

**fac-Bis(2-aminomethylbenzimidazole)(2-aminomethylbenzimidazolato)nickel(II) dicyanamide monohydrate**

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**Key indicators**

Single-crystal X-ray study  
T = 293 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$   
R factor = 0.051  
wR factor = 0.091  
Data-to-parameter ratio = 20.6

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

The title compound,  $[\text{Ni}(\text{C}_8\text{H}_9\text{N}_3)_2(\text{C}_8\text{H}_8\text{N}_3)][\text{N}(\text{CN})_2] \cdot \text{H}_2\text{O}$ , has been prepared and characterized by X-ray crystallographic analysis. The coordination environment of the nickel(II) ion is a distorted octahedron, with six N donors from two 2-aminomethylbenzimidazole (Hambi) and one  $\text{ambi}^-$  anion. The Ni—N bond distances range from 2.074 (3) to 2.152 (3) Å, and the primary amine N atoms of  $\text{ambi}^-$  possess longer Ni—N bond distances compared with the Ni—N(aromatic amine) bond distances. The three  $\text{ambi}^-$  ligands are arranged around the nickel ion in a facial fashion. The dicyanamide counter-anion was found to form extensive hydrogen bonds with both the cations and the water of crystallization.

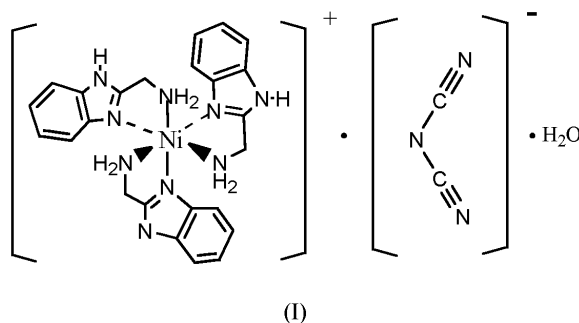
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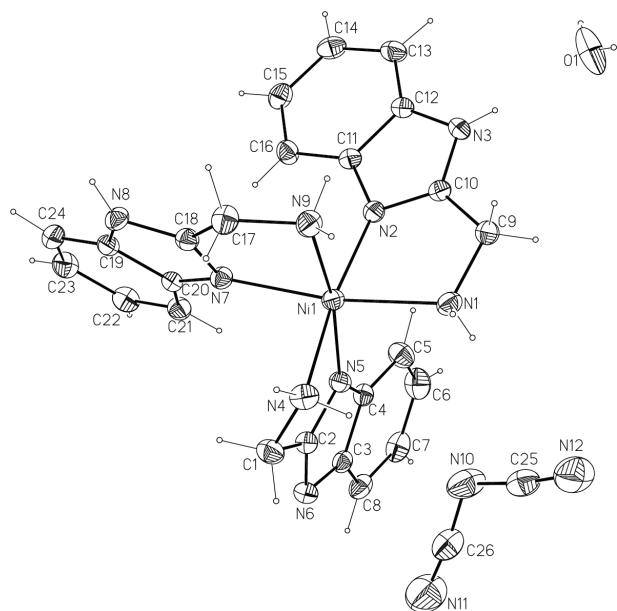
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**Comment**

2-Aminomethylbenzimidazole (Hambi) is a bidentate ligand and can chelate a 3d metal ion through two N atoms. The complex of cobalt(III) and  $\text{ambi}^-$  has been synthesized but not characterized by X-ray diffraction analysis (Gable *et al.*, 1996). The crystal structure of the mixed-ligand cobalt(III) complex with Hambi and  $\text{acac}^-$  has been reported (Cardwell *et al.*, 1997). The mixed-ligand copper(II) complex with Hambi and iminodiacetate has also been prepared and its structure determined (de la Cueva *et al.* 1998). To our knowledge, complexes of nickel(II) with Hambi ligands have not been reported. In this paper, we report the crystal structure of one such complex, (I).



A perspective view of the complex is shown in Fig. 1, and selected bond distances and angles are listed in Table 1. The coordination sphere around the nickel(II) ion is composed of two Hambi and one  $\text{ambi}^-$ , which chelate the central atom in a facial style. Nickel(II) is coordinated by six N atoms from the ligands. The bond distances between nickel(II) and the N atoms of the primary amine range from 2.138 (2) to 2.150 (2) Å, while the bond distances between nickel(II) and the N atoms of imidazole range from 2.072 (2) to 2.095 (2) Å. There is one dicyanamide counter-ion for the charge-balance



**Figure 1**  
A view of (I), with the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

ion for each complex cation. The  $[\text{N}(\text{CN})_2]^-$  anion exhibits  $C_{2v}$  symmetry, with C–N bond distances of 1.283 (3) and 1.301 (3) Å, and with C–N triple-bond distances of 1.142 (3) and 1.143 (3) Å. These results are in good agreement with the literature values for dicyanamide (Batten *et al.*, 1998, 1999; Cho *et al.*, 2002; Marshall *et al.*, 2000; Riggio *et al.*, 2001; Wang *et al.*, 2000).

For each ambi ligand the bite angle N–Ni–N varies from 78.74 (7) to 79.45 (7)°, less than the ideal angle of 90°. The ligands chelate the central ion in a facial mode, which is more stable, with less steric hindrance, compared to the meridional arrangement. Atoms C1–C8/N5/N6/Ni1 lie in the same plane, with N4 at a distance of 0.601 (4) Å from the plane. The atoms C10–C16/N1/N2/N3 are in the same plane, but C9 and Ni1 are displaced from the plane by 0.096 (5) and 0.377 (4) Å, respectively. Atoms C18–C24/N8/N9 are coplanar, but Ni1, C17 and N9 are displaced from the plane by 0.282 (4), 0.122 (5) and 0.682 (4) Å.

There are hydrogen bonds between the H atoms of the primary amine, the water of crystallization and the N atoms of dicyanamide; details are shown in Table 2. In the unit cell, the H atom attached to N8 is hydrogen bonded to N6, which was deprotonated during the synthesis.

## Experimental

2-Aminomethylbenzimidazole dihydrochloride was synthesized through a Phillips condensation of benzene-1,2-diamine with glycine in hydrochloric acid, as described in the literature (Cescon & Day, 1962).  $[\text{Ni}(\text{C}_8\text{H}_9\text{N}_3)_2(\text{C}_8\text{H}_8\text{N}_3)](\text{C}_2\text{N}_3)\cdot\text{H}_2\text{O}$  was obtained as purple crystals by the following experiment. Solid  $\text{Hambi}\cdot 2\text{HCl}$  (0.2 mmol) was dissolved in an aqueous solution (10 ml) of 0.4 mmol NaOH. To the mixture, 0.2 mmol  $\text{NiCl}_2\cdot 6\text{H}_2\text{O}$  in 5 ml water was added, resulting in some amount of pink precipitate. After the addition of an aqueous solution (5 ml) of 0.1 mmol  $\text{NaN}(\text{CN})_2$ , the mixture was heated until

the precipitate dissolved. Irregular purple crystals appeared within a few hours. Acetonitrile (10 ml) was added to redissolve the crystals and well-shaped purple crystals, suitable for X-ray diffraction analysis, were obtained by slow evaporation of the solution over two weeks.

## Crystal data

$[\text{Ni}(\text{C}_8\text{H}_9\text{N}_3)_2(\text{C}_8\text{H}_8\text{N}_3)](\text{C}_2\text{N}_3)\cdot\text{H}_2\text{O}$   
 $M_r = 583.29$   
 Monoclinic,  $P2_1/n$   
 $a = 12.168$  (2) Å  
 $b = 11.983$  (2) Å  
 $c = 18.901$  (4) Å  
 $\beta = 108.43$  (3)°  
 $V = 2614.6$  (9) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.482$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 6371 reflections  
 $\theta = 2.3$ – $25.0$ °  
 $\mu = 0.79$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Plate, purple  
 $0.30 \times 0.20 \times 0.10$  mm

## Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan (SADABS; Bruker, 2000)  
 $T_{\min} = 0.827$ ,  $T_{\max} = 0.924$   
 24 352 measured reflections

10 241 independent reflections  
 5110 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.046$   
 $\theta_{\max} = 33.5$ °  
 $h = -18 \rightarrow 18$   
 $k = -17 \rightarrow 18$   
 $l = -16 \rightarrow 29$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.051$   
 $wR(F^2) = 0.091$   
 $S = 0.82$   
 9577 reflections  
 465 parameters

H atoms treated by a mixture of constrained and independent refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.0686P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 1.05$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.46$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Ni1–N1	2.1458 (18)	Ni1–N9	2.1502 (19)
Ni1–N2	2.0874 (16)	C25–N10	1.301 (3)
Ni1–N4	2.1376 (19)	C25–N12	1.143 (3)
Ni1–N5	2.0724 (16)	C26–N10	1.283 (3)
Ni1–N7	2.0945 (16)	C26–N11	1.142 (3)
N1–Ni1–N2	79.30 (7)	N2–Ni1–N9	88.98 (8)
N1–Ni1–N4	92.69 (8)	N4–Ni1–N5	78.74 (7)
N1–Ni1–N5	95.61 (7)	N4–Ni1–N7	90.56 (8)
N1–Ni1–N7	168.66 (7)	N4–Ni1–N9	90.29 (9)
N1–Ni1–N9	89.66 (8)	N5–Ni1–N7	95.68 (6)
N2–Ni1–N4	171.96 (7)	N5–Ni1–N9	168.01 (7)
N2–Ni1–N5	102.57 (7)	N7–Ni1–N9	79.45 (7)
N2–Ni1–N7	97.18 (6)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
N1–H1B $\cdots$ N12 <sup>i</sup>	0.88 (2)	2.45 (2)	3.270 (4)	155.0 (18)
N1–H1A $\cdots$ O1 <sup>ii</sup>	0.86 (2)	2.32 (2)	3.119 (3)	154.8 (19)
N3–H3A $\cdots$ O1	0.856 (9)	2.016 (11)	2.853 (2)	166 (2)
N4–H4B $\cdots$ N10	0.87 (2)	2.35 (2)	3.184 (3)	161.1 (18)
N8–H8A $\cdots$ N6 <sup>iii</sup>	0.88 (2)	1.91 (2)	2.762 (2)	163 (2)
N9–H9D $\cdots$ N12 <sup>i</sup>	0.78 (2)	2.30 (2)	3.044 (3)	160 (2)
O1–H100 $\cdots$ N11 <sup>iv</sup>	0.85	2.17	2.851 (3)	137
O1–H101 $\cdots$ N6 <sup>iv</sup>	0.85	2.51	3.179 (3)	136

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

All H atoms were found in difference Fourier syntheses and refined isotropically, except for H100 and H101, which were found in a difference Fourier synthesis and fixed. The H atom attached to atom N6 was removed during the synthesis and no residual electron density in a chemically meaningful position was observed near N6 that could be attributed to the presence of an H atom.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2002).

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