



IUCrData

ISSN 2414-3146

trans-Diaquabis(*N,N,N'*-trimethylethylenediamine)-nickel(II) dichloride

John R. Miecznikowski,^{a*} Jerry P. Jasinski,^{b*} Nicole F. Flaherty,^a Emma E. Mircovich,^a Allison N. Smolinsky^a and Natalia R. Bertolotti^a

^aDepartment of Chemistry & Biochemistry, Fairfield University, 1073 North Benson Road, Fairfield, CT 06824, USA, and ^bDepartment of Chemistry, Keene State College, 229 Main Street, Keene, NH 03435, USA. *Correspondence e-mail: jmiecznikowski@fairfield.edu, jjasinski@keene.edu

Received 3 August 2020

Accepted 27 August 2020

Edited by M. Weil, Vienna University of Technology, Austria

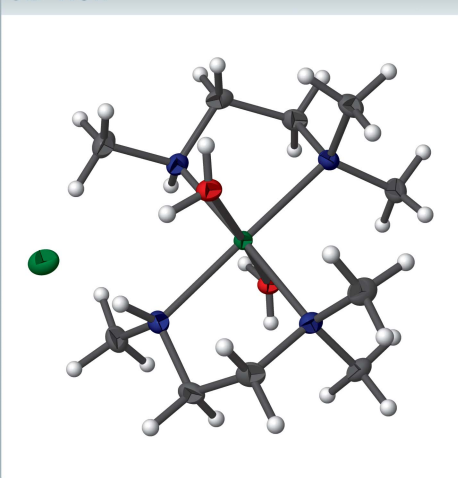
Keywords: Ligand precursor; crystal structure; substituted ethylenediamine ligand.

CCDC reference: 2025810

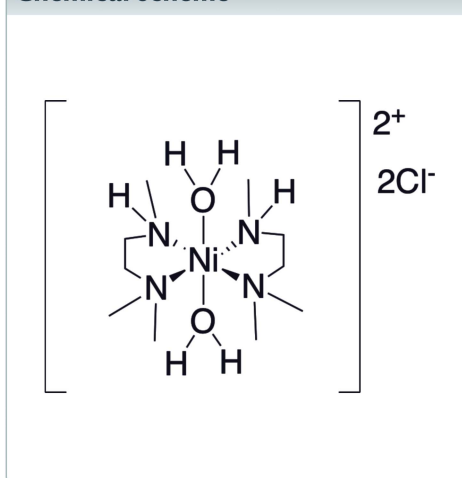
Structural data: full structural data are available from iucrdata.iucr.org

In the title salt, $[\text{Ni}(\text{C}_5\text{H}_{12}\text{N}_2)_2(\text{H}_2\text{O})_2]\text{Cl}_2$, the asymmetric unit is comprised of half of the complex cation and a chloride ion with the Ni^{II} atom of the cation situated about a twofold rotation axis. The six-coordinate Ni^{II} atom of the cation is connected to four N atoms from two methyl-substituted ethylenediamine ligands and two water molecules in a slightly distorted octahedral environment. The five-membered chelate ring is in a slight envelope conformation. The crystal packing features $\text{O}-\text{H}\cdots\text{Cl}$ and $\text{N}-\text{H}\cdots\text{Cl}$ intermolecular interactions with the Cl^- ion forming weak bifurcated hydrogen bonds with nearby water molecules and $\text{N}-\text{H}$ interactions, leading to a three-dimensional supra-molecular network structure.

3D view



Chemical scheme



Structure description

Previously, a tris-ethylenediaminenickel(II) complex has been reported (Swink & Atoji, 1960). Since then, such tris-ethylenediamine complexes have been reported for nearly all of the first row transition metals as well: scandium(III) (Wagner & Melson, 1973), titanium(II) (McDonald *et al.*, 1968), vanadium(II) (Daniels *et al.*, 1995), and vanadium(III) (Clark & Greenfield, 1967), chromium(III) (Whuler *et al.*, 1975), iron(II) (Girard *et al.*, 1998), iron(III) (Renovitch & Baker, 1968), cobalt(III) (Nakatsu, 1962), copper(II) (Cullen & Lingafelter, 1970) and zinc(II) (Emsley *et al.*, 1989). Substituted tris-ethylenediamine complexes with methyl groups instead of hydrogen atoms bonded to the nitrogen atoms have not been reported, to the best of our knowledge. In this communication, we report the preparation, spectroscopic characterization and single-crystal structure analysis of a nickel(II) complex that contains an *N,N,N'*-trimethylethylenediamine ligand.



OPEN ACCESS

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>
N2–H2···Cl1 ⁱ	1.00	2.31	3.296 (2)	169
O1–H1A···Cl1 ⁱⁱ	0.75 (3)	2.36 (3)	3.1065 (16)	172 (4)
O1–H1B···Cl1	0.85 (4)	2.24 (5)	3.0836 (19)	172 (4)

Symmetry codes: (i) $-x + \frac{1}{2}, -y + \frac{3}{2}, z$; (ii) $-x + \frac{3}{4}, y - \frac{1}{4}, z + \frac{1}{4}$.

In the title salt, the asymmetric unit is comprised of half of the cationic complex and a chloride ion with the Ni^{II} atom of the cation situated about a twofold rotation axis (Fig. 1). The chelate ring (Fig. 2) is in a slight envelope conformation on C1 with puckering parameters $Q_2 = 0.476 (2)^\circ$ and $\varphi_2 = 79.8 (2)^\circ$. The six-coordinate Ni^{II} atom of the cation is connected to four N atoms from two methyl-substituted ethylenediamine ligands and two water molecules in a slightly distorted octahedral environment, with the two substituted ethylenediamine ligands and two water molecules each coordinating *trans* to each other. The Ni–N bond lengths of 2.1906 (18) and 2.1245 (18) Å compare well to those of 2.120 (13) Å in the literature (Swink & Atoji, 1960); the Ni–O bond of 2.1189 (15) Å is the shortest of the metal–ligand bonds.

The crystal packing features O–H···Cl and N–H···Cl intermolecular interactions with the Cl[−] ions forming weak bifurcated hydrogen bonds with nearby water molecules and N–H interactions from the en moieties (Fig. 3, Table 1). Chains then form along [010], [001] and [100], generating a three-dimensional supramolecular network structure.

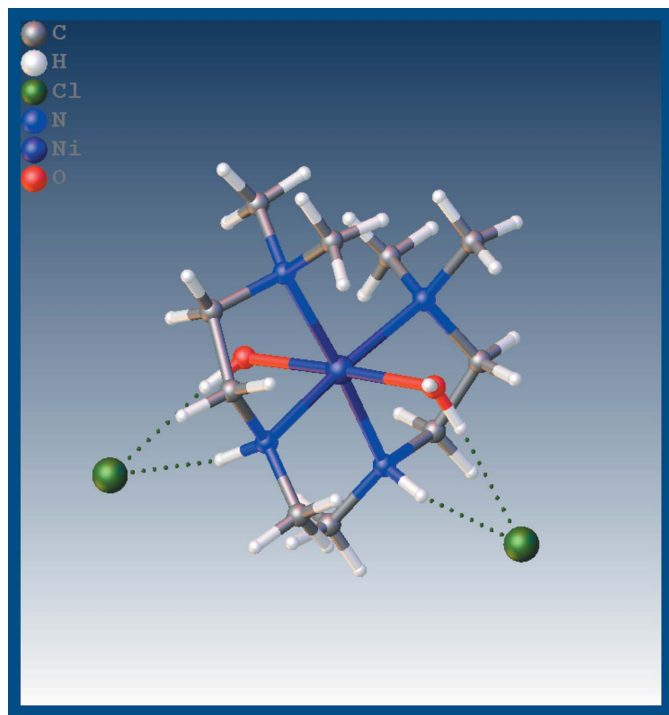


Figure 1
A view of $[\text{Ni}(\text{C}_5\text{H}_{16}\text{N}_4\text{O}_2)]^{2+}2\text{Cl}^-$, showing its structure generated from two asymmetric units containing half of the cation complex and a chloride ion situated about a twofold rotation axis on the Ni^{II} ion. The green dotted lines represent hydrogen bonds.

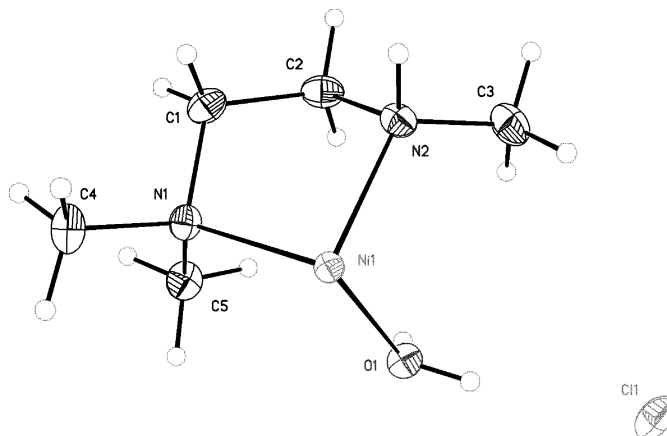


Figure 2
The molecular structure of the asymmetric unit of $[\text{Ni}(\text{C}_5\text{H}_{16}\text{N}_4\text{O}_2)]^{2+}2\text{Cl}^-$, showing the atom-labeling scheme with displacement ellipsoids drawn at the 50% probability level.

Synthesis and crystallization

N,N,N-Trimethylethylenediamine (0.47 g, 0.0046 mol) was added to 10 ml of 95%_{vol} ethanol in a round-bottom flask. To this solution, 0.32 g (0.0013 mol) of NiCl₂·6H₂O were added. The reaction mixture became green in color. The reaction contents were then refluxed for 18 h. After the reaction time, the solvent was removed under reduced pressure. The product was then re-dissolved in acetonitrile and then the acetonitrile was removed under reduced pressure in order to determine the yield of the product. (0.41 g, 82%). Single crystals of the product were obtained by dissolving the product in acetonitrile and then allowing a diethyl ether vapor to slowly diffuse into the acetonitrile solution which contained the product. Analysis calculated for $[\text{C}_{10}\text{H}_{32}\text{N}_4\text{NiO}_2]\text{Cl}_2$: C: 32.46; H: 8.72; N: 15.14. Found: C: 32.29; H: 8.59; N: 14.96. UV–Visible data: λ (nm), (ϵ ($\text{M}^{-1}\text{cm}^{-1}$)) (2.4 mM in MeCN) 390.00 (24); 228.00 (1600); 222.00 (1700).

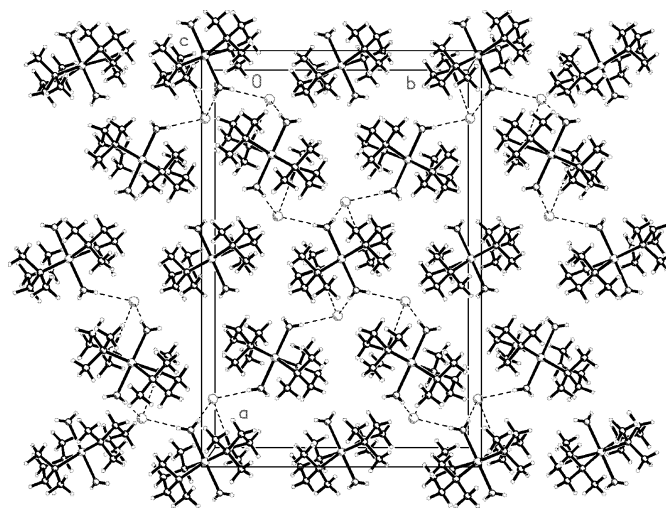


Figure 3
A partial packing diagram of the title compound viewed along the *c* axis showing the O–H···Cl and N–H···Cl intermolecular interactions (dashed lines) with the Cl[−] ion, forming weak bifurcated hydrogen bonds.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Funding information

JRM acknowledges support from The Science Institute of the College of Arts and Sciences at Fairfield University for this work. Jerry P. Jasinski expresses thanks to the National Science Foundation Major Research Instrumentation Program (grant No. CHE-1039027) for funds to purchase an X-ray diffractometer. ANS and NRB acknowledge financial support from the Klimas Fund to support their summer research at Fairfield University.

References

- Clark, R. J. H. & Greenfield, M. L. (1967). *J. Chem. Soc. A*, pp. 409–414.
- Cullen, D. L. & Lingafelter, E. C. (1970). *Inorg. Chem.* **9**, 1858–1864.
- Daniels, L. M., Murillo, C. M. & Rodríguez, K. G. (1995). *Inorg. Chim. Acta*, **229**, 27–32.
- Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
- Emsley, J., Arif, M., Bates, P. A. & Hursthouse, M. B. (1989). *Inorg. Chim. Acta*, **165**, 191–195.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Girard, M. R., Li, J. & Proserpio, D. M. (1998). *Main Group Met. Chem.* **21**, 231–236.
- McDonald, G. D., Thompson, M. & Larsen, E. M. (1968). *Inorg. Chem.* **7**, 648–655.
- Nakatsu, K. (1962). *Bull. Chem. Soc. Jpn.* **35**, 832–839.
- Renovitch, G. A. & Baker, W. A. Jr (1968). *J. Am. Chem. Soc.* **90**, 3585–3587.
- Rigaku OD (2020). *CrysAlis PRO*. Rigaku Americas, The Woodlands, TX, USA.
- Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
- Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
- Swink, L. N. & Atoji, M. (1960). *Acta Cryst.* **13**, 639–643.

Table 2

Experimental details.

Crystal data	
Chemical formula	[Ni(C ₅ H ₁₂ N ₂) ₂ (H ₂ O) ₂]Cl ₂
<i>M_r</i>	370.00
Crystal system, space group	Orthorhombic, <i>Fdd2</i>
Temperature (K)	173
<i>a</i> , <i>b</i> , <i>c</i> (Å)	24.7168 (8), 16.6156 (5), 8.3805 (3)
<i>V</i> (Å ³)	3441.75 (19)
<i>Z</i>	8
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	1.44
Crystal size (mm)	0.38 × 0.22 × 0.12
Data collection	
Diffractometer	Rigaku Oxford Diffraction Gemini Eos
Absorption correction	Multi-scan (<i>CrysAlis PRO</i> ; Rigaku OD, 2020)
<i>T_{min}</i> , <i>T_{max}</i>	0.718, 1.000
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	3481, 1940, 1866
<i>R_{int}</i>	0.018
(sin θ/λ) _{max} (Å ⁻¹)	0.758
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.025, 0.064, 1.03
No. of reflections	1940
No. of parameters	98
No. of restraints	1
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.45, -0.28
Absolute structure	Classical Flack method (Flack, 1983) preferred over Parsons because s.u. lower
Absolute structure parameter	0.011 (14)

Computer programs: *CrysAlis PRO* (Rigaku OD, 2020), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

Wagner, M. R. & Melson, G. A. (1973). *J. Inorg. Nucl. Chem.* **35**, 869–873.

Whuler, A., Brouty, C., Spinat, P. & Herpin, P. (1975). *Acta Cryst.* **B31**, 2069–2076.

full crystallographic data

IUCrData (2020). 5, x201182 [https://doi.org/10.1107/S2414314620011827]

***trans*-Diaquabis(*N,N,N'*-trimethylethylenediamine)nickel(II) dichloride**

John R. Miecznikowski, Jerry P. Jasinski, Nicole F. Flaherty, Emma E. Mircovich, Allison N. Smolinsky and Natalia R. Bertolotti

trans*-Diaquabis(*N,N,N'*-trimethylethylenediamine)nickel(II) dichlorideCrystal data*

[Ni(C₃H₁₂N₂)₂(H₂O)₂]Cl₂

M_r = 370.00

Orthorhombic, *Fdd*2

a = 24.7168 (8) Å

b = 16.6156 (5) Å

c = 8.3805 (3) Å

V = 3441.75 (19) Å³

Z = 8

F(000) = 1584

D_x = 1.428 Mg m⁻³

Mo *Kα* radiation, λ = 0.71073 Å

Cell parameters from 1975 reflections

θ = 4.5–32.7°

μ = 1.44 mm⁻¹

T = 173 K

Plate, clear light blue

0.38 × 0.22 × 0.12 mm

Data collection

Rigaku Oxford Diffraction Gemini Eos diffractometer

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

Graphite monochromator

Detector resolution: 16.0416 pixels mm⁻¹

ω scans

Absorption correction: multi-scan (*CrysAlisPro*; Rigaku OD, 2020)

T_{min} = 0.718, *T_{max}* = 1.000

3481 measured reflections

1940 independent reflections

1866 reflections with *I* > 2σ(*I*)

R_{int} = 0.018

θ_{max} = 32.6°, θ_{min} = 3.7°

h = -36→22

k = -13→23

l = -12→5

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.025

wR(*F*²) = 0.064

S = 1.03

1940 reflections

98 parameters

1 restraint

Primary atom site location: dual

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F_o*²) + (0.0416*P*)²]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

Δρ_{max} = 0.45 e Å⁻³

Δρ_{min} = -0.28 e Å⁻³

Absolute structure: Classical Flack method

(Flack, 1983) preferred over Parsons because s.u. lower

Absolute structure parameter: 0.011 (14)

Special details

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

Refinement. All of the H atoms were placed in their calculated positions and then refined with lengths of 0.99 Å (CH); 0.98 Å (CH₃) using a riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{CH}, \text{NH})$ or $1.5U_{\text{eq}}(\text{CH}_3)$ of the parent atom. The idealized methyl group was refined as a rotating group. O-bound H atoms were located from a difference Fourier map and were refined freely.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.250000	0.750000	0.50037 (3)	0.01242 (9)
O1	0.32782 (6)	0.69655 (9)	0.4955 (2)	0.0176 (3)
N1	0.21604 (8)	0.66367 (11)	0.6707 (2)	0.0168 (3)
N2	0.22374 (8)	0.66391 (11)	0.3297 (2)	0.0178 (4)
H2	0.190094	0.686465	0.280789	0.021*
C1	0.17897 (9)	0.61499 (13)	0.5691 (3)	0.0220 (4)
H1C	0.146266	0.646888	0.543559	0.026*
H1D	0.167461	0.566293	0.628112	0.026*
C2	0.20698 (10)	0.59057 (13)	0.4165 (3)	0.0218 (4)
H2A	0.239070	0.557186	0.441324	0.026*
H2B	0.182077	0.558369	0.349569	0.026*
C3	0.25933 (11)	0.64123 (16)	0.1951 (3)	0.0259 (5)
H3A	0.273671	0.689984	0.144676	0.039*
H3B	0.238542	0.610325	0.116619	0.039*
H3C	0.289369	0.608359	0.234850	0.039*
C4	0.18262 (11)	0.69845 (14)	0.8001 (3)	0.0247 (4)
H4A	0.206073	0.726192	0.876681	0.037*
H4B	0.162891	0.655298	0.854570	0.037*
H4C	0.156786	0.736879	0.754674	0.037*
C5	0.25562 (9)	0.60896 (13)	0.7464 (3)	0.0216 (4)
H5A	0.274396	0.577959	0.663706	0.032*
H5B	0.236689	0.572070	0.818502	0.032*
H5C	0.282020	0.640596	0.807014	0.032*
Cl1	0.39455 (2)	0.76479 (3)	0.21560 (8)	0.02448 (13)
H1A	0.3323 (12)	0.6516 (18)	0.495 (5)	0.026 (7)*
H1B	0.3469 (19)	0.720 (2)	0.424 (5)	0.049 (11)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01210 (15)	0.01247 (14)	0.01270 (14)	0.00142 (12)	0.000	0.000
O1	0.0163 (6)	0.0152 (6)	0.0213 (7)	0.0030 (5)	0.0004 (7)	-0.0003 (6)
N1	0.0184 (9)	0.0149 (7)	0.0172 (8)	0.0004 (6)	0.0018 (7)	0.0014 (6)
N2	0.0180 (9)	0.0181 (8)	0.0173 (8)	0.0037 (7)	-0.0023 (7)	-0.0020 (7)
C1	0.0193 (10)	0.0191 (9)	0.0274 (10)	-0.0050 (8)	0.0010 (9)	0.0010 (9)
C2	0.0223 (10)	0.0162 (8)	0.0270 (11)	-0.0012 (8)	-0.0050 (9)	-0.0036 (8)

C3	0.0315 (12)	0.0275 (11)	0.0187 (10)	0.0038 (10)	-0.0005 (10)	-0.0054 (9)
C4	0.0287 (12)	0.0233 (10)	0.0220 (9)	0.0038 (9)	0.0081 (9)	0.0024 (8)
C5	0.0237 (10)	0.0191 (9)	0.0219 (10)	0.0026 (7)	-0.0004 (10)	0.0064 (9)
C11	0.0205 (2)	0.0189 (2)	0.0340 (3)	-0.00289 (18)	0.0101 (2)	-0.0041 (2)

Geometric parameters (Å, °)

Ni1—O1 ⁱ	2.1189 (15)	C1—H1C	0.9900
Ni1—O1	2.1189 (15)	C1—H1D	0.9900
Ni1—N1 ⁱ	2.1906 (18)	C1—C2	1.509 (3)
Ni1—N1	2.1906 (18)	C2—H2A	0.9900
Ni1—N2	2.1245 (18)	C2—H2B	0.9900
Ni1—N2 ⁱ	2.1245 (18)	C3—H3A	0.9800
O1—H1A	0.75 (3)	C3—H3B	0.9800
O1—H1B	0.85 (4)	C3—H3C	0.9800
N1—C1	1.489 (3)	C4—H4A	0.9800
N1—C4	1.481 (3)	C4—H4B	0.9800
N1—C5	1.478 (3)	C4—H4C	0.9800
N2—H2	1.0000	C5—H5A	0.9800
N2—C2	1.479 (3)	C5—H5B	0.9800
N2—C3	1.479 (3)	C5—H5C	0.9800
O1 ⁱ —Ni1—O1	177.80 (10)	N1—C1—H1C	109.6
O1—Ni1—N1	94.93 (7)	N1—C1—H1D	109.6
O1 ⁱ —Ni1—N1 ⁱ	94.93 (7)	N1—C1—C2	110.35 (18)
O1 ⁱ —Ni1—N1	86.51 (7)	H1C—C1—H1D	108.1
O1—Ni1—N1 ⁱ	86.51 (7)	C2—C1—H1C	109.6
O1 ⁱ —Ni1—N2	89.54 (7)	C2—C1—H1D	109.6
O1 ⁱ —Ni1—N2 ⁱ	88.98 (7)	N2—C2—C1	108.91 (16)
O1—Ni1—N2 ⁱ	89.54 (7)	N2—C2—H2A	109.9
O1—Ni1—N2	88.98 (7)	N2—C2—H2B	109.9
N1 ⁱ —Ni1—N1	98.69 (10)	C1—C2—H2A	109.9
N2—Ni1—N1 ⁱ	175.26 (8)	C1—C2—H2B	109.9
N2—Ni1—N1	83.15 (7)	H2A—C2—H2B	108.3
N2 ⁱ —Ni1—N1	175.26 (8)	N2—C3—H3A	109.5
N2 ⁱ —Ni1—N1 ⁱ	83.15 (7)	N2—C3—H3B	109.5
N2—Ni1—N2 ⁱ	95.36 (11)	N2—C3—H3C	109.5
Ni1—O1—H1A	123 (2)	H3A—C3—H3B	109.5
Ni1—O1—H1B	109 (3)	H3A—C3—H3C	109.5
H1A—O1—H1B	111 (4)	H3B—C3—H3C	109.5
C1—N1—Ni1	102.65 (14)	N1—C4—H4A	109.5
C4—N1—Ni1	115.81 (13)	N1—C4—H4B	109.5
C4—N1—C1	106.69 (19)	N1—C4—H4C	109.5
C5—N1—Ni1	115.38 (14)	H4A—C4—H4B	109.5
C5—N1—C1	108.56 (17)	H4A—C4—H4C	109.5
C5—N1—C4	107.15 (18)	H4B—C4—H4C	109.5
Ni1—N2—H2	106.1	N1—C5—H5A	109.5
C2—N2—Ni1	108.00 (13)	N1—C5—H5B	109.5

C2—N2—H2	106.1	N1—C5—H5C	109.5
C2—N2—C3	109.40 (18)	H5A—C5—H5B	109.5
C3—N2—Ni1	120.21 (16)	H5A—C5—H5C	109.5
C3—N2—H2	106.1	H5B—C5—H5C	109.5
Ni1—N1—C1—C2	46.67 (19)	C3—N2—C2—C1	170.25 (19)
Ni1—N2—C2—C1	37.8 (2)	C4—N1—C1—C2	168.89 (17)
N1—C1—C2—N2	-59.4 (2)	C5—N1—C1—C2	-75.9 (2)

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

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2 \cdots C11 ⁱ	1.00	2.31	3.296 (2)	169
O1—H1A \cdots C11 ⁱⁱ	0.75 (3)	2.36 (3)	3.1065 (16)	172 (4)
O1—H1B \cdots C11	0.85 (4)	2.24 (5)	3.0836 (19)	172 (4)

Symmetry codes: (i) $-x+1/2, -y+3/2, z$; (ii) $-x+3/4, y-1/4, z+1/4$.