

# Bis{2-[(2-aminoethylimino)(phenyl)methyl]pyridine- $\kappa^3N$ }nickel(II) diperchlorate

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## Key indicators

Single-crystal X-ray study  
 T = 293 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.011 \text{ \AA}$   
 R factor = 0.068  
 wR factor = 0.199  
 Data-to-parameter ratio = 14.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound,  $[\text{Ni}(\text{C}_{15}\text{H}_{17}\text{N}_3)_2](\text{ClO}_4)_2$ , the Ni atom is hexacoordinated by six N atoms from two independent *N,N',N''*-tridentate 2-[(2-aminoethylimino)(phenyl)methyl]pyridine ligands, with the  $\text{NiN}_6$  group forming a distorted octahedral geometry. In the asymmetric unit, the ligand-coordinated nickel cation and two perchlorate anions are linked by one  $\text{N}-\text{H}\cdots\text{O}$  and two  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds. In the crystal structure, the complexes are linked by four  $\text{N}-\text{H}\cdots\text{O}$  bonds and three  $\text{C}-\text{H}\cdots\text{O}$  bonds.

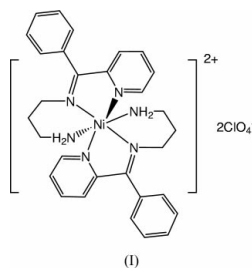
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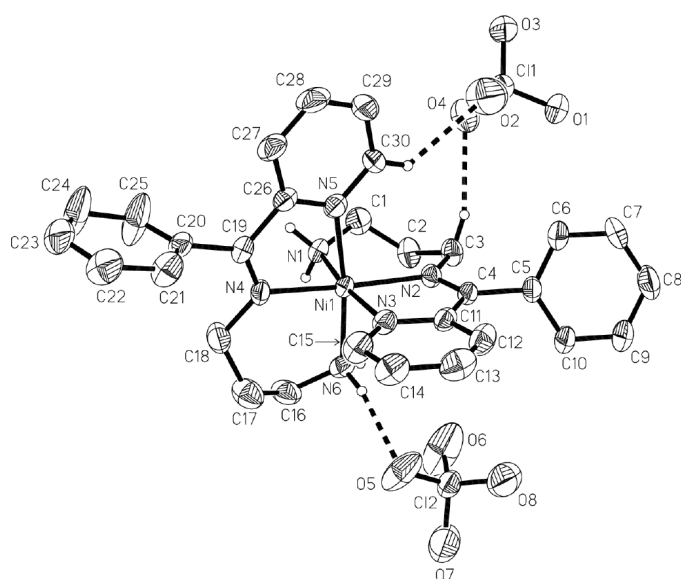
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## Comment

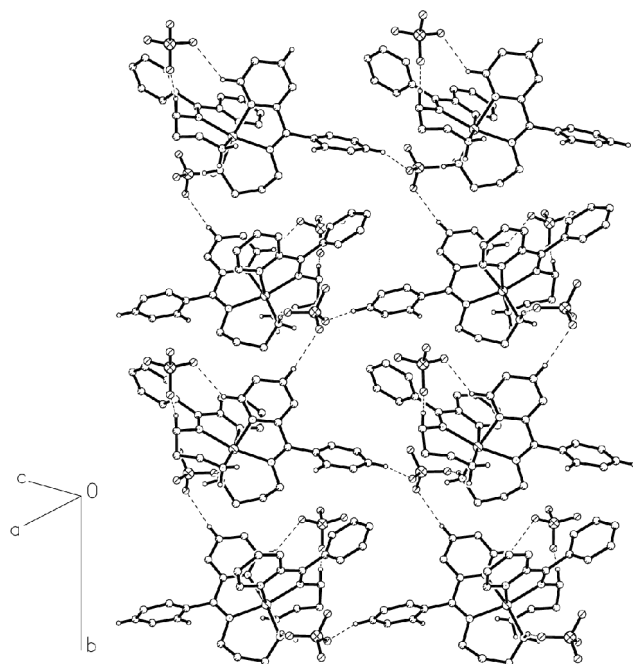
Polydentate Schiff base ligands have been widely studied because of their simple syntheses, the inherent stability associated with such systems, and different coordination to various metal ions leading to numerous complex species (Brudenell *et al.*, 1996; Chandra *et al.*, 1990; Garnovskii *et al.*, 1993; Lee *et al.*, 1996; Vigato *et al.*, 1990). The coordination chemistry of nickel with Schiff bases has also attracted much attention, owing to their versatile stereochemistry and bio-inorganic importance (Cotton *et al.*, 1999; Lancaster, 1988). Tridentate Schiff base ligands have been little studied compared with tetradentate systems (Holm *et al.*, 1966). We report here the crystal structure analysis of the title  $\text{Ni}^{\text{II}}$  complex, (I), with a tridentate ligand which was derived from the condensation of 1,3-diaminopropane and 2-benzoylpyridine in a 1:1 molar ratio.



The asymmetric unit consists of a  $\text{Ni}^{\text{II}}$  complex cation and two perchlorate anions (Fig. 1). The Ni atom is hexacoordinated by two 2-[(2-aminoethylimino)(phenyl)methyl]pyridine ligands, which act as *N,N',N''*-tridentate ligands. The  $\text{NiN}_6$  group forms a distorted octahedral geometry. The almost-linear  $\text{N1}-\text{Ni1}-\text{N3}$  group is nearly perpendicular to the basal  $\text{N2/N4/N5/N6}$  group. This is supported by the angles subtended at Ni1 (Table 1). The Ni–N bond distances [2.086 (5)–2.124 (5) Å] are normal (Allen *et al.*, 1987), and agree with those in bis(diethylenetriamine)nickel(II) [ $\text{Ni}-\text{N} = 2.094 (5)-2.129 (5) \text{ \AA}$ ; Liu-Gonzalez *et al.*, 2001].



**Figure 1**  
The structure of the title complex, showing the atom-numbering scheme, with displacement ellipsoids drawn at the 50% probability level. H atoms attached to C atoms and not involved in hydrogen bonding have been omitted for clarity.



**Figure 2**  
Packing diagram of the title complex, showing the formation of layers comprising the  $R_6^6(39)$  ring pattern.

The three coordinated N atoms of one ligand and the Ni atom form an  $\text{NiN}_3$  plane, and the two  $\text{NiN}_3$  planes are orthogonal to each other, with a dihedral angle of  $89.3(2)^\circ$ . The Ni–N–C–C–N six-membered rings are in half-chair conformations. The atoms C1 and C2 deviate from the  $\text{Ni1/N1/N2/C3}$  plane by  $-0.321(8)$  and  $0.506(7)$  Å, respectively, and the atoms C16 and C17 deviate by  $-0.328(9)$  and

$0.404(9)$  Å from the  $\text{Ni1/N4/N6/C18}$  plane. The dihedral angle between the rings C5–C10 and N3, C11–C15 is  $65.2(4)^\circ$ , and that between the rings C20–C25 and N5, C26–C30 is  $84.8(4)^\circ$ . This remarkable difference is due to the free rotation of the phenyl ring about the  $\text{C}_{\text{phenyl}}-\text{C}_{\text{methylene}}$  bond.

In the asymmetric unit, the ligand-coordinated  $\text{Ni}^{\text{II}}$  cation and two perchlorate anions are linked by  $\text{N6}-\text{H6B}\cdots\text{O5}$ ,  $\text{C3}-\text{H3C}\cdots\text{O4}$ , and  $\text{C30}-\text{H30A}\cdots\text{O2}$  hydrogen bonds (Table 2). In the crystal structure, the perchlorate anions also play an important role in the intermolecular hydrogen-bonding scheme. The complexes are linked by four intermolecular N–H $\cdots$ O bonds and three intermolecular C–H $\cdots$ O bonds involving the perchlorate anions. The  $\text{C23}-\text{H23A}\cdots\text{O6}^{\text{iii}}$  and  $\text{C28}-\text{H28A}\cdots\text{O7}^{\text{iv}}$  hydrogen bonds (see Table 2 for geometries and symmetry codes), together with the hydrogen bond in the asymmetric unit, link the complexes into layers (Fig. 2). Each layer consists of hydrogen-bonded rings,  $R_6^6(39)$  (Bernstein *et al.*, 1995), involving three symmetrically related  $\text{Ni}^{\text{II}}$  complex cations and three symmetrically related perchlorate anions. The layers are further interconnected into a three-dimensional network throughout the crystal by  $\text{N1}-\text{H1A}\cdots\text{O1}^{\text{i}}$ ,  $\text{N6}-\text{H6A}\cdots\text{O3}^{\text{i}}$ ,  $\text{N1}-\text{H1B}\cdots\text{O7}^{\text{ii}}$ ,  $\text{N1}-\text{H1B}\cdots\text{O8}^{\text{ii}}$  and  $\text{C25}-\text{H25A}\cdots\text{O5}^{\text{ii}}$  hydrogen bonds.

## Experimental

2-Benzoylpyridine (366.4 mg, 2 mmol) and 1,3-diaminopropane (148 mg, 2 mmol) were refluxed for 4–5 h. To the resulting solution was added  $\text{Ni}(\text{ClO}_4)_2\cdot 6\text{H}_2\text{O}$  (365.7 mg, 1 mmol) and the mixture was stirred for 30 min. The solution was filtered and was left to evaporate slowly; after 5–6 d yellow crystals of the title compound (I) were obtained (yield 60%).

### Crystal data

$[\text{Ni}(\text{C}_{15}\text{H}_{17}\text{N}_3)_2](\text{ClO}_4)_2$   
 $M_r = 736.24$   
 Monoclinic,  $P2_1$   
 $a = 10.0632(2)$  Å  
 $b = 16.5301(3)$  Å  
 $c = 10.2627(1)$  Å  
 $\beta = 101.991(1)^\circ$   
 $V = 1669.91(5)$  Å<sup>3</sup>  
 $Z = 2$

$D_x = 1.464$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 8192 reflections  
 $\theta = 2.5\text{--}28.3^\circ$   
 $\mu = 0.80$  mm<sup>-1</sup>  
 $T = 293(2)$  K  
 Prism, yellow  
 $0.50 \times 0.44 \times 0.20$  mm

### Data collection

Siemens SMART CCD area-detector diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\text{min}} = 0.691$ ,  $T_{\text{max}} = 0.857$   
 10219 measured reflections

5925 independent reflections  
 4981 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.078$   
 $\theta_{\text{max}} = 28.4^\circ$   
 $h = -12 \rightarrow 13$   
 $k = -9 \rightarrow 21$   
 $l = -13 \rightarrow 13$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.068$   
 $wR(F^2) = 0.199$   
 $S = 1.03$   
 5925 reflections  
 407 parameters  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.1096P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.89$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.60$  e Å<sup>-3</sup>  
 Extinction correction: SHELXTL  
 Extinction coefficient: 0.032(5)  
 Absolute structure: Flack (1983), 1608 Friedel pairs  
 Flack parameter = 0.02(2)

**Table 1**  
Selected geometric parameters (Å, °).

Ni1—N1	2.086 (5)	Ni1—N4	2.086 (5)
Ni1—N2	2.097 (4)	Ni1—N5	2.104 (5)
Ni1—N3	2.124 (5)	Ni1—N6	2.087 (5)
N1—Ni1—N4	94.0 (2)	N6—Ni1—N5	171.5 (2)
N4—Ni1—N6	94.2 (2)	N2—Ni1—N5	94.74 (19)
N1—Ni1—N6	91.2 (2)	N4—Ni1—N3	93.2 (2)
N4—Ni1—N2	168.4 (2)	N1—Ni1—N3	172.5 (2)
N1—Ni1—N2	94.7 (2)	N6—Ni1—N3	90.6 (2)
N6—Ni1—N2	93.3 (2)	N2—Ni1—N3	78.0 (2)
N4—Ni1—N5	77.5 (2)	N5—Ni1—N3	88.5 (2)
N1—Ni1—N5	90.7 (2)		

**Table 2**  
Hydrogen-bonding 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>
N1—H1A...O1 <sup>i</sup>	0.90	2.30	3.130 (8)	154
N1—H1B...O7 <sup>ii</sup>	0.90	2.48	3.265 (11)	146
N1—H1B...O8 <sup>ii</sup>	0.90	2.35	3.199 (10)	158
N6—H6A...O3 <sup>i</sup>	0.90	2.36	3.164 (9)	149
N6—H6B...O5	0.90	2.21	3.080 (8)	163
C3—H3C...O4	0.97	2.55	3.420 (11)	150
C23—H23A...O6 <sup>iii</sup>	0.93	2.49	3.155 (9)	128
C25—H25A...O5 <sup>ii</sup>	0.93	2.34	3.212 (8)	155
C28—H28A...O7 <sup>iv</sup>	0.93	2.48	3.393 (13)	169
C30—H30A...O2	0.93	2.51	3.202 (11)	131

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

Phenyl ring C20–C25 had to be constrained. This, together with the rather large  $U_{eq}$  value of C25 and the  $R_{int}$  value of 0.078, may be a result of the poor quality of the crystal. All H atoms were positioned geometrically, with C–H = 0.93–0.97 Å and N–H = 0.90 Å, and were treated as riding atoms. The largest electron-density peak and hole are located 0.03 and 0.99 Å, respectively, from atom Ni1.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*, *PARST* (Nardelli, 1995) and *PLATON* (Spek, 2003).

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