Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS
ISSN 2056-9890

Crystal structure of [2-({2-[(2-azanidylbenzylidene)-amino]benzylidene}amino)-4-chlorophenolato]-nickel(II)

Fumiya Kobayashi, Atsushi Koga, Ryo Ohtani, Shinya Hayami and Masaaki Nakamura*

Department of Chemistry, Graduate School of Science and Technology, Kumamoto University, 2-39-1 Kurokami, Kumamoto 860-8555, Japan. *Correspondence e-mail: nakamura@sci.kumamoto-u.ac.jp

Received 2 February 2017
Accepted 23 March 2017

Edited by H. Ishida, Okayama University, Japan

Keywords: crystal structure; nickel(II) complex; 2-aminobenzaldehyde; asymmetric structure; supramolecular structure.

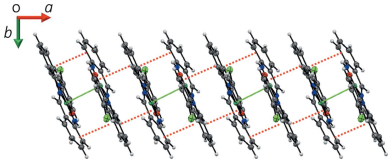
CCDC reference: 1539785

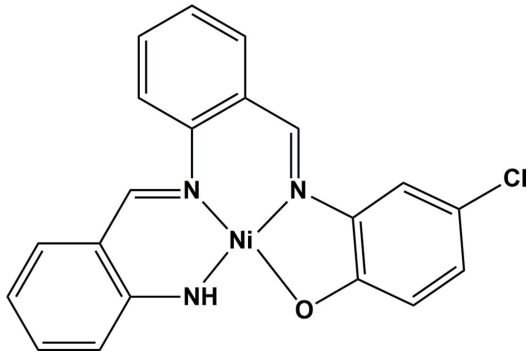
Supporting information: this article has supporting information at journals.iucr.org/e

The title complex, [Ni($C_{20}H_{14}ClN_3O$)], with an asymmetrically chloride-appended Schiff base ligand has been synthesized and structurally characterized at 100 K. In the compound, the central nickel(II) ion has a square-planar coordination geometry with N_3O donors of the π-conjugated tetradentate Schiff base ligand. In the crystal, the complexes are connected into an inversion dimer *via* an Ni···Ni interaction [3.1753 (5) Å] and a pair of π–π interactions [centroid–centroid distance = 3.8416 (16) Å]. The dimers are linked *via* a C—H···Cl hydrogen bond, forming a chain along the *c*-axis direction. The dimer chains interact with each other through π–π interactions [centroid–centroid distance = 3.8736 (16) Å], forming a layer expanding parallel to the *ac* plane.

1. Chemical context

Metal complexes with a tetradentate Schiff base ligand as represented by H_2(salen) [*N*,*N*′-ethylenebis(salicylideneimine)] and its derivatives have played extremely important roles in the field of coordination chemistry. Up to now, a large number of salen derivatives have been prepared and used for complexation in the expectation of a wide range of features such as catalytic ability, magnetic, dielectric and luminescence properties and so on (Bermejo *et al.*, 1996). In these cases, symmetric tetradentate ligands mainly produce N_2O_2 or N_4 type coordination environments. In this research, we have designed asymmetric structures, both in the coordination environment and in the molecular configuration, for the construction of the supramolecular structure through intermolecular hydrogen bonds, and synthesized the title nickel(II) complex using an asymmetrically chloride-appended tetradentate Schiff base ligand.





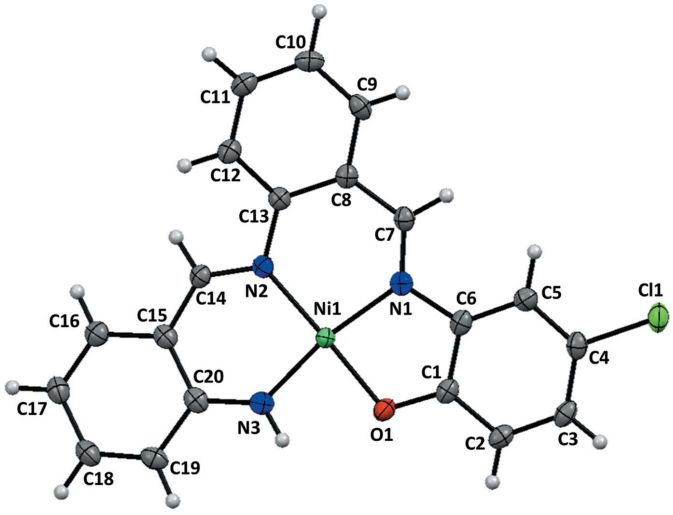


Figure 1
The molecular structure of the title compound, showing displacement ellipsoids at the 50% probability level.

The structure of the title compound, which features a widely spread π-conjugated ring system, is also useful for supramolecular assemblies through π–π interactions. The mononuclear copper(II) complex with a similar N_3O type asymmetrical ligand was reported by Ghorai & Mukherjee (2014).

2. Structural commentary

The nickel(II) atom is in a square-planar coordination with an asymmetrical coordination environment formed by the N_3O donor set including one phenolate O atom, two imine N atoms and one amino N atom of the tetradentate Schiff base ligand (Fig. 1). The Ni—O1, Ni—N1, Ni—N2, and Ni—N3 bond lengths are 1.8617 (18), 1.878 (2), 1.896 (2) and 1.831 (2) Å, respectively. The complex molecule is approximately planar; the coordination plane (N1–N3/O1/Ni1) makes dihedral angles of 4.15 (12), 10.22 (12) and 13.42 (12)°, respectively, with the C1–C6, C8–C13 and C15–C20 benzene rings.

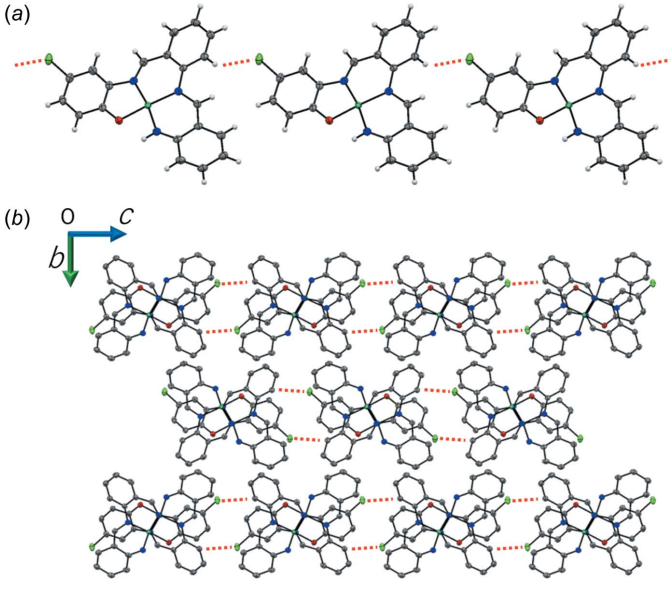


Figure 2
Packing diagrams of the title compound, showing (*a*) a chain structure running along the *c* axis formed by C—H···Cl hydrogen bonds (red dashed lines) and (*b*) the chains viewed along the *a* axis.

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12···Cl1^{i}	0.95	2.76	3.540 (3)	140
C10—H10···C20^{ii}	0.95	2.80	3.626 (4)	146

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

3. Supramolecular features

In the crystal, pairs of complex molecules related by an inversion centre are dimerized by an Ni···Ni interaction [3.1753 (5) Å] and a pair of π–π interactions between the C1–C6 and C15–C20 benzene rings [centroid–centroid distance = 3.8415 (16) Å]. Such dimerization caused by an Ni···Ni interaction has also been observed in symmetric Ni(salen) compounds (Aullón *et al.*, 1996; Siegler & Lutz, 2009). The dimeric molecules of the title compound are linked by C—H···Cl hydrogen bonds (Table 1), producing a chain of dimers along the *c* axis (Fig. 2). The dimers further interact with each other through π–π interactions between the C1–C6 and C8–C13 benzene rings [centroid–centroid distance = 3.8738 (17) Å], forming a column along the *a* axis (Fig. 3). Together, these C—H···Cl and π–π interactions result in a layer parallel to the *ac* plane. The layers are further linked by a short C—H···C contact (Table 1), giving a three-dimensional network (Fig. 4).

4. Synthesis and crystallization

The tetradentate Schiff base ligand was prepared by the reaction of 2-aminobenzaldehyde (Smith & Opie, 1948) (0.228 g, 2.0 mmol) and 2-amino-4-chlorophenol (0.144 g,

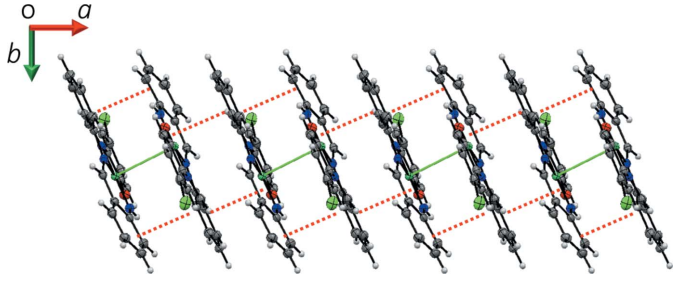


Figure 3
A packing diagram of the title compound, showing the column structure along the *a* axis formed by Ni···Ni interactions (green solid lines) and π–π interactions (red dashed lines).

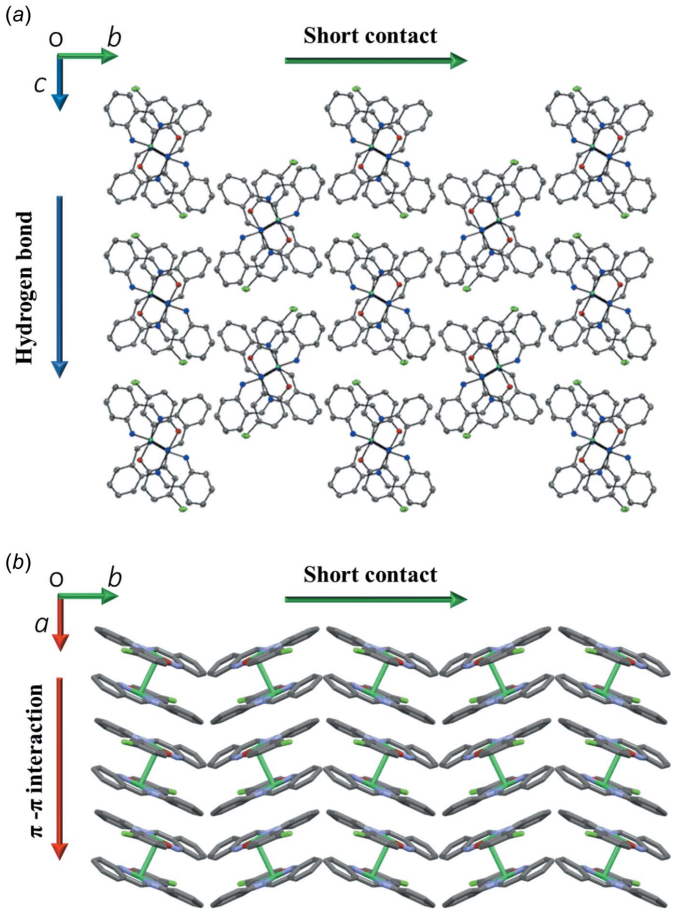


Figure 4
Packing diagrams of the title compound assembled by (*a*) C—H···Cl hydrogen bonds and C—H···C short contacts, and (*b*) π–π interactions and short contacts.

1.0 mmol) in methanol (50 ml) under stirring for 1 h. The resulting solution including the ligand was used for complexation with the Ni^{II} ion. A methanol solution (50 ml) of $Ni(CH_3COO)_2{\cdot}4H_2O$ (0.249 g, 1.0 mmol) was added to the solution and stirred for 1 h. The resulting solution was allowed to stand for a few days, during which time dark-purple block-shaped crystals precipitated. They were collected by suction filtration and dried in air to give single crystals of the title compound suitable for X-ray diffraction.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The position of the N-bound H atom was refined with N—H = 0.86 (1) Å and U_{iso}(H) = 1.5U_{eq}(N). Other H atoms were treated as riding with C—H = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C).

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Ni(C_{20}H_{14}ClN_3O)]$
M_r	406.50
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	7.5510 (4), 17.8689 (9), 12.6834 (6)
β (°)	109.9504 (14)
V (Å^3)	1608.64 (14)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	1.39
Crystal size (mm)	0.46 × 0.27 × 0.25
Data collection	
Diffractometer	Rigaku R-AXIS RAPID
Absorption correction	Multi-scan (*ABSCOR*; Higashi, 1995)
T_{min}, T_{max}	0.476, 0.712
No. of measured, independent and observed [$F^2 > 2.0\sigma(F^2)$] reflections	15243, 3638, 3177
R_{int}	0.039
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.647
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.042, 0.103, 1.04
No. of reflections	3638
No. of parameters	238
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})	1.35, −0.37

Computer programs: *RAPID-AUTO* (Rigaku, 1995), *SHELXS2013* (Sheldrick, 2008), *SHELXL2016* (Sheldrick, 2015) and *CrystalStructure* (Rigaku, 2014).

Funding information

Funding for this research was provided by: JSPS Grant-in-Aid for Young Scientists (B) (award No. JP15K17833); JSPS Grant-in-Aid for Scientific Research on Innovative Areas (Dynamical Ordering and Integrated Functions) (award No. JP16H00777); KAKENHI Grant-in-Aid for Scientific Research (B) (award No. JP26288026); Cooperative Research Program of the Network Joint Research Centre for Materials and Devices.

References

Aullón, G., Alemany, P. & Alvarez, S. (1996). *Inorg. Chem.* **35**, 5061–5067.
Bermejo, M. R., Castiñeiras, A., Garcia-Monteagudo, J. C., Rey, M., Sousa, A., Watkinson, M., McAuliffe, C. A., Pritchard, R. G. & Beddoes, R. L. (1996). *J. Chem. Soc. Dalton Trans.* pp. 2935–2944.
Ghorai, S. & Mukherjee, C. (2014). *Chem. Asian J.* **9**, 3518–3524.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Rigaku (1995). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
Rigaku (2014). *CrystalStructure*. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Siegler, M. A. & Lutz, M. (2009). *Cryst. Growth Des.* **9**, 1194–1200.
Smith, L. I. & Opie, J. W. (1948). *Org. Synth.* **28**, 11.

supporting information

Acta Cryst. (2017). E**73**, 637-639 [https://doi.org/10.1107/S2056989017004613]

Crystal structure of [2-({2-[(2-azanidylbenzylidene)amino]benzylidene}amino)-4-chlorophenolato]nickel(II)

Fumiya Kobayashi, Atsushi Koga, Ryo Ohtani, Shinya Hayami and Masaaki Nakamura

Computing details

Data collection: *RAPID-AUTO* (Rigaku, 1995); cell refinement: *RAPID-AUTO* (Rigaku, 1995); data reduction: *RAPID-AUTO* (Rigaku, 1995); program(s) used to solve structure: *SHELXS2013* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *CrystalStructure* (Rigaku, 2014); software used to prepare material for publication: *CrystalStructure* (Rigaku, 2014).

[2-({2-[(2-Azanidylbenzylidene)amino]benzylidene}amino)-4-chlorophenolato]nickel(II)

Crystal data

$[Ni(C_{20}H_{14}ClN_3O)]$
$M_r = 406.50$
Monoclinic, $P2_1/c$
$a = 7.5510$ (4) Å
$b = 17.8689$ (9) Å
$c = 12.6834$ (6) Å
$\beta = 109.9504$ (14)°
$V = 1608.64$ (14) Å^3
$Z = 4$
$F(000) = 832.00$
$D_x = 1.678$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71075$ Å
Cell parameters from 13442 reflections
$\theta = 3.0$–27.4°
$\mu = 1.39$ mm^{-1}
$T = 100$ K
Block, purple
0.46 × 0.27 × 0.25 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Detector resolution: 10.000 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)
$T_{min} = 0.476$, $T_{max} = 0.712$
15243 measured reflections
3638 independent reflections
3177 reflections with $F^2 > 2.0\sigma(F^2)$
$R_{int} = 0.039$
$\theta_{max} = 27.4°$, $\theta_{min} = 3.0°$
$h = -9 \rightarrow 8$
$k = -23 \rightarrow 23$
$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.103$
$S = 1.04$
3638 reflections
238 parameters
1 restraint
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0527P)^2 + 1.948P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.35$ e Å^{-3}
$\Delta\rho_{min} = -0.37$ 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.

Refinement. Refinement was performed using all reflections. The weighted R-factor (wR) and goodness of fit (S) are based on F^2. R-factor (gt) are based on F. The threshold expression of $F^2 > 2.0$ sigma(F^2) is used only for calculating R-factor (gt).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.29838 (4)	0.53846 (2)	0.46051 (3)	0.01597 (11)
Cl1	0.22371 (10)	0.39200 (4)	0.93185 (6)	0.03146 (17)
O1	0.3645 (3)	0.58686 (10)	0.59854 (15)	0.0230 (4)
N1	0.2079 (3)	0.46083 (11)	0.52811 (18)	0.0195 (4)
N2	0.2225 (3)	0.49436 (12)	0.31594 (18)	0.0193 (4)
N3	0.3976 (3)	0.62220 (12)	0.41867 (19)	0.0221 (4)
C1	0.3301 (4)	0.54570 (14)	0.6762 (2)	0.0205 (5)
C2	0.3738 (4)	0.56917 (15)	0.7885 (2)	0.0229 (5)
C3	0.3380 (4)	0.52243 (15)	0.8656 (2)	0.0237 (5)
C4	0.2594 (4)	0.45198 (15)	0.8321 (2)	0.0236 (5)
C5	0.2109 (4)	0.42792 (15)	0.7223 (2)	0.0224 (5)
C6	0.2447 (4)	0.47561 (15)	0.6445 (2)	0.0207 (5)
C7	0.1169 (4)	0.40146 (14)	0.4813 (2)	0.0210 (5)
C8	0.0936 (3)	0.37840 (14)	0.3689 (2)	0.0197 (5)
C9	0.0092 (4)	0.30739 (15)	0.3366 (2)	0.0235 (5)
C10	−0.0089 (4)	0.27609 (15)	0.2338 (2)	0.0259 (6)
C11	0.0649 (4)	0.31435 (15)	0.1634 (2)	0.0251 (5)
C12	0.1469 (4)	0.38395 (15)	0.1918 (2)	0.0230 (5)
C13	0.1542 (3)	0.41975 (13)	0.2923 (2)	0.0187 (5)
C14	0.2147 (4)	0.53457 (14)	0.2259 (2)	0.0199 (5)
C15	0.2954 (4)	0.60452 (14)	0.2207 (2)	0.0214 (5)
C16	0.2781 (4)	0.63380 (15)	0.1133 (2)	0.0247 (5)
C17	0.3660 (4)	0.69883 (15)	0.1023 (2)	0.0262 (5)
C18	0.4758 (4)	0.73809 (15)	0.2007 (2)	0.0267 (6)
C19	0.4922 (4)	0.71300 (14)	0.3054 (2)	0.0253 (6)
C20	0.3979 (3)	0.64586 (14)	0.3194 (2)	0.0210 (5)
H1	0.452 (4)	0.6459 (17)	0.478 (2)	0.0315*
H2	0.42785	0.61711	0.81103	0.0275*
H3	0.36681	0.5382	0.94116	0.0285*
H5	0.15584	0.38005	0.70055	0.0268*
H7	0.06228	0.37131	0.52382	0.0253*
H9	−0.03614	0.28057	0.38682	0.0282*
H10	−0.07053	0.22937	0.21193	0.0310*
H11	0.05913	0.2923	0.09418	0.0301*
H12	0.19936	0.40819	0.14264	0.0276*
H14	0.14485	0.51283	0.15561	0.0239*

H16	0.2041	0.60767	0.04782	0.0296*
H17	0.35399	0.71755	0.03007	0.0314*
H18	0.53905	0.7827	0.19338	0.0321*
H19	0.56662	0.74021	0.36959	0.0304*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01684 (17)	0.01610 (17)	0.01561 (17)	0.00035 (11)	0.00636 (13)	0.00011 (12)
Cl1	0.0320 (4)	0.0439 (4)	0.0214 (3)	−0.0047 (3)	0.0130 (3)	0.0036 (3)
O1	0.0285 (10)	0.0222 (9)	0.0181 (9)	0.0016 (8)	0.0076 (8)	−0.0014 (7)
N1	0.0167 (10)	0.0209 (11)	0.0216 (11)	0.0035 (8)	0.0072 (9)	0.0015 (8)
N2	0.0177 (10)	0.0202 (10)	0.0215 (10)	0.0012 (8)	0.0088 (9)	0.0001 (8)
N3	0.0210 (11)	0.0203 (11)	0.0238 (11)	0.0001 (9)	0.0062 (9)	−0.0002 (9)
C1	0.0183 (12)	0.0243 (13)	0.0183 (12)	0.0059 (10)	0.0054 (10)	0.0001 (10)
C2	0.0230 (12)	0.0228 (12)	0.0200 (12)	0.0049 (10)	0.0036 (10)	−0.0025 (10)
C3	0.0204 (12)	0.0315 (14)	0.0190 (12)	0.0063 (11)	0.0064 (10)	−0.0022 (11)
C4	0.0198 (12)	0.0304 (14)	0.0222 (13)	0.0036 (10)	0.0092 (10)	0.0040 (11)
C5	0.0180 (12)	0.0254 (13)	0.0241 (13)	0.0006 (10)	0.0078 (10)	−0.0024 (11)
C6	0.0171 (11)	0.0261 (13)	0.0196 (12)	0.0047 (10)	0.0070 (10)	−0.0001 (10)
C7	0.0188 (12)	0.0246 (13)	0.0211 (12)	0.0017 (10)	0.0085 (10)	0.0024 (10)
C8	0.0160 (11)	0.0228 (12)	0.0197 (12)	0.0032 (9)	0.0055 (10)	0.0023 (10)
C9	0.0195 (12)	0.0238 (13)	0.0276 (13)	−0.0001 (10)	0.0085 (11)	0.0055 (11)
C10	0.0218 (13)	0.0217 (12)	0.0310 (14)	−0.0024 (10)	0.0049 (11)	−0.0047 (11)
C11	0.0241 (13)	0.0267 (13)	0.0221 (13)	0.0019 (11)	0.0048 (11)	−0.0039 (11)
C12	0.0252 (13)	0.0232 (13)	0.0206 (12)	0.0038 (10)	0.0077 (11)	0.0003 (10)
C13	0.0167 (11)	0.0183 (12)	0.0209 (12)	0.0025 (9)	0.0062 (10)	0.0012 (10)
C14	0.0189 (12)	0.0216 (12)	0.0203 (12)	0.0019 (10)	0.0080 (10)	−0.0009 (10)
C15	0.0207 (12)	0.0182 (12)	0.0279 (13)	0.0029 (10)	0.0115 (11)	0.0015 (10)
C16	0.0242 (13)	0.0246 (13)	0.0274 (14)	0.0022 (11)	0.0116 (11)	−0.0010 (11)
C17	0.0302 (14)	0.0236 (13)	0.0291 (14)	0.0032 (11)	0.0158 (12)	0.0052 (11)
C18	0.0273 (13)	0.0204 (12)	0.0364 (15)	0.0002 (11)	0.0160 (12)	0.0038 (11)
C19	0.0216 (12)	0.0211 (13)	0.0330 (15)	−0.0002 (10)	0.0087 (11)	0.0007 (11)
C20	0.0165 (11)	0.0193 (12)	0.0285 (13)	0.0055 (9)	0.0094 (10)	0.0044 (10)

Geometric parameters (Å, º)

Ni1—N3	1.831 (2)	C8—C13	1.416 (3)
Ni1—O1	1.8617 (18)	C8—C9	1.416 (4)
Ni1—N1	1.878 (2)	C9—C10	1.382 (4)
Ni1—N2	1.896 (2)	C9—H9	0.9500
Cl1—C4	1.748 (3)	C10—C11	1.383 (4)
O1—C1	1.324 (3)	C10—H10	0.9500
N1—C7	1.293 (3)	C11—C12	1.381 (4)
N1—C6	1.430 (3)	C11—H11	0.9500
N2—C14	1.333 (3)	C12—C13	1.410 (3)
N2—C13	1.424 (3)	C12—H12	0.9500
N3—C20	1.329 (3)	C14—C15	1.402 (3)

N3—H1	0.836 (18)	C14—H14	0.9500
C1—C6	1.403 (4)	C15—C16	1.424 (4)
C1—C2	1.412 (3)	C15—C20	1.432 (4)
C2—C3	1.381 (4)	C16—C17	1.369 (4)
C2—H2	0.9500	C16—H16	0.9500
C3—C4	1.395 (4)	C17—C18	1.425 (4)
C3—H3	0.9500	C17—H17	0.9500
C4—C5	1.382 (4)	C18—C19	1.367 (4)
C5—C6	1.392 (4)	C18—H18	0.9500
C5—H5	0.9500	C19—C20	1.436 (4)
C7—C8	1.436 (3)	C19—H19	0.9500
C7—H7	0.9500		

N3—Ni1—O1	83.57 (9)	C13—C8—C7	125.0 (2)
N3—Ni1—N1	169.92 (10)	C9—C8—C7	115.8 (2)
O1—Ni1—N1	86.35 (9)	C10—C9—C8	121.7 (2)
N3—Ni1—N2	94.46 (10)	C10—C9—H9	119.1
O1—Ni1—N2	176.53 (9)	C8—C9—H9	119.1
N1—Ni1—N2	95.61 (9)	C9—C10—C11	118.5 (2)
C1—O1—Ni1	112.57 (16)	C9—C10—H10	120.8
C7—N1—C6	120.7 (2)	C11—C10—H10	120.8
C7—N1—Ni1	128.02 (18)	C12—C11—C10	121.4 (3)
C6—N1—Ni1	111.23 (16)	C12—C11—H11	119.3
C14—N2—C13	114.6 (2)	C10—C11—H11	119.3
C14—N2—Ni1	121.00 (18)	C11—C12—C13	121.3 (2)
C13—N2—Ni1	124.14 (16)	C11—C12—H12	119.3
C20—N3—Ni1	131.89 (19)	C13—C12—H12	119.3
C20—N3—H1	122 (2)	C12—C13—C8	117.5 (2)
Ni1—N3—H1	106 (2)	C12—C13—N2	121.0 (2)
O1—C1—C6	118.0 (2)	C8—C13—N2	121.5 (2)
O1—C1—C2	123.2 (2)	N2—C14—C15	128.9 (2)
C6—C1—C2	118.7 (2)	N2—C14—H14	115.6
C3—C2—C1	120.0 (3)	C15—C14—H14	115.6
C3—C2—H2	120.0	C14—C15—C16	118.3 (2)
C1—C2—H2	120.0	C14—C15—C20	122.2 (2)
C2—C3—C4	119.7 (2)	C16—C15—C20	119.5 (2)
C2—C3—H3	120.1	C17—C16—C15	121.3 (3)
C4—C3—H3	120.1	C17—C16—H16	119.3
C5—C4—C3	121.8 (2)	C15—C16—H16	119.3
C5—C4—Cl1	119.0 (2)	C16—C17—C18	119.1 (3)
C3—C4—Cl1	119.2 (2)	C16—C17—H17	120.5
C4—C5—C6	118.3 (2)	C18—C17—H17	120.5
C4—C5—H5	120.8	C19—C18—C17	121.5 (2)
C6—C5—H5	120.8	C19—C18—H18	119.3
C5—C6—C1	121.4 (2)	C17—C18—H18	119.3
C5—C6—N1	126.9 (2)	C18—C19—C20	120.6 (3)
C1—C6—N1	111.7 (2)	C18—C19—H19	119.7
N1—C7—C8	123.8 (2)	C20—C19—H19	119.7

N1—C7—H7	118.1	N3—C20—C15	119.2 (2)
C8—C7—H7	118.1	N3—C20—C19	122.9 (2)
C13—C8—C9	119.2 (2)	C15—C20—C19	117.8 (2)
N3—Ni1—O1—C1	−176.59 (18)	Ni1—N1—C7—C8	10.2 (4)
N1—Ni1—O1—C1	3.42 (17)	N1—C7—C8—C13	−4.8 (4)
N3—Ni1—N1—C7	173.9 (5)	N1—C7—C8—C9	172.8 (2)
O1—Ni1—N1—C7	174.0 (2)	C13—C8—C9—C10	2.6 (4)
N2—Ni1—N1—C7	−3.1 (2)	C7—C8—C9—C10	−175.2 (2)
N3—Ni1—N1—C6	−3.6 (6)	C8—C9—C10—C11	2.7 (4)
O1—Ni1—N1—C6	−3.50 (16)	C9—C10—C11—C12	−3.2 (4)
N2—Ni1—N1—C6	179.37 (16)	C10—C11—C12—C13	−1.7 (4)
N3—Ni1—N2—C14	−15.0 (2)	C11—C12—C13—C8	6.9 (4)
N1—Ni1—N2—C14	164.51 (19)	C11—C12—C13—N2	−173.9 (2)
N3—Ni1—N2—C13	170.91 (19)	C9—C8—C13—C12	−7.2 (3)
N1—Ni1—N2—C13	−9.6 (2)	C7—C8—C13—C12	170.3 (2)
O1—Ni1—N3—C20	−171.4 (2)	C9—C8—C13—N2	173.6 (2)
N1—Ni1—N3—C20	−171.3 (4)	C7—C8—C13—N2	−8.9 (4)
N2—Ni1—N3—C20	5.7 (2)	C14—N2—C13—C12	22.3 (3)
Ni1—O1—C1—C6	−2.6 (3)	Ni1—N2—C13—C12	−163.25 (19)
Ni1—O1—C1—C2	177.86 (19)	C14—N2—C13—C8	−158.5 (2)
O1—C1—C2—C3	−178.4 (2)	Ni1—N2—C13—C8	15.9 (3)
C6—C1—C2—C3	2.1 (4)	C13—N2—C14—C15	−169.2 (2)
C1—C2—C3—C4	0.3 (4)	Ni1—N2—C14—C15	16.1 (4)
C2—C3—C4—C5	−1.8 (4)	N2—C14—C15—C16	175.5 (2)
C2—C3—C4—Cl1	177.5 (2)	N2—C14—C15—C20	−2.7 (4)
C3—C4—C5—C6	0.9 (4)	C14—C15—C16—C17	−174.8 (2)
Cl1—C4—C5—C6	−178.37 (19)	C20—C15—C16—C17	3.5 (4)
C4—C5—C6—C1	1.5 (4)	C15—C16—C17—C18	−0.4 (4)
C4—C5—C6—N1	178.9 (2)	C16—C17—C18—C19	−1.3 (4)
O1—C1—C6—C5	177.4 (2)	C17—C18—C19—C20	−0.2 (4)
C2—C1—C6—C5	−3.0 (4)	Ni1—N3—C20—C15	4.8 (4)
O1—C1—C6—N1	−0.2 (3)	Ni1—N3—C20—C19	−177.35 (19)
C2—C1—C6—N1	179.3 (2)	C14—C15—C20—N3	−8.6 (4)
C7—N1—C6—C5	7.7 (4)	C16—C15—C20—N3	173.2 (2)
Ni1—N1—C6—C5	−174.6 (2)	C14—C15—C20—C19	173.4 (2)
C7—N1—C6—C1	−174.8 (2)	C16—C15—C20—C19	−4.8 (3)
Ni1—N1—C6—C1	2.9 (3)	C18—C19—C20—N3	−174.7 (2)
C6—N1—C7—C8	−172.5 (2)	C18—C19—C20—C15	3.2 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C12—H12···Cl1^{i}	0.95	2.76	3.540 (3)	140
C10—H10···C20^{ii}	0.95	2.80	3.626 (4)	146

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