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Bis{2-amino-2-oxo-*N*-[(1*E*)-1-(pyridin-2-yl-κN)ethylidene]acetohydrazidato-$\kappa^2 N',O^1$}nickel(II)

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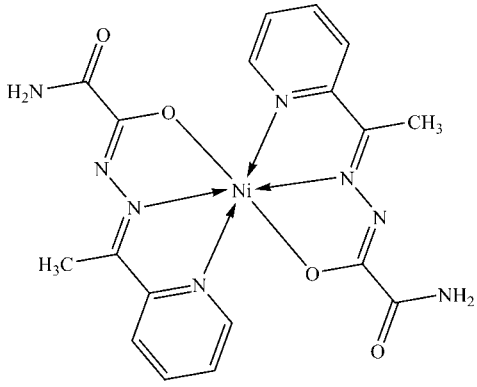
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.007 Å; R factor = 0.051; wR factor = 0.137; data-to-parameter ratio = 12.5.

In the title compound, $[Ni(C_9H_9N_4O_2)_2]$, the Ni^{II} ion is situated on a twofold rotation axis and is coordinated by two O and four N atoms from two tridentate {2-amino-2-oxo-*N*-[(1*E*)-1-(pyridin-2-yl-κN)ethylidene]acetohydrazidate ligands in a distorted octahedral geometry. In the crystal, N—H···O and N—H···N hydrogen bonds link the molecules into columns in [001]. The porous crystal packing is further stabilized *via* π–π interactions between the pyridine rings of neighbouring molecules [centroid–centroid distance = 3.746 (3) Å] with voids of 270 Å^3.

Related literature

For the structures of related nickel complexes, see: Dieng *et al.* (2004); Tamboura *et al.* (2009); Mikuriya *et al.* (1996).



Experimental

Crystal data

$[Ni(C_9H_9N_4O_2)_2]$
M_r = 469.11
Monoclinic, $C2/c$
a = 16.703 (3) Å
b = 17.878 (4) Å
c = 8.929 (2) Å
β = 114.915 (5)°
V = 2418.2 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.84 mm^{-1}
T = 293 K
0.21 × 0.14 × 0.13 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.778, T_{max} = 0.897
6288 measured reflections
1781 independent reflections
1285 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 23.5°

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.137
S = 1.04
1777 reflections
142 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4A···O2^{i}	0.86	2.22	2.976 (5)	147
N4—H4B···N3^{ii}	0.86	2.25	3.074 (5)	160

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

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1999); cell refinement: *DENZO* and *COLLECT*; data reduction: *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *CRYSTALBUILDER* (Welter, 2006); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV5274).

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supplementary materials

Acta Cryst. (2012). E**68**, m553 [doi:10.1107/S1600536812014109]

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Comment

In the title compound (Fig. 1), the Ni^{II} ion is situated on a twofold rotational and adopts a distorted octahedral geometry. The coordination of the hydrazones to Ni center results in the formation of two five-membered chelating rings. In the two rings, the Ni–$N_{pyridyl}$ bond lengths of 2.094 (3) Å are larger than those for Ni–N_{iminol} bonds [1.980 (3) Å]. The Ni–O1 involving the hydrazonic oxygen have the metal-ligand distance of 2.074 (3) Å. The Ni—N and Ni—O bond distances are similar to those observed in other mononuclear Ni^{II} complexes with similar tridentate ligands (Dieng *et al.*, 2004; Tamboura *et al.*, 2009). The following bond C6–N2 is not altered in the complex and remains with double bond character. The bond C8–N3 which was simple in character becomes a double bond after deprotonation of the N–H function. The N_{imino}–Ni–O1 and $N_{pyridyl}$–Ni–N_{imino} angles are 78.25 (13)° and 92.04 (13)° respectively. The deviation from 90° of the bond angles involving the chelation observed is presumably due to the formation of five-membered ring (Mikuriya *et al.*, 1996).

In the crystal structure, the intermolecular hydrogen-bonding network involving the acetamide groups and also the N3 atom (Table 1), propagates parallel to the crystallographic ***c*** axis (Fig.2). This contributes to display a double inverted *X* molecular pattern in the ***ab*** plane stabilized by $\pi - \pi$ stacking interactions between adjacent pyridine rings with the centroid-centroid distance of 3.746 (3) Å.

Experimental

2-Amino-2-oxo-*N*′-(1-(pyridin-2-yl)ethylidene)acetohydrazide (0.206 g, 1 mmol) was dissolved in 10 ml of ethanol and the LiOH (0.042 g, 2 mmol) was added with thorough shaking. To the resulting solution, $Ni(CH_3COO)_2.4H_2O$ (0.2489 g, 1 mmol) was added. Immediate change of the colour was observed. The mixture was stirred at room temperature during 2 h. The solution was filtered off and concentrated to tenth. Crystals that separated from the brown solution were filtered off and recrystallized in ethanol. On standing for three weeks, suitable X-rays crystals were obtained. Yield: 73.5%. Anal. Calc. for [$C_{18}H_{18}N_8O_4Ni$] (%): C, 46.09; H, 3.87; N, 23.89. Found: C, 46.06; H, 3.85; N, 23.87. Selected IR data (cm^{-1}, KBr pellet): 3214, 1728, 1645, 1585, 1459, 768.

Refinement

All H atoms were located in difference maps. They were then treated as riding in geometrically idealized positions, with C—H = 0.93 (aryl), or 0.96 Å(CH_3) and N—H = 0.86 Å, and with U_{iso}(H)=kU_{eq}(C,*N*), where k = 1.5 for the methyl groups, and 1.2 for all other H atoms. Four low-resolution reflections were omitted due to beamstop shading (*OMIT* instruction in *SHELX97-L*)). Infinite cylindrical channels of 8 Å diameters ran through the crystal packing along the crystallographic ***c*** axis at positions *x*=0, *y*=1/2, *z* and *x*=1/2, *y*=0, *z* accounting for voids of 270 $Å^3$ per unit cell but no

solvent contribution to the X-ray diffraction was found.

Computing details

Data collection: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT* (Nonius, 1999); data reduction: *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and CRYSTALBUILDER (Welter, 2006); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

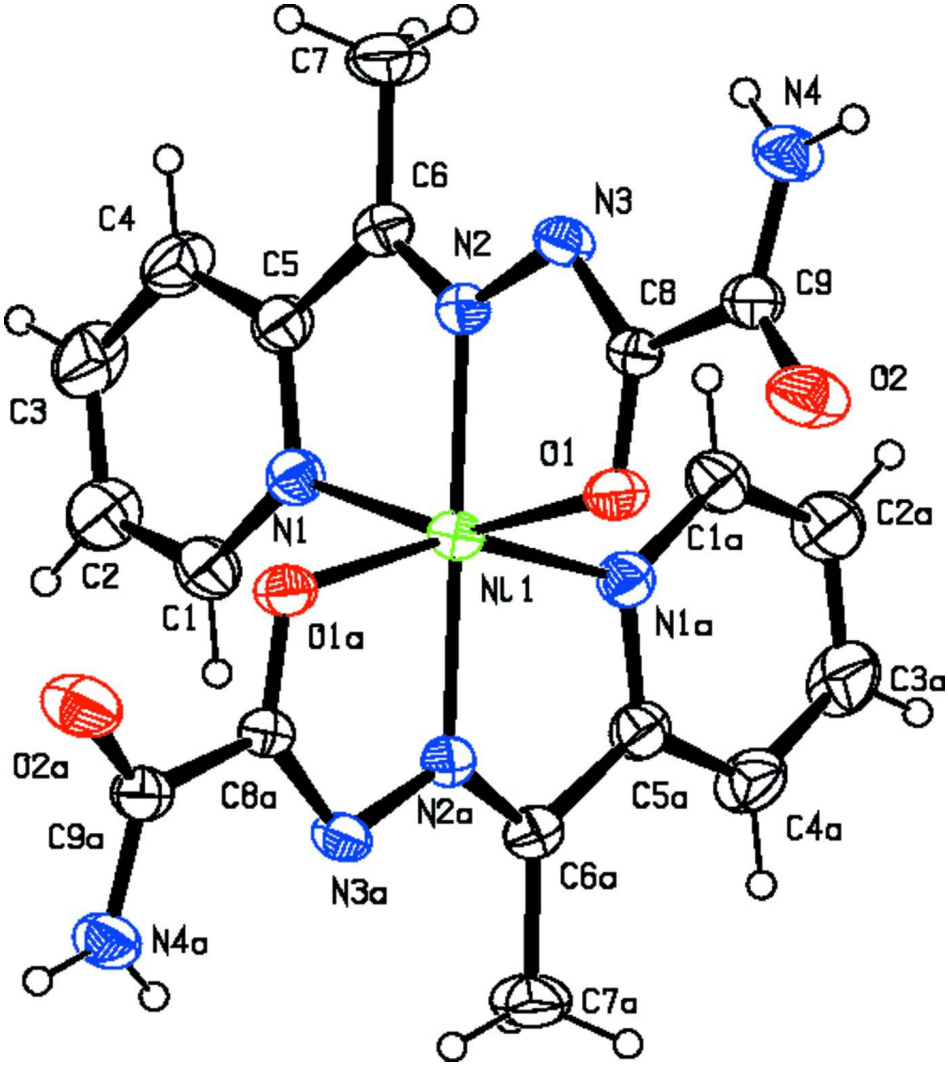

Figure 1

An *ORTEP* view of the title compound, showing the atom-numbering scheme [symmetry code: (*a*) -*x* + 1, *y*, -*z* + 1/2]. Displacement ellipsoids are plotted at the 30% probability level.

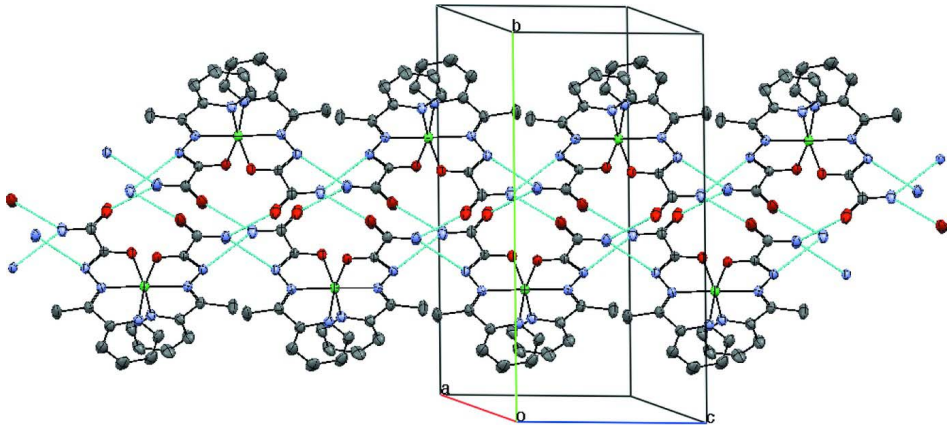

Figure 2

A portion of the crystal packing viewed down the ***a*** axis and showing hydrogen bonds as cyan lines.

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Crystal data

$[Ni(C_9H_9N_4O_2)_2]$
M_r = 469.11
Monoclinic, *C*2/*c*
Hall symbol: -C 2yc
a = 16.703 (3) Å
b = 17.878 (4) Å
c = 8.929 (2) Å
β = 114.915 (5)°
V = 2418.2 (9) Å^3
Z = 4
F(000) = 968
D_x = 1.289 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71070 Å
Cell parameters from 1780 reflections
θ = 0.4–23.5°
μ = 0.84 mm^{-1}
T = 293 K
Block, brown
0.21 × 0.14 × 0.13 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube, Nonius Kappa CCD
Graphite monochromator
Detector resolution: 9 pixels mm^{-1}
phi and *ω* scans
Absorption correction: multi-scan (*SCALEPACK*; Otwinowski & Minor, 1997)
T_{min} = 0.778, T_{max} = 0.897
6288 measured reflections
1781 independent reflections
1285 reflections with $I > 2\sigma(I)$
R_{int} = 0.046
θ_{max} = 23.5°, θ_{min} = 2.3°
h = −18→18
k = −18→20
l = −9→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.137
S = 1.04
1777 reflections
142 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0757P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-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.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger. Five low-resolution reflections were omitted due to beamstop shading (*OMIT* instruction in *SHELX97-L*).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.5000	0.30602 (4)	0.2500	0.0392 (3)
O1	0.41866 (19)	0.38561 (16)	0.2833 (3)	0.0451 (8)
O2	0.3304 (2)	0.4879 (2)	0.3757 (4)	0.0722 (11)
N1	0.5999 (2)	0.22513 (19)	0.3236 (4)	0.0438 (9)
N2	0.5383 (2)	0.30400 (18)	0.4922 (4)	0.0368 (8)
N3	0.4949 (2)	0.35081 (19)	0.5577 (4)	0.0406 (9)
N4	0.3876 (3)	0.4413 (2)	0.6353 (4)	0.0572 (11)
H4A	0.3576	0.4710	0.6676	0.069*
H4B	0.4232	0.4094	0.7031	0.069*
C1	0.6314 (3)	0.1867 (3)	0.2321 (6)	0.0567 (13)
H1	0.6064	0.1948	0.1187	0.068*
C2	0.6990 (4)	0.1356 (3)	0.2970 (7)	0.0708 (16)
H2	0.7189	0.1097	0.2290	0.085*
C3	0.7360 (4)	0.1241 (3)	0.4635 (7)	0.0733 (17)
H3	0.7822	0.0902	0.5109	0.088*
C4	0.7050 (3)	0.1624 (3)	0.5594 (6)	0.0631 (14)
H4	0.7302	0.1550	0.6731	0.076*
C5	0.6359 (3)	0.2127 (2)	0.4885 (5)	0.0475 (12)
C6	0.5976 (3)	0.2576 (2)	0.5825 (5)	0.0453 (11)
C7	0.6273 (4)	0.2469 (3)	0.7638 (5)	0.0713 (17)
H7A	0.5935	0.2786	0.8020	0.107*
H7B	0.6887	0.2595	0.8202	0.107*
H7C	0.6189	0.1956	0.7856	0.107*
C8	0.4349 (3)	0.3894 (2)	0.4339 (5)	0.0369 (10)
C9	0.3792 (3)	0.4445 (3)	0.4806 (5)	0.0482 (12)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0409 (5)	0.0462 (5)	0.0311 (5)	0.000	0.0158 (4)	0.000
O1	0.0491 (19)	0.0503 (18)	0.0330 (16)	0.0100 (15)	0.0144 (14)	0.0013 (14)
O2	0.091 (3)	0.080 (3)	0.052 (2)	0.042 (2)	0.036 (2)	0.0173 (19)
N1	0.044 (2)	0.047 (2)	0.040 (2)	0.0055 (18)	0.0176 (18)	−0.0014 (18)
N2	0.037 (2)	0.0394 (19)	0.0332 (19)	0.0013 (18)	0.0144 (16)	0.0023 (17)
N3	0.049 (2)	0.045 (2)	0.0321 (19)	0.0077 (18)	0.0208 (18)	0.0014 (17)
N4	0.064 (3)	0.069 (3)	0.042 (2)	0.023 (2)	0.026 (2)	0.002 (2)

C1	0.058 (3)	0.065 (3)	0.052 (3)	0.008 (3)	0.028 (3)	−0.009 (3)
C2	0.069 (4)	0.075 (4)	0.065 (4)	0.019 (3)	0.025 (3)	−0.019 (3)
C3	0.062 (4)	0.072 (4)	0.072 (4)	0.032 (3)	0.016 (3)	−0.009 (3)
C4	0.058 (3)	0.067 (3)	0.051 (3)	0.020 (3)	0.010 (3)	−0.001 (3)
C5	0.045 (3)	0.051 (3)	0.043 (3)	0.004 (2)	0.015 (2)	−0.001 (2)
C6	0.043 (3)	0.053 (3)	0.036 (2)	0.004 (2)	0.013 (2)	0.004 (2)
C7	0.082 (4)	0.091 (4)	0.036 (3)	0.034 (3)	0.020 (3)	0.012 (3)
C8	0.041 (3)	0.039 (2)	0.031 (2)	−0.001 (2)	0.016 (2)	−0.001 (2)
C9	0.050 (3)	0.057 (3)	0.038 (3)	0.008 (2)	0.018 (2)	0.002 (2)

Geometric parameters (Å, º)

Ni1—N2^{i}	1.980 (3)	N4—H4B	0.8600
Ni1—N2	1.980 (3)	C1—C2	1.376 (6)
Ni1—O1^{i}	2.074 (3)	C1—H1	0.9300
Ni1—O1	2.074 (3)	C2—C3	1.364 (7)
Ni1—N1^{i}	2.094 (3)	C2—H2	0.9300
Ni1—N1	2.094 (3)	C3—C4	1.359 (7)
O1—C8	1.257 (5)	C3—H3	0.9300
O2—C9	1.225 (5)	C4—C5	1.388 (6)
N1—C1	1.333 (6)	C4—H4	0.9300
N1—C5	1.354 (5)	C5—C6	1.487 (6)
N2—C6	1.283 (5)	C6—C7	1.492 (6)
N2—N3	1.387 (5)	C7—H7A	0.9600
N3—C8	1.330 (5)	C7—H7B	0.9600
N4—C9	1.329 (5)	C7—H7C	0.9600
N4—H4A	0.8600	C8—C9	1.528 (6)
N2^{i}—Ni1—N2	177.92 (19)	C2—C1—H1	118.3
N2^{i}—Ni1—O1^{i}	77.63 (12)	C3—C2—C1	118.3 (5)
N2—Ni1—O1^{i}	103.84 (12)	C3—C2—H2	120.8
N2^{i}—Ni1—O1	103.84 (12)	C1—C2—H2	120.8
N2—Ni1—O1	77.63 (12)	C4—C3—C2	119.5 (5)
O1^{i}—Ni1—O1	93.34 (17)	C4—C3—H3	120.3
N2^{i}—Ni1—N1^{i}	78.26 (13)	C2—C3—H3	120.3
N2—Ni1—N1^{i}	100.27 (13)	C3—C4—C5	120.3 (5)
O1^{i}—Ni1—N1^{i}	155.88 (12)	C3—C4—H4	119.9
O1—Ni1—N1^{i}	92.02 (13)	C5—C4—H4	119.9
N2^{i}—Ni1—N1	100.27 (13)	N1—C5—C4	120.4 (4)
N2—Ni1—N1	78.26 (13)	N1—C5—C6	115.2 (4)
O1^{i}—Ni1—N1	92.02 (13)	C4—C5—C6	124.4 (4)
O1—Ni1—N1	155.88 (12)	N2—C6—C5	113.3 (4)
N1^{i}—Ni1—N1	92.6 (2)	N2—C6—C7	125.5 (4)
C8—O1—Ni1	109.4 (2)	C5—C6—C7	121.2 (4)
C1—N1—C5	118.2 (4)	C6—C7—H7A	109.5
C1—N1—Ni1	129.2 (3)	C6—C7—H7B	109.5
C5—N1—Ni1	112.6 (3)	H7A—C7—H7B	109.5
C6—N2—N3	121.8 (3)	C6—C7—H7C	109.5
C6—N2—Ni1	120.5 (3)	H7A—C7—H7C	109.5
N3—N2—Ni1	117.6 (2)	H7B—C7—H7C	109.5

C8—N3—N2	107.9 (3)	O1—C8—N3	127.4 (4)
C9—N4—H4A	120.0	O1—C8—C9	116.4 (4)
C9—N4—H4B	120.0	N3—C8—C9	116.2 (3)
H4A—N4—H4B	120.0	O2—C9—N4	124.6 (4)
N1—C1—C2	123.4 (5)	O2—C9—C8	119.0 (4)
N1—C1—H1	118.3	N4—C9—C8	116.4 (4)
N2^{i}—Ni1—O1—C8	177.3 (3)	Ni1—N1—C1—C2	178.8 (4)
N2—Ni1—O1—C8	−1.2 (3)	N1—C1—C2—C3	−0.4 (8)
O1^{i}—Ni1—O1—C8	−104.6 (3)	C1—C2—C3—C4	0.5 (9)
N1^{i}—Ni1—O1—C8	98.9 (3)	C2—C3—C4—C5	0.4 (9)
N1—Ni1—O1—C8	−2.1 (5)	C1—N1—C5—C4	1.5 (7)
N2^{i}—Ni1—N1—C1	3.4 (4)	Ni1—N1—C5—C4	−178.0 (4)
N2—Ni1—N1—C1	−178.1 (4)	C1—N1—C5—C6	179.9 (4)
O1^{i}—Ni1—N1—C1	−74.4 (4)	Ni1—N1—C5—C6	0.4 (5)
O1—Ni1—N1—C1	−177.2 (3)	C3—C4—C5—N1	−1.4 (8)
N1^{i}—Ni1—N1—C1	81.9 (4)	C3—C4—C5—C6	−179.6 (5)
N2^{i}—Ni1—N1—C5	−177.3 (3)	N3—N2—C6—C5	179.9 (3)
N2—Ni1—N1—C5	1.2 (3)	Ni1—N2—C6—C5	4.1 (5)
O1^{i}—Ni1—N1—C5	104.9 (3)	N3—N2—C6—C7	0.5 (7)
O1—Ni1—N1—C5	2.1 (5)	Ni1—N2—C6—C7	−175.3 (4)
N1^{i}—Ni1—N1—C5	−98.7 (3)	N1—C5—C6—N2	−2.8 (6)
O1^{i}—Ni1—N2—C6	−92.3 (3)	C4—C5—C6—N2	175.5 (4)
O1—Ni1—N2—C6	177.3 (3)	N1—C5—C6—C7	176.7 (4)
N1^{i}—Ni1—N2—C6	87.5 (3)	C4—C5—C6—C7	−5.0 (7)
N1—Ni1—N2—C6	−3.1 (3)	Ni1—O1—C8—N3	1.1 (5)
O1^{i}—Ni1—N2—N3	91.7 (3)	Ni1—O1—C8—C9	−178.8 (3)
O1—Ni1—N2—N3	1.3 (3)	N2—N3—C8—O1	−0.1 (6)
N1^{i}—Ni1—N2—N3	−88.5 (3)	N2—N3—C8—C9	179.8 (3)
N1—Ni1—N2—N3	−179.1 (3)	O1—C8—C9—O2	−8.8 (6)
C6—N2—N3—C8	−177.0 (4)	N3—C8—C9—O2	171.4 (4)
Ni1—N2—N3—C8	−1.1 (4)	O1—C8—C9—N4	171.0 (4)
C5—N1—C1—C2	−0.6 (7)	N3—C8—C9—N4	−8.9 (6)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4*A*···O2^{ii}	0.86	2.22	2.976 (5)	147
N4—H4*B*···N3^{iii}	0.86	2.25	3.074 (5)	160

Symmetry codes: (ii) *x*, −*y*+1, *z*+1/2; (iii) −*x*+1, *y*, −*z*+3/2.