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-κ^3N,N',O)bromidonicke(I)

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The title compound, [NiBr(C_{25}H_{29}N_{2}O)], contains an NiII 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–methyl–phenolate 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-κ^3N,N',O)bromidonicke(I), (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
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), \([\text{Ni}(\text{NNO})\text{OAc}]\) (II) (NNO = 2-[[2-aminophenyl]iminomethyl]-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 \(O1—\text{Ni1—Br1}\) of 90.32 (7)°, which connects individual molecules into dimers. The crystal-packing of (I) is steered by a number of medium strength and weak intermolecular interactions. Most prominent is an intermolecular \(\text{Ni}—\text{H}···\text{Br}\) hydrogen bond, Table 2, which connects individual molecules into dimers. The hydrogen bond involves \(\text{H}2\text{B}\) of the amine group. The other amine \(\text{H}\) atom, \(\text{H}2\text{A}\), does not form a hydrogen bond. Instead, it interacts with the \(\pi\) electron cloud of the phenolate ring, with two close \(\text{N}—\text{H}···\text{C}(\pi)\) contacts (Table 2). These latter interactions appear to provide additional synergy for 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 \(\text{NiN}_{2}\text{OBr}\) 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 \(\text{Ni}_{2}\text{OBr}\) 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.

### Table 1

Selected geometric parameters (Å, °).

|  |  |  |  |  |
|---|---|---|---|---|
| N1—Ni1 | 1.880 (3) | Ni1—Br1 | 2.3330 (5) |
| N2—Ni1 | 1.922 (3) | Cl—O1 | 1.312 (4) |
| O1—Ni1 | 1.850 (2) | C7—Ni1 | 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—O1 | 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···Cl1\(^{i}\) | 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\(^{ii}\) | 0.98 | 2.96 | 3.804 (6) | 145 |
| C11—H11B···C14\(^{ii}\) | 0.98 | 2.77 | 3.741 (5) | 169 |
| C9—H9C···C5\(^{ii}\) | 0.98 | 2.76 | 3.730 (5) | 169 |
| C7—H7C···C19\(^{i}\) | 0.95 | 2.71 | 3.518 (5) | 144 |

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

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 \(\text{N}—\text{H}···\text{Br}\) hydrogen bond, Table 2, which connects individual molecules into dimers. The hydrogen bond involves \(\text{H}2\text{B}\) of the amine group. The other amine \(\text{H}\) atom, \(\text{H}2\text{A}\), does not form a hydrogen bond. Instead, it interacts with the \(\pi\) electron cloud of the phenolate ring, with two close \(\text{N}—\text{H}···\text{C}(\pi)\) contacts (Table 2). These latter interactions appear to provide additional synergy for the interaction.

Figure 1

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

Figure 2

The molecular structure of (I), showing atom labels, with displacement ellipsoids at the 50% probability level.
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 (El Tayeb et al., 2007), and one tin (Yearwood et al., 2002) complexes.
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%).\(^1\)H NMR (300 MHz, C6D6, 8.1 Hz, Ar, 8.76 (s, H), 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, NH2), 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-aminoanaphthalen-1-yl]iminomethyl]-4,6-di-tertbutylphenol (80 mg, 0.21 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 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), (1 0 2) and (0 1 3) were obstructed by the beam stop and were omitted from the refinement.

### Funding information

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Crystall structure of (2-[(8-aminonaphthalen-1-yl)imino]methyl)-4,6-di-tert-butylphenolato-κ³N,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-κ³N,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  
\(β = 98.0315\) (14)°  
\(V = 2325.43\) (13) Å³  
\(Z = 4\)  

\(F(000) = 1056\)  
\(D_\lambda = 1.463\) Mg m⁻³  
Mo Kα radiation, \(λ = 0.71073\) Å  
Cell parameters from 11680 reflections  
\(θ = 2.1–30.1°\)  
\(µ = 2.57\) mm⁻¹  
\(T = 100\) K  
Plate, black  
0.55 × 0.44 × 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 \(I > 2\sigma(I)\)  
\(R_{int} = 0.045\)  
\(θ_{max} = 30.1°, θ_{min} = 2.1°\)  
h = 0→13  
k = 0→15  
l = −30→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  
\(w = 1/[σ^2(F^2)+ (0.0631P)^2 + 4.3983P]\)  
where \(P = (F^2 + 2F^2)/3\)  
\((Δ/σ)_{max} < 0.001\)  
\(Δρ_{max} = 1.07\) e Å⁻³  
\(Δρ_{min} = −1.25\) 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 (Å²)**

|    | x        | y        | z        | \(U_{eq}\)/\(U_{eq}\) |
|----|----------|----------|----------|------------------------|
| C1 | -0.0553  | 0.4478   | 0.1442   | 0.0207 (6)             |
| C2 | -0.1176  | 0.5200   | 0.1876   | 0.0215 (6)             |
| C3 | -0.2474  | 0.4849   | 0.1996   | 0.0231 (6)             |
| C4 | -0.3239  | 0.3836   | 0.1729   | 0.0230 (6)             |
| C5 | -0.2624  | 0.3152   | 0.1323   | 0.0228 (6)             |
| C6 | -0.1295  | 0.3445   | 0.1176   | 0.0202 (6)             |
| C7 | -0.0640  | 0.2563   | 0.0836   | 0.0208 (6)             |
| C8 | -0.11370 | 0.1809   | 0.0745   | 0.025*                 |
| C9 | 0.0896   | 0.5782   | 0.2614   | 0.0295 (7)             |
| H9A| 0.061397 | 0.5178   | 0.2901   | 0.044*                 |
| H9B| 0.138719 | 0.6458   | 0.2842   | 0.044*                 |
| C10| 0.0052 (4)| 0.7237 (3)| 0.1756 (16)| 0.0301 (7)             |
| H10A| 0.064332 | 0.683952 | 0.149067 | 0.045*                 |
| H10B| 0.056620 | 0.790083 | 0.198582 | 0.045*                 |
| C11| -0.077039| 0.757407 | 0.150692 | 0.045*                 |
| C12| -0.4634  | 0.3499   | 0.1929   | 0.0281 (7)             |
| C13| -0.5585 (5)| 0.4609 (5)| 0.1875 (3)| 0.0651 (16)           |
| C14| -0.5341 (5)| 0.2460 (6)| 0.1546 (3)| 0.075 (2)             |
| C15| -0.4382 (5)| 0.3110 (5)| 0.2604 (2)| 0.0546 (13)           |
| C16| 0.1225 (3)| 0.1628 (3)| 0.0455 (14)| 0.0218 (6)           |
| C17| 0.1062 (3)| 0.0524 (3)| 0.0744 (15)| 0.0247 (6)           |
| H17| 0.048093 | 0.048630 | 0.105510 | 0.030*                 |
### 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—C7   | 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) |
| C9—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    |
| C11—H11A| 0.9800    | C24—C25 | 1.364 (5) |
| C11—H11B| 0.9800    | C24—H24 | 0.9500    |
| 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|

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| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|----------------------|--------------|----------------------|--------------|
| 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        | C1—C16—C21          | 121.1 (3)    |
| C5—C6—C5            | 119.1        | C16—C17—C18         | 121.3 (3)    |
| 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—C1            | 121.0 (3)    | 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)   |
Hydrogen-bond geometry (Å, °)

| D—H···A | D—H  | H···A  | D···A  | D—H···A |
|---------|------|--------|--------|---------|
| N2—H28···Br1i | 0.88 (2) | 2.98 (2) | 3.827 (3) | 162 (4) |
| N2—H24···C1i | 0.88 (2) | 2.84 (4) | 3.285 (4) | 113 (3) |
| N2—H24···C6i | 0.88 (2) | 2.90 (3) | 3.589 (4) | 137 (3) |
| C18—H18···Br1i | 0.95 | 2.93 | 3.624 (4) | 131 |

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

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