

# Crystal structure of *trans*-(1,8-dibutyl-1,3,6,8,10,13-hexaazacyclotetradecane- $\kappa^4N^3,N^6,N^{10},N^{13}$ )bis(isonicotinato- $\kappa O$ )nickel(II) determined from synchrotron data

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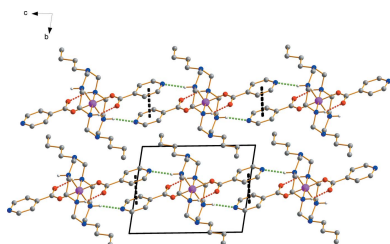
**Supporting information:** this article has supporting information at journals.iucr.org/e

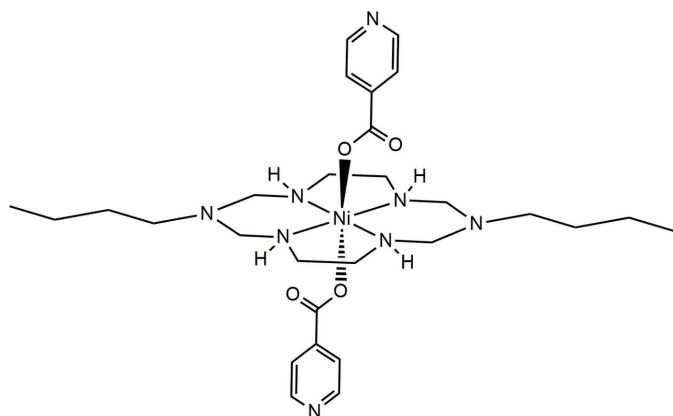
The title compound,  $[\text{Ni}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{C}_{16}\text{H}_{38}\text{N}_6)]$ , was prepared through self-assembly of a nickel(II) azamacrocyclic complex with isonicotinic acid. The  $\text{Ni}^{\text{II}}$  atom is located on an inversion center and exhibits a distorted octahedral  $\text{N}_4\text{O}_2$  coordination environment, with the four secondary N atoms of the azamacrocyclic ligand in the equatorial plane [average  $\text{Ni}-\text{N}_{\text{eq}} = 2.064(11) \text{ \AA}$ ] and two O atoms of monodentate isonicotinate anions in axial positions [ $\text{Ni}-\text{O}_{\text{ax}} = 2.137(1) \text{ \AA}$ ]. Intramolecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bonds between one of the secondary amine N atoms of the azamacrocyclic ligand and the non-coordinating carboxylate O atom of the anion stabilize the molecular structure. Intermolecular  $\text{N}-\text{H}\cdots\text{N}$  hydrogen bonds, as well as  $\pi$ - $\pi$  interactions between neighbouring pyridine rings, give rise to the formations of supramolecular ribbons extending parallel to [001].

## 1. Chemical context

The molecular design and synthesis of coordination polymers with macrocyclic ligands have attracted considerable attention because of their potential applications in chemistry, environmental chemistry, and materials science (Churchard *et al.*, 2010; Lehn, 2015). To obtain specific molecular compounds through assembly of supramolecular building blocks with properties such as guest recognition or catalytic effects, macrocyclic complexes involving vacant sites in an axial position are good candidates. Moreover, these complexes can also be easily derivatized by carboxylic acid moieties, such as 1,3,5-BTC (1,3,5-benzenetricarboxylic acid), 2,7-NDC (2,7-naphthalenedicarboxylic acid) or 1,3,5-CTC (1,3,5-cyclohexanetricarboxylic acid), forming interesting coordination compounds with supramolecular structures ranging from chains to networks (Min & Suh, 2001; Shin *et al.*, 2016*b*). For example,  $[\text{Ni}(L^R, R)]_3[\text{BTC}^{3-}]_2 \cdot 12\text{H}_2\text{O} \cdot \text{CH}_3\text{CN}$  ( $L^R, R = 1,8$ -bis[(*R*)- $\alpha$ -methylbenzyl]-1,3,6,8,10,13-hexaazacyclotetradecane) displays a two-dimensional supramolecular network structure and exhibits a selective chiral recognition for racemic material (Ryoo *et al.*, 2010). Isonicotinic acid as another building unit can easily bind or interact with transition metal ions through its possible bridging or coordination modes associated with the carboxylic group and pyridine moieties, respectively, thus allowing the assembly of compounds with supramolecular structures or the formation of heterometallic complexes (Xie *et al.*, 2014).

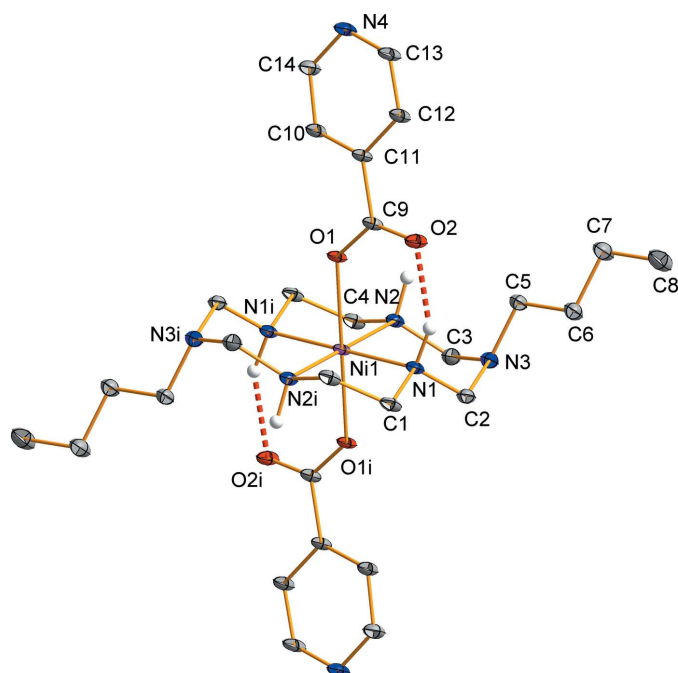
Here, we report on the synthesis and crystal structure of an  $\text{Ni}^{\text{II}}$  azamacrocyclic complex including isonicotinate anions,  $[\text{Ni}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{C}_{16}\text{H}_{38}\text{N}_6)]$ , (**I**).





## 2. Structural commentary

Compound (**1**) is isotopic with its copper(II) analogue (Shin *et al.*, 2015). The nickel(II) atom is located on an inversion center. The coordination environment around the nickel(II) atom is distorted octahedral with the four secondary amine N atoms of the azamacrocyclic ligand in the equatorial plane and two O atoms of two monodentate isonicotinate anions in axial positions (Fig. 1). The average Ni–N<sub>eq</sub> bond lengths is 2.064 (11) Å and the Ni–O<sub>ax</sub> bond length is 2.137 (1) Å. The longer axial bonds can be attributed to a ring contraction of the azamacrocyclic ligand (Melson, 1979). The six-membered NiC<sub>2</sub>N<sub>3</sub> ring (Ni1–N1–C2–N3–C3–N2) adopts the expected



**Figure 1**  
View of the molecular structure of the title compound, showing the atom-labelling scheme, with displacement ellipsoids drawn at the 30% probability level. H atoms bonded to C atoms have been omitted for clarity. Intramolecular N–H...O hydrogen bonds are shown as red dashed lines. [Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ .]

**Table 1**  
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...O2	1.00	1.98	2.892 (2)	150
N2–H2...N4 <sup>i</sup>	1.00	2.23	3.143 (2)	151

Symmetry code: (i)  $-x + 1, -y + 1, -z$ .

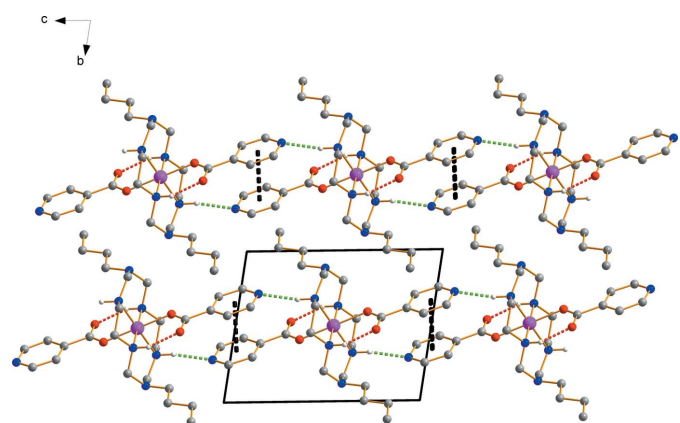
chair conformation, whereas the five-membered NiC<sub>2</sub>N<sub>2</sub> ring (Ni1–N1–C1–C4–N2) has a *gauche* conformation (Min & Suh, 2001). Since the carboxylate group is fully delocalized, the two C–O bonds and the bond angle (O1–C9–O2) are 1.267 (2), 1.248 (2) Å and 126.9 (2)°, respectively. The bond angles around the nickel(II) atom are in the normal range for an octahedral complex. Intramolecular N–H...O hydrogen bonds between one of the secondary amine groups of the azamacrocyclic ligand and the non-coordinating carboxylate O atom of the isonicotinate anion form six-membered rings and stabilize the molecular structure (Fig. 1, Table 1).

## 3. Supramolecular features

The N4 atom of the isonicotinate anion forms an intermolecular hydrogen bond with an adjacent secondary amine group of the azamacrocyclic ligand (Fig. 2, Table 1) (Steed & Atwood, 2009). In addition, parallel pyridine rings (Hunter & Sanders, 1990) of the isonicotinate anions participate in  $\pi$ – $\pi$  interactions with a centroid-to-centroid distance of 3.741 (1) Å and an interplanar separation of 3.547 (1) Å. The interplay between hydrogen bonds and  $\pi$ – $\pi$  interactions give rise to the formation of supramolecular ribbons extending parallel to [001].

## 4. Database survey

A search of the Cambridge Structural Database (Version 5.36, May 2014 with 3 updates; Groom & Allen, 2014) reveals two



**Figure 2**  
View of the crystal packing of the title compound, showing hydrogen bonds and  $\pi$ – $\pi$  interactions (red: intramolecular N–H...O hydrogen bonds, green: intermolecular N–H...N hydrogen bonds, black:  $\pi$ – $\pi$  interactions).

complexes with the same nickel(II) azamacrocyclic building block (Kim *et al.*, 2015*a,b*) for which synthesis, FT-IR spectroscopic data and the crystal structure have been reported.

## 5. Synthesis and crystallization

The starting complex,  $[\text{Ni}(\text{C}_{16}\text{H}_{38}\text{N}_6)(\text{ClO}_4)_2]$ , was prepared in a slightly modified procedure with respect to the reported method (Kim *et al.*, 2015*b*). To an acetonitrile solution (14 mL) of  $[\text{Ni}(\text{C}_{16}\text{H}_{38}\text{N}_6)(\text{ClO}_4)_2]$  (0.298 g, 0.52 mmol) was slowly added an acetonitrile solution (8 mL) containing isonicotinic acid (0.128 g, 1.04 mmol) and excess triethylamine (0.12 g, 1.20 mmol) at room temperature. The purple precipitate was filtered off, washed with acetonitrile and diethyl ether, and dried in air. Single crystals of compound (**1**) were obtained by layering of the acetonitrile solution of isonicotinic acid on the acetonitrile solution of  $[\text{Ni}(\text{C}_{16}\text{H}_{38}\text{N}_6)(\text{ClO}_4)_2]$  for several days. Yield: 0.167 g (52%). FT-IR (ATR,  $\text{cm}^{-1}$ ): 3145, 3075, 2951, 2920, 1571, 1457, 1351, 1272, 1014, 915.

**Safety note:** Although we have experienced no problems with the compounds reported in this study, perchlorate salts of metal complexes are often explosive and should be handled with great caution.

## 6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.95 (ring H atoms) or 0.98–0.99 Å (open-chain H atoms), and an N—H distance of 1.0 Å, with  $U_{\text{iso}}(\text{H})$  values of 1.2 or  $1.5U_{\text{eq}}$  of the parent atoms.

## Acknowledgements

This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (NRF-2014R1A1A2058815) and supported by the Institute for Basic Science (IBS-R007-D1-2016-a01). The X-ray crystallography BL2D-SMC beamline and FT-IR experiment at the PLS-II are supported in part by MSIP and POSTECH.

## References

- Churchard, A. J., Cyranski, M. K., Dobrzycki, Ł., Budzianowski, A. & Grochala, W. (2010). *Energ. Environ. Sci.* **3**, 1973–1978.  
Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.  
Hunter, C. A. & Sanders, K. M. (1990). *J. Am. Chem. Soc.* **112**, 5525–5534.

**Table 2**  
Experimental details.

Crystal data	
Chemical formula	$[\text{Ni}(\text{C}_6\text{H}_4\text{NO}_2)_2(\text{C}_{16}\text{H}_{38}\text{N}_6)]$
$M_r$	617.44
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
$a, b, c$ (Å)	8.0630 (16), 8.5110 (17), 10.927 (2)
$\alpha, \beta, \gamma$ (°)	80.52 (3), 88.26 (3), 86.44 (3)
$V$ (Å <sup>3</sup> )	738.0 (3)
$Z$	1
Radiation type	Synchrotron, $\lambda = 0.62998$ Å
$\mu$ (mm <sup>-1</sup> )	0.51
Crystal size (mm)	0.01 × 0.004 × 0.004
Data collection	
Diffractometer	ADSC Q210 CCD area detector
Absorption correction	Empirical ( <i>HKL-3000SM SCALE-PAK</i> ; Otwinowski & Minor, 1997)
$T_{\text{min}}, T_{\text{max}}$	0.995, 0.998
No. of measured, independent and observed [ $I > 2\sigma(I)$ ] reflections	7634, 3879, 3326
$R_{\text{int}}$	0.023
$(\sin \theta/\lambda)_{\text{max}}$ (Å <sup>-1</sup> )	0.696
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.040, 0.110, 1.04
No. of reflections	3879
No. of parameters	188
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	1.12, -0.95

Computer programs: *PAL BL2D-SMDC* (Shin *et al.*, 2016*a*), *HKL-3000SM* (Otwinowski & Minor, 1997), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *DIAMOND* (Putz & Brandenburg, 2014) and *PUBLICIF* (Westrip, 2010).

- Kim, D.-W., Kim, J. J., Shin, J. W., Kim, J. H. & Moon, D. (2015*a*). *Acta Cryst.* **E71**, 779–782.  
Kim, D.-W., Shin, J. W. & Moon, D. (2015*b*). *Acta Cryst.* **E71**, 136–138.  
Lehn, J.-M. (2015). *Angew. Chem. Int. Ed.* **54**, 3276–3289.  
Melson, G. A. (1979). In *Coordination Chemistry of Macrocyclic Compounds*, 1st ed. New York: Plenum Press.  
Min, K. S. & Suh, M. P. (2001). *Chem. Eur. J.* **7**, 303–313.  
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography, Part A*, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.  
Putz, H. & Brandenburg, K. (2014). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.  
Ryoo, J. J., Shin, J. W., Dho, H.-S. & Min, K. S. (2010). *Inorg. Chem.* **49**, 7232–7234.  
Sheldrick, G. M. (2015*a*). *Acta Cryst.* **A71**, 3–8.  
Sheldrick, G. M. (2015*b*). *Acta Cryst.* **C71**, 3–8.  
Shin, J. W., Eom, K. & Moon, D. (2016*a*). *J. Synchrotron Rad.* **23**, 369–373.  
Shin, J. W., Kim, D.-W., Kim, J. H. & Moon, D. (2015). *Acta Cryst.* **E71**, 203–205.  
Shin, J. W., Kim, D.-W. & Moon, D. (2016*b*). *Polyhedron*, **105**, 62–70.  
Steed, J. W. & Atwood, J. L. (2009). *Supramol. Chem.* 2nd ed. Chichester: John Wiley & Sons Ltd.  
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.  
Xie, W.-P., Wang, N., Long, Y., Ran, X.-R., Gao, J.-Y., Chen, C.-J., Yue, S.-T. & Cai, Y.-P. (2014). *Inorg. Chem. Commun.* **40**, 151–156.

## supporting information

*Acta Cryst.* (2016). E72, 223-225 [doi:10.1107/S2056989016001031]

## Crystal structure of *trans*-(1,8-dibutyl-1,3,6,8,10,13-hexaazacyclotetradecane- $\kappa^4N^3,N^6,N^{10},N^{13}$ )bis(isonicotinato- $\kappa O$ )nickel(II) determined from synchrotron data

Jong Won Shin, Dae-Woong Kim and Dohyun Moon

### Computing details

Data collection: *PAL BL2D-SMDC* (Shin *et al.*, 2016a); cell refinement: *HKL-3000SM* (Otwinowski & Minor, 1997); data reduction: *HKL-3000SM* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Putz & Brandenburg, 2014); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

*trans*-(1,8-Dibutyl-1,3,6,8,10,13-hexaazacyclotetradecane- $\kappa^4N^3,N^6,N^{10},N^{13}$ )bis(isonicotinato- $\kappa O$ )nickel(II)

### Crystal data

[Ni(C<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>)<sub>2</sub>(C<sub>16</sub>H<sub>38</sub>N<sub>6</sub>)]

$M_r = 617.44$

Triclinic,  $P\bar{1}$

$a = 8.0630$  (16) Å

$b = 8.5110$  (17) Å

$c = 10.927$  (2) Å

$\alpha = 80.52$  (3)°

$\beta = 88.26$  (3)°

$\gamma = 86.44$  (3)°

$V = 738.0$  (3) Å<sup>3</sup>

$Z = 1$

$F(000) = 330$

$D_x = 1.389$  Mg m<sup>-3</sup>

Synchrotron radiation,  $\lambda = 0.62998$  Å

Cell parameters from 20128 reflections

$\theta = 0.4$ – $33.6$ °

$\mu = 0.51$  mm<sup>-1</sup>

$T = 100$  K

Needle, pale pink

$0.01 \times 0.004 \times 0.004$  mm

### Data collection

ADSC Q210 CCD area-detector  
diffractometer

Radiation source: PLSII 2D bending magnet

$\omega$  scan

Absorption correction: empirical (using  
intensity measurements)

(*HKL-3000SM SCALEPACK*; Otwinowski &  
Minor, 1997)

$T_{\min} = 0.995$ ,  $T_{\max} = 0.998$

7634 measured reflections

3879 independent reflections

3326 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.023$

$\theta_{\max} = 26.0$ °,  $\theta_{\min} = 2.5$ °

$h = -11 \rightarrow 11$

$k = -11 \rightarrow 11$

$l = -15 \rightarrow 15$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.040$

$wR(F^2) = 0.110$

$S = 1.04$

3879 reflections

188 parameters

0 restraints

Hydrogen site location: inferred from  
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0649P)^2 + 0.1918P]$$

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

$$\Delta\rho_{\max} = 1.12 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.95 \text{ e } \text{\AA}^{-3}$$

### Special details

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

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.5000	0.5000	0.5000	0.02066 (10)
O1	0.43513 (15)	0.41029 (17)	0.33736 (11)	0.0257 (3)
O2	0.18613 (16)	0.52908 (19)	0.28022 (12)	0.0322 (3)
N1	0.27809 (18)	0.6311 (2)	0.50735 (13)	0.0244 (3)
H1	0.2171	0.6276	0.4296	0.029*
N2	0.61452 (18)	0.67953 (19)	0.38249 (13)	0.0241 (3)
H2	0.5798	0.6766	0.2959	0.029*
N3	0.3946 (2)	0.8835 (2)	0.41256 (14)	0.0304 (3)
N4	0.3686 (2)	0.2837 (2)	-0.09149 (14)	0.0335 (4)
C1	0.1835 (2)	0.5457 (3)	0.61221 (15)	0.0276 (4)
H1A	0.0642	0.5807	0.6057	0.033*
H1B	0.2242	0.5692	0.6915	0.033*
C2	0.3004 (2)	0.8006 (2)	0.51521 (16)	0.0296 (4)
H2A	0.1895	0.8566	0.5192	0.036*
H2B	0.3574	0.8058	0.5933	0.036*
C3	0.5703 (2)	0.8414 (2)	0.41070 (18)	0.0308 (4)
H3A	0.6153	0.8493	0.4926	0.037*
H3B	0.6249	0.9202	0.3480	0.037*
C4	0.7938 (2)	0.6330 (3)	0.39084 (16)	0.0280 (4)
H4A	0.8376	0.6572	0.4689	0.034*
H4B	0.8552	0.6932	0.3203	0.034*
C5	0.3160 (2)	0.9034 (2)	0.29077 (17)	0.0310 (4)
H5A	0.2983	0.7968	0.2700	0.037*
H5B	0.3922	0.9575	0.2269	0.037*
C6	0.1502 (3)	0.9999 (3)	0.28701 (18)	0.0341 (4)
H6A	0.0727	0.9447	0.3493	0.041*
H6B	0.1671	1.1058	0.3093	0.041*
C7	0.0730 (3)	1.0223 (3)	0.15954 (19)	0.0390 (5)
H7A	0.1527	1.0726	0.0966	0.047*
H7B	0.0507	0.9166	0.1390	0.047*
C8	-0.0882 (3)	1.1257 (4)	0.1543 (2)	0.0502 (6)
H8A	-0.1692	1.0739	0.2140	0.075*
H8B	-0.1328	1.1395	0.0705	0.075*
H8C	-0.0667	1.2302	0.1750	0.075*
C9	0.3163 (2)	0.4477 (2)	0.26295 (15)	0.0235 (3)
C10	0.4760 (2)	0.2978 (3)	0.10910 (16)	0.0294 (4)

H10	0.5631	0.2691	0.1666	0.035*
C11	0.3367 (2)	0.3884 (2)	0.13963 (14)	0.0234 (3)
C12	0.2134 (2)	0.4252 (3)	0.05120 (16)	0.0300 (4)
H12	0.1158	0.4874	0.0676	0.036*
C13	0.2347 (2)	0.3703 (3)	−0.06044 (17)	0.0339 (4)
H13	0.1486	0.3957	−0.1191	0.041*
C14	0.4868 (2)	0.2496 (3)	−0.00601 (17)	0.0340 (4)
H14	0.5838	0.1887	−0.0256	0.041*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ni1	0.01767 (15)	0.03464 (19)	0.00987 (14)	0.00142 (11)	−0.00201 (9)	−0.00504 (11)
O1	0.0246 (6)	0.0412 (7)	0.0122 (5)	0.0012 (5)	−0.0054 (4)	−0.0073 (5)
O2	0.0235 (6)	0.0543 (9)	0.0207 (6)	0.0047 (6)	−0.0043 (5)	−0.0139 (6)
N1	0.0225 (7)	0.0384 (8)	0.0122 (6)	0.0027 (6)	−0.0022 (5)	−0.0048 (6)
N2	0.0227 (7)	0.0355 (8)	0.0142 (6)	0.0007 (6)	−0.0016 (5)	−0.0049 (6)
N3	0.0338 (8)	0.0354 (9)	0.0209 (7)	0.0055 (7)	−0.0018 (6)	−0.0041 (7)
N4	0.0344 (8)	0.0525 (11)	0.0148 (6)	0.0002 (7)	−0.0027 (6)	−0.0091 (7)
C1	0.0186 (7)	0.0485 (11)	0.0149 (7)	0.0026 (7)	0.0012 (5)	−0.0052 (7)
C2	0.0331 (9)	0.0384 (10)	0.0169 (8)	0.0078 (8)	−0.0008 (6)	−0.0068 (7)
C3	0.0339 (9)	0.0350 (10)	0.0240 (8)	−0.0011 (7)	−0.0018 (7)	−0.0063 (8)
C4	0.0205 (8)	0.0460 (11)	0.0173 (7)	−0.0038 (7)	0.0002 (6)	−0.0043 (7)
C5	0.0376 (10)	0.0345 (10)	0.0188 (8)	0.0059 (8)	−0.0014 (7)	−0.0011 (7)
C6	0.0356 (10)	0.0414 (11)	0.0227 (9)	0.0064 (8)	−0.0008 (7)	−0.0009 (8)
C7	0.0394 (11)	0.0506 (13)	0.0243 (9)	0.0048 (9)	−0.0033 (7)	−0.0006 (9)
C8	0.0400 (12)	0.0733 (18)	0.0320 (11)	0.0119 (11)	−0.0033 (9)	0.0018 (11)
C9	0.0213 (7)	0.0366 (9)	0.0128 (7)	−0.0044 (6)	−0.0018 (5)	−0.0040 (6)
C10	0.0258 (8)	0.0468 (11)	0.0160 (7)	0.0028 (7)	−0.0044 (6)	−0.0071 (7)
C11	0.0222 (7)	0.0365 (9)	0.0119 (7)	−0.0038 (7)	−0.0016 (5)	−0.0047 (7)
C12	0.0257 (8)	0.0484 (11)	0.0158 (7)	0.0020 (8)	−0.0044 (6)	−0.0062 (8)
C13	0.0307 (9)	0.0562 (13)	0.0157 (8)	0.0009 (8)	−0.0073 (6)	−0.0085 (8)
C14	0.0306 (9)	0.0534 (12)	0.0186 (8)	0.0056 (8)	−0.0017 (7)	−0.0106 (8)

*Geometric parameters (Å, °)*

Ni1—N1 <sup>i</sup>	2.0559 (16)	C3—H3B	0.9900
Ni1—N1	2.0559 (16)	C4—C1 <sup>i</sup>	1.526 (3)
Ni1—N2	2.0720 (17)	C4—H4A	0.9900
Ni1—N2 <sup>i</sup>	2.0720 (17)	C4—H4B	0.9900
Ni1—O1 <sup>i</sup>	2.1371 (13)	C5—C6	1.523 (3)
Ni1—O1	2.1372 (13)	C5—H5A	0.9900
O1—C9	1.2669 (19)	C5—H5B	0.9900
O2—C9	1.248 (2)	C6—C7	1.521 (3)
N1—C1	1.471 (2)	C6—H6A	0.9900
N1—C2	1.481 (3)	C6—H6B	0.9900
N1—H1	1.0000	C7—C8	1.521 (3)
N2—C4	1.477 (2)	C7—H7A	0.9900



N2—C3	1.481 (3)	C7—H7B	0.9900
N2—H2	1.0000	C8—H8A	0.9800
N3—C3	1.440 (3)	C8—H8B	0.9800
N3—C2	1.444 (2)	C8—H8C	0.9800
N3—C5	1.471 (2)	C9—C11	1.516 (2)
N4—C13	1.336 (3)	C10—C14	1.384 (3)
N4—C14	1.340 (2)	C10—C11	1.386 (3)
C1—C4 <sup>i</sup>	1.526 (3)	C10—H10	0.9500
C1—H1A	0.9900	C11—C12	1.393 (2)
C1—H1B	0.9900	C12—C13	1.379 (3)
C2—H2A	0.9900	C12—H12	0.9500
C2—H2B	0.9900	C13—H13	0.9500
C3—H3A	0.9900	C14—H14	0.9500
N1 <sup>i</sup> —Ni1—N1	180.0	H3A—C3—H3B	107.6
N1 <sup>i</sup> —Ni1—N2	85.97 (6)	N2—C4—C1 <sup>i</sup>	108.14 (15)
N1—Ni1—N2	94.03 (6)	N2—C4—H4A	110.1
N1 <sup>i</sup> —Ni1—N2 <sup>i</sup>	94.03 (6)	C1 <sup>i</sup> —C4—H4A	110.1
N1—Ni1—N2 <sup>i</sup>	85.97 (6)	N2—C4—H4B	110.1
N2—Ni1—N2 <sup>i</sup>	180.0	C1 <sup>i</sup> —C4—H4B	110.1
N1 <sup>i</sup> —Ni1—O1 <sup>i</sup>	93.29 (6)	H4A—C4—H4B	108.4
N1—Ni1—O1 <sup>i</sup>	86.71 (6)	N3—C5—C6	112.79 (16)
N2—Ni1—O1 <sup>i</sup>	92.90 (6)	N3—C5—H5A	109.0
N2 <sup>i</sup> —Ni1—O1 <sup>i</sup>	87.10 (6)	C6—C5—H5A	109.0
N1 <sup>i</sup> —Ni1—O1	86.71 (6)	N3—C5—H5B	109.0
N1—Ni1—O1	93.29 (6)	C6—C5—H5B	109.0
N2—Ni1—O1	87.10 (6)	H5A—C5—H5B	107.8
N2 <sup>i</sup> —Ni1—O1	92.90 (6)	C7—C6—C5	111.93 (17)
O1 <sup>i</sup> —Ni1—O1	180.0	C7—C6—H6A	109.2
C9—O1—Ni1	131.99 (12)	C5—C6—H6A	109.2
C1—N1—C2	114.34 (14)	C7—C6—H6B	109.2
C1—N1—Ni1	105.52 (11)	C5—C6—H6B	109.2
C2—N1—Ni1	112.75 (11)	H6A—C6—H6B	107.9
C1—N1—H1	108.0	C8—C7—C6	111.81 (19)
C2—N1—H1	108.0	C8—C7—H7A	109.3
Ni1—N1—H1	108.0	C6—C7—H7A	109.3
C4—N2—C3	113.96 (15)	C8—C7—H7B	109.3
C4—N2—Ni1	104.76 (11)	C6—C7—H7B	109.3
C3—N2—Ni1	113.72 (11)	H7A—C7—H7B	107.9
C4—N2—H2	108.0	C7—C8—H8A	109.5
C3—N2—H2	108.0	C7—C8—H8B	109.5
Ni1—N2—H2	108.0	H8A—C8—H8B	109.5
C3—N3—C2	115.84 (15)	C7—C8—H8C	109.5
C3—N3—C5	114.58 (15)	H8A—C8—H8C	109.5
C2—N3—C5	115.55 (16)	H8B—C8—H8C	109.5
C13—N4—C14	116.05 (17)	O2—C9—O1	126.88 (16)
N1—C1—C4 <sup>i</sup>	108.60 (14)	O2—C9—C11	117.12 (15)
N1—C1—H1A	110.0	O1—C9—C11	115.99 (16)

C4 <sup>i</sup> —C1—H1A	110.0	C14—C10—C11	119.30 (17)
N1—C1—H1B	110.0	C14—C10—H10	120.4
C4 <sup>i</sup> —C1—H1B	110.0	C11—C10—H10	120.4
H1A—C1—H1B	108.4	C10—C11—C12	117.25 (16)
N3—C2—N1	114.07 (15)	C10—C11—C9	122.61 (15)
N3—C2—H2A	108.7	C12—C11—C9	120.14 (16)
N1—C2—H2A	108.7	C13—C12—C11	119.15 (18)
N3—C2—H2B	108.7	C13—C12—H12	120.4
N1—C2—H2B	108.7	C11—C12—H12	120.4
H2A—C2—H2B	107.6	N4—C13—C12	124.30 (17)
N3—C3—N2	114.51 (16)	N4—C13—H13	117.8
N3—C3—H3A	108.6	C12—C13—H13	117.8
N2—C3—H3A	108.6	N4—C14—C10	123.94 (18)
N3—C3—H3B	108.6	N4—C14—H14	118.0
N2—C3—H3B	108.6	C10—C14—H14	118.0
C2—N1—C1—C4 <sup>i</sup>	-166.23 (14)	C5—C6—C7—C8	-177.2 (2)
Ni1—N1—C1—C4 <sup>i</sup>	-41.74 (15)	Ni1—O1—C9—O2	-15.1 (3)
C3—N3—C2—N1	-72.6 (2)	Ni1—O1—C9—C11	164.15 (12)
C5—N3—C2—N1	65.5 (2)	C14—C10—C11—C12	0.4 (3)
C1—N1—C2—N3	179.49 (14)	C14—C10—C11—C9	-179.18 (18)
Ni1—N1—C2—N3	58.94 (17)	O2—C9—C11—C10	179.64 (18)
C2—N3—C3—N2	70.3 (2)	O1—C9—C11—C10	0.3 (3)
C5—N3—C3—N2	-68.2 (2)	O2—C9—C11—C12	0.1 (3)
C4—N2—C3—N3	-175.30 (14)	O1—C9—C11—C12	-179.24 (17)
Ni1—N2—C3—N3	-55.32 (18)	C10—C11—C12—C13	0.3 (3)
C3—N2—C4—C1 <sup>i</sup>	167.84 (13)	C9—C11—C12—C13	179.86 (18)
Ni1—N2—C4—C1 <sup>i</sup>	42.93 (14)	C14—N4—C13—C12	0.4 (3)
C3—N3—C5—C6	-160.49 (18)	C11—C12—C13—N4	-0.7 (3)
C2—N3—C5—C6	60.9 (2)	C13—N4—C14—C10	0.4 (3)
N3—C5—C6—C7	178.71 (18)	C11—C10—C14—N4	-0.8 (3)

Symmetry code: (i)  $-x+1, -y+1, -z+1$ .

*Hydrogen-bond geometry* ( $\text{\AA}, ^\circ$ )

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1 $\cdots$ O2	1.00	1.98	2.892 (2)	150
N2—H2 $\cdots$ N4 <sup>ii</sup>	1.00	2.23	3.143 (2)	151

Symmetry code: (ii)  $-x+1, -y+1, -z$ .