Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis({1-[(1-iminoethyl)imino]ethyl}-azanido-κ^2N^1,N^5)nickel(II) methanol monosolvate

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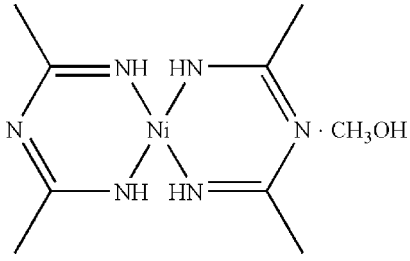
Received 6 November 2012; accepted 15 November 2012

Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.029; wR factor = 0.082; data-to-parameter ratio = 14.9.

The title compound, $[Ni(C_4H_8N_3)_2]\cdot CH_3OH$, contains two independent Ni^{II} atoms, each located on an inversion center and coordinated by four N atoms from two 1-[(1-iminoethyl)-imino]ethyl}azanide ligands in a square-planar geometry. N—H···N, N—H···O and O—H···N hydrogen bonds link the complex molecules and methanol solvent molecules into a corrugated layer parallel to (001).

Related literature

For structures and applications of related compounds, see: Aromi *et al.* (2011); Guzei *et al.* (2006); Kopylovich *et al.* (2007); Kryatov *et al.* (2001); Norrestam *et al.* (1983).



Experimental

Crystal data

$[Ni(C_4H_8N_3)_2]\cdot CH_4O$
M_r = 287.02
Monoclinic, $P2_1/c$
a = 9.2768 (7) Å
b = 11.4347 (3) Å
c = 12.9774 (3) Å
β = 92.961 (3)°
V = 1374.77 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.41 mm^{-1}
T = 298 K
0.23 × 0.21 × 0.19 mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.603, T_{max} = 0.766
9293 measured reflections
2421 independent reflections
1738 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.082
S = 1.04
2421 reflections
163 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.33 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1A^{i}	0.86	2.19	3.049 (3)	172
N2—H2···O1A^{ii}	0.86	2.23	3.079 (3)	169
N4—H4···N3^{iii}	0.86	2.44	3.264 (3)	160
N5—H5···N3	0.86	2.31	3.153 (3)	165
O1A—H1A4···N6	0.82	1.90	2.711 (3)	172

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, -y, -z$; (iii) $-x+1, -y+1, -z$.

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

This work was supported by the National Natural Science Foundation of China (grant Nos. 21064006 and 21161018), the Natural Science Foundation of Gansu Province (1010RJZA018) and the Program for Changjiang Scholars and the Innovative Research Team in Universities of the Ministry of Education of China (IRT1177).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2604).

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supporting information

Acta Cryst. (2013). E**69**, m3 [https://doi.org/10.1107/S1600536812046958]

Bis({1-[(1-iminoethyl)imino]ethyl}azanido-κ^2N^1,N^5)nickel(II) methanol monosolvate

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S1. Comment

Acetonitrile is one of the common solvents that is widely used to study processes in solution. With most 3d-transition metal ions, acetonitrile behaves as a relatively weak monodentate ligand (Kopylovich *et al.*, 2007; Kryatov *et al.*, 2001), providing inorganic chemists with a perfect media for numerous reactions. As a whole, metal-promoted reactions of nitriles have proven to be a significant tool for the synthesis of diverse compounds, and several reviews on this topic have appeared in literatures in the past decades (Aromi *et al.*, 2011). However, a few reports showed the application of solvothermal synthetic techniques to reactions of nitriles with transition metal sources as a mean for the preparation of coordination compounds with molecular or extended structures (Guzei *et al.*, 2006). Here we study reactions of 3d-transition metal ions with acetonitrile in order to understand the reaction system and elucidate structural features of the resultant mononuclear metal complexes.

The asymmetric unit of the title compound contains two independent Ni^{II} atoms, each of which lies on an inversion center, and a methanol molecule, as shown in Fig. 1. Each Ni^{II} atom is in a square-planar geometry, coordinated by four N atoms from two 1-[(1-iminoethyl)imino]ethyl}azanide ligands. Two six-membered rings around the Ni^{II} atom is slightly distorted toward a boat conformation. In one six-membered ring, Ni1 and N2 atoms exist in the apex positions, while in the other ring Ni2 and N5 atoms do. The bond distances in the ligands are very similar to those observed for the simple acetamidine molecule (Norrestam *et al.*, 1983). In the crystal, the complex molecules are linked into a one-dimensional supramolecular architecture *via* N4—H4···N3^{i}, N5—H5···N3 hydrogen bonds (Table 1) [symmetry code: (i) -*x*+1, -*y*+1, -*z*]. The one-dimensional architectures are further linked into a two-dimensional supramolecular structure with highly corrugated architecture *via* O—H···N and N—H···O hydrogen bonds between the ligands and the lattice methanol molecules, as shown in Fig. 2.

S2. Experimental

A mixture of $Ni(NO_3)_2.6H_2O$ (0.029 g, 0.1 mmol) in 12 ml of acetonitrile/methanol (3:1, *v*/*v*) and 0.1 ml of 2*M* NaOH solution was sealed in a Teflon-lined autoclave and heated under autogenous pressure to 160°C for 3 days and then allowed to cool to room temperature at a rate of 1°C per minute. Block-shaped tan crystals of the title complex were collected in 71% yield.

S3. Refinement

H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.96, N—H = 0.86 and O—H = 0.82 Å and with U_{iso}(H) = 1.2U_{eq}(N) or 1.5U_{eq}(C, O).

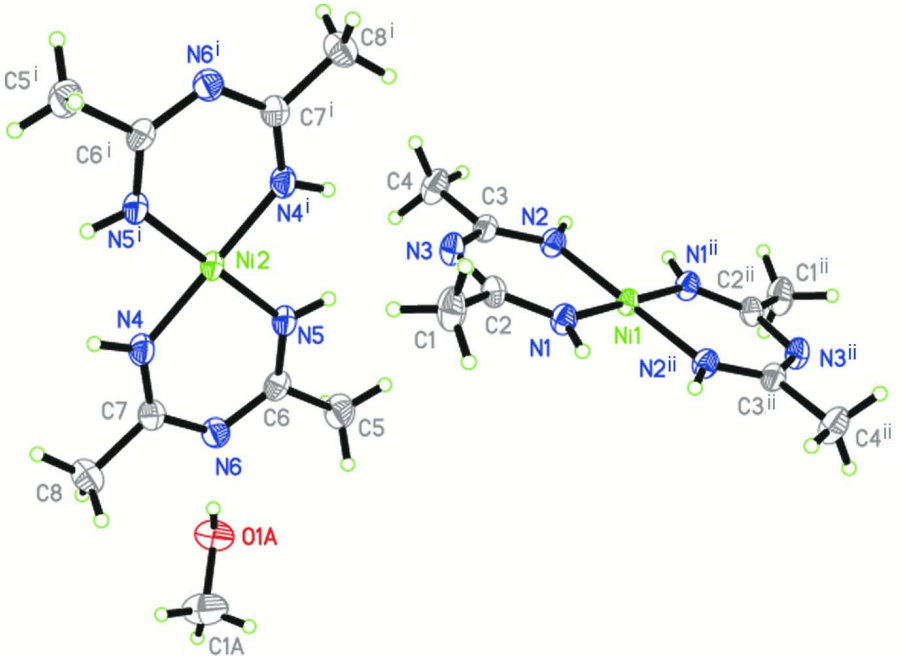

Figure 1

The molecular structure of the title complex. Displacement ellipsoids are drawn at the 30% probability level. [Symmetry codes: (i) 1-x, 1-y, -z; (ii) 2-x, -y, -z.]

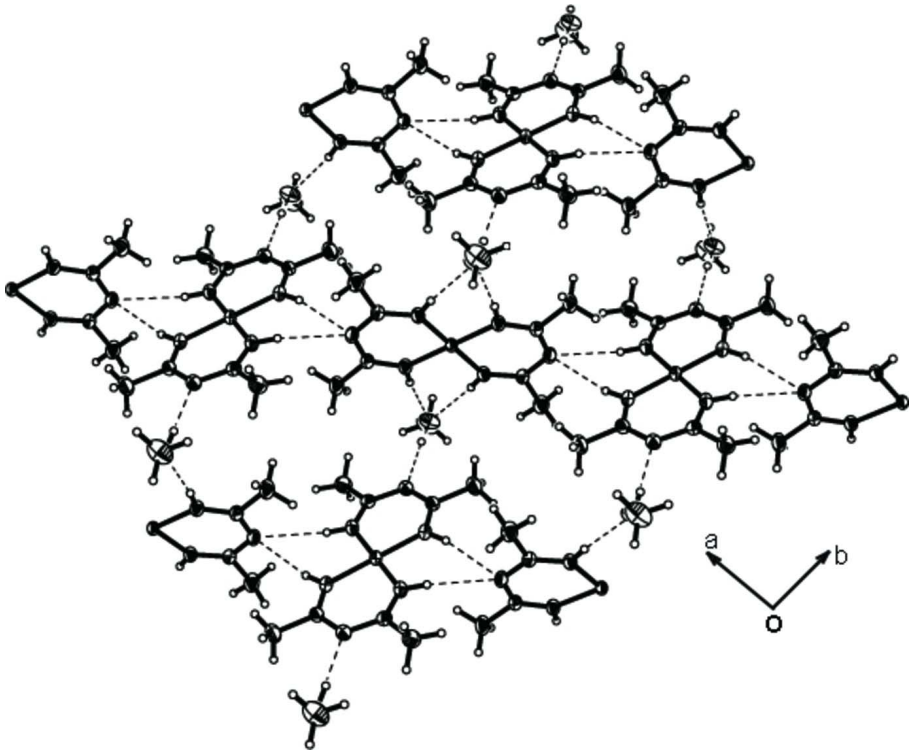

Figure 2

The two-dimensional supramolecular structure of the title complex.

Bis({1-[(1-iminoethyl)imino]ethyl}azanido- κ^2N^1,N^5)nickel(II) methanol monosolvate

Crystal data

$[Ni(C_4H_8N_3)_2]\cdot CH_4O$
$M_r = 287.02$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 9.2768$ (7) Å
$b = 11.4347$ (3) Å
$c = 12.9774$ (3) Å
$\beta = 92.961$ (3)°
$V = 1374.77$ (11) Å^3
$Z = 4$
$F(000) = 608$
$D_x = 1.387$ Mg m^{-3}
$D_m = 1.37$ Mg m^{-3}
D_m measured by not measured
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9999 reflections
$\theta = 2.4$–$27.7°$
$\mu = 1.41$ mm^{-1}
$T = 298$ K
Block, green
0.23 × 0.21 × 0.19 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
$T_{min} = 0.603$, $T_{max} = 0.766$
9293 measured reflections
2421 independent reflections
1738 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.2°$
$h = -9\rightarrow11$
$k = -13\rightarrow13$
$l = -15\rightarrow15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.082$
$S = 1.04$
2421 reflections
163 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0344P)^2 + 0.7499P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.33$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.051 (2)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
C1	0.8993 (3)	0.3445 (2)	0.0859 (3)	0.0599 (8)
H1A	0.9269	0.3305	0.1572	0.090*

H1B	0.8074	0.3832	0.0810	0.090*
H1C	0.9704	0.3929	0.0558	0.090*
C2	0.8886 (3)	0.2297 (2)	0.02917 (19)	0.0394 (6)
C3	0.7796 (3)	0.1309 (2)	−0.10996 (19)	0.0383 (6)
C4	0.6614 (3)	0.1373 (3)	−0.1938 (2)	0.0578 (8)
H4A	0.6647	0.0688	−0.2365	0.087*
H4B	0.6747	0.2057	−0.2351	0.087*
H4C	0.5695	0.1413	−0.1632	0.087*
N1	0.9732 (2)	0.14471 (17)	0.05897 (16)	0.0391 (5)
H1	1.0248	0.1577	0.1148	0.047*
N2	0.8599 (2)	0.03823 (17)	−0.10115 (15)	0.0379 (5)
H2	0.8460	−0.0129	−0.1493	0.045*
N3	0.7895 (2)	0.22670 (18)	−0.05010 (16)	0.0423 (5)
Ni1	1.0000	0.0000	0.0000	0.03187 (16)
C5	0.4642 (3)	0.1559 (2)	0.1102 (3)	0.0606 (8)
H5A	0.3862	0.1150	0.0746	0.091*
H5B	0.4685	0.1344	0.1818	0.091*
H5C	0.5535	0.1357	0.0805	0.091*
C6	0.4397 (3)	0.2853 (2)	0.1004 (2)	0.0407 (6)
C7	0.3098 (3)	0.4450 (2)	0.1593 (2)	0.0402 (6)
C8	0.2071 (4)	0.4860 (2)	0.2380 (2)	0.0561 (8)
H8A	0.2570	0.4901	0.3046	0.084*
H8B	0.1282	0.4319	0.2407	0.084*
H8C	0.1707	0.5620	0.2190	0.084*
N4	0.3630 (2)	0.52029 (17)	0.09697 (17)	0.0423 (6)
H4	0.3296	0.5902	0.1014	0.051*
N5	0.5126 (2)	0.34436 (18)	0.03568 (17)	0.0406 (5)
H5	0.5765	0.3050	0.0047	0.049*
N6	0.3410 (2)	0.32978 (18)	0.16225 (16)	0.0431 (5)
Ni2	0.5000	0.5000	0.0000	0.03481 (17)
C1A	0.1695 (5)	0.1778 (3)	0.3585 (3)	0.0868 (12)
H1A1	0.2617	0.1556	0.3894	0.130*
H1A2	0.0962	0.1268	0.3826	0.130*
H1A3	0.1484	0.2570	0.3771	0.130*
O1A	0.1728 (2)	0.16916 (17)	0.25194 (14)	0.0601 (6)
H1A4	0.2242	0.2210	0.2302	0.090*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0588 (19)	0.0430 (17)	0.076 (2)	0.0143 (15)	−0.0105 (16)	−0.0205 (15)
C2	0.0371 (15)	0.0335 (14)	0.0476 (15)	0.0039 (12)	0.0022 (12)	−0.0055 (11)
C3	0.0365 (14)	0.0359 (14)	0.0422 (14)	0.0038 (12)	−0.0001 (11)	0.0030 (11)
C4	0.0597 (19)	0.0530 (18)	0.0582 (18)	0.0117 (15)	−0.0199 (15)	−0.0022 (14)
N1	0.0408 (12)	0.0349 (11)	0.0408 (12)	0.0056 (10)	−0.0048 (10)	−0.0067 (9)
N2	0.0414 (13)	0.0322 (11)	0.0395 (12)	0.0048 (10)	−0.0037 (9)	−0.0048 (9)
N3	0.0400 (13)	0.0359 (12)	0.0502 (13)	0.0094 (10)	−0.0044 (10)	−0.0036 (10)
Ni1	0.0320 (3)	0.0273 (3)	0.0360 (3)	0.00400 (18)	−0.00116 (18)	−0.00203 (18)

C5	0.064 (2)	0.0380 (16)	0.081 (2)	0.0033 (15)	0.0155 (17)	0.0081 (15)
C6	0.0399 (15)	0.0325 (13)	0.0490 (16)	−0.0001 (12)	−0.0043 (12)	0.0039 (12)
C7	0.0347 (15)	0.0402 (15)	0.0454 (15)	−0.0010 (12)	−0.0012 (12)	−0.0033 (12)
C8	0.0558 (18)	0.0507 (19)	0.063 (2)	−0.0025 (14)	0.0164 (15)	−0.0092 (14)
N4	0.0429 (13)	0.0323 (12)	0.0521 (13)	0.0071 (10)	0.0051 (11)	−0.0004 (10)
N5	0.0389 (13)	0.0343 (12)	0.0484 (12)	0.0081 (10)	0.0023 (10)	0.0000 (10)
N6	0.0426 (13)	0.0376 (12)	0.0493 (13)	−0.0005 (10)	0.0061 (11)	0.0016 (10)
Ni2	0.0339 (3)	0.0292 (3)	0.0413 (3)	0.00597 (19)	0.00096 (19)	0.00100 (19)
C1A	0.124 (4)	0.078 (3)	0.058 (2)	−0.018 (2)	0.006 (2)	0.0053 (19)
O1A	0.0711 (15)	0.0590 (13)	0.0505 (12)	−0.0232 (11)	0.0049 (10)	−0.0076 (10)

Geometric parameters (Å, º)

C1—C2	1.506 (3)	C5—H5C	0.9600
C1—H1A	0.9600	C6—N5	1.296 (3)
C1—H1B	0.9600	C6—N6	1.348 (3)
C1—H1C	0.9600	C7—N4	1.297 (3)
C2—N1	1.295 (3)	C7—N6	1.349 (3)
C2—N3	1.344 (3)	C7—C8	1.507 (4)
C3—N2	1.296 (3)	C8—H8A	0.9600
C3—N3	1.344 (3)	C8—H8B	0.9600
C3—C4	1.506 (3)	C8—H8C	0.9600
C4—H4A	0.9600	N4—Ni2	1.848 (2)
C4—H4B	0.9600	N4—H4	0.8600
C4—H4C	0.9600	N5—Ni2	1.841 (2)
N1—Ni1	1.8452 (19)	N5—H5	0.8600
N1—H1	0.8600	Ni2—N5^{ii}	1.841 (2)
N2—Ni1	1.851 (2)	Ni2—N4^{ii}	1.848 (2)
N2—H2	0.8600	C1A—O1A	1.388 (4)
Ni1—N1^{i}	1.8452 (19)	C1A—H1A1	0.9600
Ni1—N2^{i}	1.851 (2)	C1A—H1A2	0.9600
C5—C6	1.501 (3)	C1A—H1A3	0.9600
C5—H5A	0.9600	O1A—H1A4	0.8200
C5—H5B	0.9600		

C2—C1—H1A	109.5	H5A—C5—H5C	109.5
C2—C1—H1B	109.5	H5B—C5—H5C	109.5
H1A—C1—H1B	109.5	N5—C6—N6	125.6 (2)
C2—C1—H1C	109.5	N5—C6—C5	119.2 (3)
H1A—C1—H1C	109.5	N6—C6—C5	115.2 (2)
H1B—C1—H1C	109.5	N4—C7—N6	125.3 (3)
N1—C2—N3	126.1 (2)	N4—C7—C8	119.4 (2)
N1—C2—C1	119.0 (2)	N6—C7—C8	115.3 (2)
N3—C2—C1	114.9 (2)	C7—C8—H8A	109.5
N2—C3—N3	126.4 (2)	C7—C8—H8B	109.5
N2—C3—C4	119.8 (2)	H8A—C8—H8B	109.5
N3—C3—C4	113.8 (2)	C7—C8—H8C	109.5
C3—C4—H4A	109.5	H8A—C8—H8C	109.5

C3—C4—H4B	109.5	H8B—C8—H8C	109.5
H4A—C4—H4B	109.5	C7—N4—Ni2	129.69 (19)
C3—C4—H4C	109.5	C7—N4—H4	115.2
H4A—C4—H4C	109.5	Ni2—N4—H4	115.2
H4B—C4—H4C	109.5	C6—N5—Ni2	129.70 (18)
C2—N1—Ni1	129.87 (18)	C6—N5—H5	115.1
C2—N1—H1	115.1	Ni2—N5—H5	115.1
Ni1—N1—H1	115.1	C6—N6—C7	120.2 (2)
C3—N2—Ni1	129.38 (18)	N5^{ii}—Ni2—N5	180.00 (13)
C3—N2—H2	115.3	N5^{ii}—Ni2—N4	90.74 (9)
Ni1—N2—H2	115.3	N5—Ni2—N4	89.26 (9)
C3—N3—C2	119.1 (2)	N5^{ii}—Ni2—N4^{ii}	89.26 (9)
N1—Ni1—N1^{i}	180.00 (13)	N5—Ni2—N4^{ii}	90.74 (9)
N1—Ni1—N2	88.73 (9)	N4—Ni2—N4^{ii}	180.0
N1^{i}—Ni1—N2	91.27 (9)	O1A—C1A—H1A1	109.5
N1—Ni1—N2^{i}	91.27 (9)	O1A—C1A—H1A2	109.5
N1^{i}—Ni1—N2^{i}	88.73 (9)	H1A1—C1A—H1A2	109.5
N2—Ni1—N2^{i}	180.00 (17)	O1A—C1A—H1A3	109.5
C6—C5—H5A	109.5	H1A1—C1A—H1A3	109.5
C6—C5—H5B	109.5	H1A2—C1A—H1A3	109.5
H5A—C5—H5B	109.5	C1A—O1A—H1A4	109.5
C6—C5—H5C	109.5		

N3—C2—N1—Ni1	6.0 (4)	N6—C7—N4—Ni2	−3.4 (4)
C1—C2—N1—Ni1	−173.5 (2)	C8—C7—N4—Ni2	174.9 (2)
N3—C3—N2—Ni1	6.1 (4)	N6—C6—N5—Ni2	−4.4 (4)
C4—C3—N2—Ni1	−173.7 (2)	C5—C6—N5—Ni2	175.8 (2)
N2—C3—N3—C2	−1.7 (4)	N5—C6—N6—C7	0.6 (4)
C4—C3—N3—C2	178.2 (2)	C5—C6—N6—C7	−179.6 (2)
N1—C2—N3—C3	−4.4 (4)	N4—C7—N6—C6	3.3 (4)
C1—C2—N3—C3	175.1 (2)	C8—C7—N6—C6	−175.1 (2)
C2—N1—Ni1—N2	−1.8 (2)	C6—N5—Ni2—N4	3.5 (2)
C2—N1—Ni1—N2^{i}	178.2 (2)	C6—N5—Ni2—N4^{ii}	−176.5 (2)
C3—N2—Ni1—N1	−3.9 (2)	C7—N4—Ni2—N5^{ii}	−179.8 (2)
C3—N2—Ni1—N1^{i}	176.1 (2)	C7—N4—Ni2—N5	0.2 (2)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O1*A*^{iii}	0.86	2.19	3.049 (3)	172
N2—H2···O1*A*^{iv}	0.86	2.23	3.079 (3)	169
N4—H4···N3^{ii}	0.86	2.44	3.264 (3)	160
N5—H5···N3	0.86	2.31	3.153 (3)	165
O1*A*—H1*A*4···N6	0.82	1.90	2.711 (3)	172

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