

Crystal structure of *trans*-(1,8-dibutyl-1,3,6,8,10,13-hexaazacyclotetradecane- $\kappa^4N^3,N^6,N^{10},N^{13}$)bis(5-methyltetrazolato- κN)-nickel(II) from synchrotron data

Dae-Woong Kim, Jong Won Shin, Jin Hong Kim and Dohyun Moon*

Received 8 January 2015
 Accepted 13 January 2015

Beamline Department, Pohang Accelerator Laboratory, 80 Jigokro-127-beongil, Nam-Gu Pohang, Gyeongbuk 790-784, Republic of Korea. *Correspondence e-mail: dmoon@postech.ac.kr

Edited by H. Ishida, Okayama University, Japan

Keywords: crystal structure; azamacrocyclic ligand; Jahn–Teller distortion; tetrazole derivatives; synchrotron data

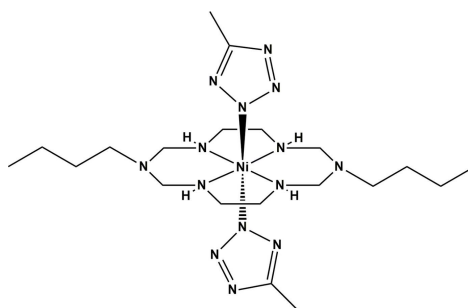
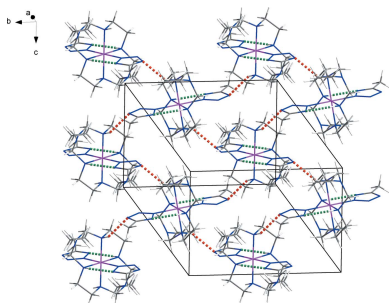
CCDC reference: 1043241

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

The structure of the title compound, $[\text{Ni}(\text{C}_2\text{H}_3\text{N}_4)_2(\text{C}_{16}\text{H}_{38}\text{N}_6)]$, has been characterized from synchrotron radiation. The asymmetric unit consists of one half of the Ni^{II} complex molecule, which is related to the other half-molecule by an inversion center. The Ni^{II} ion is coordinated by four secondary N atoms of the macrocyclic ligand in a square-planar fashion in the equatorial plane and by two N atoms of the 5-methyltetrazolate anions in axial positions, resulting in a tetragonally distorted octahedral geometry. The average equatorial Ni–N bond length [2.060 (8) Å] is shorter than the axial Ni–N bond length [2.2183 (11) Å]. An intramolecular N–H \cdots N hydrogen bond between the secondary amine N atom of the macrocyclic ligand and the non-coordinating N atom of the 5-methyltetrazolate ion stabilizes the molecular structure. Moreover, an intermolecular N–H \cdots N hydrogen bond between the macrocyclic ligand and 5-methyltetrazolate group gives rise to a supramolecular sheet structure parallel to the *bc* plane.

1. Chemical context

Coordination compounds with macrocyclic ligands have been studied widely in chemistry, metalloenzymes and materials science (Lehn, 1995). In particular, Ni^{II} macrocyclic complexes having vacant sites in the axial positions are good building blocks for assembling supramolecular frameworks (Min & Suh, 2001), with potential applications in gas adsorption/desorption (Lee & Suh, 2004), carbon dioxide reduction (Froehlich & Kubiak, 2012) and chiral separation (Ryoo *et al.*, 2010). For example, Ni^{II} complexes with tetra-azamacrocyclic ligands have been studied as catalysts for water oxidation at neutral pH (Zhang *et al.*, 2014) and their magnetic properties have been investigated with various auxiliary anionic moieties such as azide, dicyanamide and ferricyanide (Yuan *et al.*, 2011). Moreover, tetrazole derivatives are versatile anions which can easily bridge to transition metal ions, thus allowing the assembly of multi-dimensional compounds (Zhao *et al.*, 2008).



Here, we report the synthesis and crystal structure of an Ni^{II} azamacrocyclic complex with two tetrazole derivatives, *trans*-(1,8-dibutyl-1,3,6,8,10,13-hexaazacyclotetradecane- $\kappa^4N^3,N^6,N^{10},N^{13}$)bis(5-methyltetrazolato- κN)nickel(II), (I).

2. Structural commentary

In the title compound, the coordination environment around the Ni^{II} ion, in which the Ni^{II} ion lies on an inversion center, has a tetragonally distorted octahedral geometry. The Ni^{II} ion is bonded to four secondary N atoms of the azamacrocyclic ligand in a square-planar fashion in the equatorial plane, and to two N atoms from the 5-methyltetrazolate anions at the axial positions, as shown in Fig. 1. The average Ni–N_{eq} bond length and the Ni–N_{ax} length are 2.060 (8) and 2.2183 (11) Å, respectively. The axial bond lengths are much longer than the equatorial bond lengths, which can be attributed to a rather large Jahn–Teller distortion of the Ni^{II} ion and/or ring contraction of the azamacrocyclic ligand (Halcrow, 2013). The six-membered chelate rings adopt chair conformations and the five-membered chelate rings assume *gauche* conformations (Min & Suh, 2001). The N–N bond lengths in the 5-methyltetrazolate ion range from 1.3182 (15) to 1.3543 (16) Å, indicating that the tetrazolate ring is fully delocalized. An intramolecular N–H···N hydrogen bond between the secondary amine group of the macrocyclic ligand and the N atom of the 5-methyltetrazolate ion stabilizes the molecular structure (Fig. 1 and Table 1).

3. Supramolecular features

The packing in the structure involves an intermolecular N–H···N hydrogen bond between the secondary amine group of

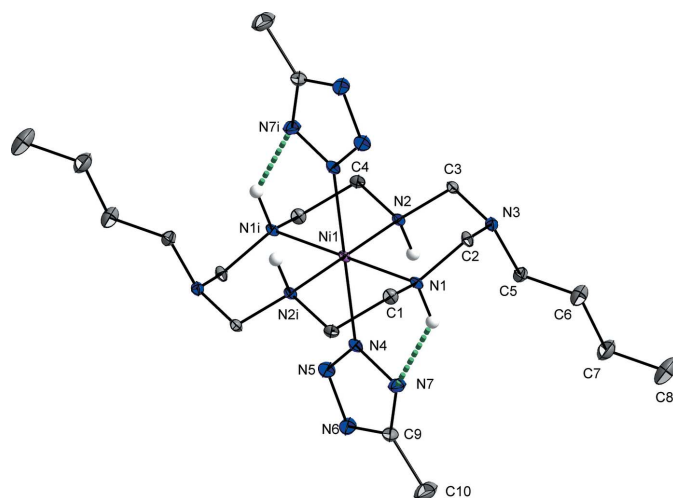


Figure 1

View of the molecular structure of the title compound, showing the atom-labelling scheme, with displacement ellipsoids drawn at the 50% probability level. H atoms bonded to C atoms have been omitted for clarity. Intramolecular N–H···N hydrogen bonds are shown as green dashed lines. [Symmetry code: (i) $-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.]

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···N7	1.00	2.07	2.8508 (16)	133
N2–H2···N6 ⁱ	1.00	2.35	3.1403 (16)	135

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

the macrocyclic ligand and the non-coordinating N atom of the 5-methyltetrazolate ion (Table 1), which forms a rigid supramolecular sheet structure parallel to the *bc* plane (Fig. 2).

4. Database survey

A search of the Cambridge Structural Database (Version 5.35, May 2014 with 3 updates; Groom & Allen, 2014) indicated that 71 Ni^{II} azamacrocyclic complexes with alkyl pendant groups have been reported. These complexes with various alkyl pendant groups were investigated as good building blocks for supramolecular chemistry and also studied for their magnetic properties and gas sorption abilities due to the anions such as cyanido groups and carboxylic acid derivatives (Hyun *et al.*, 2013; Shen *et al.*, 2012). No corresponding Ni^{II} azamacrocyclic complex with a butyl pendant group and tetrazole derivatives has been reported, and the title compound was newly synthesized for this research.

5. Synthesis and crystallization

The title compound (I) was prepared as follows. The starting complex, [Ni(C₁₆H₃₈N₆)(ClO₄)₂], was prepared by a slight modification of the reported method (Jung *et al.*, 1989). To an MeCN (10 mL) solution of [Ni(C₁₆H₃₈N₆)(ClO₄)₂] (0.10 g, 0.17 mmol) was slowly added an MeCN solution (5 mL) containing 5-methyl-1*H*-tetrazole (0.029 g, 0.34 mmol) and

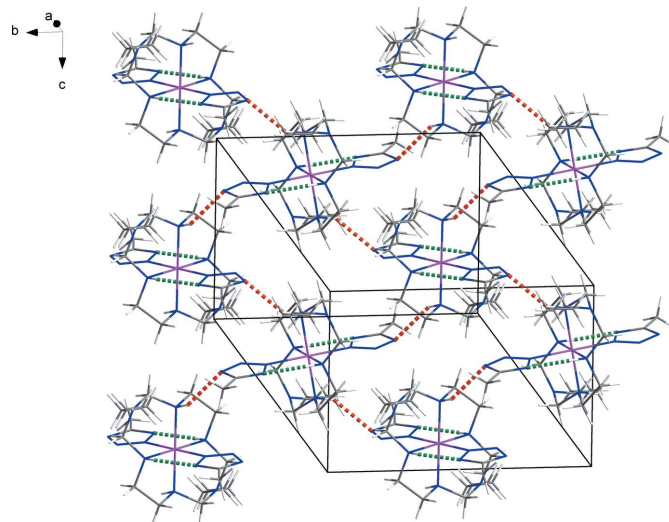


Figure 2

View of the crystal packing of the title compound, with N–H···N hydrogen bonds drawn as green (intramolecular) and red (intermolecular) dashed lines.

excess triethylamine (0.04 g, 0.40 mmol) at room temperature. The color of the solution turned from yellow to pale pink and a pale-pink precipitate was formed, which was filtered off, washed with MeCN, and diethyl ether, and dried in air. Single crystals of the title compound were obtained by layering of the MeCN solution of 5-methyl-1*H*-tetrazole on the MeCN solution of $[\text{Ni}(\text{C}_{16}\text{H}_{38}\text{N}_6)(\text{ClO}_4)_2]$ for several days. Yield: 0.057 g (62%). FT-IR (ATR, cm^{-1}): 3215, 2954, 1590, 1488, 1457, 1376, 1237, 1019, 933.

Safety note: Although we have experienced no problem 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 = 0.98–0.99 Å and N–H = 1.00 Å, and 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 the 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, IBS-R007-D1-2014-a01). The X-ray crystallography 2D-SMC beamline and the FT-IR experiment at the PLS-II were supported in part by MSIP and POSTECH.

References

- Arvai, A. J. & Nielsen, C. (1983). *ADSC Quantum-210 ADX*. Area Detector System Corporation, Poway, CA, USA.
- Froehlich, J. E. & Kubiak, C. P. (2012). *Inorg. Chem.* **51**, 3932–3934.
- Groom, C. R. & Allen, F. H. (2014). *Angew. Chem. Int. Ed.* **53**, 662–671.
- Halcrow, M. A. (2013). *Chem. Soc. Rev.* **42**, 1784–1795.
- Hyun, S.-M., Kim, T. K., Kim, Y. K., Moon, D. & Moon, H. R. (2013). *Inorg. Chem. Commun.* **33**, 52–56.
- Jung, S. K., Kang, S. G. & Suh, M. P. (1989). *Bull. Korean Chem. Soc.* **10**, 362–366.
- Lee, E. Y. & Suh, M. P. (2004). *Angew. Chem. Int. Ed.* **43**, 2798–2801.
- Lehn, J.-M. (1995). *Supramolecular Chemistry: Concepts and Perspectives*. Weinheim: John Wiley & Sons.
- Min, K. S. & Suh, M. P. (2001). *Chem. Eur. J.* **7**, 303–313.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[\text{Ni}(\text{C}_2\text{H}_3\text{N}_4)_2(\text{C}_{16}\text{H}_{38}\text{N}_6)]$
M_r	539.40
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	100
a, b, c (Å)	24.040 (5), 12.923 (3), 8.7170 (17)
β (°)	98.94 (3)
V (Å ³)	2675.1 (9)
Z	4
Radiation type	Synchrotron, $\lambda = 0.62998$ Å
μ (mm ⁻¹)	0.55
Crystal size (mm)	0.05 × 0.04 × 0.04
Data collection	
Diffractometer	ADSC Q210 CCD area detector
Absorption correction	Empirical (using intensity measurements) (<i>HKL3000sm SCALEPACK</i> ; Otwinowski & Minor, 1997)
$T_{\text{min}}, T_{\text{max}}$	0.973, 0.978
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12808, 3761, 3150
R_{int}	0.042
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.696
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.032, 0.090, 1.08
No. of reflections	3761
No. of parameters	162
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.32, -0.79

Computer programs: *PAL ADSC Quantum-210 ADX* (Arvai & Nielsen, 1983), *HKL3000sm* (Otwinowski & Minor, 1997), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2014/7* (Sheldrick, 2008, 2015b), *DIAMOND4* (Putz & Brandenburg, 2014) and *publCIF* (Westrip, 2010).

- 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). *DIAMOND4*. 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. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Shen, X., Zhou, H., Zhang, Q., Xu, Y. & Zhou, H. (2012). *Eur. J. Inorg. Chem.* **31**, 5050–5057.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Yuan, A.-H., Qian, S.-Y., Liu, W.-Y., Zhou, H. & Song, Y. (2011). *Dalton Trans.* **40**, 5302–5306.
- Zhang, M., Zhang, M.-T., Hou, C., Ke, Z.-F. & Lu, T.-B. (2014). *Angew. Chem. Int. Ed.* **53**, 13042–13048.
- Zhao, H., Qu, Z.-R., Ye, H.-Y. & Xiong, R.-G. (2008). *Chem. Soc. Rev.* **37**, 84–100.

supporting information

Acta Cryst. (2015). E71, 173-175 [doi:10.1107/S2056989015000651]

Crystal structure of *trans*-(1,8-dibutyl-1,3,6,8,10,13-hexaazacyclotetradecane- $\kappa^4N^3,N^6,N^{10},N^{13}$)bis(5-methyltetrazolato- κN)nickel(II) from synchrotron data

Dae-Woong Kim, Jong Won Shin, Jin Hong Kim and Dohyun Moon

Computing details

Data collection: *PAL ADSC Quantum-210 ADX* (Arvai & Nielsen, 1983); cell refinement: *HKL3000sm* (Otwinowski & Minor, 1997); data reduction: *HKL3000sm* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014/7* (Sheldrick, 2008, 2015b); molecular graphics: *DIAMOND4* (Putz & Brandenburg, 2014); software used to prepare material for publication: *publCIF* (Westrip, 2010).

trans-(1,8-Dibutyl-1,3,6,8,10,13-hexaazacyclotetradecane- $\kappa^4N^3,N^6,N^{10},N^{13}$)bis(5-methyltetrazolato- κN^2)nickel(II)

Crystal data

[Ni(C₂H₃N₄)₂(C₁₆H₃₈N₆)]

$M_r = 539.40$

Monoclinic, *C2/c*

$a = 24.040$ (5) Å

$b = 12.923$ (3) Å

$c = 8.7170$ (17) Å

$\beta = 98.94$ (3)°

$V = 2675.1$ (9) Å³

$Z = 4$

$F(000) = 1160$

$D_x = 1.339$ Mg m⁻³

Synchrotron radiation, $\lambda = 0.62998$ Å

Cell parameters from 25946 reflections

$\theta = 0.4$ – 33.6 °

$\mu = 0.55$ mm⁻¹

$T = 100$ K

Block, pink

$0.05 \times 0.04 \times 0.04$ mm

Data collection

ADSC Q210 CCD area-detector
diffractometer

Radiation source: PLSII 2D bending magnet

ω scan

Absorption correction: empirical (using
intensity measurements)

(*HKL3000sm SCALEPACK*; Otwinowski &
Minor, 1997)

$T_{\min} = 0.973$, $T_{\max} = 0.978$

12808 measured reflections

3761 independent reflections

3150 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$

$\theta_{\max} = 26.0$ °, $\theta_{\min} = 1.6$ °

$h = -33$ → 33

$k = -17$ → 17

$l = -12$ → 12

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.090$

$S = 1.08$

3761 reflections

162 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0565P)^2 + 0.106P]$$

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

$$\Delta\rho_{\max} = 0.32 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.79 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.2500	0.7500	0.5000	0.00596 (8)
N1	0.31782 (5)	0.83411 (8)	0.60560 (11)	0.0073 (2)
H1	0.3488	0.7841	0.6424	0.009*
N2	0.28136 (5)	0.73476 (8)	0.29352 (12)	0.0076 (2)
H2	0.3095	0.6773	0.3067	0.009*
N3	0.35616 (5)	0.86428 (8)	0.36376 (12)	0.0095 (2)
C1	0.29951 (5)	0.88036 (9)	0.74420 (13)	0.0094 (2)
H1A	0.2752	0.9411	0.7137	0.011*
H1B	0.3327	0.9038	0.8177	0.011*
C2	0.34005 (6)	0.90993 (9)	0.50278 (14)	0.0097 (2)
H2A	0.3110	0.9634	0.4716	0.012*
H2B	0.3733	0.9448	0.5621	0.012*
C3	0.31026 (6)	0.82902 (9)	0.24815 (14)	0.0096 (2)
H3A	0.3251	0.8147	0.1505	0.011*
H3B	0.2823	0.8854	0.2270	0.011*
C4	0.23296 (6)	0.70064 (10)	0.17841 (14)	0.0095 (2)
H4A	0.2464	0.6706	0.0864	0.011*
H4B	0.2083	0.7603	0.1441	0.011*
C5	0.40350 (6)	0.79167 (10)	0.39114 (15)	0.0119 (2)
H5A	0.4070	0.7560	0.2926	0.014*
H5B	0.3955	0.7386	0.4666	0.014*
C6	0.45926 (6)	0.84385 (12)	0.45282 (18)	0.0188 (3)
H6A	0.4686	0.8939	0.3747	0.023*
H6B	0.4553	0.8829	0.5483	0.023*
C7	0.50699 (7)	0.76635 (13)	0.4891 (2)	0.0237 (3)
H7A	0.5101	0.7263	0.3940	0.028*
H7B	0.4977	0.7172	0.5685	0.028*
C8	0.56368 (7)	0.81669 (16)	0.5480 (2)	0.0334 (4)
H8A	0.5737	0.8641	0.4688	0.050*
H8B	0.5926	0.7630	0.5696	0.050*
H8C	0.5612	0.8554	0.6434	0.050*
N4	0.30074 (5)	0.61260 (8)	0.58628 (12)	0.0100 (2)
N5	0.29007 (5)	0.51298 (9)	0.56721 (14)	0.0156 (2)
N6	0.33266 (5)	0.45876 (9)	0.64836 (16)	0.0185 (3)
N7	0.35088 (5)	0.62585 (9)	0.67914 (13)	0.0146 (2)
C9	0.36869 (6)	0.52976 (10)	0.71493 (17)	0.0157 (3)

C10	0.42228 (7)	0.50538 (13)	0.8200 (2)	0.0298 (4)
H10A	0.4139	0.4869	0.9230	0.045*
H10B	0.4470	0.5661	0.8285	0.045*
H10C	0.4411	0.4472	0.7773	0.045*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.00867 (12)	0.00459 (12)	0.00474 (11)	-0.00101 (8)	0.00141 (8)	-0.00027 (7)
N1	0.0102 (5)	0.0052 (5)	0.0069 (4)	-0.0004 (4)	0.0021 (4)	-0.0002 (4)
N2	0.0092 (5)	0.0077 (5)	0.0061 (4)	-0.0007 (4)	0.0016 (4)	-0.0005 (4)
N3	0.0085 (5)	0.0105 (5)	0.0097 (5)	-0.0006 (4)	0.0024 (4)	0.0003 (4)
C1	0.0120 (6)	0.0083 (5)	0.0080 (5)	-0.0012 (4)	0.0016 (4)	-0.0031 (4)
C2	0.0114 (6)	0.0068 (5)	0.0115 (5)	-0.0016 (4)	0.0032 (4)	0.0001 (4)
C3	0.0112 (6)	0.0095 (6)	0.0084 (5)	-0.0012 (4)	0.0026 (4)	0.0022 (4)
C4	0.0112 (6)	0.0109 (6)	0.0062 (5)	0.0000 (5)	0.0012 (4)	-0.0009 (4)
C5	0.0099 (6)	0.0126 (6)	0.0136 (6)	0.0010 (5)	0.0029 (5)	0.0006 (5)
C6	0.0117 (7)	0.0189 (7)	0.0250 (7)	-0.0002 (5)	0.0008 (5)	-0.0032 (6)
C7	0.0128 (7)	0.0257 (8)	0.0316 (8)	0.0019 (6)	-0.0001 (6)	0.0016 (6)
C8	0.0139 (8)	0.0426 (10)	0.0409 (10)	0.0023 (7)	-0.0038 (7)	-0.0053 (8)
N4	0.0123 (5)	0.0071 (5)	0.0108 (5)	-0.0002 (4)	0.0024 (4)	0.0009 (4)
N5	0.0149 (6)	0.0081 (5)	0.0233 (6)	0.0003 (4)	0.0017 (5)	0.0026 (4)
N6	0.0129 (6)	0.0099 (5)	0.0323 (7)	0.0017 (4)	0.0025 (5)	0.0051 (5)
N7	0.0134 (6)	0.0110 (5)	0.0180 (5)	0.0013 (4)	-0.0016 (4)	0.0027 (4)
C9	0.0127 (6)	0.0113 (6)	0.0233 (7)	0.0019 (5)	0.0028 (5)	0.0060 (5)
C10	0.0194 (8)	0.0199 (7)	0.0460 (10)	0.0024 (6)	-0.0079 (7)	0.0092 (7)

Geometric parameters (Å, °)

Ni1—N1	2.0543 (12)	C5—C6	1.522 (2)
Ni1—N2	2.0661 (11)	C5—H5A	0.9900
Ni1—N4	2.2183 (11)	C5—H5B	0.9900
N1—C1	1.4752 (15)	C6—C7	1.519 (2)
N1—C2	1.4826 (15)	C6—H6A	0.9900
N1—H1	1.0000	C6—H6B	0.9900
N2—C4	1.4807 (17)	C7—C8	1.525 (2)
N2—C3	1.4860 (16)	C7—H7A	0.9900
N2—H2	1.0000	C7—H7B	0.9900
N3—C3	1.4474 (17)	C8—H8A	0.9800
N3—C2	1.4535 (16)	C8—H8B	0.9800
N3—C5	1.4657 (17)	C8—H8C	0.9800
C1—C4 ⁱ	1.5244 (17)	N4—N5	1.3182 (15)
C1—H1A	0.9900	N4—N7	1.3543 (16)
C1—H1B	0.9900	N5—N6	1.3469 (17)
C2—H2A	0.9900	N6—C9	1.3314 (19)
C2—H2B	0.9900	N7—C9	1.3347 (17)
C3—H3A	0.9900	C9—C10	1.494 (2)
C3—H3B	0.9900	C10—H10A	0.9800

C4—C1 ⁱ	1.5244 (17)	C10—H10B	0.9800
C4—H4A	0.9900	C10—H10C	0.9800
C4—H4B	0.9900		
N1 ⁱ —Ni1—N1	180.0	H3A—C3—H3B	107.6
N1 ⁱ —Ni1—N2	86.04 (4)	N2—C4—C1 ⁱ	107.88 (10)
N1—Ni1—N2	93.96 (4)	N2—C4—H4A	110.1
N1 ⁱ —Ni1—N2 ⁱ	93.96 (4)	C1 ⁱ —C4—H4A	110.1
N1—Ni1—N2 ⁱ	86.04 (4)	N2—C4—H4B	110.1
N2—Ni1—N2 ⁱ	180.0	C1 ⁱ —C4—H4B	110.1
N1 ⁱ —Ni1—N4 ⁱ	85.15 (4)	H4A—C4—H4B	108.4
N1—Ni1—N4 ⁱ	94.86 (4)	N3—C5—C6	113.12 (11)
N2—Ni1—N4 ⁱ	92.11 (4)	N3—C5—H5A	109.0
N2 ⁱ —Ni1—N4 ⁱ	87.89 (4)	C6—C5—H5A	109.0
N1 ⁱ —Ni1—N4	94.86 (4)	N3—C5—H5B	109.0
N1—Ni1—N4	85.14 (4)	C6—C5—H5B	109.0
N2—Ni1—N4	87.89 (4)	H5A—C5—H5B	107.8
N2 ⁱ —Ni1—N4	92.11 (4)	C7—C6—C5	112.13 (12)
N4 ⁱ —Ni1—N4	180.0	C7—C6—H6A	109.2
C1—N1—C2	114.13 (10)	C5—C6—H6A	109.2
C1—N1—Ni1	105.32 (8)	C7—C6—H6B	109.2
C2—N1—Ni1	114.48 (8)	C5—C6—H6B	109.2
C1—N1—H1	107.5	H6A—C6—H6B	107.9
C2—N1—H1	107.5	C6—C7—C8	113.29 (14)
Ni1—N1—H1	107.5	C6—C7—H7A	108.9
C4—N2—C3	114.49 (10)	C8—C7—H7A	108.9
C4—N2—Ni1	105.31 (8)	C6—C7—H7B	108.9
C3—N2—Ni1	113.75 (7)	C8—C7—H7B	108.9
C4—N2—H2	107.7	H7A—C7—H7B	107.7
C3—N2—H2	107.7	C7—C8—H8A	109.5
Ni1—N2—H2	107.7	C7—C8—H8B	109.5
C3—N3—C2	115.80 (10)	H8A—C8—H8B	109.5
C3—N3—C5	113.60 (10)	C7—C8—H8C	109.5
C2—N3—C5	115.15 (10)	H8A—C8—H8C	109.5
N1—C1—C4 ⁱ	108.83 (10)	H8B—C8—H8C	109.5
N1—C1—H1A	109.9	N5—N4—N7	109.66 (11)
C4 ⁱ —C1—H1A	109.9	N5—N4—Ni1	130.78 (9)
N1—C1—H1B	109.9	N7—N4—Ni1	119.52 (8)
C4 ⁱ —C1—H1B	109.9	N4—N5—N6	108.96 (11)
H1A—C1—H1B	108.3	C9—N6—N5	105.08 (11)
N3—C2—N1	113.80 (10)	C9—N7—N4	104.21 (11)
N3—C2—H2A	108.8	N6—C9—N7	112.09 (13)
N1—C2—H2A	108.8	N6—C9—C10	124.23 (13)
N3—C2—H2B	108.8	N7—C9—C10	123.67 (13)
N1—C2—H2B	108.8	C9—C10—H10A	109.5
H2A—C2—H2B	107.7	C9—C10—H10B	109.5
N3—C3—N2	114.21 (10)	H10A—C10—H10B	109.5
N3—C3—H3A	108.7	C9—C10—H10C	109.5

N2—C3—H3A	108.7	H10A—C10—H10C	109.5
N3—C3—H3B	108.7	H10B—C10—H10C	109.5
N2—C3—H3B	108.7		
C2—N1—C1—C4 ⁱ	168.66 (10)	C2—N3—C5—C6	-68.36 (14)
Ni1—N1—C1—C4 ⁱ	42.26 (11)	N3—C5—C6—C7	176.68 (12)
C3—N3—C2—N1	70.86 (14)	C5—C6—C7—C8	178.80 (14)
C5—N3—C2—N1	-65.05 (14)	N7—N4—N5—N6	0.63 (15)
C1—N1—C2—N3	-177.96 (10)	Ni1—N4—N5—N6	-177.06 (9)
Ni1—N1—C2—N3	-56.49 (12)	N4—N5—N6—C9	-0.27 (16)
C2—N3—C3—N2	-71.26 (14)	N5—N4—N7—C9	-0.72 (15)
C5—N3—C3—N2	65.32 (14)	Ni1—N4—N7—C9	177.28 (9)
C4—N2—C3—N3	177.73 (10)	N5—N6—C9—N7	-0.20 (17)
Ni1—N2—C3—N3	56.58 (12)	N5—N6—C9—C10	178.68 (15)
C3—N2—C4—C1 ⁱ	-167.67 (10)	N4—N7—C9—N6	0.56 (16)
Ni1—N2—C4—C1 ⁱ	-41.97 (10)	N4—N7—C9—C10	-178.32 (14)
C3—N3—C5—C6	154.78 (11)		

Symmetry code: (i) $-x+1/2, -y+3/2, -z+1$.

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...N7	1.00	2.07	2.8508 (16)	133
N2—H2...N6 ⁱⁱ	1.00	2.35	3.1403 (16)	135

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