

Bis[μ -3-(pyridin-2-yl)pyrazolato]bis[acetato(3,5-dimethyl-1*H*-pyrazole)nickel(II)]

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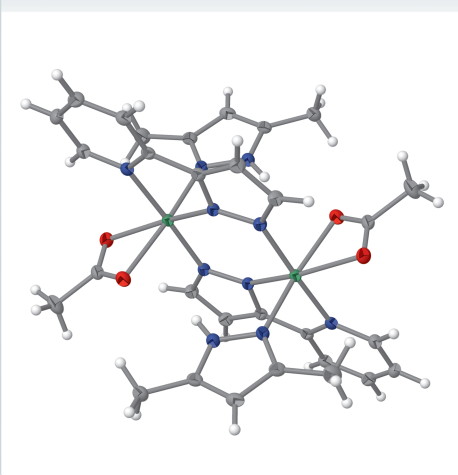
Keywords: coordination compound; nickel; 3,5-dimethylpyrazole; 3-(pyridin-2-yl) pyrazole; heteroleptic complex; crystal structure.

CCDC reference: 2346359

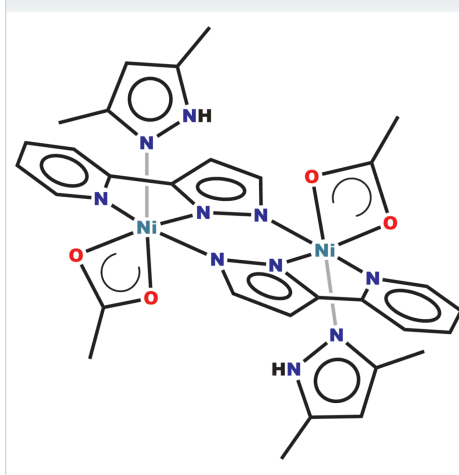
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $[\text{Ni}_2(\text{C}_8\text{H}_6\text{N}_3)_2(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_5\text{H}_8\text{N}_2)_2]$ or $[\text{Ni}(\mu\text{-OOCCH}_3\text{-}(2\text{-PyPz})(\text{Me}_2\text{PzH})_2]$ (**1**) [2-PyPz = 3-(pyridin-2-yl) pyrazole; Me_2PzH = 3,5-dimethyl pyrazole] was synthesized from $\text{Ni}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}$, 2-PyPzH, Me_2PzH and triethylamine as a base. Compound **1** $\{[\text{Ni}_2(\text{C}_{30}\text{H}_{34}\text{N}_{10}\text{Ni}_2\text{O}_4)]\}$ at 100 K has monoclinic ($P2_1/n$) symmetry and the molecules have crystallographic inversion symmetry. Molecules of **1** comprise an almost planar dinuclear Ni^{II} core with an N_4O_2 coordination environment. The equatorial plane consists of N_3O coordination derived from one of the bidentate acetate O atoms and three of the N atoms of the chelating 2-PyPz ligand while the axial positions are occupied by neutral Me_2PzH and the second O atom of the acetate unit. The Ni atoms are bridged by the nitrogen atom of a deprotonated 2-PyPz ligand. Compound **1** exhibits various inter- and intramolecular C—H \cdots O and N—H \cdots O hydrogen bonds.

3D view



Chemical scheme



Structure description

Noble metals such as palladium, platinum or iridium are widely used in catalysis due to their desirable properties such as the ability to tolerate variable coordination states and oxidation states that predispose them towards catalysing two-electron redox processes, while at the same time also being sufficiently stable and thermally stable to be of practical use. A major drawback is, however, their high price and limited availability. As an alternative to scarce 4 and 5*d* metals, their more earth-abundant 3*d* congeners have been investigated, and in particular several nickel-catalysed organic transformation strategies were developed and established (Wilke, 1988; Keim, 1990; Montgomery, 2004; Tasker *et al.*, 2014; Dicciani *et al.*, 2020). These include C—C and C—X (*X* = heteroatom) cross-coupling (Rosen *et al.*, 2011), cycloaddition (Lautens *et al.*, 1996; Komagawa *et al.*, 2013),

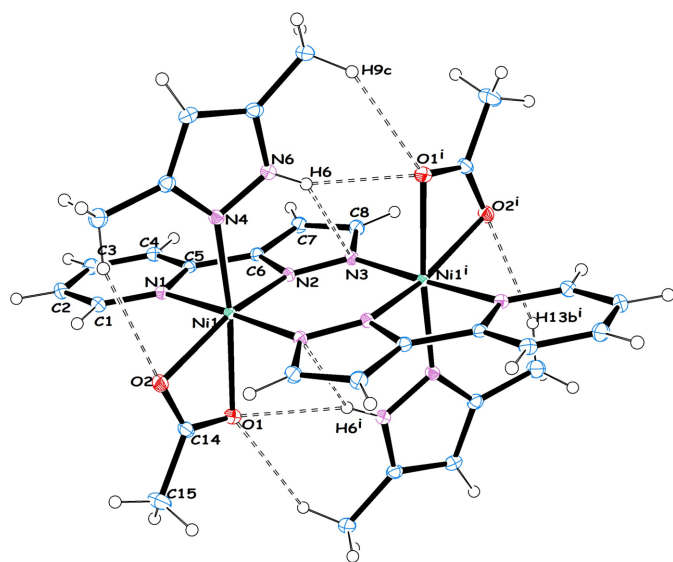


Figure 1
The molecule of **1** (with 50% displacement ellipsoids) with the unlabelled atoms related by crystallographic inversion symmetry ($-x, -y, 1 - z$). Intramolecular C–H...O, N–H...O and N–H...N hydrogen bonds are shown as dashed lines.

asymmetric hydrogenation (Vermaak *et al.*, 2024), photoredox catalysis (Milligan *et al.*, 2019; Cuesta-Galisteo *et al.*, 2024), reductive coupling (Day *et al.*, 2023) and reductive cyclization reactions (Montgomery, 2004) to name just a few. The inability of nickel to catalyse two-electron transformations can be overcome by the placement of more than one metal atom at the catalytic centre, and dinuclear nickel complexes show an enhanced catalytic activity and a higher robustness that can be traced back to the synergistic interaction between the two metals in the active site (Uyeda & Farley 2021; Xu *et al.*, 2020). Nickel is also a micronutrient and essential for the biosynthesis of hydrogenase, carbon monoxide dehydrogenase (CODH) and urease. These enzymes require more than one metal active site to catalyse the enzymatic process. This also substantiates the crucial role of the presence of more than one metal centre for 3*d*-metal-based catalysts.

We are interested in synthesizing dimeric Ni^{II} complexes utilizing chelating ligands such as 2-PyPzH [3-(2-pyridyl)pyrazole, C₈H₇N₃]. The use of pyrazole ligands in coordination and organometallic chemistry is well established (Trofimenko, 1972; Mukherjee, 2000; Halcrow, 2009; Viciano-Chumillas *et al.*, 2010). 2-PyPzH usually forms planar dimeric [*M*(μ -2-PyPz)₂]₂ units that are thermally stable. Copper-based dimeric complexes with a {[Cu(μ -2-PyPz)₂]₂}_{*n*} core have been described (Jeffery *et al.*, 1997; Hu *et al.*, 2006; Das *et al.*, 2019). However, to the best of our knowledge, the analogous nickel complex with an [Ni(μ -2-PyPz)₂]_{*n*} core is unknown. Thus, a reaction was carried out between nickel(II)acetate tetrahydrate, 2-PyPzH as the primary ligand and highly lipophilic 3,5-dimethylpyrazole (Me₂PzH) as an ancillary ligand and a small excess of triethylamine base in methanol solvent. This was done in a 1:1:5:3.5 ratio, which resulted in the formation of a green solid, which was then recrystallized from methanol

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>
N6–H6...N2	0.859 (18)	2.571 (18)	2.9931 (18)	111.4 (14)
N6–H6...N3	0.859 (18)	2.591 (19)	3.3065 (18)	141.4 (16)
N6–H6...O1 ⁱ	0.859 (18)	2.332 (19)	3.0800 (17)	145.6 (16)
C1–H1...O2	0.95	2.61	3.1281 (19)	115
C2–H2...O2 ⁱⁱ	0.95	2.37	3.2692 (19)	158
C4–H4...O1 ⁱⁱⁱ	0.95	2.62	3.4696 (19)	149
C9–H9C...O1 ⁱ	0.98	2.61	3.426 (2)	141
C13–H13B...O2	0.98	2.60	3.530 (2)	159

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

solvent to obtain blue crystals of [Ni₂(μ -OOCCH₃)₂(2-PyPz)₂(Me₂PzH)₂] (**1**). Interestingly, the initial reaction between nickel(II)acetate tetrahydrate, 2-PyPzH and triethylamine base in a 1:1:1.5 stoichiometry failed and led to an intractable mixture. However, the addition of a large excess of Me₂PzH allowed us to isolate the soluble molecular assembly of **1** (Fig. 1).

Compound **1** crystallizes in the monoclinic *P2₁/n* space group, in which the asymmetric unit contains half of the molecule. Compound **1** is a dinuclear heteroleptic nickel(II) complex consisting of two each of anionic 2-PyPz, anionic CH₃COO[−] and neutral Me₂PzH ligands and the complex molecules have crystallographic inversion symmetry. Overall, the two nickel atoms (Ni1 and Ni1ⁱ) are bridged through the 2-PyPz ligand and each Ni atom has an N₄O₂ octahedral coordination environment around it. The three N-donors (N1, N2 and N3ⁱ) are derived from the 2-PyPz unit, which forms the basal plane of the dimer while the fourth N-coordination (N4) is obtained from the axial neutral Me₂PzH ligand. The acetate ligand (O1 and O2) exhibits a *syn-syn* symmetric binding mode (κ^2 mode) in which O2 is in the equatorial position while the sixth axial position is occupied by O1.

The following is a summary of the bonding parameters found in compound **1** in which each Ni atom exhibits three different Ni–N distances and two different Ni–O distances. The Ni–N distance involving the anionic pyrazole unit is shorter [Ni1–N2 = 2.0245 (12); Ni1–N3ⁱ = 2.0409 (13) Å] compared to the pyridinic N of 2-PyPz [Ni1–N1 = 2.0964 (13) Å] and the neutral Me₂PzH ligand [Ni1–N4 = 2.0884 (12) Å]. Additionally, the axial Ni–O distances are longer [Ni1–O1 = 2.1848 (11) Å] than the equatorial distance [Ni1–O2 = 2.1232 (11) Å]. Furthermore, the C–O distances are not equal [C14–O1 = 1.2576 (19); C14–O2 = 1.2641 (19) Å]. It is noteworthy that the dimeric [Ni(μ -2-PyPz)(COOCH₃)₂]₂ unit is almost planar, with the two basal *trans* angles being less than 180° [O1–Ni1–N4 = 170.18 (5); N1–Ni1–N3ⁱ = 177.68 (5)°]. The angle between the two apical positions is the most acute [O2–Ni1–N2 = 157.80 (5)°]. Finally, of the twelve right angles around Ni1, seven are closer to 90° [average O–Ni–N = 89.16 (4) and average N–Ni–N = 91.03 (6)°], and the remaining three are obtuse [N2–Ni1–N3ⁱ = 100.88 (5); O1–Ni1–N2 = 99.02 (5); O2–Ni1–N4 = 109.07 (5)°].

Compound **1** exhibits several intra- and intermolecular hydrogen bonds (Table 1, Fig. 2), with atom N6 of Me₂PzH

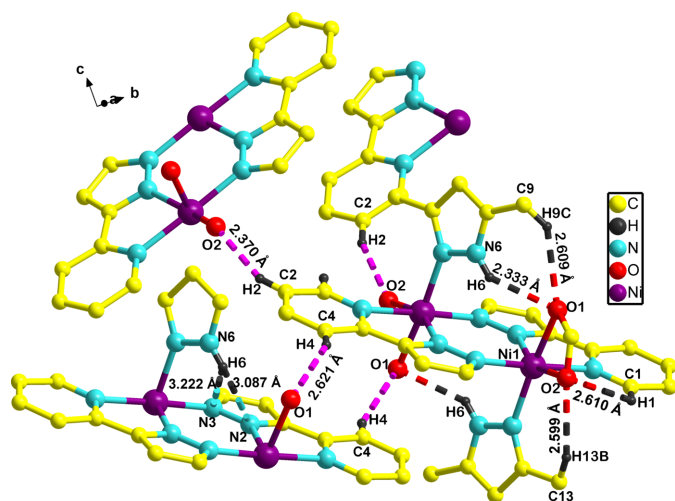


Figure 2
Perspective view of **1** showing the intra- (red and black dotted lines) and intermolecular C—H···O (pink dotted lines) and intramolecular N—H···N (blue and black dotted lines) interactions with bond distances (several atoms were removed for clarity).

forming intramolecular hydrogen bonds with O1 of the acetate (N6—H6···O1ⁱ and the reciprocal N6ⁱ—H6ⁱ···O1 3.0800 (17) Å; symmetry code: (i) $-x, -y, -z + 1$), with N2 [N6—H6···N2 2.9931 (18) Å] and N3 [N6—H6···N3 3.3065 (18) Å] of 2-PyPz, while the two O atoms of acetate (O1 and O2) interact with the pyridine C—H of 2-PyPz and pyrazolyl C—H of Me₂PzH. Thus, the hydrogen bonding between C2—H2···O2ⁱⁱ [3.2692 (19) Å; symmetry code: (ii) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$] and C4—H4···O1ⁱⁱⁱ [3.4696 (19) Å; symmetry code: (iii) $-x, -y + 1, -z + 1$] are intermolecular in nature while the C9—H9C···O1ⁱ [3.426 (2) Å], C1—H1···O2 [3.1281 (19) Å] and C13—H13B···O2 [3.530 (2) Å] are of intramolecular type.

Synthesis and crystallization

0.5 mmol of Ni(OOCCH₃)₂·4H₂O (0.1244 g) was dissolved in 30 ml of methanol. Then, 0.5 mmol of 2-PyPzH (0.0726 g) and 0.79 mmol of triethylamine (0.11 ml) were added to the solution. Upon addition of these, the solution became milky white and insoluble. It was stirred for 2 h. After every 30 minutes of stirring, 0.5 mmol of lipophilic Me₂PzH (0.2402 g, 2.5 mmol) and equal portions of triethylamine (0.11 ml, 0.79 mmol) were added. The solution slowly turned green and was further stirred for 12 h. It was then filtered and solvents were evaporated *in vacuo* to obtain a pale-green solid. Finally, the solid was recrystallized from methanol solution, which afforded blue crystals of **1**. Crystal yield 45% [based on Ni(OOCCH₃)₂·4H₂O], m.p. 212°C. ESI-MS: [M - 2H]⁺ 713.479; [M₁ + Li]⁺ where [M₁ = M-2(Me₂PzH)-CH₃CO] 487.309. FT-IR (KBr, ν, cm⁻¹): 3122 (s), 3114 (s), 3000 (m), 2937 (s), 2738 (m), 2677 (s), 2015 (m, br), 1470 (m), 1307 (m), 1268 (m), 1407 (m), 1094 (s, br), 1032 (m), 941 (s), 898 (s), 855 (m), 811 (s), 624 (s), 554 (m).

Table 2
Experimental details.

Crystal data	
Chemical formula	[Ni ₂ (C ₈ H ₆ N ₃) ₂ (C ₂ H ₃ O ₂) ₂ ·(C ₅ H ₈ N ₂) ₂]
<i>M</i> _r	716.09
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>n</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	11.1045 (7), 9.1489 (6), 15.8088 (11)
β (°)	92.210 (1)
<i>V</i> (Å ³)	1604.88 (18)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	1.23
Crystal size (mm)	0.12 × 0.10 × 0.10
Data collection	
Diffractometer	Bruker <i>APEX</i>
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
<i>T</i> _{min} , <i>T</i> _{max}	0.875, 0.905
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	10468, 3946, 3617
<i>R</i> _{int}	0.025
(sin θ/λ) _{max} (Å ⁻¹)	0.667
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.030, 0.079, 1.04
No. of reflections	3946
No. of parameters	214
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.44, -0.27

Computer programs: *SMART* and *SAINT* (Bruker, 2012), *SHELXT* (Sheldrick, 2015a), *SHELXL2019/2* (Sheldrick, 2015b), *ORTEP-3 for Windows* (Farrugia, 2012), *DIAMOND* (Brandenburg *et al.*, 2014) and *pubCIF* (Westrip, 2010).

Refinement

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

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full crystallographic data

IUCrData (2024). **9**, x240810 [https://doi.org/10.1107/S2414314624008101]

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Bis[μ -3-(pyridin-2-yl)pyrazolato]bis[acetato(3,5-dimethyl-1*H*-pyrazole)nickel(II)]

Crystal data

$[\text{Ni}_2(\text{C}_8\text{H}_6\text{N}_3)_2(\text{C}_2\text{H}_3\text{O}_2)_2(\text{C}_5\text{H}_8\text{N}_2)_2]$

$M_r = 716.09$

Monoclinic, $P2_1/n$

$a = 11.1045$ (7) Å

$b = 9.1489$ (6) Å

$c = 15.8088$ (11) Å

$\beta = 92.210$ (1)°

$V = 1604.88$ (18) Å³

$Z = 2$

$F(000) = 744$

$D_x = 1.482$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 5987 reflections

$\theta = 2.6$ – 28.3 °

$\mu = 1.23$ mm⁻¹

$T = 100$ K

Prism, blue

$0.12 \times 0.10 \times 0.10$ mm

Data collection

Bruker APEX
diffractometer

Radiation source: sealed tube

φ and ω scans

Absorption correction: multi-scan
(SADABS; Krause *et al.*, 2015)

$T_{\min} = 0.875$, $T_{\max} = 0.905$

10468 measured reflections

3946 independent reflections

3617 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\max} = 28.3$ °, $\theta_{\min} = 2.2$ °

$h = -14 \rightarrow 14$

$k = -12 \rightarrow 12$

$l = -21 \rightarrow 14$

4 standard reflections every 22 reflections

intensity decay: none

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.030$

$wR(F^2) = 0.079$

$S = 1.04$

3946 reflections

214 parameters

0 restraints

Primary atom site location: difference Fourier
map

Secondary atom site location: inferred from
neighbouring sites

Hydrogen site location: mixed

H atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0457P)^2 + 0.5264P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.44$ e Å⁻³

$\Delta\rho_{\min} = -0.27$ 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. All the non-hydrogen atoms were refined anisotropically using full-matrix least-square procedures while carbon bound hydrogen atoms were included in idealized positions and the methyl CH₃ were allowed to rotate using a riding model. C—H bonds were constrained to 0.95 Å for aromatic C—H ($U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$) and 0.98 Å for CH₃ [$U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$] units, respectively. The N—H proton was added from the difference Fourier map and refined with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{N})$.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.11107 (14)	0.40306 (17)	0.31691 (10)	0.0189 (3)
H1	0.177134	0.357829	0.290855	0.023*
C2	0.08185 (14)	0.54516 (18)	0.29476 (10)	0.0212 (3)
H2	0.125431	0.595694	0.253272	0.025*
C3	−0.01268 (15)	0.61225 (16)	0.33456 (11)	0.0213 (3)
H3	−0.033162	0.710881	0.321898	0.026*
C4	−0.07701 (13)	0.53426 (17)	0.39297 (9)	0.0184 (3)
H4	−0.142463	0.578183	0.420430	0.022*
C5	−0.04392 (13)	0.39056 (15)	0.41058 (9)	0.0152 (3)
C6	−0.10578 (12)	0.29590 (16)	0.46928 (9)	0.0154 (3)
C7	−0.21072 (13)	0.31154 (17)	0.51418 (10)	0.0192 (3)
H7	−0.263572	0.393132	0.515024	0.023*
C8	−0.21990 (13)	0.18053 (17)	0.55720 (10)	0.0191 (3)
H8	−0.282715	0.156611	0.593911	0.023*
C9	−0.31184 (15)	−0.1728 (2)	0.28848 (11)	0.0268 (4)
H9A	−0.325502	−0.242347	0.241949	0.040*
H9B	−0.377717	−0.101487	0.288064	0.040*
H9C	−0.308875	−0.225503	0.342481	0.040*
C10	−0.19552 (14)	−0.09537 (16)	0.27774 (10)	0.0195 (3)
C11	−0.12922 (14)	−0.06840 (18)	0.20783 (10)	0.0206 (3)
H11	−0.149648	−0.094806	0.150952	0.025*
C12	−0.02518 (13)	0.00603 (17)	0.23726 (9)	0.0189 (3)
C13	0.07636 (15)	0.0650 (2)	0.18861 (11)	0.0272 (4)
H13A	0.101087	−0.008066	0.147390	0.041*
H13B	0.144532	0.087654	0.227618	0.041*
H13C	0.050240	0.154119	0.158824	0.041*
C14	0.30155 (13)	0.17584 (17)	0.44170 (10)	0.0207 (3)
C15	0.43466 (15)	0.2066 (2)	0.45627 (13)	0.0363 (4)
H15A	0.473384	0.211363	0.401669	0.054*
H15B	0.471550	0.128286	0.490694	0.054*
H15C	0.445230	0.300123	0.485868	0.054*
N1	0.05042 (11)	0.32623 (14)	0.37348 (8)	0.0158 (2)
N2	−0.05658 (10)	0.16361 (14)	0.48562 (7)	0.0143 (2)
N3	−0.12709 (11)	0.09133 (14)	0.53973 (8)	0.0157 (2)

N4	-0.02724 (11)	0.02391 (14)	0.32099 (8)	0.0161 (2)
N6	-0.13244 (11)	-0.03814 (14)	0.34435 (8)	0.0179 (3)
O1	0.23062 (10)	0.19619 (12)	0.50069 (7)	0.0213 (2)
O2	0.26366 (10)	0.12852 (12)	0.37041 (7)	0.0204 (2)
Ni1	0.08662 (2)	0.11295 (2)	0.41577 (2)	0.01351 (7)
H6	-0.1496 (16)	-0.046 (2)	0.3967 (12)	0.016*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0153 (7)	0.0217 (8)	0.0195 (7)	-0.0015 (5)	0.0013 (6)	0.0017 (6)
C2	0.0190 (7)	0.0229 (8)	0.0218 (8)	-0.0039 (6)	0.0009 (6)	0.0061 (6)
C3	0.0223 (8)	0.0164 (7)	0.0249 (8)	0.0001 (6)	-0.0022 (6)	0.0037 (6)
C4	0.0164 (7)	0.0188 (7)	0.0198 (7)	0.0007 (5)	-0.0014 (6)	-0.0008 (6)
C5	0.0139 (6)	0.0180 (7)	0.0136 (6)	-0.0012 (5)	-0.0024 (5)	-0.0015 (5)
C6	0.0146 (6)	0.0171 (7)	0.0143 (6)	-0.0001 (5)	-0.0008 (5)	-0.0009 (5)
C7	0.0171 (7)	0.0205 (8)	0.0200 (7)	0.0040 (6)	0.0022 (6)	0.0005 (6)
C8	0.0152 (7)	0.0234 (8)	0.0189 (7)	0.0029 (6)	0.0037 (5)	0.0013 (6)
C9	0.0225 (8)	0.0303 (9)	0.0271 (8)	-0.0091 (7)	-0.0076 (6)	0.0063 (7)
C10	0.0183 (7)	0.0166 (7)	0.0229 (8)	-0.0001 (5)	-0.0054 (6)	0.0023 (6)
C11	0.0212 (7)	0.0217 (7)	0.0183 (7)	0.0017 (6)	-0.0044 (6)	-0.0010 (6)
C12	0.0180 (7)	0.0200 (7)	0.0186 (7)	0.0032 (6)	-0.0006 (6)	0.0015 (6)
C13	0.0226 (8)	0.0396 (10)	0.0197 (8)	-0.0009 (7)	0.0034 (6)	-0.0011 (7)
C14	0.0144 (7)	0.0201 (7)	0.0275 (8)	-0.0013 (5)	-0.0002 (6)	0.0065 (6)
C15	0.0161 (8)	0.0456 (11)	0.0467 (11)	-0.0063 (7)	-0.0028 (7)	0.0064 (9)
N1	0.0134 (6)	0.0186 (6)	0.0154 (6)	-0.0008 (5)	-0.0005 (4)	0.0009 (5)
N2	0.0126 (5)	0.0166 (6)	0.0136 (6)	-0.0005 (5)	0.0013 (4)	0.0009 (5)
N3	0.0129 (6)	0.0196 (6)	0.0147 (6)	0.0006 (5)	0.0023 (4)	0.0016 (5)
N4	0.0134 (6)	0.0165 (6)	0.0183 (6)	0.0001 (4)	0.0011 (5)	0.0012 (5)
N6	0.0162 (6)	0.0204 (6)	0.0172 (6)	-0.0022 (5)	-0.0003 (5)	0.0016 (5)
O1	0.0176 (5)	0.0256 (6)	0.0205 (5)	-0.0023 (4)	-0.0009 (4)	0.0005 (4)
O2	0.0164 (5)	0.0240 (6)	0.0210 (6)	0.0005 (4)	0.0043 (4)	0.0027 (4)
Ni1	0.01067 (11)	0.01613 (12)	0.01377 (11)	-0.00014 (6)	0.00125 (7)	0.00074 (6)

Geometric parameters (Å, °)

C1—N1	1.3393 (19)	C11—C12	1.405 (2)
C1—C2	1.382 (2)	C11—H11	0.9500
C1—H1	0.9500	C12—N4	1.3348 (19)
C2—C3	1.388 (2)	C12—C13	1.490 (2)
C2—H2	0.9500	C13—H13A	0.9800
C3—C4	1.387 (2)	C13—H13B	0.9800
C3—H3	0.9500	C13—H13C	0.9800
C4—C5	1.390 (2)	C14—O1	1.2576 (19)
C4—H4	0.9500	C14—O2	1.2641 (19)
C5—N1	1.3547 (19)	C14—C15	1.514 (2)
C5—C6	1.460 (2)	C14—Ni1	2.4738 (15)
C6—N2	1.3488 (19)	C15—H15A	0.9800

C6—C7	1.395 (2)	C15—H15B	0.9800
C7—C8	1.384 (2)	C15—H15C	0.9800
C7—H7	0.9500	N1—Ni1	2.0964 (13)
C8—N3	1.3514 (19)	N2—N3	1.3541 (17)
C8—H8	0.9500	N2—Ni1	2.0245 (12)
C9—C10	1.489 (2)	N3—Ni1 ⁱ	2.0409 (13)
C9—H9A	0.9800	N4—N6	1.3626 (17)
C9—H9B	0.9800	N4—Ni1	2.0884 (12)
C9—H9C	0.9800	N6—H6	0.859 (18)
C10—N6	1.3479 (19)	O1—Ni1	2.1848 (11)
C10—C11	1.374 (2)	O2—Ni1	2.1232 (11)
N1—C1—C2	122.95 (15)	O1—C14—Ni1	61.93 (8)
N1—C1—H1	118.5	O2—C14—Ni1	59.12 (8)
C2—C1—H1	118.5	C15—C14—Ni1	177.13 (13)
C1—C2—C3	118.39 (14)	C14—C15—H15A	109.5
C1—C2—H2	120.8	C14—C15—H15B	109.5
C3—C2—H2	120.8	H15A—C15—H15B	109.5
C4—C3—C2	119.50 (14)	C14—C15—H15C	109.5
C4—C3—H3	120.2	H15A—C15—H15C	109.5
C2—C3—H3	120.2	H15B—C15—H15C	109.5
C3—C4—C5	118.75 (14)	C1—N1—C5	118.57 (13)
C3—C4—H4	120.6	C1—N1—Ni1	127.31 (10)
C5—C4—H4	120.6	C5—N1—Ni1	114.10 (10)
N1—C5—C4	121.80 (14)	C6—N2—N3	108.63 (12)
N1—C5—C6	114.08 (13)	C6—N2—Ni1	114.95 (10)
C4—C5—C6	124.12 (14)	N3—N2—Ni1	135.91 (10)
N2—C6—C7	109.55 (13)	C8—N3—N2	107.36 (12)
N2—C6—C5	117.19 (13)	C8—N3—Ni1 ⁱ	129.94 (10)
C7—C6—C5	133.25 (14)	N2—N3—Ni1 ⁱ	122.68 (9)
C8—C7—C6	103.89 (13)	C12—N4—N6	105.39 (12)
C8—C7—H7	128.1	C12—N4—Ni1	136.57 (11)
C6—C7—H7	128.1	N6—N4—Ni1	118.01 (9)
N3—C8—C7	110.57 (13)	C10—N6—N4	112.04 (13)
N3—C8—H8	124.7	C10—N6—H6	126.3 (12)
C7—C8—H8	124.7	N4—N6—H6	121.3 (12)
C10—C9—H9A	109.5	C14—O1—Ni1	87.55 (9)
C10—C9—H9B	109.5	C14—O2—Ni1	90.15 (9)
H9A—C9—H9B	109.5	N2—Ni1—N3 ⁱ	100.88 (5)
C10—C9—H9C	109.5	N2—Ni1—N4	90.81 (5)
H9A—C9—H9C	109.5	N3 ⁱ —Ni1—N4	90.53 (5)
H9B—C9—H9C	109.5	N2—Ni1—N1	79.39 (5)
N6—C10—C11	106.28 (14)	N3 ⁱ —Ni1—N1	177.68 (5)
N6—C10—C9	121.53 (15)	N4—Ni1—N1	91.77 (5)
C11—C10—C9	132.18 (15)	N2—Ni1—O2	157.80 (5)
C10—C11—C12	106.26 (13)	N3 ⁱ —Ni1—O2	89.05 (5)
C10—C11—H11	126.9	N4—Ni1—O2	109.07 (5)
C12—C11—H11	126.9	N1—Ni1—O2	89.92 (4)

N4—C12—C11	110.03 (14)	N2—Ni1—O1	99.02 (5)
N4—C12—C13	120.64 (14)	N3 ⁱ —Ni1—O1	87.78 (5)
C11—C12—C13	129.31 (14)	N4—Ni1—O1	170.18 (5)
C12—C13—H13A	109.5	N1—Ni1—O1	89.91 (4)
C12—C13—H13B	109.5	O2—Ni1—O1	61.24 (4)
H13A—C13—H13B	109.5	N2—Ni1—C14	129.01 (5)
C12—C13—H13C	109.5	N3 ⁱ —Ni1—C14	87.58 (5)
H13A—C13—H13C	109.5	N4—Ni1—C14	139.74 (5)
H13B—C13—H13C	109.5	N1—Ni1—C14	90.48 (5)
O1—C14—O2	121.02 (14)	O2—Ni1—C14	30.73 (5)
O1—C14—C15	119.71 (15)	O1—Ni1—C14	30.52 (5)
O2—C14—C15	119.27 (15)		
N1—C1—C2—C3	1.7 (2)	C7—C6—N2—N3	0.44 (16)
C1—C2—C3—C4	-2.0 (2)	C5—C6—N2—N3	-178.96 (12)
C2—C3—C4—C5	0.6 (2)	C7—C6—N2—Ni1	173.56 (10)
C3—C4—C5—N1	1.2 (2)	C5—C6—N2—Ni1	-5.84 (16)
C3—C4—C5—C6	-178.64 (14)	C7—C8—N3—N2	0.27 (17)
N1—C5—C6—N2	5.98 (19)	C7—C8—N3—Ni1 ⁱ	178.58 (10)
C4—C5—C6—N2	-174.14 (13)	C6—N2—N3—C8	-0.43 (15)
N1—C5—C6—C7	-173.25 (15)	Ni1—N2—N3—C8	-171.45 (11)
C4—C5—C6—C7	6.6 (3)	C6—N2—N3—Ni1 ⁱ	-178.89 (9)
N2—C6—C7—C8	-0.27 (17)	Ni1—N2—N3—Ni1 ⁱ	10.09 (18)
C5—C6—C7—C8	179.01 (15)	C11—C12—N4—N6	-0.36 (17)
C6—C7—C8—N3	0.00 (17)	C13—C12—N4—N6	178.19 (14)
N6—C10—C11—C12	0.30 (17)	C11—C12—N4—Ni1	177.84 (11)
C9—C10—C11—C12	-178.23 (17)	C13—C12—N4—Ni1	-3.6 (2)
C10—C11—C12—N4	0.04 (18)	C11—C10—N6—N4	-0.55 (17)
C10—C11—C12—C13	-178.35 (16)	C9—C10—N6—N4	178.17 (14)
C2—C1—N1—C5	0.1 (2)	C12—N4—N6—C10	0.57 (16)
C2—C1—N1—Ni1	-178.23 (11)	Ni1—N4—N6—C10	-178.03 (10)
C4—C5—N1—C1	-1.6 (2)	O2—C14—O1—Ni1	1.96 (15)
C6—C5—N1—C1	178.30 (13)	C15—C14—O1—Ni1	-177.31 (14)
C4—C5—N1—Ni1	176.96 (11)	O1—C14—O2—Ni1	-2.01 (15)
C6—C5—N1—Ni1	-3.15 (15)	C15—C14—O2—Ni1	177.26 (14)

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

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

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N6—H6 \cdots N2	0.859 (18)	2.571 (18)	2.9931 (18)	111.4 (14)
N6—H6 \cdots N3	0.859 (18)	2.591 (19)	3.3065 (18)	141.4 (16)
N6—H6 \cdots O1 ⁱ	0.859 (18)	2.332 (19)	3.0800 (17)	145.6 (16)
C1—H1 \cdots O2	0.95	2.61	3.1281 (19)	115
C2—H2 \cdots O2 ⁱⁱ	0.95	2.37	3.2692 (19)	158
C4—H4 \cdots O1 ⁱⁱⁱ	0.95	2.62	3.4696 (19)	149

C9—H9C···O1 ⁱ	0.98	2.61	3.426 (2)	141
C13—H13B···O2	0.98	2.60	3.530 (2)	159

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