N5      | 0.015 (2)  | 0.012 (3)  | 0.037 (3)  | 0.005 (2)   | −0.0038 (19) | −0.002 (2)  |
| C8      | 0.024 (3)  | 0.020 (3)  | 0.051 (4)  | −0.007 (3)  | −0.007 (3)  | −0.009 (3)  |
| N8      | 0.058 (4)  | 0.029 (3)  | 0.037 (3)  | −0.005 (3)  | −0.004 (3)  | −0.001 (3)  |
| N3      | 0.022 (2)  | 0.025 (3)  | 0.029 (3)  | −0.002 (2)  | −0.0016 (19) | 0.002 (2)   |
| N6      | 0.055 (4)  | 0.045 (4)  | 0.037 (4)  | −0.012 (3)  | 0.000 (3)   | −0.002 (3)  |
| N2      | 0.020 (2)  | 0.023 (3)  | 0.028 (3)  | −0.001 (2)  | −0.0050 (18) | −0.003 (2)  |
| C11     | 0.024 (3)  | 0.019 (3)  | 0.020 (3)  | −0.007 (2)  | −0.006 (2)  | −0.001 (2)  |
| O2W     | 0.041 (2)  | 0.030 (3)  | 0.039 (3)  | −0.004 (2)  | −0.0061 (19) | 0.005 (2)   |
| C14     | 0.020 (3)  | 0.014 (3)  | 0.044 (4)  | 0.004 (2)   | −0.005 (2)  | −0.002 (3)  |
| C10     | 0.035 (3)  | 0.029 (4)  | 0.029 (3)  | −0.001 (3)  | −0.002 (2)  | −0.005 (3)  |
| N1      | 0.022 (2)  | 0.018 (3)  | 0.026 (3)  | −0.0045 (19) | 0.0040 (18) | 0.000 (2)   |
| C3      | 0.032 (3)  | 0.025 (4)  | 0.046 (4)  | −0.008 (3)  | −0.008 (3)  | −0.011 (3)  |
| N7      | 0.017 (2)  | 0.014 (3)  | 0.034 (3)  | 0.002 (2)   | −0.0014 (18) | 0.003 (2)   |
| C4      | 0.028 (3)  | 0.034 (4)  | 0.023 (3)  | −0.006 (3)  | −0.001 (2)  | −0.003 (3)  |
| C12     | 0.027 (3)  | 0.015 (3)  | 0.039 (4)  | −0.005 (2)  | 0.003 (2)   | 0.005 (3)   |
| O1W     | 0.038 (2)  | 0.033 (3)  | 0.042 (3)  | −0.003 (2)  | −0.0109 (19) | −0.006 (2)  |
| C1      | 0.019 (3)  | 0.012 (3)  | 0.057 (4)  | −0.004 (2)  | 0.008 (2)   | 0.007 (3)   |

*Fixed atomic displacement parameters are given in parentheses.*
### Geometric parameters (Å, °)

| Bond                  | Distance (Å) | Angle (°)   |
|-----------------------|--------------|-------------|
| Ni1—N5                | 2.100 (4)    | N2—C4       | 1.482 (7) |
| Ni1—N5i               | 2.100 (4)    | O2W—H2WA    | 0.8491    |
| Ni1—N2                | 2.070 (4)    | O2W—H2WB    | 0.8493    |
| Ni1—N2i               | 2.070 (4)    | C10—H10A    | 0.9700    |
| Ni1—N1i               | 2.082 (4)    | C10—H10B    | 0.9700    |
| Ni1—N1                | 2.082 (4)    | C10—C9      | 1.528 (8) |
| Ni2—N3                | 2.069 (4)    | N1—H1       | 0.9800    |
| Ni2—N3i               | 2.069 (4)    | N1—C1       | 1.468 (7) |
| Ni2—N7                | 2.095 (4)    | N1—C5i      | 1.474 (6) |
| Ni2—N7ii              | 2.095 (4)    | C3—H3A      | 0.9700    |
| Ni2—N4                | 2.079 (4)    | C3—H3B      | 0.9700    |
| Ni2—N4ii              | 2.079 (4)    | C3—C2       | 1.512 (8) |
| Ni3—C11               | 1.874 (6)    | C4—H4A      | 0.9700    |
| Ni3—C11ii             | 1.874 (6)    | C4—H4B      | 0.9700    |
| Ni3—C12               | 1.857 (6)    | C4—C5       | 1.514 (8) |
| Ni3—C12ii             | 1.857 (6)    | O1W—H1WA    | 0.8499    |
| Ni4—C13               | 1.866 (6)    | O1W—H1WB    | 0.8492    |
| Ni4—C13i              | 1.866 (6)    | C1—H1A      | 0.9700    |
| Ni4—C14               | 1.863 (6)    | C1—H1B      | 0.9700    |
| Ni4—C14i              | 1.863 (6)    | C1—C2       | 1.511 (8) |
| C13—N7                | 1.145 (7)    | N4—H4       | 0.9800    |
| N5—C11                | 1.132 (7)    | N4—C9       | 1.475 (7) |
| C8—H8A                | 0.9700       | C2—H2A      | 0.9700    |
| C8—H8B                | 0.9700       | C2—H2B      | 0.9700    |
| C8—N4                 | 1.470 (6)    | C6—H6A      | 0.9700    |
| C8—C7                 | 1.521 (8)    | C6—H6B      | 0.9700    |
| N8—C14                | 1.156 (7)    | C6—C7       | 1.521 (8) |
| N3—H3                 | 0.9800       | C5—H5A      | 0.9700    |
| N3—C10i               | 1.466 (7)    | C5—H5B      | 0.9700    |
| N3—C6                 | 1.468 (7)    | C9—H9A      | 0.9700    |
| N6—C12                | 1.154 (7)    | C9—H9B      | 0.9700    |
| N2—H2                 | 0.9800       | C7—H7A      | 0.9700    |
| N2—C3                 | 1.467 (7)    | C7—H7B      | 0.9700    |

| Bond                  | Distance (Å) |
|-----------------------|--------------|
| C13v—Ni4—C13         | 180.0        |
| C14v—Ni4—C13i        | 89.7 (2)     |
| C14—Ni4—C13i         | 90.3 (2)     |
| C14v—Ni4—C13         | 90.3 (2)     |
| C14—Ni4—C13          | 89.7 (2)     |
| Bond | Angle | Bond | Angle |
|------|-------|------|-------|
| C14ii—Ni4—C14 | 180.0 | C1—N1—Ni1 | 115.1 (3) |
| C11—Ni3—C11ii | 180.0 | C1—N1—H1 | 107.1 |
| C12—Ni3—C11 | 90.1 (2) | C1—N1—C5i | 114.3 (4) |
| C12ii—Ni3—C11ii | 90.1 (2) | C5i—N1—Ni1 | 105.7 (3) |
| C12ii—Ni3—C12 | 89.9 (2) | C5i—N1—H1 | 107.1 |
| N5ii—Ni1—N5 | 180.0 | N2—C3—H3A | 109.2 |
| N2—Ni1—N5 | 180.0 | N2—C3—H3B | 109.2 |
| N2—Ni1—N5i | 89.31 (17) | N2—C3—C2 | 111.9 (5) |
| N2—Ni1—N5i | 90.69 (17) | C13—N7—Ni2 | 166.1 (4) |
| N2—Ni1—N5 | 90.69 (17) | C5i—N1—H1 | 107.1 |
| N2—Ni1—N2 | 90.69 (17) | N2—C4—H4A | 109.8 |
| N2—Ni1—N2 | 90.69 (17) | N2—C4—H4B | 109.8 |
| N2—Ni1—N1i | 85.61 (17) | N2—C4—C5 | 109.6 (5) |
| N2—Ni1—N1i | 85.61 (17) | H4A—C4—H4B | 108.2 |
| N2—Ni1—N1 | 94.39 (17) | C5—C4—H4A | 109.8 |
| N2—Ni1—N1 | 94.39 (17) | C5—C4—H4B | 109.8 |
| N1i—Ni1—N5i | 90.34 (17) | N6—C12—Ni3 | 176.9 (5) |
| N1i—Ni1—N5i | 89.66 (17) | H1WA—O1W—H1WB | 109.4 |
| N1—Ni1—N1 | 90.34 (17) | N1—C1—H1A | 109.2 |
| N1i—Ni1—N1 | 90.00 (11) | N1—C1—H1B | 109.2 |
| N3i—Ni2—N3 | 180.0 | N1—C1—C2 | 111.9 (4) |
| N3i—Ni2—N3 | 180.0 | N2—C4—H4B | 109.8 |
| N3—Ni2—N7ii | 89.44 (17) | N2—C4—C5 | 109.6 (5) |
| N3—Ni2—N7ii | 90.56 (17) | H4A—C4—H4B | 108.2 |
| N3—Ni2—N7 | 90.56 (17) | C5—C4—H4A | 109.8 |
| N3—Ni2—N7 | 90.56 (17) | C5—C4—H4B | 109.8 |
| N3—Ni2—N4 | 85.36 (17) | C8—N4—Ni2 | 115.6 (3) |
| N3—Ni2—N4i | 85.36 (17) | C8—N4—H4 | 107.0 |
| N3—Ni2—N4 | 94.64 (17) | C8—N4—C9 | 113.8 (4) |
| N3—Ni2—N4 | 94.64 (17) | C9—N4—Ni2 | 105.9 (3) |
| N3—Ni2—N7ii | 180.0 | C9—N4—H4 | 107.0 |
| N4—Ni2—N7ii | 180.0 | C9—N4—H4 | 107.0 |
| N4—Ni2—N7ii | 89.87 (17) | C3—C2—H2A | 108.1 |
| N4—Ni2—N7ii | 90.13 (17) | C3—C2—H2B | 108.1 |
| N4—Ni2—N7ii | 90.13 (17) | C1—C2—C3 | 116.7 (4) |
| N4—Ni2—N7ii | 89.87 (17) | C1—C2—H2A | 108.1 |
| N4—Ni2—N4 | 89.87 (17) | C1—C2—H2B | 108.1 |
| N7—C13—Ni4 | 176.4 (5) | H2A—C2—H2B | 107.3 |
| C11—N5—Ni1 | 166.1 (4) | N3—C6—H6A | 109.2 |
| H8A—C8—H8B | 107.9 | N3—C6—H6B | 109.2 |
| N4—C8—H8A | 109.2 | N3—C6—C7 | 111.9 (4) |
| N4—C8—H8B | 109.2 | H6A—C6—H6B | 107.9 |
| N4—C8—C7 | 112.1 (5) | C7—C6—H6A | 109.2 |
| C7—C8—H8A | 109.2 | C7—C6—H6B | 109.2 |
| C7—C8—H8B | 109.2 | N1i—C5—C4 | 109.3 (3) |
| Ni2—N3—H3 | 106.9 | N1i—C5—H5A | 109.8 |
| C10ii—N3—Ni2 | 105.8 (3) | N1i—C5—H5B | 109.8 |
| C10ii—N3—H3 | 106.9 | C4—C5—H5A | 109.8 |
C10ii—N3—C6 113.3 (4) C4—C5—H5B 109.8
C6—N3—Ni2 116.6 (4) C5A—C5—H5B 108.3
C6—N3—H3 106.9 C10—C9—H9A 110.1
Ni1—N2—H2 107.0 C10—C9—H9B 110.1
C3—N2—Ni1 116.2 (3) N4—C9—C10 108.2 (5)
C3—N2—H2 107.0 N4—C9—H9A 110.1
C3—N2—C4 113.7 (4) N4—C9—H9B 110.1
C4—N2—Ni1 105.5 (3) H9A—C9—H9B 108.4
C4—N2—H2 107.0 C8—C7—C6 117.0 (4)
N5—C11—Ni3 176.5 (5) C8—C7—H7A 108.1
H2WA—O2W—H2WB 109.4 C8—C7—H7B 108.1
N8—C14—Ni4 178.0 (5) C6—C7—H7A 108.1
N3ii—C10—H10A 109.8 C6—C7—H7B 108.1
N3ii—C10—H10B 109.8 H7A—C7—H7B 107.3

Ni1—N2—C3—C2 54.8 (5) N2—C4—C5—N1i 56.3 (6)
Ni1—N2—C4—C5 −40.9 (5) C10ii—N3—C6—C7 −177.7 (5)
Ni1—N1—C1—C2 −56.5 (5) N1—C1—C2—C3 71.8 (7)
Ni2—N3—C6—C7 −54.5 (5) C3—N2—C4—C5 −169.4 (4)
Ni2—N4—C9—C10 −40.9 (5) C4—N2—C3—C2 177.5 (4)
C8—N4—C9—C10 −169.0 (4) N4—C8—C7—C6 −70.7 (6)
N3ii—C10—C9—N4 57.3 (6) C5i—N1—C1—C2 −179.1 (4)
N3—C6—C7—C8 69.7 (6) C7—C8—N4—Ni2 55.4 (5)
N2—C3—C2—C1 −70.5 (7) C7—C8—N4—C9 178.2 (4)

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

Hydrogen-bond geometry (Å, °)

| D—H···A          | D—H | H···A | D···A | D—H···A |
|------------------|------|-------|-------|---------|
| N1—H1···O1Wvi    | 0.98 | 2.28  | 3.115 (6) | 143     |
| N2—H2···O1Wvi    | 0.98 | 2.10  | 3.020 (6) | 156     |
| N3—H3···O2Wvi    | 0.98 | 2.15  | 3.083 (7) | 159     |
| N4—H4···O2Wvi    | 0.98 | 2.26  | 3.080 (6) | 140     |
| O1W—H1WA···N8    | 0.85 | 2.03  | 2.872 (7) | 173     |
| O1W—H1WB···N6iii | 0.85 | 2.27  | 3.112 (7) | 171     |
| O2W—H2WA···N6    | 0.85 | 2.03  | 2.853 (6) | 164     |
| O2W—H2WB···N8v   | 0.85 | 2.30  | 3.149 (7) | 175     |

Symmetry codes: (iv) −x, −y+1, −z+1; (v) x, y, −z; (vi) x, y−1, z; (vii) −x, −y+2, −z+1.

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