



# 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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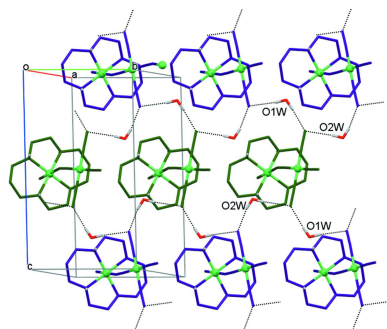
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The asymmetric unit of the title compound, *catena*-poly[[[(1,4,8,11-tetraazacyclotetradecane- $\kappa^4 N^1, N^4, N^8, N^{11}$ )nickel(II)]- $\mu$ -cyanido- $\kappa^2 N:C$ -[bis(cyanido- $\kappa C$ )nickel(II)]- $\mu$ -cyanido- $\kappa^2 C:N$ ] dihydrate],  $\{[\text{Ni}_2(\text{CN})_4(\text{C}_{10}\text{H}_{24}\text{N}_4)] \cdot 2\text{H}_2\text{O}\}_n$  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  $\bar{1}$ ) 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  $[1\bar{1}0]$  direction. The water molecules of crystallization play a pivotal role in the three-dimensional supramolecular organization of the crystal. Acting as acceptors, they form  $\text{N}-\text{H} \cdots \text{O}_w$  ( $w$  = 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*  $\text{O}_w-\text{H} \cdots \text{N}_c$  ( $c$  = cyanide) hydrogen bonds, giving two-dimensional layers oriented parallel to the (100) plane and thus generating a three-dimensional network.

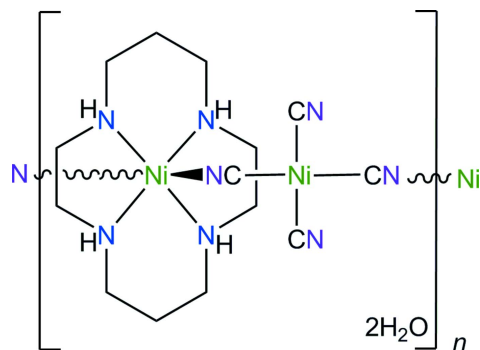
## 1. Chemical context

Transition-metal complexes of tetraazamacrocyclic 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.*,



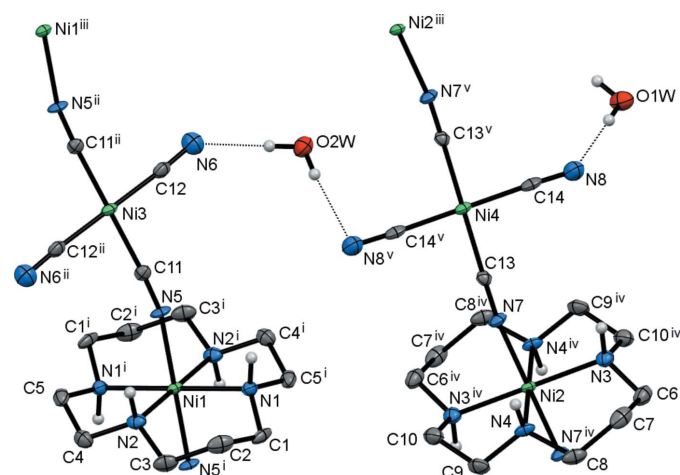
2019). Among such linkers, the tetracyanonickelate(II) dianion has attracted less attention compared to hexa- and octacyanomethylates and only one work describing the structure of the coordination polymer formed by the metal(cyclam) complex and this anion, *i.e.*,  $\{Cu(L)[Ni(CN)_4]\}_n$ , has been published to date (Černák *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*-[bis( $\mu_2$ -cyano- $\kappa^2$ C,N)-dicyano-(1,4,8,11-tetraazacyclotetradecane- $\kappa^4$ N<sup>1</sup>,N<sup>4</sup>,N<sup>8</sup>,N<sup>11</sup>)-dinickel(II) dihydrate],  $[[Ni(L)][Ni(CN)_4]\cdot 2H_2O]_n$  (**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



**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). C-bound H atoms are omitted for clarity. Dotted lines represent hydrogen-bonding interactions. Symmetry codes: (i)  $-x + 1, -y + 1, -z$ ; (ii)  $-x, -y + 2, -z$ ; (iii)  $x - 1, y + 1, z$ ; (iv)  $-x + 1, -y, -z + 1$ ; (v)  $-x, -y + 1, -z + 1$ .

**Table 1**  
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	1.866 (6)
Ni2—N7	2.095 (4)	Ni4—C14	1.863 (6)

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O1W <sup>i</sup>	0.98	2.28	3.115 (6)	143
N2—H2...O1W <sup>ii</sup>	0.98	2.10	3.020 (6)	156
N3—H3...O2W <sup>i</sup>	0.98	2.15	3.083 (7)	159
N4—H4...O2W <sup>iii</sup>	0.98	2.26	3.080 (6)	140
O1W—H1WA...N8	0.85	2.03	2.872 (7)	173
O1W—H1WB...N6 <sup>iv</sup>	0.85	2.27	3.112 (7)	171
O2W—H2WA...N6	0.85	2.03	2.853 (6)	164
O2W—H2WB...N8 <sup>i</sup>	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)  $-x, -y + 2, -z + 1$ .

macrocyclic  $[Ni(L)]^{2+}$  cations and tetracyanonickelate anions  $[Ni(CN)_4]^{2-}$ . 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  $[1\bar{1}0]$  direction.

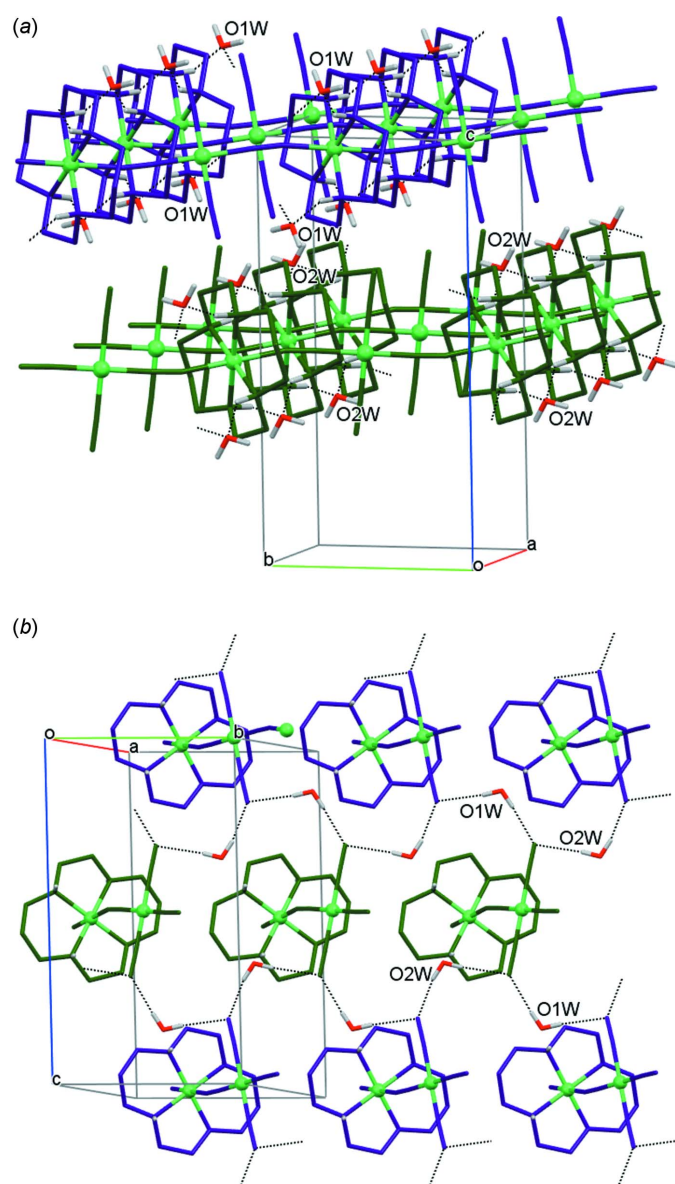
The location of the metal ions on inversion centres enforces strict planarity of the Ni(N<sub>4</sub>) and Ni(C<sub>4</sub>) coordination moieties. The macrocyclic ligand in the complex cations adopts the most common and energetically favorable *trans*-III (*R,R,S,S*) conformation (Bosnich *et al.*, 1965) with almost equal Ni—N bond lengths (Table 1). The five-membered chelate rings are present in *gauche* (bite angles *ca* 85.5°) and the six-membered in *chair* (bite angles *ca* 94.5°) conformations (Table 1). The geometric parameters observed are characteristic of high-spin *d*<sup>8</sup> nickel(II) complexes with macrocyclic 14-membered tetraamine ligands (Lampeka & Tsybmal, 2004; Tsybmal *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<sub>4</sub>N<sub>2</sub> 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  $[Ni-N-C = 166.1 (4)^\circ]$ , giving rise to a linear polymeric chain, whereas the two remaining *trans* CN<sup>−</sup> 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  $[Ni(L)]^{2+}$  cations bridged by the  $[Ni(CN)_4]^{2-}$  anions, which propagate along the  $[1\bar{1}0]$  direction. There are no direct contacts between the chains and the water molecules of

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.



**Figure 2**  
View of the sheets of polymeric chains formed due to the hydrogen-bond acceptor (a) and donor (b) properties of the water molecules of crystallization. The macrocyclic ligands in the crystallographically non-equivalent nickel ions are shown in violet (Ni1/Ni3) and green (Ni2/Ni4) colors.

#### 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-hexaazacyclotetradecane) 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)]<sup>2+</sup> cation with [Ni(CN)<sub>4</sub>]<sup>2-</sup> (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)(ClO<sub>4</sub>)<sub>2</sub> was prepared according to procedures described previously (Barefield *et al.*, 1976).

**[[Ni(L)][Ni(CN)<sub>4</sub>]]·2H<sub>2</sub>O<sub>n</sub>, (I):** A solution of 121 mg (0.50 mmol) of K<sub>2</sub>[Ni(CN)<sub>4</sub>] in 15 ml of water was added under stirring to a solution of 290 mg (0.50 mmol) Ni(L)(ClO<sub>4</sub>)<sub>2</sub> 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 C<sub>14</sub>H<sub>28</sub>N<sub>8</sub>Ni<sub>2</sub>O<sub>2</sub>: 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 *U*<sub>iso</sub>(H) values of 1.2 or 1.5*U*<sub>eq</sub> of the parent atoms.

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**Table 3**  
Experimental details.

Crystal data	
Chemical formula	[Ni <sub>2</sub> (CN) <sub>4</sub> (C <sub>10</sub> H <sub>24</sub> N <sub>4</sub> )]·2H <sub>2</sub> O
<i>M<sub>r</sub></i>	457.86
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	180
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.7325 (6), 8.8809 (7), 15.7780 (12)
$\alpha$ , $\beta$ , $\gamma$ (°)	88.673 (6), 85.682 (7), 74.623 (7)
<i>V</i> (Å <sup>3</sup> )	1041.74 (15)
<i>Z</i>	2
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	1.83
Crystal size (mm)	0.30 × 0.20 × 0.06
Data collection	
Diffractometer	Rigaku Xcalibur, Eos
Absorption correction	Multi-scan ( <i>CrysAlis PRO</i> ; Rigaku OD, 2018)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.852, 1.000
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	7144, 3673, 2417
<i>R<sub>int</sub></i>	0.036
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.595
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.059, 0.159, 1.07
No. of reflections	3673
No. of parameters	247
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	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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## supporting information

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## 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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### 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- $\kappa^4\text{N}^1, \text{N}^4, \text{N}^8, \text{N}^{11}$ )nickel(II)]- $\mu$ -cyanido- $\kappa^2\text{N}:\text{C}$ -[bis(cyanido- $\kappa\text{C}$ )nickel(II)]- $\mu$ -cyanido- $\kappa^2\text{C}:\text{N}$ ] dihydrate]

### Crystal data

$[\text{Ni}_2(\text{CN})_4(\text{C}_{10}\text{H}_{24}\text{N}_4)] \cdot 2\text{H}_2\text{O}$

$M_r = 457.86$

Triclinic,  $P\bar{1}$

$a = 7.7325$  (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<sup>3</sup>

$Z = 2$

$F(000) = 480$

$D_x = 1.460$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 2303 reflections

$\theta = 2.7\text{--}28.8^\circ$

$\mu = 1.83$  mm<sup>-1</sup>

$T = 180$  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<sup>-1</sup>

$\omega$  scans

Absorption correction: multi-scan

(CrysAlisPro; Rigaku OD, 2018)

$T_{\min} = 0.852$ ,  $T_{\max} = 1.000$

7144 measured reflections

3673 independent reflections

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

$R_{\text{int}} = 0.036$

$\theta_{\max} = 25.0^\circ$ ,  $\theta_{\min} = 2.4^\circ$

$h = -9 \rightarrow 9$

$k = -9 \rightarrow 10$

$l = -17 \rightarrow 18$

### 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

$$w = 1/[\sigma^2(F_o^2) + (0.064P)^2 + 1.1599P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 1.31 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni4	0.000000	0.500000	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)

H1WA	-0.004667	0.541681	0.798936	0.057*
H1WB	0.027685	0.675211	0.830710	0.057*
C1	0.3698 (7)	0.2153 (6)	0.0457 (4)	0.0300 (14)
H1A	0.303586	0.163745	0.086184	0.036*
H1B	0.491913	0.149679	0.037738	0.036*
N4	0.3896 (5)	-0.1378 (5)	0.4269 (3)	0.0225 (10)
H4	0.267023	-0.077143	0.417091	0.027*
C2	0.2837 (7)	0.2331 (7)	-0.0382 (4)	0.0373 (15)
H2A	0.169263	0.311348	-0.031187	0.045*
H2B	0.258498	0.135002	-0.050764	0.045*
C6	0.3638 (7)	-0.2135 (7)	0.6248 (4)	0.0336 (15)
H6A	0.295970	-0.222107	0.678108	0.040*
H6B	0.483387	-0.283061	0.627483	0.040*
C5	0.5424 (7)	0.6439 (7)	-0.1614 (3)	0.0295 (14)
H5A	0.619798	0.672475	-0.206694	0.035*
H5B	0.428831	0.723764	-0.157782	0.035*
C9	0.4941 (7)	-0.1553 (7)	0.3439 (3)	0.0323 (14)
H9A	0.427445	-0.187587	0.301267	0.039*
H9B	0.607290	-0.234112	0.347689	0.039*
C7	0.2724 (7)	-0.2638 (7)	0.5524 (4)	0.0364 (16)
H7A	0.244558	-0.361196	0.568747	0.044*
H7B	0.159067	-0.186226	0.546429	0.044*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
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)

N4	0.021 (2)	0.013 (2)	0.034 (3)	-0.0037 (19)	-0.0065 (18)	-0.006 (2)
C2	0.025 (3)	0.026 (4)	0.064 (4)	-0.011 (3)	-0.003 (3)	-0.010 (3)
C6	0.027 (3)	0.027 (4)	0.045 (4)	-0.006 (3)	0.003 (3)	0.010 (3)
C5	0.024 (3)	0.030 (4)	0.028 (3)	0.002 (3)	0.003 (2)	0.009 (3)
C9	0.038 (3)	0.030 (4)	0.026 (3)	-0.002 (3)	-0.004 (2)	-0.012 (3)
C7	0.018 (3)	0.027 (4)	0.064 (5)	-0.008 (3)	-0.002 (3)	0.010 (3)

*Geometric parameters (Å, °)*

Ni1—N5	2.100 (4)	N2—C4	1.482 (7)
Ni1—N5 <sup>i</sup>	2.100 (4)	O2W—H2WA	0.8491
Ni1—N2 <sup>i</sup>	2.070 (4)	O2W—H2WB	0.8493
Ni1—N2	2.070 (4)	C10—H10A	0.9700
Ni1—N1 <sup>i</sup>	2.082 (4)	C10—H10B	0.9700
Ni1—N1	2.082 (4)	C10—C9	1.528 (8)
Ni2—N3 <sup>ii</sup>	2.069 (4)	N1—H1	0.9800
Ni2—N3	2.069 (4)	N1—C1	1.468 (7)
Ni2—N7	2.095 (4)	N1—C5 <sup>i</sup>	1.474 (6)
Ni2—N7 <sup>ii</sup>	2.095 (4)	C3—H3A	0.9700
Ni2—N4	2.079 (4)	C3—H3B	0.9700
Ni2—N4 <sup>ii</sup>	2.079 (4)	C3—C2	1.512 (8)
Ni3—C11	1.874 (6)	C4—H4A	0.9700
Ni3—C11 <sup>iii</sup>	1.874 (6)	C4—H4B	0.9700
Ni3—C12 <sup>iii</sup>	1.857 (6)	C4—C5	1.514 (8)
Ni3—C12	1.857 (6)	O1W—H1WA	0.8499
Ni4—C13 <sup>iv</sup>	1.866 (6)	O1W—H1WB	0.8492
Ni4—C13	1.866 (6)	C1—H1A	0.9700
Ni4—C14 <sup>iv</sup>	1.863 (6)	C1—H1B	0.9700
Ni4—C14	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—C10 <sup>ii</sup>	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
C13 <sup>iv</sup> —Ni4—C13	180.0	N3 <sup>ii</sup> —C10—C9	109.3 (4)
C14 <sup>iv</sup> —Ni4—C13 <sup>iv</sup>	89.7 (2)	H10A—C10—H10B	108.3
C14—Ni4—C13 <sup>iv</sup>	90.3 (2)	C9—C10—H10A	109.8
C14 <sup>iv</sup> —Ni4—C13	90.3 (2)	C9—C10—H10B	109.8
C14—Ni4—C13	89.7 (2)	Ni1—N1—H1	107.1



C14 <sup>iv</sup> —Ni4—C14	180.0	C1—N1—Ni1	115.1 (3)
C11—Ni3—C11 <sup>iii</sup>	180.0	C1—N1—H1	107.1
C12—Ni3—C11	90.1 (2)	C1—N1—C5 <sup>i</sup>	114.3 (4)
C12 <sup>iii</sup> —Ni3—C11 <sup>iii</sup>	90.1 (2)	C5 <sup>i</sup> —N1—Ni1	105.7 (3)
C12—Ni3—C11 <sup>iii</sup>	89.9 (2)	C5 <sup>i</sup> —N1—H1	107.1
C12 <sup>iii</sup> —Ni3—C11	89.9 (2)	N2—C3—H3A	109.2
C12 <sup>iii</sup> —Ni3—C12	180.0	N2—C3—H3B	109.2
N5 <sup>i</sup> —Ni1—N5	180.0	N2—C3—C2	111.9 (5)
N2—Ni1—N5	89.31 (17)	H3A—C3—H3B	107.9
N2—Ni1—N5 <sup>i</sup>	90.69 (17)	C2—C3—H3A	109.2
N2 <sup>i</sup> —Ni1—N5 <sup>i</sup>	89.31 (17)	C2—C3—H3B	109.2
N2 <sup>i</sup> —Ni1—N5	90.69 (17)	C13—N7—Ni2	166.1 (4)
N2 <sup>i</sup> —Ni1—N2	180.00 (11)	N2—C4—H4A	109.8
N2—Ni1—N1 <sup>i</sup>	85.61 (17)	N2—C4—H4B	109.8
N2 <sup>i</sup> —Ni1—N1	85.61 (17)	N2—C4—C5	109.6 (5)
N2 <sup>i</sup> —Ni1—N1 <sup>i</sup>	94.39 (17)	H4A—C4—H4B	108.2
N2—Ni1—N1	94.39 (17)	C5—C4—H4A	109.8
N1 <sup>i</sup> —Ni1—N5	90.34 (17)	C5—C4—H4B	109.8
N1—Ni1—N5	89.66 (17)	N6—C12—Ni3	176.9 (5)
N1 <sup>i</sup> —Ni1—N5 <sup>i</sup>	89.66 (17)	H1WA—O1W—H1WB	109.4
N1—Ni1—N5 <sup>i</sup>	90.34 (17)	N1—C1—H1A	109.2
N1 <sup>i</sup> —Ni1—N1	180.0	N1—C1—H1B	109.2
N3 <sup>ii</sup> —Ni2—N3	180.0	N1—C1—C2	111.9 (4)
N3 <sup>ii</sup> —Ni2—N7 <sup>ii</sup>	89.44 (17)	H1A—C1—H1B	107.9
N3—Ni2—N7 <sup>ii</sup>	90.56 (17)	C2—C1—H1A	109.2
N3 <sup>ii</sup> —Ni2—N7	90.56 (17)	C2—C1—H1B	109.2
N3—Ni2—N7	89.44 (17)	Ni2—N4—H4	107.0
N3 <sup>ii</sup> —Ni2—N4	85.36 (17)	C8—N4—Ni2	115.6 (3)
N3—Ni2—N4 <sup>ii</sup>	85.36 (17)	C8—N4—H4	107.0
N3—Ni2—N4	94.64 (17)	C8—N4—C9	113.8 (4)
N3 <sup>ii</sup> —Ni2—N4 <sup>ii</sup>	94.64 (17)	C9—N4—Ni2	105.9 (3)
N7 <sup>ii</sup> —Ni2—N7	180.0	C9—N4—H4	107.0
N4 <sup>ii</sup> —Ni2—N7 <sup>ii</sup>	89.87 (17)	C3—C2—H2A	108.1
N4 <sup>ii</sup> —Ni2—N7	90.13 (17)	C3—C2—H2B	108.1
N4—Ni2—N7 <sup>ii</sup>	90.13 (17)	C1—C2—C3	116.7 (4)
N4—Ni2—N7	89.87 (17)	C1—C2—H2A	108.1
N4 <sup>ii</sup> —Ni2—N4	180.0	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	N1 <sup>i</sup> —C5—C4	109.3 (4)
Ni2—N3—H3	106.9	N1 <sup>i</sup> —C5—H5A	109.8
C10 <sup>ii</sup> —N3—Ni2	105.8 (3)	N1 <sup>i</sup> —C5—H5B	109.8
C10 <sup>ii</sup> —N3—H3	106.9	C4—C5—H5A	109.8

C10 <sup>ii</sup> —N3—C6	113.3 (4)	C4—C5—H5B	109.8
C6—N3—Ni2	116.6 (4)	H5A—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
N3 <sup>ii</sup> —C10—H10A	109.8	C6—C7—H7B	108.1
N3 <sup>ii</sup> —C10—H10B	109.8	H7A—C7—H7B	107.3
Ni1—N2—C3—C2	54.8 (5)	N2—C4—C5—N1 <sup>i</sup>	56.3 (6)
Ni1—N2—C4—C5	-40.9 (5)	C10 <sup>ii</sup> —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)
N3 <sup>ii</sup> —C10—C9—N4	57.3 (6)	C5 <sup>i</sup> —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 ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 $\cdots$ O1W <sup>iv</sup>	0.98	2.28	3.115 (6)	143
N2—H2 $\cdots$ O1W <sup>v</sup>	0.98	2.10	3.020 (6)	156
N3—H3 $\cdots$ O2W <sup>iv</sup>	0.98	2.15	3.083 (7)	159
N4—H4 $\cdots$ O2W <sup>vi</sup>	0.98	2.26	3.080 (6)	140
O1W—H1WA $\cdots$ N8	0.85	2.03	2.872 (7)	173
O1W—H1WB $\cdots$ N6 <sup>vii</sup>	0.85	2.27	3.112 (7)	171
O2W—H2WA $\cdots$ N6	0.85	2.03	2.853 (6)	164
O2W—H2WB $\cdots$ N8 <sup>iv</sup>	0.85	2.30	3.149 (7)	175

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