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## Structure Reports

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**[N,N,N',N'-Tetrakis(benzimidazol-2-ylmethyl)cyclohexane-1,2-diamine]-nickel(II) dinitrate dihydrate**

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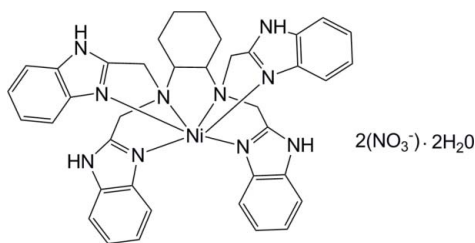
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Key indicators: single-crystal X-ray study;  $T = 292$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å; H-atom completeness 91%; disorder in solvent or counterion;  $R$  factor = 0.056;  $wR$  factor = 0.133; data-to-parameter ratio = 12.7.

In the title compound,  $[\text{Ni}(\text{C}_{38}\text{H}_{38}\text{N}_{10})](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , the  $\text{Ni}^{\text{II}}$  ion is located on a crystallographic twofold rotation axis and is in a distorted octahedral coordination environment. The crystal structure is stabilized by intermolecular  $\text{N}-\text{H} \cdots \text{O}$  and  $\text{C}-\text{H} \cdots \text{O}$  hydrogen bonds, and weak  $\text{C}-\text{H} \cdots \pi$  interactions. The O atoms of the unique nitrate ion are disordered over two sites with occupancies of 0.63 (1) and 0.37 (1). In addition, the O atom of the unique solvent water molecule is disordered over two sites with equal occupancies.

## Related literature

For background information, see: Oki *et al.* (1996); Hendriks *et al.* (1982); Main (1992); Zhao *et al.* (2005). For the structure of the free ligand of the title compound, see: Li *et al.* (2005).



## Experimental

## Crystal data

 $[\text{Ni}(\text{C}_{38}\text{H}_{38}\text{N}_{10})](\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  $M_r = 853.55$ Monoclinic,  $C2/c$  $a = 15.3395$  (16) Å $b = 13.1695$  (14) Å $c = 19.606$  (2) Å $\beta = 98.501$  (2)° $V = 3917.2$  (7) Å<sup>3</sup> $Z = 4$ Mo  $K\alpha$  radiation $\mu = 0.56$  mm<sup>-1</sup> $T = 292$  (2) K

0.32 × 0.20 × 0.10 mm

## Data collection

Bruker SMART APEX CCD

diffractometer

Absorption correction: multi-scan

(SADABS; Sheldrick, 1996)

 $T_{\text{min}} = 0.840$ ,  $T_{\text{max}} = 0.946$ 

10917 measured reflections

3847 independent reflections

2618 reflections with  $I > 2\sigma(I)$  $R_{\text{int}} = 0.074$ 

## Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.056$  $wR(F^2) = 0.133$  $S = 0.95$ 

3847 reflections

303 parameters

65 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{\text{max}} = 0.43$  e Å<sup>-3</sup> $\Delta\rho_{\text{min}} = -0.34$  e Å<sup>-3</sup>

Table 1

Selected geometric parameters (Å, °).

Ni1—N2	2.061 (2)	Ni1—N1	2.190 (3)
Ni1—N4	2.071 (3)		
N2—Ni1—N2 <sup>i</sup>	175.20 (15)	N4—Ni1—N1 <sup>i</sup>	79.11 (10)
N2—Ni1—N4	90.83 (10)	N2—Ni1—N1	94.90 (10)
N2—Ni1—N4 <sup>i</sup>	91.53 (10)	N4—Ni1—N1	158.69 (10)
N2—Ni1—N1 <sup>i</sup>	81.44 (10)	N1 <sup>i</sup> —Ni1—N1	81.47 (14)

Symmetry code: (i)  $-x, y, -z + \frac{3}{2}$ .

Table 2

Hydrogen-bond geometry (Å, °).

Cg1 and Cg2 are the centroids defined by atoms C7–C12 and C14–C19, respectively.

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
N3—H3 <sup>iii</sup> ···O1 <sup>ii</sup>	0.86	1.94	2.774 (10)	165
N5—H5 <sup>iii</sup> ···O2 <sup>iii</sup>	0.86	2.14	2.923 (7)	151
C4—H4B <sup>iv</sup> ···O4	0.97	2.37	3.268 (12)	154
C11—H11 <sup>iv</sup> ···Cg1 <sup>iv</sup>	0.93	2.73	3.542	147
C16—H16 <sup>v</sup> ···Cg2 <sup>v</sup>	0.93	2.79	3.680	160

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

Data collection: SMART (Bruker, 2007); cell refinement: SAINT-Plus (Bruker, 2007); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: SHELXTL (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2699).

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**supplementary materials**

*Acta Cryst.* (2008). E64, m1361-m1362 [ doi:10.1107/S1600536808031553 ]

**[*N,N,N',N'*-Tetrakis(benzimidazol-2-ylmethyl)cyclohexane-1,2-diamine]nickel(II) dinitrate dihydrate**

**D. Zhan and Z.-A. Xiao**

**Comment**

*N,N,N',N'*-Tetrakis(2-benzimidazolymethyl) cyclohexane-1,2-diamine (CTB) is a polybenzimidazole ligand, which has the advantage that the basicity of the coordinating group approximates that of histidine (pK<sub>b</sub>: histidine = 7.96 and benzimidazole = 8.47; Main, 1992). Recently, studies of ligand CTB and its metal coordination compounds have been widely carried out (Li *et al.*, 2005; Zhao *et al.*, 2005). In a continuation of this work, the title compound, (I), was prepared as part of a series of syntheses to produce new benzimidazole derivatives. We report the crystal structure of the title compound herein.

In the molecule structure of (I), the Ni<sup>II</sup> ion is located on a crystallographic twofold rotation axis and is coordinated by four benzimidazolyl(bzim) N atoms and two amino N atoms of the ligand CTB, in a distorted octahedral environment (Fig.1). The amino N atoms are slightly further away from the Ni<sup>II</sup> ion than the benzimidazolyl N atoms. The Ni-N bond lengths are similar to the values reported in a related structure (Oki *et al.*, 1996). As shown in Fig. 2, the crystal structure is stabilized by intermolecular N—H···O, C—H···O hydrogen bonds and weak C—H···π interactions.

**Experimental**

All reagents and solvents were used as obtained without further purification. The ligand CTB was prepared according to literature methods (Hendriks *et al.*, 1982). Compound (I) was synthesized by refluxing stoichiometric quantities (1:1 molar ratio) of CTB (0.64 g, 1 mmol) and nickel(II) dinitrate hexahydrate (0.29 g, 1 mmol) in 95% ethanol (30 ml) at 333 K for 6 h. The solution was cooled to room temperature, filtered and evaporated to obtain the product (yield 72%). Crystals of (I) were grown from an ethanol solution by slow evaporation.

**Refinement**

In (I), the nitrate O atoms are disordered over two positions with the final refined occupancies of 0.63 (1):0.37 (1). Water atom O4 is also disordered over two positions with both the occupancies being set to 0.5. H atoms bonded to water molecules were not located and were not included in the refinement but are included in the molecular formula. All H atoms (except for H3A) were included in geometrical positions with C—H=0.97 Å (methylene), 0.93 Å (aromatic), 0.86 Å (imine) and all the *U*<sub>iso</sub> values were set 1.2 times of their carrier atoms. The positional parameters of atom H3A were refined.

Figures

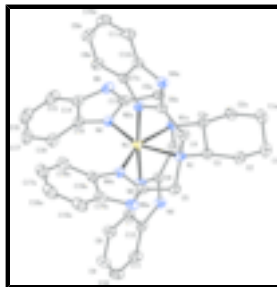


Fig. 1. The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The nitrate anions, water molecules and H atoms are omitted for clarity [symmetry code: (a)  $-x, y, -z+3/2$ ].

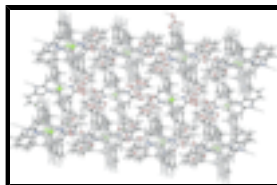


Fig. 2. Part of the crystal structure showing the linking of molecules by H-bonding and weak C—H... $\pi$  interactions as dashed lines.

**[N,N,N',N'-Tetrakis(benzimidazol-2-ylmethyl)cyclohexane-1,2-diamine]nickel(II) dinitrate dihydrate**

*Crystal data*

[Ni(C<sub>38</sub>H<sub>38</sub>N<sub>10</sub>)](NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O

$M_r = 853.55$

Monoclinic,  $C2/c$

Hall symbol:  $-C\ 2yc$

$a = 15.3395\ (16)\ \text{\AA}$

$b = 13.1695\ (14)\ \text{\AA}$

$c = 19.606\ (2)\ \text{\AA}$

$\beta = 98.501\ (2)^\circ$

$V = 3917.2\ (7)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1784$

$D_x = 1.447\ \text{Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2061 reflections

$\theta = 2.4\text{--}22.1^\circ$

$\mu = 0.57\ \text{mm}^{-1}$

$T = 292\ (2)\ \text{K}$

Plate, purple

$0.32 \times 0.20 \times 0.10\ \text{mm}$

*Data collection*

Bruker SMART APEX CCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 292\ (2)\ \text{K}$

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.840, T_{\max} = 0.946$

10917 measured reflections

3847 independent reflections

2618 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.074$

$\theta_{\max} = 26.0^\circ$

$\theta_{\min} = 2.1^\circ$

$h = -18 \rightarrow 17$

$k = -10 \rightarrow 16$

$l = -24 \rightarrow 24$

Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.056$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.133$	$w = 1/[\sigma^2(F_o^2) + (0.0618P)^2]$
$S = 0.95$	where $P = (F_o^2 + 2F_c^2)/3$
3847 reflections	$(\Delta/\sigma)_{\max} = 0.001$
303 parameters	$\Delta\rho_{\max} = 0.43 \text{ e } \text{\AA}^{-3}$
65 restraints	$\Delta\rho_{\min} = -0.34 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > \sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Ni1	0.0000	0.06922 (5)	0.7500	0.0383 (2)	
N1	0.08499 (16)	0.1952 (2)	0.79130 (13)	0.0411 (7)	
N2	0.03564 (16)	0.0758 (2)	0.65276 (12)	0.0420 (7)	
N3	0.01367 (17)	0.1461 (2)	0.54912 (12)	0.0461 (7)	
H3	-0.0083	0.1852	0.5158	0.055*	
N4	-0.11459 (17)	-0.0078 (2)	0.71196 (12)	0.0419 (7)	
N5	-0.25584 (18)	0.0113 (3)	0.66910 (14)	0.0552 (8)	
H5	-0.3063	0.0401	0.6586	0.066*	
N6	0.8994 (3)	0.3077 (5)	0.4093 (3)	0.139 (2)	
O1	0.9736 (6)	0.2879 (13)	0.4445 (5)	0.268 (8)	0.630 (9)
O2	0.8880 (3)	0.3273 (6)	0.3471 (3)	0.119 (3)	0.630 (9)
O3	0.8392 (5)	0.3165 (5)	0.4456 (4)	0.142 (3)	0.630 (9)
O1'	0.9621 (5)	0.2465 (7)	0.4281 (4)	0.058 (3)	0.370 (9)
O2'	0.9055 (8)	0.4029 (8)	0.4173 (8)	0.161 (7)	0.370 (9)
O3'	0.8270 (19)	0.2712 (14)	0.377 (3)	0.29 (12)*	0.370 (9)
O4	0.0215 (8)	0.4055 (10)	0.9433 (5)	0.169 (6)	0.50 (2)

## supplementary materials

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O4'	0.0237 (12)	0.491 (2)	0.9646 (10)	0.279 (12)	0.50 (2)
C1	0.0479 (3)	0.4797 (3)	0.7444 (2)	0.0738 (12)	
H1A	0.0765	0.5412	0.7635	0.089*	
H1B	0.0512	0.4784	0.6954	0.089*	
C2	0.0954 (2)	0.3874 (3)	0.7790 (2)	0.0609 (10)	
H2A	0.1560	0.3873	0.7704	0.073*	
H2B	0.0958	0.3916	0.8284	0.073*	
C3	0.0508 (2)	0.2889 (3)	0.75205 (18)	0.0454 (8)	
H3A	0.063 (2)	0.280 (2)	0.7048 (16)	0.054*	
C4	0.0837 (2)	0.2029 (3)	0.86709 (16)	0.0494 (9)	
H4A	0.1394	0.1790	0.8917	0.059*	
H4B	0.0767	0.2734	0.8795	0.059*	
C5	0.1735 (2)	0.1638 (3)	0.77788 (18)	0.0492 (9)	
H5A	0.2189	0.2039	0.8052	0.059*	
H5B	0.1787	0.1722	0.7295	0.059*	
C6	-0.0106 (2)	0.1420 (3)	0.61190 (15)	0.0412 (8)	
C7	0.0944 (2)	0.0319 (3)	0.61274 (15)	0.0412 (8)	
C8	0.1581 (2)	-0.0419 (3)	0.62782 (19)	0.0570 (10)	
H8	0.1678	-0.0735	0.6707	0.068*	
C9	0.2069 (3)	-0.0668 (3)	0.5766 (2)	0.0644 (11)	
H9	0.2502	-0.1165	0.5852	0.077*	
C10	0.1936 (3)	-0.0204 (3)	0.51282 (19)	0.0658 (11)	
H10	0.2289	-0.0386	0.4801	0.079*	
C11	0.1299 (2)	0.0515 (3)	0.49675 (17)	0.0561 (10)	
H11	0.1204	0.0823	0.4536	0.067*	
C12	0.0804 (2)	0.0764 (3)	0.54747 (15)	0.0441 (8)	
C13	-0.1819 (2)	0.0548 (3)	0.70208 (16)	0.0453 (8)	
C14	-0.2356 (2)	-0.0880 (3)	0.65533 (18)	0.0546 (10)	
C15	-0.2841 (3)	-0.1652 (4)	0.6196 (2)	0.0793 (14)	
H15	-0.3432	-0.1566	0.6015	0.095*	
C16	-0.2408 (3)	-0.2551 (4)	0.6122 (2)	0.0862 (15)	
H16	-0.2710	-0.3084	0.5883	0.103*	
C17	-0.1518 (3)	-0.2677 (3)	0.6401 (2)	0.0800 (14)	
H17	-0.1248	-0.3298	0.6346	0.096*	
C18	-0.1031 (3)	-0.1913 (3)	0.67524 (18)	0.0601 (10)	
H18	-0.0439	-0.2002	0.6931	0.072*	
C19	-0.1463 (2)	-0.1002 (3)	0.68280 (16)	0.0468 (9)	

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ni1	0.0387 (4)	0.0453 (4)	0.0307 (3)	0.000	0.0044 (2)	0.000
N1	0.0380 (15)	0.0490 (17)	0.0366 (14)	-0.0011 (13)	0.0062 (11)	0.0024 (13)
N2	0.0414 (15)	0.0507 (17)	0.0342 (14)	0.0041 (14)	0.0066 (11)	0.0015 (14)
N3	0.0536 (17)	0.0550 (18)	0.0292 (14)	0.0030 (15)	0.0044 (12)	0.0085 (13)
N4	0.0433 (16)	0.0469 (17)	0.0347 (15)	-0.0039 (14)	0.0028 (12)	-0.0051 (13)
N5	0.0393 (17)	0.071 (2)	0.0544 (19)	-0.0096 (16)	0.0027 (14)	0.0030 (17)
N6	0.087 (4)	0.119 (5)	0.203 (8)	0.000 (4)	-0.007 (5)	0.038 (5)

O1	0.179 (10)	0.317 (15)	0.290 (14)	0.021 (10)	-0.025 (9)	0.206 (12)
O2	0.079 (4)	0.176 (7)	0.097 (4)	0.031 (4)	-0.003 (3)	0.091 (5)
O3	0.127 (6)	0.125 (6)	0.191 (7)	0.023 (5)	0.082 (5)	-0.025 (5)
O1'	0.052 (5)	0.076 (6)	0.044 (4)	0.027 (4)	0.005 (3)	0.023 (4)
O2'	0.115 (9)	0.170 (13)	0.184 (13)	0.027 (9)	-0.025 (8)	0.000 (10)
O4	0.239 (11)	0.123 (10)	0.149 (8)	0.023 (7)	0.043 (7)	-0.076 (6)
O4'	0.311 (17)	0.28 (2)	0.247 (17)	0.064 (15)	0.042 (12)	0.007 (16)
C1	0.084 (3)	0.050 (2)	0.088 (3)	-0.011 (2)	0.013 (3)	-0.001 (2)
C2	0.061 (2)	0.053 (2)	0.069 (3)	-0.011 (2)	0.012 (2)	-0.003 (2)
C3	0.0481 (19)	0.045 (2)	0.0440 (19)	-0.0006 (17)	0.0101 (16)	0.0002 (17)
C4	0.047 (2)	0.059 (2)	0.0403 (19)	-0.0071 (18)	0.0007 (15)	-0.0039 (17)
C5	0.0388 (19)	0.058 (2)	0.050 (2)	-0.0037 (17)	0.0064 (15)	0.0022 (18)
C6	0.0418 (18)	0.047 (2)	0.0339 (17)	-0.0018 (16)	0.0043 (14)	-0.0007 (16)
C7	0.0434 (18)	0.047 (2)	0.0335 (17)	-0.0016 (16)	0.0075 (14)	-0.0021 (15)
C8	0.060 (2)	0.063 (3)	0.049 (2)	0.013 (2)	0.0106 (18)	0.0008 (19)
C9	0.063 (2)	0.073 (3)	0.059 (2)	0.017 (2)	0.0133 (19)	-0.008 (2)
C10	0.060 (3)	0.094 (3)	0.047 (2)	-0.002 (2)	0.0188 (19)	-0.017 (2)
C11	0.059 (2)	0.075 (3)	0.0358 (18)	-0.004 (2)	0.0118 (17)	-0.0019 (19)
C12	0.0461 (19)	0.051 (2)	0.0345 (17)	-0.0066 (18)	0.0051 (14)	-0.0027 (16)
C13	0.0402 (19)	0.059 (2)	0.0372 (18)	-0.0065 (18)	0.0069 (14)	0.0005 (17)
C14	0.052 (2)	0.068 (3)	0.044 (2)	-0.016 (2)	0.0081 (17)	0.0011 (19)
C15	0.073 (3)	0.094 (4)	0.069 (3)	-0.042 (3)	0.005 (2)	-0.005 (3)
C16	0.105 (4)	0.079 (4)	0.073 (3)	-0.048 (3)	0.010 (3)	-0.014 (3)
C17	0.121 (4)	0.055 (3)	0.067 (3)	-0.024 (3)	0.023 (3)	-0.009 (2)
C18	0.076 (3)	0.058 (3)	0.046 (2)	-0.008 (2)	0.0063 (19)	-0.0029 (19)
C19	0.057 (2)	0.053 (2)	0.0319 (17)	-0.0085 (18)	0.0091 (15)	0.0018 (16)

*Geometric parameters (Å, °)*

Ni1—N2	2.061 (2)	C2—H2B	0.9700
Ni1—N2 <sup>i</sup>	2.062 (2)	C3—C3 <sup>i</sup>	1.549 (6)
Ni1—N4	2.071 (3)	C3—H3A	0.98 (3)
Ni1—N4 <sup>i</sup>	2.071 (3)	C4—C6 <sup>i</sup>	1.485 (4)
Ni1—N1 <sup>i</sup>	2.190 (3)	C4—H4A	0.9700
Ni1—N1	2.190 (3)	C4—H4B	0.9700
N1—C5	1.479 (4)	C5—C13 <sup>i</sup>	1.489 (5)
N1—C4	1.493 (4)	C5—H5A	0.9700
N1—C3	1.506 (4)	C5—H5B	0.9700
N2—C6	1.318 (4)	C6—C4 <sup>i</sup>	1.485 (4)
N2—C7	1.404 (4)	C7—C8	1.379 (5)
N3—C6	1.339 (4)	C7—C12	1.395 (4)
N3—C12	1.378 (4)	C8—C9	1.378 (5)
N3—H3	0.8600	C8—H8	0.9300
N4—C13	1.313 (4)	C9—C10	1.378 (5)
N4—C19	1.400 (4)	C9—H9	0.9300
N5—C13	1.348 (4)	C10—C11	1.364 (5)
N5—C14	1.379 (5)	C10—H10	0.9300
N5—H5	0.8600	C11—C12	1.378 (4)



## supplementary materials

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N6—O2	1.233 (6)	C11—H11	0.9300
N6—O3	1.252 (6)	C13—C5 <sup>i</sup>	1.489 (5)
N6—O2'	1.265 (8)	C14—C15	1.387 (5)
N6—O1'	1.267 (7)	C14—C19	1.405 (5)
N6—O1	1.268 (7)	C15—C16	1.375 (7)
N6—O3'	1.286 (9)	C15—H15	0.9300
O4'—O4 <sup>iii</sup>	1.68 (4)	C16—C17	1.403 (6)
C1—C1 <sup>i</sup>	1.519 (8)	C16—H16	0.9300
C1—C2	1.524 (5)	C17—C18	1.376 (5)
C1—H1A	0.9700	C17—H17	0.9300
C1—H1B	0.9700	C18—C19	1.389 (5)
C2—C3	1.524 (5)	C18—H18	0.9300
C2—H2A	0.9700		
N2—Ni1—N2 <sup>i</sup>	175.20 (15)	C2—C3—C3 <sup>i</sup>	114.5 (2)
N2—Ni1—N4	90.83 (10)	N1—C3—H3A	106.6 (19)
N2 <sup>i</sup> —Ni1—N4	91.53 (10)	C2—C3—H3A	106.6 (19)
N2—Ni1—N4 <sup>i</sup>	91.53 (10)	C3 <sup>i</sup> —C3—H3A	106.6 (19)
N2 <sup>i</sup> —Ni1—N4 <sup>i</sup>	90.82 (10)	C6 <sup>i</sup> —C4—N1	111.2 (3)
N4—Ni1—N4 <sup>i</sup>	121.31 (16)	C6 <sup>i</sup> —C4—H4A	109.4
N2—Ni1—N1 <sup>i</sup>	81.44 (10)	N1—C4—H4A	109.4
N2 <sup>i</sup> —Ni1—N1 <sup>i</sup>	94.90 (10)	C6 <sup>i</sup> —C4—H4B	109.4
N4—Ni1—N1 <sup>i</sup>	79.11 (10)	N1—C4—H4B	109.4
N4 <sup>i</sup> —Ni1—N1 <sup>i</sup>	158.69 (11)	H4A—C4—H4B	108.0
N2—Ni1—N1	94.90 (10)	N1—C5—C13 <sup>i</sup>	105.6 (3)
N2 <sup>i</sup> —Ni1—N1	81.43 (10)	N1—C5—H5A	110.6
N4—Ni1—N1	158.69 (10)	C13 <sup>i</sup> —C5—H5A	110.6
N4 <sup>i</sup> —Ni1—N1	79.11 (10)	N1—C5—H5B	110.6
N1 <sup>i</sup> —Ni1—N1	81.47 (14)	C13 <sup>i</sup> —C5—H5B	110.6
C5—N1—C4	110.1 (2)	H5A—C5—H5B	108.8
C5—N1—C3	113.4 (2)	N2—C6—N3	112.8 (3)
C4—N1—C3	113.5 (3)	N2—C6—C4 <sup>i</sup>	123.3 (3)
C5—N1—Ni1	103.5 (2)	N3—C6—C4 <sup>i</sup>	123.8 (3)
C4—N1—Ni1	108.93 (19)	C8—C7—C12	120.1 (3)
C3—N1—Ni1	106.76 (18)	C8—C7—N2	131.6 (3)
C6—N2—C7	105.4 (3)	C12—C7—N2	108.3 (3)
C6—N2—Ni1	113.4 (2)	C9—C8—C7	117.1 (3)
C7—N2—Ni1	141.2 (2)	C9—C8—H8	121.5
C6—N3—C12	107.6 (3)	C7—C8—H8	121.5
C6—N3—H3	126.2	C8—C9—C10	122.2 (4)
C12—N3—H3	126.2	C8—C9—H9	118.9
C13—N4—C19	105.5 (3)	C10—C9—H9	118.9
C13—N4—Ni1	110.6 (2)	C11—C10—C9	121.4 (3)
C19—N4—Ni1	142.9 (2)	C11—C10—H10	119.3
C13—N5—C14	107.4 (3)	C9—C10—H10	119.3
C13—N5—H5	126.3	C10—C11—C12	116.8 (3)

C14—N5—H5	126.3	C10—C11—H11	121.6
O2—N6—O3	122.3 (5)	C12—C11—H11	121.6
O2—N6—O2'	85.0 (9)	C11—C12—N3	131.8 (3)
O3—N6—O2'	83.4 (9)	C11—C12—C7	122.4 (3)
O2—N6—O1'	114.3 (7)	N3—C12—C7	105.8 (3)
O3—N6—O1'	119.1 (7)	N4—C13—N5	113.0 (3)
O2'—N6—O1'	123.7 (6)	N4—C13—C5 <sup>i</sup>	122.1 (3)
O2—N6—O1	124.5 (6)	N5—C13—C5 <sup>i</sup>	124.8 (3)
O3—N6—O1	112.8 (6)	N5—C14—C15	132.4 (4)
O2'—N6—O1	95.3 (11)	N5—C14—C19	105.5 (3)
O2'—N6—O3'	118.3 (7)	C15—C14—C19	122.0 (4)
O1'—N6—O3'	117.9 (7)	C16—C15—C14	116.9 (4)
O1—N6—O3'	146.2 (13)	C16—C15—H15	121.5
C1 <sup>i</sup> —C1—C2	110.1 (3)	C14—C15—H15	121.5
C1 <sup>i</sup> —C1—H1A	109.6	C15—C16—C17	121.2 (5)
C2—C1—H1A	109.6	C15—C16—H16	119.4
C1 <sup>i</sup> —C1—H1B	109.6	C17—C16—H16	119.4
C2—C1—H1B	109.6	C18—C17—C16	122.3 (5)
H1A—C1—H1B	108.1	C18—C17—H17	118.9
C3—C2—C1	111.4 (3)	C16—C17—H17	118.9
C3—C2—H2A	109.4	C17—C18—C19	116.9 (4)
C1—C2—H2A	109.4	C17—C18—H18	121.6
C3—C2—H2B	109.4	C19—C18—H18	121.6
C1—C2—H2B	109.4	C18—C19—N4	130.6 (3)
H2A—C2—H2B	108.0	C18—C19—C14	120.8 (4)
N1—C3—C2	114.5 (3)	N4—C19—C14	108.5 (3)
N1—C3—C3 <sup>i</sup>	107.3 (2)		
N2—Ni1—N1—C5	-55.5 (2)	Ni1—N1—C5—C13 <sup>i</sup>	-44.1 (3)
N2 <sup>i</sup> —Ni1—N1—C5	127.6 (2)	C7—N2—C6—N3	-0.9 (4)
N4—Ni1—N1—C5	-160.6 (2)	Ni1—N2—C6—N3	179.5 (2)
N4 <sup>i</sup> —Ni1—N1—C5	35.10 (19)	C7—N2—C6—C4 <sup>i</sup>	177.3 (3)
N1 <sup>i</sup> —Ni1—N1—C5	-136.1 (2)	Ni1—N2—C6—C4 <sup>i</sup>	-2.3 (4)
N2—Ni1—N1—C4	-172.7 (2)	C12—N3—C6—N2	0.9 (4)
N2 <sup>i</sup> —Ni1—N1—C4	10.5 (2)	C12—N3—C6—C4 <sup>i</sup>	-177.3 (3)
N4—Ni1—N1—C4	82.3 (3)	C6—N2—C7—C8	-179.7 (4)
N4 <sup>i</sup> —Ni1—N1—C4	-82.0 (2)	Ni1—N2—C7—C8	-0.2 (6)
N1 <sup>i</sup> —Ni1—N1—C4	106.8 (2)	C6—N2—C7—C12	0.5 (4)
N2—Ni1—N1—C3	64.4 (2)	Ni1—N2—C7—C12	180.0 (3)
N2 <sup>i</sup> —Ni1—N1—C3	-112.4 (2)	C12—C7—C8—C9	1.3 (5)
N4—Ni1—N1—C3	-40.6 (3)	N2—C7—C8—C9	-178.5 (3)
N4 <sup>i</sup> —Ni1—N1—C3	155.1 (2)	C7—C8—C9—C10	0.3 (6)
N1 <sup>i</sup> —Ni1—N1—C3	-16.12 (14)	C8—C9—C10—C11	-1.3 (6)
N4—Ni1—N2—C6	74.0 (2)	C9—C10—C11—C12	0.8 (6)
N4 <sup>i</sup> —Ni1—N2—C6	-164.6 (2)	C10—C11—C12—N3	178.2 (4)
N1 <sup>i</sup> —Ni1—N2—C6	-4.9 (2)	C10—C11—C12—C7	0.8 (5)

## supplementary materials

N1—Ni1—N2—C6	-85.4 (2)	C6—N3—C12—C11	-178.2 (4)
N4—Ni1—N2—C7	-105.4 (3)	C6—N3—C12—C7	-0.5 (4)
N4 <sup>i</sup> —Ni1—N2—C7	15.9 (3)	C8—C7—C12—C11	-1.9 (5)
N1 <sup>i</sup> —Ni1—N2—C7	175.7 (4)	N2—C7—C12—C11	178.0 (3)
N1—Ni1—N2—C7	95.1 (3)	C8—C7—C12—N3	-179.8 (3)
N2—Ni1—N4—C13	-98.7 (2)	N2—C7—C12—N3	0.0 (4)
N2 <sup>i</sup> —Ni1—N4—C13	77.1 (2)	C19—N4—C13—N5	0.4 (4)
N4 <sup>i</sup> —Ni1—N4—C13	169.0 (2)	Ni1—N4—C13—N5	171.9 (2)
N1 <sup>i</sup> —Ni1—N4—C13	-17.6 (2)	C19—N4—C13—C5 <sup>i</sup>	-176.2 (3)
N1—Ni1—N4—C13	7.0 (4)	Ni1—N4—C13—C5 <sup>i</sup>	-4.6 (4)
N2—Ni1—N4—C19	67.7 (3)	C14—N5—C13—N4	-0.7 (4)
N2 <sup>i</sup> —Ni1—N4—C19	-116.5 (3)	C14—N5—C13—C5 <sup>i</sup>	175.7 (3)
N4 <sup>i</sup> —Ni1—N4—C19	-24.6 (3)	C13—N5—C14—C15	-175.8 (4)
N1 <sup>i</sup> —Ni1—N4—C19	148.8 (3)	C13—N5—C14—C19	0.7 (4)
N1—Ni1—N4—C19	173.5 (3)	N5—C14—C15—C16	176.1 (4)
C1 <sup>i</sup> —C1—C2—C3	57.5 (5)	C19—C14—C15—C16	0.1 (6)
C5—N1—C3—C2	-73.2 (4)	C14—C15—C16—C17	0.4 (6)
C4—N1—C3—C2	53.5 (4)	C15—C16—C17—C18	-0.8 (7)
Ni1—N1—C3—C2	173.5 (2)	C16—C17—C18—C19	0.7 (6)
C5—N1—C3—C3 <sup>i</sup>	158.5 (3)	C17—C18—C19—N4	-176.0 (3)
C4—N1—C3—C3 <sup>i</sup>	-74.8 (3)	C17—C18—C19—C14	-0.1 (5)
Ni1—N1—C3—C3 <sup>i</sup>	45.2 (3)	C13—N4—C19—C18	176.4 (3)
C1—C2—C3—N1	-171.0 (3)	Ni1—N4—C19—C18	9.6 (6)
C1—C2—C3—C3 <sup>i</sup>	-46.4 (5)	C13—N4—C19—C14	0.1 (3)
C5—N1—C4—C6 <sup>i</sup>	-126.7 (3)	Ni1—N4—C19—C14	-166.7 (3)
C3—N1—C4—C6 <sup>i</sup>	104.9 (3)	N5—C14—C19—C18	-177.2 (3)
Ni1—N1—C4—C6 <sup>i</sup>	-13.8 (3)	C15—C14—C19—C18	-0.3 (5)
C4—N1—C5—C13 <sup>i</sup>	72.2 (3)	N5—C14—C19—N4	-0.5 (4)
C3—N1—C5—C13 <sup>i</sup>	-159.4 (3)	C15—C14—C19—N4	176.5 (3)

Symmetry codes: (i)  $-x, y, -z+3/2$ ; (ii)  $-x, -y+1, -z+2$ .

### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3—H3 $\cdots$ O1 <sup>iii</sup>	0.86	1.94	2.774 (10)	165
N5—H5 $\cdots$ O2 <sup>iv</sup>	0.86	2.14	2.923 (7)	151
C4—H4B $\cdots$ O4	0.97	2.37	3.268 (12)	154
C11—H11 $\cdots$ Cg1 <sup>v</sup>	0.93	2.73	3.542	147
C16—H16 $\cdots$ Cg2 <sup>vi</sup>	0.93	2.79	3.680	160

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

Fig. 1

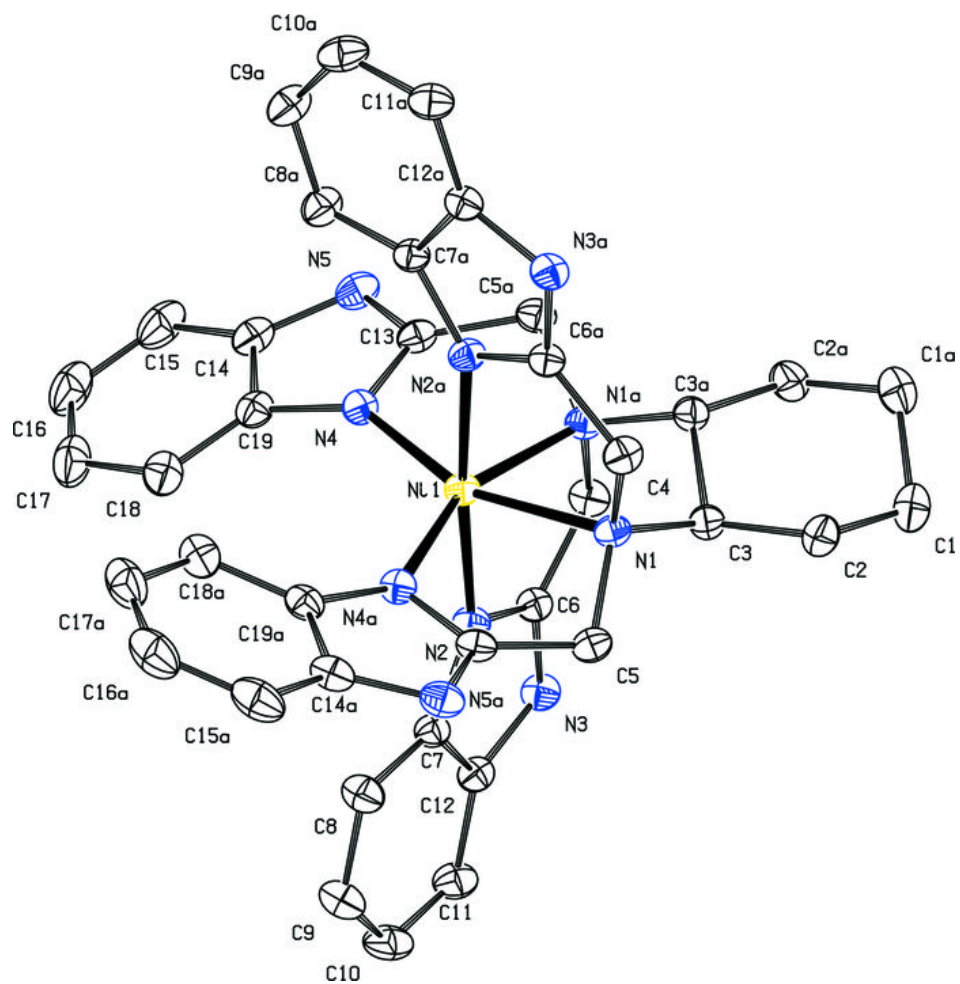


Fig. 2

