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Crystal Structure of (2-[[[(8-aminonaphthalen-1-yl)imino]methyl]-4,6-di-tert-butylphenolato-κ³N,N',O)]bromidonickel(II)

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Crystal structure of (2-[[[(8-aminonaphthalen-1-yl)imino]methyl]-4,6-di-*tert*-butylphenolato- $\kappa^3 N, N', O$]bromidonickel(II)

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Keywords: crystal structure; nickel complex; tridentate ligand; square-planar coordination.**CCDC reference:** 1827007**Supporting information:** this article has supporting information at journals.iucr.org/e

The title compound, [NiBr(C₂₅H₂₉N₂O)], contains an Ni^{II} atom with a slightly distorted square-planar coordination environment defined by one O and two N atoms from the 2-[[[(8-aminonaphthalen-1-yl)imino]methyl]-4,6-di-*tert*-butylphenolate ligand and a bromide anion. The Ni–O and Ni–N bond lengths are slightly longer than those observed in the phenyl backbone counterpart, which can be attributed to the larger steric hindrance of the naphthyl group in the structure of the title compound. The molecule as a whole is substantially distorted, with both the planar naphthalene-1,8-diamine and imino-methylphenolate substituents rotated against the NiN₂OBr plane by 38.92 (7) and 37.22 (8)°, respectively, giving the molecule a twisted appearance. N–H···Br hydrogen bonds and N–H···C(π) contacts connect the molecules into dimers, and additional C–H···Br contacts, C–H··· π interactions, and an offset stacking interaction between naphthyl units interconnect these dimers into a three-dimensional network.

1. Chemical context

There has been an emergent interest in the design and synthesis of non-symmetrical iminoaryl bis(salen)-based ligands because of their facile synthesis and tunable properties. As a result, their nickel complexes have been used in a variety of applications and properties, including metal–organic frameworks (Crane & MacLachlan, 2012), catalysis for styrene polymerization (Ding *et al.*, 2017), unique redox behavior (Rotthaus *et al.*, 2006; Kochem *et al.*, 2013), and non-linear optics (Cisterna *et al.*, 2015; Trujillo *et al.*, 2010). One of the synthetic methods utilizes the half-unit Schiff base as a precursor for the preparation of non-symmetrical iminoaryl bis(salen) ligands. Surprisingly, ligands are mostly limited to phenyl derivatives as the backbone. Some metal complexes bearing non-symmetrical iminonaphthyl bis(salen) ligands have been reported in the literature (Villaverde *et al.*, 2011; Boghaei & Mohebi, 2002; Sundaravadivel *et al.*, 2013, 2014), but their crystal structures were not determined. As part of our work on the synthesis of nickel complexes bearing non-symmetrical iminoaryl bis(salen)-based ligands, we report here the crystal structure of (2-[[[(8-aminonaphthalen-1-yl)imino]methyl]-4,6-di-*tert*-butylphenolato- $\kappa^3 N, N', O$]bromidonickel(II), (I).

2. Structural commentary

The molecular structure of the title compound, (I), is given in Fig. 1, with selected bond lengths and angles collated in

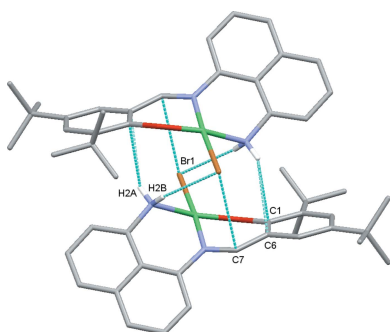
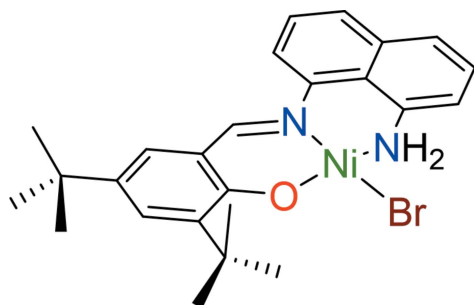


Table 1. The structure confirms the nickel cation to be four-coordinate and bound by two N atoms (imine N1 and amine N2), the phenolic O atom (O1), and the Br atom (Br1). The amino nitrogen atom (N2H₂) is neutral, with both hydrogen atoms well-defined in difference electron density maps. The O1—C1 bond length of 1.312 (4) Å indicates a phenolate resonance form for the ligand. The Schiff base double N1=C7 bond is within the range expected for a metal-coordinating Schiff base–imine fragment.



The coordination environment around the Ni^{II} cation can be best described as slightly distorted square-planar, with an r.m.s deviation from planarity for the NiN₂OBr fragment of 0.0943 Å. Interestingly, the Ni1—N1, Ni1—N2, and Ni1—O1 bond lengths are slightly longer than those observed in the phenyl backbone counterpart of (I), [Ni(NNO)OAc] (II) (NNO = 2-[[[(2-aminophenyl)imino]methyl]-4,6-di-*tert*-butylphenolate]; Ding *et al.*, 2017), which could be attributed to the increased steric bulk of the naphthyl backbone in (I). In line with this increased steric demand are the value for the angle N2—Ni1—O1 [170.15 (11)°], and that of the torsion angle C6—C7—N1—C16 [163.1 (3)°], which are significantly larger than those observed for (II) (176 and 178°, respectively). The steric profile of the aryl backbone appears to play an important role in altering both bond lengths and angles around the coordination center.

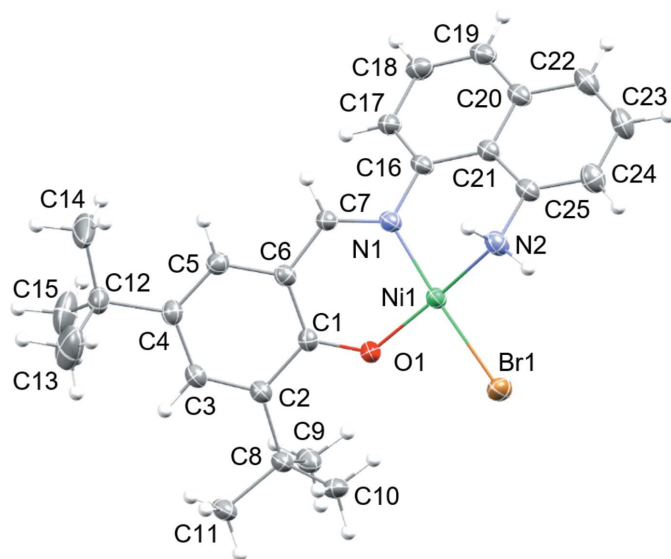


Figure 1 The molecular structure of the title compound showing atom labels, with displacement ellipsoids at the 50% probability level.

Table 1 Selected geometric parameters (Å, °).

N1—Ni1	1.880 (3)	Ni1—Br1	2.3330 (5)
N2—Ni1	1.922 (3)	C1—O1	1.312 (4)
O1—Ni1	1.850 (2)	C7—N1	1.305 (4)
O1—Ni1—N1	92.82 (10)	O1—Ni1—Br1	90.32 (7)
O1—Ni1—N2	170.15 (11)	N1—Ni1—Br1	176.24 (8)
N1—Ni1—N2	87.66 (12)	N2—Ni1—Br1	89.61 (9)
C6—C7—N1—C16	163.1 (3)		

Table 2 Hydrogen-bond geometry (Å, °).

D—H...A	D—H	H...A	D...A	D—H...A
N2—H2B...Br1 ⁱ	0.88 (2)	2.98 (2)	3.827 (3)	162 (4)
N2—H2A...C1 ⁱ	0.88 (2)	2.84 (4)	3.285 (4)	113 (3)
N2—H2A...C6 ⁱ	0.88 (2)	2.90 (3)	3.589 (4)	137 (3)
C18—H18...Br1 ⁱⁱ	0.95	2.93	3.624 (4)	131
C13—H13A...Br1 ⁱⁱⁱ	0.98	2.96	3.804 (6)	145
C11—H11B...C1 ^{iv}	0.98	2.77	3.741 (5)	169
C9—H9C...C5 ^v	0.98	2.76	3.730 (5)	169
C7—H7...C19 ^v	0.95	2.71	3.518 (5)	144

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

The increased steric demand in (I) does not substantially affect the bond lengths and angles of the individual ligand fragments. Both the naphthyl as well as the iminomethyl phenolate fragments are essentially planar, with r.m.s deviations from planarity of only 0.062 and 0.072 Å, respectively (the least-squares planes include the N and O atoms attached to the fragments). They do, however, yield to the steric strain by substantially rotating out of the plane of the NiN₂OBr plane, and with respect to each other, giving the molecule as a whole a twisted appearance. The dihedral angle of the naphthalene-1,8-diamine unit with the central NiN₂OBr plane is 38.92 (7)°, the equivalent angle of the iminomethyl phenolate substituent is 37.22 (8)°. The interplanar angle between the two organic fragments is 50.33 (5)°. This contrasts starkly with (II). The less sterically strained counterpart of (I) is essentially planar, with interplanar angles of the NiN₂O₂ fragment with the phenylene di-amine of only 5.91 and 7.39° [note that there are two independent molecules in the structure of (II)], and of only 7.08 and 3.58° towards the iminomethyl phenolate fragments.

3. Supramolecular features

The crystal-packing of (I) is steered by a number of medium strength and weak intermolecular interactions. Most prominent is an intermolecular N—H...Br hydrogen bond, Table 2, which connects individual molecules into dimers. The hydrogen bond involves H2B of the amine group. The other amine H atom, H2A, does not form a hydrogen bond. Instead, it interacts with the π electron cloud of the phenolate ring, with two close N—H...C(π) contacts (Table 2). These latter interactions appear to provide additional synergy for the

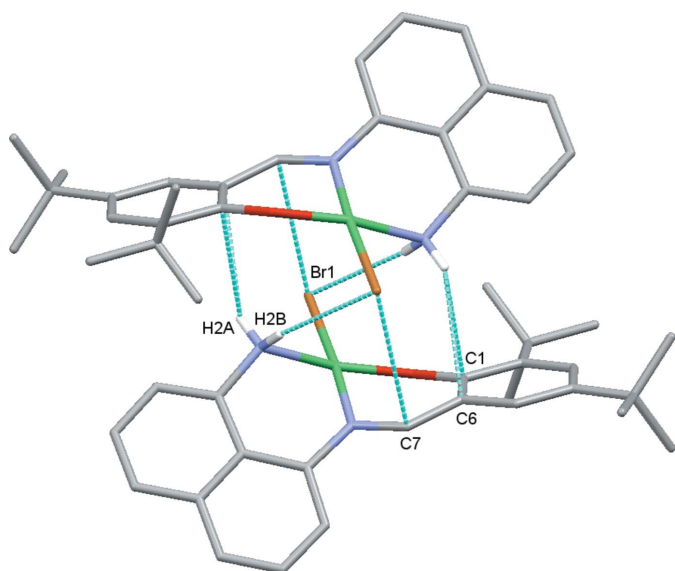


Figure 2
View of one of the dimers in (I), showing the N–H...Br hydrogen bonds and N–H...C(π) contacts. H atoms not involved in the interactions are omitted for clarity.

formation of the N–H...Br bridged dimers, Fig. 2. Other intermolecular interactions in (I) are less directional. They

involve a series of C–H...Br contacts, C–H... π interactions, and an offset stacking interaction between naphthyl units of neighboring molecules. Combined, these interactions connect the more tightly bound dimers into a three-dimensional network, Fig. 3.

4. Database survey

The most recent version of the Cambridge Structural Database (Version 5.39, updated November 2017; Groom *et al.*, 2016) has no entries related to iminonaphthyl mono(salen) supported metal complexes. However, a closely related compound, a nickel(II) complex bearing an iminophenyl mono(salen) ligand, has been reported as its acetate complex, and has been compared to the title compound in the *Structural commentary*. A broader exploration showed eight entries corresponding to iminophenyl mono(salen) ligands, including two aluminum (Muñoz-Hernández *et al.*, 2000), one copper (Ding *et al.*, 2014), two palladium (Vicente *et al.*, 1993, Liu *et al.*, 2010), one rhenium (Lane *et al.*, 2011), one ruthenium (Eltayeb *et al.*, 2007), and one tin (Yearwood *et al.*, 2002) complexes.

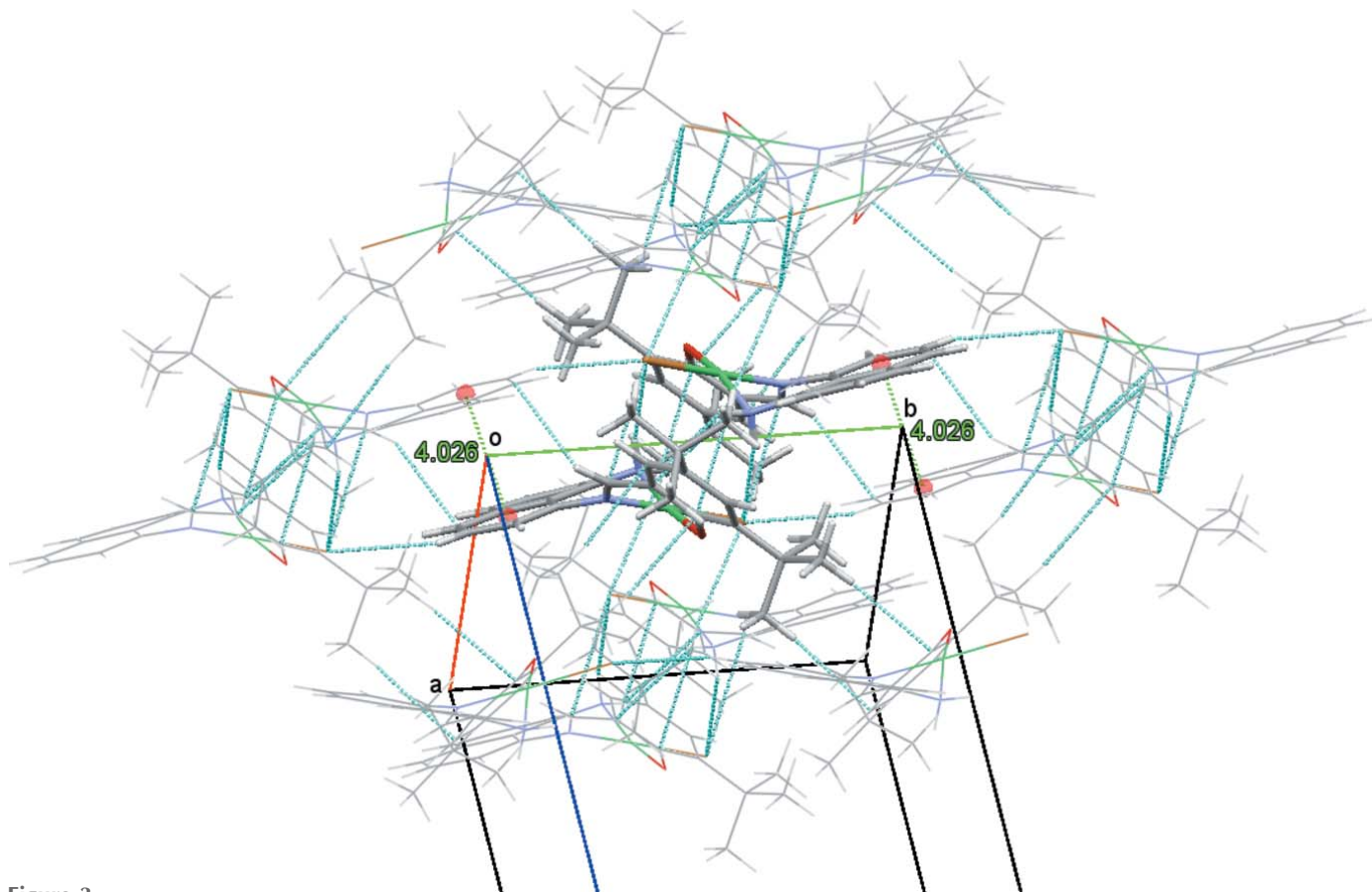


Figure 3
View of the intermolecular interactions for (I), showing N–H...Br hydrogen bonds and N–H...C(π) contacts as well as C–H...Br contacts, C–H... π interactions, and the offset stacking interaction between naphthyl units that interconnects dimers into a three-dimensional framework. For clarity, only one central dimer is shown in stick mode, the surrounding molecules in wireframe style.

5. Synthesis and crystallization

Starting materials were commercially available and were used without further purification.

Ligand synthesis: 3,5-di-tertbutyl-2-hydrobenzaldehyde (1.00 g, 4.27 mmol) dissolved in ethanol (20 ml) was added to 1,8-diaminonaphthalene (1.36 g, 8.53 mmol) in ethanol (20 ml) in a 100 ml round-bottom flask. The reaction mixture was refluxed for 24 h. Volatiles were removed under reduced pressure, and the residue was crystallized at 253 K to yield light-purple crystals (1.17 g, 73%). ¹H NMR (300 MHz, C₆D₆, *d*): δ, 8.76 (*s*, 1H, *CH*), 7.63 (*d*, 1H, *J* = 2.1 Hz, *ArH*), 7.26 (*d*, 2H, *J* = 8.1 Hz, *ArH*), 7.18–7.13 (*m*, 2H, *ArH*), 6.81 (*d*, 1H, *J* = 1.8 Hz, *ArH*), 6.05 (*d*, 2H, *J* = 7.2 Hz, *ArH*), 4.66 (*s*, 1H, *OH*), 3.72 (*s*, 2H, *NH*₂), 1.71 [*s*, 9H, *ArC*(CH₃)], 1.41 [*s*, 9H, *ArC*(CH₃)].

Synthesis of the title compound: To a stirred solution of (*E*)-2-[[[(8-aminonaphthalen-1-yl)imino]methyl]-4,6-di-tert-butylphenol (80 mg, 0.21 mmol) in THF (3 mL) at ambient temperature under an N₂ atmosphere was added a suspension of potassium *tert*-butoxide (26 mg, 0.24 mmol) in THF (2 mL) for 2 h. Solid NiBr₂(DME) (69 mg, 0.22 mmol) was added, and the resulting slurry was stirred for 18 h at ambient temperature. Volatiles were removed under reduced pressure, and the residue was extracted with toluene and filtered through Celite. The filtrate was dried *in vacuo* to yield a dark-red solid (21 mg, 95%). Crystals suitable for X-ray diffraction were grown from a concentrated solution in Et₂O at ambient temperature.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. H atoms attached to carbon atoms were positioned geometrically and constrained to ride on their parent atoms, with C–H bond lengths of 0.95 Å for alkene and aromatic moieties, and 0.98 Å for aliphatic CH₃ moieties, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. Amine H atom positions were refined with N–H distances restrained to 0.88 (2) Å. *U*_{iso}(H) values were set to a multiple of *U*_{eq}(C/N) with 1.5 for CH₃, and 1.2 for C–H and N–H units, respectively. Reflections (0 0 2), (1̄ 0 2) and (0 1 3) were obstructed by the beam stop and were omitted from the refinement.

Funding information

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 Ding, L., Zhang, Y., Chen, X. & Lü, X. (2017). *Inorg. Chem. Commun.* **76**, 100–102.

Table 3

Experimental details.

Crystal data	
Chemical formula	[NiBr(C ₂₅ H ₂₉ N ₂ O)]
<i>M</i> _r	512.12
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.7626 (3), 10.9008 (4), 22.0679 (7)
β (°)	98.0315 (14)
<i>V</i> (Å ³)	2325.43 (13)
<i>Z</i>	4
Radiation type	Mo Kα
μ (mm ⁻¹)	2.57
Crystal size (mm)	0.55 × 0.44 × 0.12
Data collection	
Diffractometer	Nonius KappaCCD
Absorption correction	Multi-scan (SCALEPACK; Otwinowski & Minor, 1997)
<i>T</i> _{min} , <i>T</i> _{max}	0.245, 0.735
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	11680, 5755, 4738
<i>R</i> _{int}	0.045
(sin θ/λ) _{max} (Å ⁻¹)	0.705
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.046, 0.128, 1.07
No. of reflections	5755
No. of parameters	283
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.07, -1.25

Computer programs: COLLECT (Nonius, 1998), HKL-3000 (Otwinowski & Minor, 1997), SHELXS97 (Sheldrick, 2008), SHELXL2018 (Sheldrick, 2015) and shelXle (Hübschle *et al.*, 2011), Mercury (Macrae *et al.*, 2006) and publCIF (Westrip, 2010).

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supporting information

Acta Cryst. (2018). E74, 469-473 [https://doi.org/10.1107/S2056989018003651]

Crystal structure of (2-[[8-aminonaphthalen-1-yl]imino]methyl)-4,6-di-*tert*-butylphenolato- κ^3N,N',O)bromidonickel(II)

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Computing details

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL-3000* (Otwinowski & Minor, 1997); data reduction: *HKL-3000* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2018* (Sheldrick, 2015) and *shelXle* (Hübschle *et al.*, 2011); molecular graphics: *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

(2-[[8-Aminonaphthalen-1-yl]imino]methyl)-4,6-di-*tert*-butylphenolato- κ^3N,N',O)bromidonickel(II)

Crystal data

[NiBr(C₂₅H₂₉N₂O)]
 $M_r = 512.12$
 Monoclinic, $P2_1/c$
 $a = 9.7626$ (3) Å
 $b = 10.9008$ (4) Å
 $c = 22.0679$ (7) Å
 $\beta = 98.0315$ (14)°
 $V = 2325.43$ (13) Å³
 $Z = 4$

$F(000) = 1056$
 $D_x = 1.463$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 11680 reflections
 $\theta = 2.1$ – 30.1 °
 $\mu = 2.57$ mm⁻¹
 $T = 100$ K
 Plate, black
 $0.55 \times 0.44 \times 0.12$ mm

Data collection

Nonius KappaCCD
 diffractometer
 Radiation source: fine focus X-ray tube
 Graphite monochromator
 ω and φ scans
 Absorption correction: multi-scan
 (SCALEPACK; Otwinowski & Minor, 1997)
 $T_{\min} = 0.245$, $T_{\max} = 0.735$

11680 measured reflections
 5755 independent reflections
 4738 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.045$
 $\theta_{\max} = 30.1$ °, $\theta_{\min} = 2.1$ °
 $h = 0 \rightarrow 13$
 $k = 0 \rightarrow 15$
 $l = -30 \rightarrow 31$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.128$
 $S = 1.07$
 5755 reflections
 283 parameters
 2 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: mixed
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0631P)^2 + 4.3983P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 1.07$ e Å⁻³
 $\Delta\rho_{\min} = -1.25$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	−0.0553 (3)	0.4478 (3)	0.14421 (13)	0.0207 (6)
C2	−0.1176 (3)	0.5200 (3)	0.18765 (13)	0.0215 (6)
C3	−0.2474 (3)	0.4849 (3)	0.19962 (14)	0.0231 (6)
H3	−0.288647	0.532890	0.228138	0.028*
C4	−0.3239 (3)	0.3836 (3)	0.17296 (14)	0.0230 (6)
C5	−0.2624 (3)	0.3152 (3)	0.13236 (14)	0.0228 (6)
H5	−0.310127	0.246173	0.113465	0.027*
C6	−0.1295 (3)	0.3445 (3)	0.11769 (13)	0.0202 (6)
C7	−0.0640 (3)	0.2563 (3)	0.08365 (13)	0.0208 (6)
H7	−0.111370	0.180965	0.074598	0.025*
C8	−0.0394 (3)	0.6284 (3)	0.22098 (14)	0.0230 (6)
C9	0.0896 (3)	0.5782 (3)	0.26142 (16)	0.0295 (7)
H9A	0.150747	0.538983	0.235565	0.044*
H9B	0.061397	0.517857	0.290193	0.044*
H9C	0.138719	0.645847	0.284265	0.044*
C10	0.0052 (4)	0.7237 (3)	0.17568 (16)	0.0301 (7)
H10A	0.064332	0.683952	0.149067	0.045*
H10B	0.056620	0.790083	0.198582	0.045*
H10C	−0.077039	0.757407	0.150692	0.045*
C11	−0.1291 (4)	0.6966 (3)	0.26186 (15)	0.0281 (7)
H11A	−0.213815	0.725748	0.236934	0.042*
H11B	−0.077523	0.766708	0.281208	0.042*
H11C	−0.153307	0.640822	0.293557	0.042*
C12	−0.4634 (3)	0.3499 (4)	0.19290 (16)	0.0288 (7)
C13	−0.5585 (5)	0.4609 (5)	0.1875 (3)	0.0651 (16)
H13A	−0.573130	0.489421	0.144959	0.098*
H13B	−0.516131	0.526707	0.214029	0.098*
H13C	−0.647545	0.438227	0.199999	0.098*
C14	−0.5341 (5)	0.2460 (6)	0.1546 (3)	0.075 (2)
H14A	−0.550635	0.270893	0.111563	0.112*
H14B	−0.622540	0.227022	0.168740	0.112*
H14C	−0.474709	0.173182	0.158954	0.112*
C15	−0.4382 (5)	0.3110 (5)	0.2604 (2)	0.0546 (13)
H15A	−0.526967	0.293766	0.274528	0.082*
H15B	−0.390898	0.377284	0.284997	0.082*
H15C	−0.380507	0.237058	0.264654	0.082*
C16	0.1225 (3)	0.1628 (3)	0.04555 (14)	0.0218 (6)
C17	0.1062 (3)	0.0524 (3)	0.07443 (15)	0.0247 (6)
H17	0.048093	0.048630	0.105510	0.030*

C18	0.1736 (4)	-0.0540 (3)	0.05882 (16)	0.0283 (7)
H18	0.158249	-0.129379	0.078375	0.034*
C19	0.2612 (3)	-0.0504 (3)	0.01577 (15)	0.0277 (7)
H19	0.306526	-0.123154	0.005685	0.033*
C20	0.2850 (3)	0.0613 (3)	-0.01401 (14)	0.0246 (6)
C21	0.2139 (3)	0.1693 (3)	0.00004 (13)	0.0220 (6)
C22	0.3818 (4)	0.0675 (4)	-0.05633 (15)	0.0307 (8)
H22	0.426691	-0.005268	-0.066781	0.037*
C23	0.4111 (4)	0.1759 (4)	-0.08210 (16)	0.0322 (8)
H23	0.479367	0.179134	-0.108810	0.039*
C24	0.3404 (4)	0.2833 (4)	-0.06927 (15)	0.0310 (7)
H24	0.360980	0.358951	-0.087370	0.037*
C25	0.2425 (3)	0.2789 (3)	-0.03089 (14)	0.0238 (6)
N1	0.0550 (3)	0.2692 (3)	0.06375 (11)	0.0217 (5)
N2	0.1631 (3)	0.3879 (3)	-0.02205 (12)	0.0259 (6)
H2A	0.205 (4)	0.450 (3)	-0.0365 (18)	0.031*
H2B	0.076 (2)	0.376 (4)	-0.0368 (18)	0.031*
O1	0.0677 (2)	0.4768 (2)	0.13117 (10)	0.0229 (4)
Ni1	0.12898 (4)	0.42762 (4)	0.05935 (2)	0.02024 (11)
Br1	0.23263 (4)	0.61856 (3)	0.05095 (2)	0.02840 (11)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0199 (13)	0.0223 (16)	0.0202 (13)	0.0005 (11)	0.0044 (10)	0.0015 (11)
C2	0.0218 (14)	0.0229 (17)	0.0196 (13)	0.0028 (11)	0.0026 (10)	-0.0005 (11)
C3	0.0237 (14)	0.0261 (17)	0.0200 (13)	0.0030 (12)	0.0047 (11)	-0.0005 (12)
C4	0.0185 (13)	0.0284 (18)	0.0221 (14)	0.0012 (12)	0.0032 (11)	0.0018 (12)
C5	0.0244 (15)	0.0221 (17)	0.0220 (13)	-0.0017 (12)	0.0035 (11)	0.0000 (11)
C6	0.0222 (14)	0.0196 (16)	0.0189 (13)	0.0023 (11)	0.0037 (10)	0.0006 (11)
C7	0.0228 (14)	0.0192 (16)	0.0208 (13)	-0.0014 (11)	0.0042 (10)	-0.0018 (11)
C8	0.0238 (14)	0.0224 (17)	0.0234 (14)	0.0001 (12)	0.0056 (11)	-0.0047 (11)
C9	0.0249 (16)	0.034 (2)	0.0285 (16)	0.0002 (13)	0.0018 (12)	-0.0083 (14)
C10	0.0367 (19)	0.0199 (18)	0.0345 (17)	-0.0037 (13)	0.0081 (14)	-0.0065 (13)
C11	0.0293 (16)	0.0271 (19)	0.0284 (15)	0.0013 (13)	0.0062 (12)	-0.0089 (13)
C12	0.0220 (15)	0.035 (2)	0.0311 (16)	-0.0027 (13)	0.0090 (12)	-0.0011 (14)
C13	0.026 (2)	0.060 (3)	0.112 (5)	0.010 (2)	0.021 (2)	0.019 (3)
C14	0.049 (3)	0.107 (5)	0.078 (4)	-0.048 (3)	0.040 (3)	-0.055 (3)
C15	0.038 (2)	0.081 (4)	0.047 (2)	-0.013 (2)	0.0134 (19)	0.019 (2)
C16	0.0240 (14)	0.0201 (16)	0.0216 (13)	0.0020 (11)	0.0040 (11)	-0.0047 (11)
C17	0.0294 (16)	0.0200 (17)	0.0257 (14)	-0.0015 (12)	0.0078 (12)	-0.0027 (12)
C18	0.0323 (17)	0.0193 (18)	0.0332 (17)	-0.0002 (13)	0.0038 (13)	-0.0007 (13)
C19	0.0280 (16)	0.0242 (18)	0.0303 (16)	0.0030 (13)	0.0027 (12)	-0.0071 (13)
C20	0.0230 (14)	0.0266 (18)	0.0236 (14)	0.0031 (12)	0.0017 (11)	-0.0053 (12)
C21	0.0221 (14)	0.0228 (17)	0.0209 (13)	0.0022 (12)	0.0019 (11)	-0.0023 (11)
C22	0.0285 (17)	0.038 (2)	0.0263 (15)	0.0092 (14)	0.0057 (13)	-0.0048 (14)
C23	0.0296 (17)	0.043 (2)	0.0264 (15)	0.0091 (15)	0.0109 (13)	0.0027 (14)
C24	0.0334 (18)	0.036 (2)	0.0242 (15)	0.0051 (14)	0.0075 (13)	0.0040 (14)

C25	0.0254 (15)	0.0248 (18)	0.0209 (13)	0.0040 (12)	0.0023 (11)	-0.0026 (12)
N1	0.0243 (13)	0.0207 (14)	0.0206 (11)	0.0014 (10)	0.0051 (9)	-0.0025 (10)
N2	0.0311 (15)	0.0260 (16)	0.0218 (12)	0.0034 (11)	0.0081 (11)	0.0010 (11)
O1	0.0234 (11)	0.0219 (12)	0.0251 (10)	-0.0017 (9)	0.0086 (8)	-0.0029 (9)
Ni1	0.0229 (2)	0.0184 (2)	0.02046 (19)	0.00083 (14)	0.00663 (14)	-0.00010 (14)
Br1	0.03690 (19)	0.0209 (2)	0.02905 (17)	-0.00314 (13)	0.01042 (13)	0.00202 (12)

Geometric parameters (Å, °)

N1—Ni1	1.880 (3)	C12—C13	1.520 (6)
N2—Ni1	1.922 (3)	C12—C14	1.520 (6)
N2—H2A	0.878 (19)	C12—C15	1.535 (5)
N2—H2B	0.878 (19)	C13—H13A	0.9800
O1—Ni1	1.850 (2)	C13—H13B	0.9800
Ni1—Br1	2.3330 (5)	C13—H13C	0.9800
C1—O1	1.312 (4)	C14—H14A	0.9800
C1—C6	1.420 (4)	C14—H14B	0.9800
C1—C2	1.439 (4)	C14—H14C	0.9800
C2—C3	1.384 (4)	C15—H15A	0.9800
C2—C8	1.537 (4)	C15—H15B	0.9800
C3—C4	1.414 (5)	C15—H15C	0.9800
C3—H3	0.9500	C16—C17	1.381 (5)
C4—C5	1.367 (4)	C16—N1	1.420 (4)
C4—C12	1.533 (4)	C16—C21	1.435 (4)
C5—C6	1.418 (4)	C17—C18	1.400 (5)
C5—H5	0.9500	C17—H17	0.9500
C6—C7	1.426 (4)	C18—C19	1.365 (5)
C7—N1	1.305 (4)	C18—H18	0.9500
C7—H7	0.9500	C19—C20	1.418 (5)
C8—C11	1.534 (4)	C19—H19	0.9500
C8—C9	1.538 (5)	C20—C22	1.420 (5)
C8—C10	1.546 (5)	C20—C21	1.423 (5)
C9—H9A	0.9800	C21—C25	1.422 (5)
C9—H9B	0.9800	C22—C23	1.359 (6)
C9—H9C	0.9800	C22—H22	0.9500
C10—H10A	0.9800	C23—C24	1.408 (5)
C10—H10B	0.9800	C23—H23	0.9500
C10—H10C	0.9800	C24—C25	1.364 (5)
C11—H11A	0.9800	C24—H24	0.9500
C11—H11B	0.9800	C25—N2	1.447 (4)
C11—H11C	0.9800		
O1—C1—C6	122.0 (3)	C12—C14—H14B	109.5
O1—C1—C2	120.0 (3)	H14A—C14—H14B	109.5
C6—C1—C2	118.0 (3)	C12—C14—H14C	109.5
C3—C2—C1	117.4 (3)	H14A—C14—H14C	109.5
C3—C2—C8	121.8 (3)	H14B—C14—H14C	109.5
C1—C2—C8	120.8 (3)	C12—C15—H15A	109.5

C2—C3—C4	125.5 (3)	C12—C15—H15B	109.5
C2—C3—H3	117.3	H15A—C15—H15B	109.5
C4—C3—H3	117.3	C12—C15—H15C	109.5
C5—C4—C3	116.4 (3)	H15A—C15—H15C	109.5
C5—C4—C12	123.1 (3)	H15B—C15—H15C	109.5
C3—C4—C12	120.4 (3)	C17—C16—N1	119.5 (3)
C4—C5—C6	121.8 (3)	C17—C16—C21	119.3 (3)
C4—C5—H5	119.1	N1—C16—C21	121.1 (3)
C6—C5—H5	119.1	C16—C17—C18	121.3 (3)
C5—C6—C1	121.0 (3)	C16—C17—H17	119.4
C5—C6—C7	117.4 (3)	C18—C17—H17	119.4
C1—C6—C7	120.8 (3)	C19—C18—C17	120.6 (3)
N1—C7—C6	126.2 (3)	C19—C18—H18	119.7
N1—C7—H7	116.9	C17—C18—H18	119.7
C6—C7—H7	116.9	C18—C19—C20	120.4 (3)
C11—C8—C2	111.6 (3)	C18—C19—H19	119.8
C11—C8—C9	108.6 (3)	C20—C19—H19	119.8
C2—C8—C9	108.4 (3)	C19—C20—C22	120.9 (3)
C11—C8—C10	106.9 (3)	C19—C20—C21	119.6 (3)
C2—C8—C10	111.9 (3)	C22—C20—C21	119.6 (3)
C9—C8—C10	109.4 (3)	C25—C21—C20	117.1 (3)
C8—C9—H9A	109.5	C25—C21—C16	124.1 (3)
C8—C9—H9B	109.5	C20—C21—C16	118.7 (3)
H9A—C9—H9B	109.5	C23—C22—C20	121.0 (3)
C8—C9—H9C	109.5	C23—C22—H22	119.5
H9A—C9—H9C	109.5	C20—C22—H22	119.5
H9B—C9—H9C	109.5	C22—C23—C24	120.1 (3)
C8—C10—H10A	109.5	C22—C23—H23	120.0
C8—C10—H10B	109.5	C24—C23—H23	120.0
H10A—C10—H10B	109.5	C25—C24—C23	120.1 (3)
C8—C10—H10C	109.5	C25—C24—H24	120.0
H10A—C10—H10C	109.5	C23—C24—H24	120.0
H10B—C10—H10C	109.5	C24—C25—C21	122.0 (3)
C8—C11—H11A	109.5	C24—C25—N2	119.3 (3)
C8—C11—H11B	109.5	C21—C25—N2	118.7 (3)
H11A—C11—H11B	109.5	C7—N1—C16	118.5 (3)
C8—C11—H11C	109.5	C7—N1—Ni1	118.9 (2)
H11A—C11—H11C	109.5	C16—N1—Ni1	122.6 (2)
H11B—C11—H11C	109.5	C25—N2—Ni1	118.5 (2)
C13—C12—C14	108.9 (4)	C25—N2—H2A	108 (3)
C13—C12—C4	110.2 (3)	Ni1—N2—H2A	108 (3)
C14—C12—C4	111.8 (3)	C25—N2—H2B	110 (3)
C13—C12—C15	108.1 (4)	Ni1—N2—H2B	95 (3)
C14—C12—C15	109.4 (4)	H2A—N2—H2B	117 (4)
C4—C12—C15	108.4 (3)	C1—O1—Ni1	122.3 (2)
C12—C13—H13A	109.5	O1—Ni1—N1	92.82 (10)
C12—C13—H13B	109.5	O1—Ni1—N2	170.15 (11)
H13A—C13—H13B	109.5	N1—Ni1—N2	87.66 (12)

C12—C13—H13C	109.5	O1—Ni1—Br1	90.32 (7)
H13A—C13—H13C	109.5	N1—Ni1—Br1	176.24 (8)
H13B—C13—H13C	109.5	N2—Ni1—Br1	89.61 (9)
C12—C14—H14A	109.5		
O1—C1—C2—C3	-179.9 (3)	C18—C19—C20—C21	-1.7 (5)
C6—C1—C2—C3	-1.3 (4)	C19—C20—C21—C25	179.6 (3)
O1—C1—C2—C8	-2.3 (4)	C22—C20—C21—C25	1.4 (4)
C6—C1—C2—C8	176.3 (3)	C19—C20—C21—C16	1.7 (4)
C1—C2—C3—C4	0.3 (5)	C22—C20—C21—C16	-176.4 (3)
C8—C2—C3—C4	-177.3 (3)	C17—C16—C21—C25	-177.6 (3)
C2—C3—C4—C5	0.4 (5)	N1—C16—C21—C25	-1.2 (5)
C2—C3—C4—C12	176.4 (3)	C17—C16—C21—C20	0.1 (4)
C3—C4—C5—C6	-0.2 (5)	N1—C16—C21—C20	176.5 (3)
C12—C4—C5—C6	-176.1 (3)	C19—C20—C22—C23	-175.9 (3)
C4—C5—C6—C1	-0.8 (5)	C21—C20—C22—C23	2.2 (5)
C4—C5—C6—C7	169.1 (3)	C20—C22—C23—C24	-3.0 (5)
O1—C1—C6—C5	-179.8 (3)	C22—C23—C24—C25	0.1 (5)
C2—C1—C6—C5	1.6 (4)	C23—C24—C25—C21	3.7 (5)
O1—C1—C6—C7	10.6 (5)	C23—C24—C25—N2	-175.1 (3)
C2—C1—C6—C7	-168.0 (3)	C20—C21—C25—C24	-4.4 (5)
C5—C6—C7—N1	176.8 (3)	C16—C21—C25—C24	173.3 (3)
C1—C6—C7—N1	-13.2 (5)	C20—C21—C25—N2	174.4 (3)
C3—C2—C8—C11	-6.1 (4)	C16—C21—C25—N2	-7.9 (5)
C1—C2—C8—C11	176.4 (3)	C6—C7—N1—C16	163.1 (3)
C3—C2—C8—C9	113.5 (3)	C6—C7—N1—Ni1	-17.6 (4)
C1—C2—C8—C9	-64.0 (4)	C17—C16—N1—C7	-31.8 (4)
C3—C2—C8—C10	-125.7 (3)	C21—C16—N1—C7	151.9 (3)
C1—C2—C8—C10	56.7 (4)	C17—C16—N1—Ni1	149.0 (2)
C5—C4—C12—C13	-130.8 (4)	C21—C16—N1—Ni1	-27.3 (4)
C3—C4—C12—C13	53.5 (5)	C24—C25—N2—Ni1	-137.7 (3)
C5—C4—C12—C14	-9.5 (5)	C21—C25—N2—Ni1	43.4 (4)
C3—C4—C12—C14	174.8 (4)	C6—C1—O1—Ni1	23.3 (4)
C5—C4—C12—C15	111.1 (4)	C2—C1—O1—Ni1	-158.1 (2)
C3—C4—C12—C15	-64.6 (4)	C1—O1—Ni1—N1	-41.9 (2)
N1—C16—C17—C18	-178.5 (3)	C1—O1—Ni1—Br1	140.2 (2)
C21—C16—C17—C18	-2.1 (5)	C7—N1—Ni1—O1	37.9 (2)
C16—C17—C18—C19	2.1 (5)	C16—N1—Ni1—O1	-142.9 (2)
C17—C18—C19—C20	-0.2 (5)	C7—N1—Ni1—N2	-132.3 (2)
C18—C19—C20—C22	176.4 (3)	C16—N1—Ni1—N2	46.9 (2)

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>
N2—H2 <i>B</i> ...Br1 ⁱ	0.88 (2)	2.98 (2)	3.827 (3)	162 (4)
N2—H2 <i>A</i> ...C1 ⁱ	0.88 (2)	2.84 (4)	3.285 (4)	113 (3)
N2—H2 <i>A</i> ...C6 ⁱ	0.88 (2)	2.90 (3)	3.589 (4)	137 (3)
C18—H18...Br1 ⁱⁱ	0.95	2.93	3.624 (4)	131

C13—H13A···Br1 ⁱⁱⁱ	0.98	2.96	3.804 (6)	145
C11—H11B···C1 ^{iv}	0.98	2.77	3.741 (5)	169
C9—H9C···C5 ^{iv}	0.98	2.76	3.730 (5)	169
C7—H7···C19 ^v	0.95	2.71	3.518 (5)	144

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