Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Crystal structure of bis[4-(allyloxy)-*N*′-(but-2-en-1-ylidene)benzohydrazidato]nickel(II)

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Received 24 February 2023
Accepted 27 March 2023

Edited by S. Parkin, University of Kentucky, USA

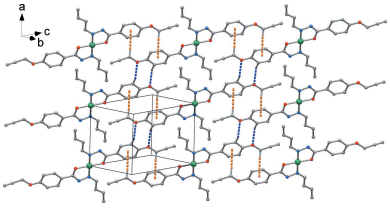
Keywords: crystal structure; nickel complex; allyloxy; benzohydrazide.

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

In the title complex, $[Ni(C_{14}H_{15}N_2O_2)_2]$, the nickel(II) atom exhibits a square-planar coordination geometry, being coordinated by two negatively charged *N*,*O* chelating ligands in a *trans* configuration, with the metal located on a crystallographic center of symmetry. The X-ray structural characterization showed the complex to be disordered over two orientations with refined occupancies of 0.898 (2) and 0.102 (2). The whole molecule is close to planar, the five- and six-membered rings subtending a dihedral angle of 7.5 (2)°. The crystal packing is supported by C—H···π and C—H···O interactions that form a di-periodic layered network.

1. Chemical context

Hydrazones are a specific class of Schiff-base compounds that are distinguished by the presence of a –CO—NH—N= pharmacophore group, and exhibit a wide range of biological activity (Khan *et al.*, 2003; Joshi *et al.*, 2008; Terzioglu & Gürsoy, 2003). Hydrazone molecules display a number of features, such as their degree of flexibility, a conjugated π-system and an NH unit that readily participates in hydrogen bonding and may be easily deprotonated. In addition, hydrazone molecules behave as bidentate ligands through their carbonyl oxygen and azomethine nitrogen atoms, and are widely used in coordination chemistry for their ability to form complexes with metal ions in variable oxidation states (Abou-Melha, 2021; Abser *et al.*, 2013; Saygıdeğer Demir *et al.*, 2021; Gond *et al.*, 2022; Velásquez *et al.*, 2020). In this respect, the formation of metal complexes plays an important role in enhancing the biological activity of hydrazones (Sathyadevi *et al.*, 2012). In addition, providing the molecule with additional donor sites in this type of ligand can modulate the nuclearity of complexes (Vrdoljak *et al.*, 2023). As part of our studies in this area, this paper describes the crystal structure of a bis-[benzohydrazidato]nickel(II) complex.



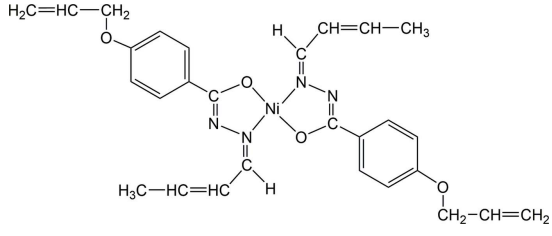


Table 1
Hydrogen-bond geometry (Å, °).

*Cg*1 is the centroid of the C6–C11 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O1^{i}	0.95	2.46	2.975 (3)	114
C8—H8···O2^{ii}	0.95	2.55	3.466 (5)	161
C11a—H11a···O1a	0.95	2.48	2.801 (3)	100
C12—H12b···*Cg*1^{iii}	0.95	2.88	3.781 (4)	152

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

2. Structural commentary

The nickel(II) cation of the title complex, $[Ni(C_{14}H_{15}N_2O_2)_2]$, is located on a crystallographic inversion centre and exhibits a square-planar coordination geometry, with a *trans* configuration of the *N*,*O*-chelating ligands, as imposed by the crystal symmetry. An ellipsoid plot of the complex is shown Fig. 1. The structural characterization revealed that the complex is disordered over two orientations (Fig. 2) with refined occupancies of 0.898 (2) and 0.102 (2). As a result of the low percentage of the second component, the discussion is limited to the species at higher occupancy (Fig. 1). The Ni—O and Ni—N bond lengths are 1.8432 (16) and 1.8596 (18) Å, respectively, and the O1—Ni—N1 chelating angle is 84.13 (7)°. The C2—C3 and C13—C14 bond lengths are 1.319 (4) and 1.258 (5) Å, respectively, which confirm their double bond character (Allen *et al.*, 1987). Intramolecular C4—H4···O1 and C11a—H11a···O1a interactions (Table 1), where the C···O distances are 2.975 (3) and 2.801 (3) Å, respectively, reinforce the crystal structure.

The X-ray diffraction analysis revealed that non-hydrogen atoms of the ligand are nearly coplanar; the maximum deviations being 0.308 (3) and 0.313 (5) Å for the allyl carbon atoms C13 and C14, respectively, on either side of the molecular mean plane. The five- and six-membered rings form a dihedral angle of 7.5 (2)°. This conformation, which is rather common for this type of molecule (Al-Qadsy *et al.*, 2021; Al Banna *et al.*, 2022; Krishnamoorthy *et al.*, 2012), allows for electron delocalization throughout the molecule.

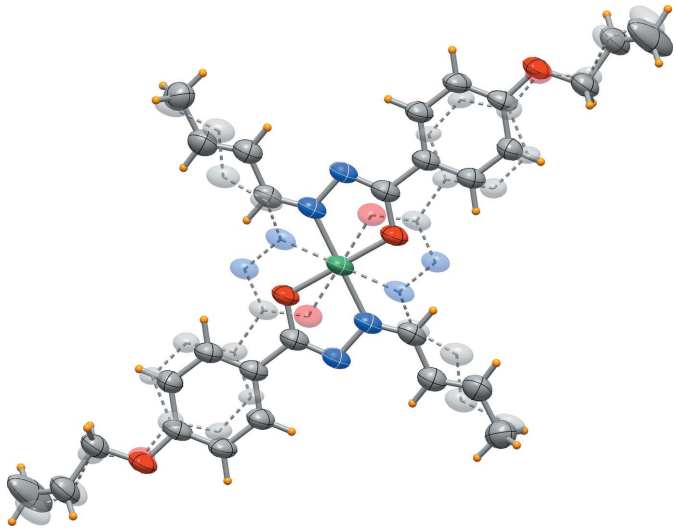


Figure 2
The two disordered species in the crystal with occupancies of *ca* 0.90/0.10.

3. Supramolecular features

Despite the presence of phenyl rings in the ligands, there is no evidence of π–π stacking. The crystal packing is, however, supported by unconventional hydrogen bonds of type C—H···O, *e.g.* C8—H8···O2($-x+1, -y+1, -z+1$) that connect complexes to form ribbons in the [111] direction (Fig. 3, Table 1). In addition, C—H···π interactions are realized by centrosymmetrically related complexes (H···phenyl centroid distance = 2.88 Å, Table 1) and give rise to a polymeric chain in the crystallographic [011] direction (Fig. 4). These interactions form a di-periodic architecture, as depicted in Fig. 5.

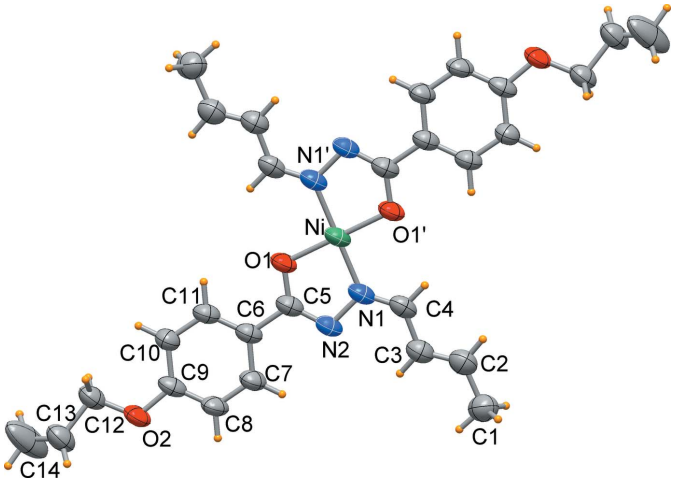


Figure 1
An ellipsoid plot (probability at 50%) of the Ni^{II} complex with atom labels for the crystallographically independent part.

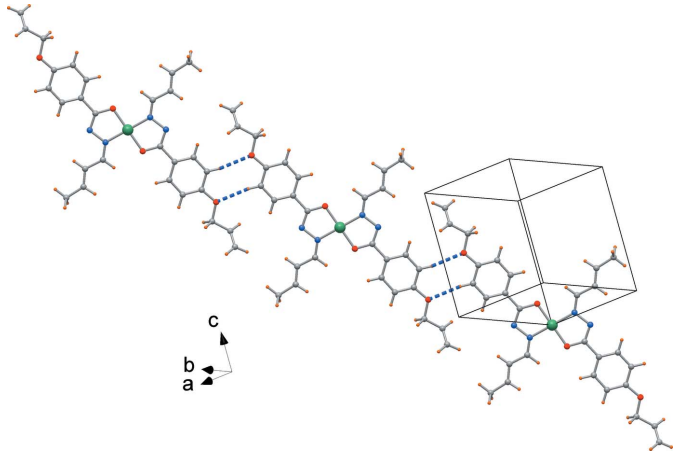


Figure 3
Mono-periodic chain formed by unconventional C—H···O hydrogen bonds (dotted lines) parallel to the [111] direction.

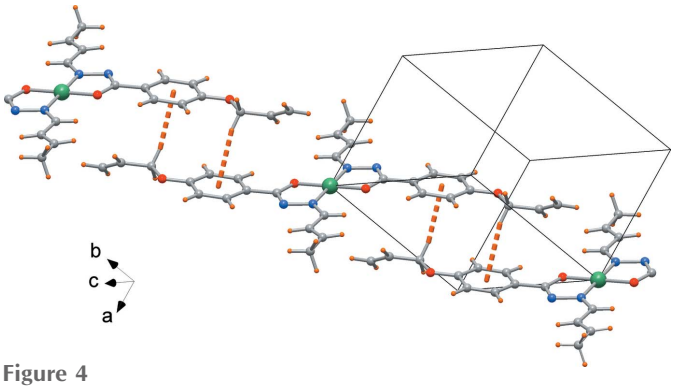


Figure 4
Detail of the crystal packing showing C—H···π interactions, forming a mono-periodic chain in the [011] direction.

4. Synthesis and crystallization

To a solution of 4-(allyloxy)benzohydrazide (0.514 g, 2.6 mmol in 20 mL of ethanol), crotonaldehyde (0.187 g, 2.6 mmol) was added and the mixture was refluxed for an hour. Then a solution of nickel(II) acetate tetrahydrate (0.335 g, 1.3 mmol in 10 mL of ethanol) was added and refluxing was continued for an additional two hours. The resulting orange precipitate was filtered off and washed with hot ethanol. The product was recrystallized from a mixture of chloroform and toluene (1:1, *v*/*v*), and orange crystals, suitable for X-ray diffraction, were formed. Yield: 0.44 g, 60%, melting point: 511–513 K.

FT–IR (KBr), (cm^{-1}): 1636 for ν(C═N—N═C) moiety. Absence of ν(N—H) and ν(C═O) bands. ^{1}H NMR ($CDCl_3$, 400 MHz), δ: 7.85 (*d*, 2×2H, *J* = 8.8 Hz, C-2, 6), 6.85 (*d*, 2×2H, *J* = 9.2 Hz, C-3, 5), 6.92 (*d*, 2×1H, *J* = 10 Hz, –CH═N,) , 6.41 (*m*, 2×1H, –CH═CH—CH_3), 4.56 (*dt*, 2×1H, *J* = 5.2 Hz, ═CH—CH_3), 1.99 (*dd*, 2×3H, *J* = 6.8 Hz, 2.8 Hz, –CH_3), 4.56 (*d*, 2×2H, *J* = 6.8 Hz, –OCH_2), 5.42 (*dq*, 2×H_a, *J* = 17.2 Hz, 3.2 Hz, ═CH_2), 5.30 (*dq*, 2×H_b, *J* = 10.8 Hz, 3.2 Hz, ═CH_2) , 6.05 (*m*, 2×H_c, –CH═CH_2). HRMS (FAB) calculated for $C_{28}H_{30}N_4O_4Ni$, $[M + H]^+$: 545.1692, found: 545.1693.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The structure is disordered, having a second component with a low occupancy of about 10%. The whole component at lower occupancy was refined with DELU and RIGU restraints, with bond lengths restrained to those at higher occupancy by use of the instruction SAME (Sheldrick, 2015*b*). The hydrogen atoms were included at idealized positions, using a riding model with fixed isotropic displacement parameters [C—H = 0.95–0.99 Å; U_{iso}(H) = 1.2 or 1.5 U_{eq}(C)].

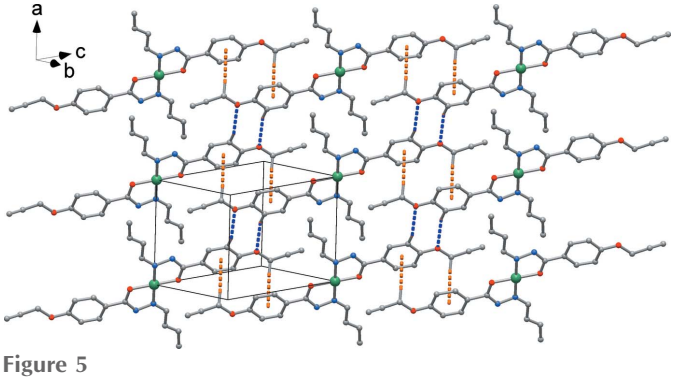


Figure 5
The di-periodic network built by C—H···O (blue dotted lines) and C—H···π (orange dotted lines) interactions. Only H atoms involved in the interactions are shown.

Table 2
Experimental details.

Crystal data	
Chemical formula	$[Ni(C_{14}H_{15}N_2O_2)_2]$
M_r	545.27
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	173
a, *b*, *c* (Å)	8.0978 (8), 9.2021 (9), 9.3316 (10)
α, β, γ (°)	84.027 (6), 88.091 (6), 84.170 (6)
V (Å^3)	687.83 (12)
Z	1
Radiation type	Mo *K*α
μ (mm^{-1})	0.74
Crystal size (mm)	0.29 × 0.19 × 0.11
Data collection	
Diffractometer	Rigaku R-AXIS RAPID
Absorption correction	Multi-scan (*ABSCOR*; Higashi, 1995)
T_{min}, T_{max}	0.739, 0.988
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6566, 3120, 2678
R_{int}	0.027
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.040, 0.098, 1.03
No. of reflections	3120
No. of parameters	333
No. of restraints	196
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.64, −0.20

Computer programs: *RAPID-AUTO* (Rigaku, 2018), *SHELXT2018/2* (Sheldrick, 2015*a*), *SHELXL2019/2* (Sheldrick, 2015*b*), *DIAMOND* (Brandenburg, 1999) and *WinGX* publication routines (Farrugia, 2012).

Acknowledgements

MBHH and SSK are grateful to the Department of Chemistry, Rajshahi University for the provision of laboratory facilities. MCS and RM acknowledge the Center for Environmental Conservation and Research Safety, University of Toyama, for providing facilities for single-crystal X-ray analyses.

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supporting information

Acta Cryst. (2023). E**79**, 465-468 [https://doi.org/10.1107/S2056989023002918]

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Computing details

Cell refinement: *RAPID-AUTO* (Rigaku, 2018); data reduction: *RAPID-AUTO* (Rigaku, 2018); program(s) used to solve structure: *SHELXT2018/2* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2019/2* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* publication routines (Farrugia, 2012).

Bis[4-(allyloxy)-*N*′-(but-2-en-1-ylidene)benzohydrazidato]nickel(II)

Crystal data

$[Ni(C_{14}H_{15}N_2O_2)_2]$
M_r = 545.27
Triclinic, $P\overline{1}$
a = 8.0978 (8) Å
b = 9.2021 (9) Å
c = 9.3316 (10) Å
α = 84.027 (6)°
β = 88.091 (6)°
γ = 84.170 (6)°
V = 687.83 (12) Å^3
Z = 1
$F(000)$ = 286
D_x = 1.316 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71075 Å
Cell parameters from 8347 reflections
θ = 2.0–27.4°
μ = 0.74 mm^{-1}
T = 173 K
Prism, colorless
0.29 × 0.19 × 0.11 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} = 0.739, T_{max} = 0.988
6566 measured reflections
3120 independent reflections
2678 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 27.5°, θ_{min} = 3.0°
h = −10→10
k = −11→10
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.098
S = 1.03
3120 reflections
333 parameters
196 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0653P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.64 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Ni1	0.000000	0.000000	0.000000	0.05459 (14)	
O1	0.0243 (2)	0.07363 (16)	0.17356 (18)	0.0578 (4)	0.898 (2)
O2	0.2723 (5)	0.4718 (5)	0.6267 (4)	0.0674 (10)	0.898 (2)
N1	0.2013 (2)	0.07530 (17)	−0.04863 (19)	0.0579 (4)	0.898 (2)
N2	0.2596 (2)	0.15342 (17)	0.05752 (18)	0.0576 (4)	0.898 (2)
C1	0.6805 (6)	0.1843 (6)	−0.3689 (5)	0.0823 (13)	0.898 (2)
H1A	0.716800	0.236081	−0.290787	0.123*	0.898 (2)
H1B	0.663757	0.253188	−0.455829	0.123*	0.898 (2)
H1C	0.765440	0.104813	−0.388854	0.123*	0.898 (2)
C2	0.5204 (4)	0.1213 (3)	−0.3251 (3)	0.0697 (7)	0.898 (2)
H2	0.469034	0.073371	−0.394546	0.084*	0.898 (2)
C3	0.4453 (3)	0.1270 (2)	−0.1979 (2)	0.0630 (5)	0.898 (2)
H3	0.496134	0.171140	−0.125341	0.076*	0.898 (2)
C4	0.2889 (4)	0.0685 (4)	−0.1661 (4)	0.0568 (9)	0.898 (2)
H4	0.245553	0.019621	−0.239171	0.068*	0.898 (2)
C5	0.1563 (3)	0.1451 (2)	0.1675 (2)	0.0552 (5)	0.898 (2)
C6	0.1878 (3)	0.2237 (2)	0.2942 (2)	0.0541 (5)	0.898 (2)
C7	0.3212 (3)	0.3097 (2)	0.2903 (2)	0.0596 (5)	0.898 (2)
H7	0.395956	0.312765	0.209668	0.072*	0.898 (2)
C8	0.3441 (4)	0.3901 (3)	0.4036 (3)	0.0620 (6)	0.898 (2)
H8	0.434157	0.449102	0.399809	0.074*	0.898 (2)
C9	0.2377 (6)	0.3857 (6)	0.5226 (4)	0.0582 (9)	0.898 (2)
C10	0.1064 (4)	0.2975 (3)	0.5305 (3)	0.0568 (6)	0.898 (2)
H10	0.034480	0.291804	0.613008	0.068*	0.898 (2)
C11	0.0832 (3)	0.2176 (2)	0.4142 (3)	0.0570 (6)	0.898 (2)
H11	−0.006304	0.158031	0.417885	0.068*	0.898 (2)
C12	0.1649 (5)	0.4721 (5)	0.7530 (4)	0.0683 (10)	0.898 (2)
H12A	0.175044	0.374580	0.809471	0.082*	0.898 (2)
H12B	0.047605	0.497658	0.725636	0.082*	0.898 (2)
C13	0.2227 (4)	0.5876 (3)	0.8394 (3)	0.0822 (7)	0.898 (2)
H13	0.250302	0.677449	0.789198	0.099*	0.898 (2)
C14	0.2360 (9)	0.5703 (6)	0.9742 (5)	0.159 (3)	0.898 (2)
H14A	0.209241	0.481443	1.026860	0.190*	0.898 (2)
H14B	0.272886	0.646034	1.023245	0.190*	0.898 (2)
O1′	0.1078 (17)	0.0981 (16)	0.1178 (14)	0.061 (3)	0.102 (2)
O2′	0.262 (3)	0.459 (4)	0.634 (3)	0.052 (6)	0.102 (2)
N1′	−0.1507 (14)	−0.0071 (12)	0.1524 (15)	0.054 (3)	0.102 (2)
N2′	−0.1064 (15)	0.0573 (14)	0.2739 (15)	0.055 (3)	0.102 (2)
C1′	−0.664 (4)	−0.157 (3)	0.394 (3)	0.055 (5)	0.102 (2)

H1′1	−0.755231	−0.211867	0.369214	0.082*	0.102 (2)
H1′2	−0.605399	−0.210640	0.476523	0.082*	0.102 (2)
H1′3	−0.708624	−0.059756	0.418061	0.082*	0.102 (2)
C2′	−0.545 (2)	−0.142 (3)	0.267 (3)	0.066 (5)	0.102 (2)
H2′	−0.564913	−0.182154	0.179826	0.079*	0.102 (2)
C3′	−0.4083 (19)	−0.0693 (19)	0.278 (2)	0.064 (4)	0.102 (2)
H3′	−0.380715	−0.041637	0.368440	0.077*	0.102 (2)
C4′	−0.305 (2)	−0.034 (3)	0.152 (3)	0.048 (5)	0.102 (2)
H4′	−0.355132	−0.029991	0.061133	0.057*	0.102 (2)
C5′	0.0340 (17)	0.1135 (17)	0.2405 (17)	0.054 (3)	0.102 (2)
C6′	0.115 (3)	0.199 (2)	0.345 (2)	0.057 (5)	0.102 (2)
C7′	0.248 (2)	0.2777 (18)	0.3065 (17)	0.045 (3)	0.102 (2)
H7′	0.303354	0.273720	0.215557	0.054*	0.102 (2)
C8′	0.295 (3)	0.363 (3)	0.408 (2)	0.057 (5)	0.102 (2)
H8′	0.390159	0.415000	0.389954	0.069*	0.102 (2)
C9′	0.205 (5)	0.374 (5)	0.538 (3)	0.047 (5)	0.102 (2)
C10′	0.067 (3)	0.299 (3)	0.578 (3)	0.058 (6)	0.102 (2)
H10′	0.005157	0.306756	0.665513	0.070*	0.102 (2)
C11′	0.031 (2)	0.211 (2)	0.475 (2)	0.057 (5)	0.102 (2)
H11′	−0.059768	0.152927	0.495134	0.069*	0.102 (2)
C12′	0.181 (3)	0.489 (3)	0.766 (2)	0.043 (4)	0.102 (2)
H12C	0.123609	0.403449	0.807081	0.052*	0.102 (2)
H12D	0.096411	0.574476	0.749571	0.052*	0.102 (2)
C13′	0.310 (3)	0.522 (2)	0.872 (2)	0.067 (5)	0.102 (2)
H13′	0.419193	0.474347	0.874300	0.080*	0.102 (2)
C14′	0.260 (4)	0.618 (4)	0.956 (4)	0.090 (11)	0.102 (2)
H14C	0.149387	0.663448	0.950229	0.108*	0.102 (2)
H14D	0.333053	0.643923	1.024081	0.108*	0.102 (2)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0642 (2)	0.04564 (18)	0.0584 (2)	−0.01815 (13)	−0.01564 (14)	−0.00945 (13)
O1	0.0649 (9)	0.0544 (8)	0.0601 (9)	−0.0232 (7)	−0.0120 (8)	−0.0138 (7)
O2	0.082 (2)	0.0662 (17)	0.0625 (12)	−0.0312 (13)	−0.0128 (11)	−0.0200 (11)
N1	0.0698 (10)	0.0464 (8)	0.0617 (10)	−0.0166 (7)	−0.0183 (8)	−0.0099 (7)
N2	0.0645 (9)	0.0519 (8)	0.0613 (10)	−0.0190 (7)	−0.0158 (8)	−0.0114 (7)
C1	0.078 (2)	0.075 (3)	0.095 (3)	−0.0150 (15)	0.004 (2)	−0.0096 (17)
C2	0.0775 (16)	0.0562 (13)	0.0769 (17)	−0.0096 (11)	−0.0073 (14)	−0.0095 (12)
C3	0.0672 (13)	0.0575 (11)	0.0676 (14)	−0.0134 (10)	−0.0136 (11)	−0.0111 (10)
C4	0.0702 (15)	0.041 (2)	0.0612 (15)	−0.0112 (14)	−0.0175 (12)	−0.0067 (13)
C5	0.0619 (11)	0.0455 (9)	0.0613 (12)	−0.0135 (8)	−0.0175 (10)	−0.0067 (8)
C6	0.0590 (13)	0.0477 (11)	0.0592 (12)	−0.0166 (10)	−0.0154 (9)	−0.0073 (9)
C7	0.0623 (13)	0.0613 (12)	0.0605 (12)	−0.0236 (10)	−0.0126 (10)	−0.0106 (9)
C8	0.0648 (16)	0.0640 (15)	0.0636 (13)	−0.0295 (11)	−0.0125 (11)	−0.0111 (10)
C9	0.065 (3)	0.0514 (15)	0.0631 (17)	−0.0172 (17)	−0.0226 (13)	−0.0110 (14)
C10	0.0567 (15)	0.0579 (12)	0.0596 (15)	−0.0159 (11)	−0.0068 (11)	−0.0125 (12)
C11	0.0588 (15)	0.0527 (11)	0.0640 (17)	−0.0199 (11)	−0.0138 (13)	−0.0089 (13)

C12	0.084 (2)	0.061 (2)	0.0657 (17)	−0.0187 (15)	−0.0127 (14)	−0.0189 (14)
C13	0.109 (2)	0.0719 (15)	0.0724 (16)	−0.0207 (15)	−0.0135 (14)	−0.0226 (13)
C14	0.294 (7)	0.114 (4)	0.083 (2)	−0.071 (4)	−0.069 (3)	−0.011 (2)
O1′	0.053 (6)	0.068 (8)	0.066 (6)	−0.017 (6)	−0.012 (5)	−0.012 (5)
O2′	0.033 (8)	0.057 (11)	0.070 (8)	−0.009 (7)	−0.009 (6)	−0.013 (7)
N1′	0.045 (5)	0.034 (5)	0.084 (7)	0.002 (4)	−0.020 (5)	−0.014 (5)
N2′	0.054 (5)	0.044 (6)	0.070 (7)	−0.012 (5)	−0.010 (4)	−0.010 (5)
C1′	0.053 (8)	0.030 (9)	0.083 (11)	−0.007 (7)	−0.029 (7)	−0.006 (8)
C2′	0.062 (8)	0.055 (10)	0.084 (12)	−0.010 (7)	−0.020 (8)	−0.010 (9)
C3′	0.055 (6)	0.051 (8)	0.089 (9)	−0.009 (6)	−0.022 (6)	−0.003 (7)
C4′	0.046 (6)	0.017 (10)	0.077 (9)	0.005 (5)	−0.034 (5)	0.007 (6)
C5′	0.054 (6)	0.042 (7)	0.068 (7)	−0.014 (5)	−0.016 (5)	−0.007 (5)
C6′	0.055 (8)	0.056 (9)	0.064 (8)	−0.028 (7)	0.000 (6)	−0.011 (7)
C7′	0.037 (7)	0.038 (7)	0.062 (7)	−0.018 (6)	−0.001 (5)	−0.006 (6)
C8′	0.050 (9)	0.056 (10)	0.070 (8)	−0.029 (7)	0.005 (6)	−0.011 (7)
C9′	0.034 (8)	0.048 (11)	0.060 (8)	−0.007 (7)	−0.005 (5)	−0.006 (7)
C10′	0.044 (9)	0.070 (11)	0.069 (9)	−0.033 (8)	0.007 (7)	−0.024 (8)
C11′	0.052 (9)	0.059 (9)	0.067 (8)	−0.022 (7)	0.000 (6)	−0.013 (7)
C12′	0.047 (8)	0.022 (8)	0.058 (8)	−0.001 (6)	−0.009 (6)	0.007 (6)
C13′	0.071 (10)	0.053 (9)	0.077 (9)	0.003 (7)	−0.027 (8)	−0.014 (8)
C14′	0.071 (12)	0.084 (19)	0.12 (2)	0.011 (13)	−0.038 (12)	−0.051 (18)

Geometric parameters (Å, º)

Ni1—O1′^{i}	1.793 (13)	C13—C14	1.258 (5)
Ni1—O1′	1.793 (13)	C13—H13	0.9500
Ni1—O1	1.8432 (16)	C14—H14A	0.9500
Ni1—O1^{i}	1.8432 (16)	C14—H14B	0.9500
Ni1—N1′^{i}	1.843 (14)	O1′—C5′	1.287 (15)
Ni1—N1′	1.843 (14)	O2′—C9′	1.363 (16)
Ni1—N1	1.8596 (18)	O2′—C12′	1.423 (17)
Ni1—N1^{i}	1.8596 (18)	N1′—C4′	1.301 (17)
O1—C5	1.308 (2)	N1′—N2′	1.406 (14)
O2—C9	1.369 (3)	N2′—C5′	1.311 (14)
O2—C12	1.442 (4)	C1′—C2′	1.509 (18)
N1—C4	1.289 (4)	C1′—H1′1	0.9800
N1—N2	1.4034 (19)	C1′—H1′2	0.9800
N2—C5	1.304 (3)	C1′—H1′3	0.9800
C1—C2	1.501 (4)	C2′—C3′	1.360 (16)
C1—H1A	0.9800	C2′—H2′	0.9500
C1—H1B	0.9800	C3′—C4′	1.441 (19)
C1—H1C	0.9800	C3′—H3′	0.9500
C2—C3	1.319 (4)	C4′—H4′	0.9500
C2—H2	0.9500	C5′—C6′	1.519 (15)
C3—C4	1.436 (4)	C6′—C7′	1.368 (16)
C3—H3	0.9500	C6′—C11′	1.386 (17)
C4—H4	0.9500	C7′—C8′	1.381 (16)
C5—C6	1.490 (3)	C7′—H7′	0.9500

C6—C11	1.381 (4)	C8′—C9′	1.401 (17)
C6—C7	1.400 (3)	C8′—H8′	0.9500
C7—C8	1.379 (3)	C9′—C10′	1.397 (17)
C7—H7	0.9500	C10′—C11′	1.374 (16)
C8—C9	1.383 (4)	C10′—H10′	0.9500
C8—H8	0.9500	C11′—H11′	0.9500
C9—C10	1.397 (3)	C12′—C13′	1.534 (18)
C10—C11	1.401 (3)	C12′—H12C	0.9900
C10—H10	0.9500	C12′—H12D	0.9900
C11—H11	0.9500	C13′—C14′	1.263 (18)
C12—C13	1.518 (3)	C13′—H13′	0.9500
C12—H12A	0.9900	C14′—H14C	0.9500
C12—H12B	0.9900	C14′—H14D	0.9500

O1′^{i}—Ni1—O1′	180.0	H12A—C12—H12B	108.8
O1—Ni1—O1^{i}	180.00 (4)	C14—C13—C12	123.3 (4)
O1′^{i}—Ni1—N1′^{i}	82.3 (5)	C14—C13—H13	118.4
O1′—Ni1—N1′^{i}	97.7 (5)	C12—C13—H13	118.4
O1—Ni1—N1′^{i}	125.4 (3)	C13—C14—H14A	120.0
O1^{i}—Ni1—N1′^{i}	54.6 (3)	C13—C14—H14B	120.0
O1′^{i}—Ni1—N1′	97.7 (5)	H14A—C14—H14B	120.0
O1′—Ni1—N1′	82.3 (5)	C5′—O1′—Ni1	114.5 (12)
N1′^{i}—Ni1—N1′	180.0	C9′—O2′—C12′	125 (2)
O1—Ni1—N1	84.13 (7)	C4′—N1′—N2′	114.5 (17)
O1^{i}—Ni1—N1	95.87 (7)	C4′—N1′—Ni1	128.3 (15)
O1—Ni1—N1^{i}	95.87 (7)	N2′—N1′—Ni1	115.4 (8)
O1^{i}—Ni1—N1^{i}	84.13 (7)	C5′—N2′—N1′	106.7 (12)
N1—Ni1—N1^{i}	180.0	C2′—C1′—H1′1	109.5
C5—O1—Ni1	109.78 (15)	C2′—C1′—H1′2	109.5
C9—O2—C12	117.6 (3)	H1′1—C1′—H1′2	109.5
C4—N1—N2	117.3 (2)	C2′—C1′—H1′3	109.5
C4—N1—Ni1	128.85 (17)	H1′1—C1′—H1′3	109.5
N2—N1—Ni1	113.84 (14)	H1′2—C1′—H1′3	109.5
C5—N2—N1	107.80 (16)	C3′—C2′—C1′	119 (2)
C2—C1—H1A	109.5	C3′—C2′—H2′	120.4
C2—C1—H1B	109.5	C1′—C2′—H2′	120.4
H1A—C1—H1B	109.5	C2′—C3′—C4′	120.4 (18)
C2—C1—H1C	109.5	C2′—C3′—H3′	119.8
H1A—C1—H1C	109.5	C4′—C3′—H3′	119.8
H1B—C1—H1C	109.5	N1′—C4′—C3′	126 (2)
C3—C2—C1	125.3 (3)	N1′—C4′—H4′	116.9
C3—C2—H2	117.4	C3′—C4′—H4′	116.9
C1—C2—H2	117.4	O1′—C5′—N2′	121.1 (14)
C2—C3—C4	121.9 (2)	O1′—C5′—C6′	117.6 (13)
C2—C3—H3	119.1	N2′—C5′—C6′	121.3 (13)
C4—C3—H3	119.1	C7′—C6′—C11′	121.5 (13)
N1—C4—C3	126.8 (3)	C7′—C6′—C5′	123.1 (15)
N1—C4—H4	116.6	C11′—C6′—C5′	114.7 (15)

C3—C4—H4	116.6	C6′—C7′—C8′	115.9 (13)
N2—C5—O1	124.2 (2)	C6′—C7′—H7′	122.1
N2—C5—C6	118.43 (19)	C8′—C7′—H7′	122.1
O1—C5—C6	117.4 (2)	C7′—C8′—C9′	121.2 (15)
C11—C6—C7	119.07 (18)	C7′—C8′—H8′	119.4
C11—C6—C5	120.9 (2)	C9′—C8′—H8′	119.4
C7—C6—C5	120.0 (2)	O2′—C9′—C10′	118.7 (18)
C8—C7—C6	120.0 (2)	O2′—C9′—C8′	117.2 (18)
C8—C7—H7	120.0	C10′—C9′—C8′	124.0 (16)
C6—C7—H7	120.0	C11′—C10′—C9′	112.0 (16)
C7—C8—C9	120.8 (2)	C11′—C10′—H10′	124.0
C7—C8—H8	119.6	C9′—C10′—H10′	124.0
C9—C8—H8	119.6	C10′—C11′—C6′	125.4 (15)
O2—C9—C8	115.2 (3)	C10′—C11′—H11′	117.3
O2—C9—C10	124.7 (3)	C6′—C11′—H11′	117.3
C8—C9—C10	120.2 (2)	O2′—C12′—C13′	109.1 (19)
C9—C10—C11	118.5 (2)	O2′—C12′—H12C	109.9
C9—C10—H10	120.7	C13′—C12′—H12C	109.9
C11—C10—H10	120.7	O2′—C12′—H12D	109.9
C6—C11—C10	121.4 (2)	C13′—C12′—H12D	109.9
C6—C11—H11	119.3	H12C—C12′—H12D	108.3
C10—C11—H11	119.3	C14′—C13′—C12′	115.3 (19)
O2—C12—C13	105.3 (3)	C14′—C13′—H13′	122.3
O2—C12—H12A	110.7	C12′—C13′—H13′	122.3
C13—C12—H12A	110.7	C13′—C14′—H14C	120.0
O2—C12—H12B	110.7	C13′—C14′—H14D	120.0
C13—C12—H12B	110.7	H14C—C14′—H14D	120.0

N1—Ni1—O1—C5	4.34 (13)	N1′^{i}—Ni1—O1′—C5′	−179.7 (12)
N1^{i}—Ni1—O1—C5	−175.66 (13)	N1′—Ni1—O1′—C5′	0.3 (12)
O1—Ni1—N1—C4	177.9 (3)	O1′^{i}—Ni1—N1′—C4′	−18 (2)
O1^{i}—Ni1—N1—C4	−2.1 (3)	O1′—Ni1—N1′—C4′	162 (2)
O1—Ni1—N1—N2	−4.24 (12)	O1′^{i}—Ni1—N1′—N2′	178.1 (9)
O1^{i}—Ni1—N1—N2	175.76 (12)	O1′—Ni1—N1′—N2′	−1.9 (9)
C4—N1—N2—C5	−178.9 (2)	C4′—N1′—N2′—C5′	−163.0 (18)
Ni1—N1—N2—C5	3.05 (18)	Ni1—N1′—N2′—C5′	3.0 (14)
C1—C2—C3—C4	177.7 (4)	C1′—C2′—C3′—C4′	−171 (2)
N2—N1—C4—C3	3.1 (5)	N2′—N1′—C4′—C3′	−30 (4)
Ni1—N1—C4—C3	−179.1 (2)	Ni1—N1′—C4′—C3′	165.8 (19)
C2—C3—C4—N1	−176.1 (3)	C2′—C3′—C4′—N1′	−158 (3)
N1—N2—C5—O1	0.8 (3)	Ni1—O1′—C5′—N2′	2 (2)
N1—N2—C5—C6	−178.15 (15)	Ni1—O1′—C5′—C6′	−178.4 (14)
Ni1—O1—C5—N2	−4.2 (2)	N1′—N2′—C5′—O1′	−3 (2)
Ni1—O1—C5—C6	174.79 (13)	N1′—N2′—C5′—C6′	177.0 (16)
N2—C5—C6—C11	−179.42 (19)	O1′—C5′—C6′—C7′	10 (3)
O1—C5—C6—C11	1.6 (3)	N2′—C5′—C6′—C7′	−169.9 (19)
N2—C5—C6—C7	3.0 (3)	O1′—C5′—C6′—C11′	−179 (2)
O1—C5—C6—C7	−175.96 (18)	N2′—C5′—C6′—C11′	1 (3)

C11—C6—C7—C8	−1.8 (3)	C11′—C6′—C7′—C8′	3 (4)
C5—C6—C7—C8	175.8 (2)	C5′—C6′—C7′—C8′	173 (2)
C6—C7—C8—C9	0.7 (5)	C6′—C7′—C8′—C9′	−4 (4)
C12—O2—C9—C8	179.7 (5)	C12′—O2′—C9′—C10′	−8 (7)
C12—O2—C9—C10	−0.5 (9)	C12′—O2′—C9′—C8′	176 (4)
C7—C8—C9—O2	−179.1 (4)	C7′—C8′—C9′—O2′	179 (4)
C7—C8—C9—C10	1.0 (7)	C7′—C8′—C9′—C10′	2 (7)
O2—C9—C10—C11	178.5 (5)	O2′—C9′—C10′—C11′	−176 (4)
C8—C9—C10—C11	−1.7 (7)	C8′—C9′—C10′—C11′	0 (6)
C7—C6—C11—C10	1.1 (3)	C9′—C10′—C11′—C6′	−2 (5)
C5—C6—C11—C10	−176.5 (2)	C7′—C6′—C11′—C10′	0 (5)
C9—C10—C11—C6	0.6 (5)	C5′—C6′—C11′—C10′	−171 (2)
C9—O2—C12—C13	−174.3 (5)	C9′—O2′—C12′—C13′	154 (4)
O2—C12—C13—C14	−138.1 (6)	O2′—C12′—C13′—C14′	145 (3)

Symmetry code: (i) −*x*, −*y*, −*z*.

Hydrogen-bond geometry (Å, º)

*Cg*1 is the centroid of the C6–C11 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O1^{i}	0.95	2.46	2.975 (3)	114
C8—H8···O2^{ii}	0.95	2.55	3.466 (5)	161
C11a—H11a···O1a	0.95	2.48	2.801 (3)	100
C12—H12b···*Cg*1^{iii}	0.95	2.88	3.781 (4)	152

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