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Bis(di-2-pyridylmethanediol-κ^3N,O,N')-nickel(II) dinitrate

Seung Man Yu,[a] Young Joo Song,[a] Kang Chul Kim,[b] Cheal Kim[a]* and Youngmee Kim[c]*

[a]Department of Fine Chemistry and Eco-Product and Materials Education Center, Seoul National University of Technology, Seoul 139-743, Republic of Korea, [b]Department of Computer Engineering, Yeosu Campus, Chonnam National University, Yeosu 550-749, Republic of Korea, and [c]Department of Chemistry and Nano Science, Ewha Women's University, Seoul 120-750, Republic of Korea
Correspondence e-mail: chealkim@sunt.ac.kr, ymeekim@ewha.ac.kr

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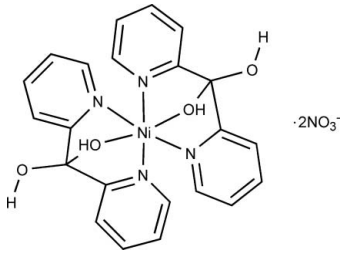
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; disorder in main residue; R factor = 0.046; wR factor = 0.135; data-to-parameter ratio = 13.6.

The title compound, $[Ni(C_{11}H_{10}N_2O_2)_2](NO_3)_2$, consists of an Ni^{II} atom coordinated by two tridentate chelating di-2-pyridylmethanediol $[(2\text{-py})_2C(OH)_2]$ ligands. The Ni^{II} atom is located on an inversion center. The geometry around the Ni^{II} atom is distorted octahedral. The *gem*-diol $(2\text{-py})_2C(OH)_2$ ligand adopts the coordination mode $\eta^1{:}\eta^1{:}\eta^1$. The Ni—N and Ni—O bond lengths are typical for high-spin Ni^{II} in an octahedral environment [Ni—N = 2.094 (2) and 2.124 (3) Å, and Ni—O = 2.108 (3) Å]. One of the hydroxy H atoms is split over two positions which both interact with the nitrate anion. The occurence of different O—H···O hydrogen bonds leads to the formation of a layer parallel to the (101) plane.

Related literature

For background information, see: Efthymiou *et al.* (2006); Moragues-Cánovas *et al.* (2004); Papaefstathiou & Perlepes (2002); Papatriantafyllopoulou *et al.* (2007); Stoumpos *et al.* (2008, 2009). For related structures, see: Li *et al.* (2005); Wang *et al.* (1986).



Experimental

Crystal data

$[Ni(C_{11}H_{10}N_2O_2)_2](NO_3)_2$
M_r = 587.15
Monoclinic, $P2_1/n$
a = 8.4077 (9) Å
b = 15.5098 (16) Å
c = 9.5556 (10) Å
β = 94.644 (2)°
V = 1242.0 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.85 mm^{-1}
T = 293 K
0.20 × 0.10 × 0.03 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: none
7646 measured reflections
2442 independent reflections
1826 reflections with $I > 2\sigma(I)$
R_{int} = 0.057

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.135
S = 1.06
2442 reflections
179 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O4	0.82	2.22	2.810 (4)	129
O1—H1B···O3	0.86	2.13	2.933 (4)	155
O1—H1A···O5^{i}	0.87	2.04	2.884 (4)	165

Symmetry code: (i) $x+\frac{1}{2}, -y+\frac{3}{2}, z-\frac{1}{2}$.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Financial support from the Korean Environment Ministry 'ET–Human Resource Development Project' and the Korean Science and Engineering Foundation (grant No. R01-2008-000-20704-0) is gratefully acknowledged.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2454).

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supporting information

Acta Cryst. (2009). E**65**, m678–m679 [doi:10.1107/S1600536809018728]

Bis(di-2-pyridylmethanediol-κ^3N,O,N')nickel(II) dinitrate

Seung Man Yu, Young Joo Song, Kang Chul Kim, Cheal Kim and Youngmee Kim

S1. Comment

Di-2-pyridyl ketone ($(py)_2CO$) has been employed to form structurally interesting new complexes with 3 d-metal ions (Stoumpos *et al.*, 2009). Water and alcohols (ROH) have been shown to add to the carbonyl group forming the ligands $(2\text{-py})_2C(OH)_2$ [the *gem*-diol form of $(2\text{-py})_2CO$] and $(2\text{-py})_2C(OR)(OH)$ [the hemiacetal form of $(2\text{- py})_2CO$], respectively (Efthymiou *et al.*, 2006). The neutral ligands $(py)_2C(OH)_2$ and $(py)_2C(OR)(OH)$ coordinate to the metal centres as *N*,*N*′,*O* chelates (Papaefstathiou & Perlepes, 2002). The different interesting coordination modes have been seen when the ligands $(py)_2C(OH)_2$ and $(py)_2C(OR)(OH)$ are deprotonated to form mono- or dianion. The deprotonation of hydroxyl groups leads to a coordinative flexibility (Papatriantafyllopoulou *et al.*, 2007; Stoumpos *et al.*, 2008). Some Ni^{II} complexes of the neutral ligand, $(py)_2C(OH)_2$ have been structuraly characterized (Wang *et al.*, 1986; Li *et al.*, 2005), but no structure with a nitrate ion as the counter-ion has been reported to date.

The Ni^{II} atom is located on an inversion center and is coordinated by two tridentate chelating $(2\text{-py})_2C(OH)_2$ ligand to form a distorted octahedral geometry. The *gem*-diol ligand $(2\text{-py})_2C(OH)_2$ adopts the coordination mode $\eta^1{:}\eta^1{:}\eta^1$ (Fig. 1). The Ni—N and Ni—O bond lengths are typical for high-spin Ni(II) in octahedral environments [Ni—N = 2.094 (2) and 2.124 (3) Å, Ni—O = 2.108 (3) Å] (Moragues-Cánovas *et al.*, 2004). The hydrogen attached to O1 is splitting on two positions which are both in interaction with the NO_3^- anion. The O—H···O hydrogen bonds build up a layer parallel to the (101) plane (Table 1, Fig. 2).

S2. Experimental

36.7 mg (0.125 mmol) of $Ni(NO_3)_2.6H_2O$ and 35.5 mg (0.25 mmol) of $C_6H_5COONH_4$ were dissolved in 4 ml water and carefully layered by 4 ml solution of amixture of acetone, methanol and ethanol (2/2/2) of di-2-pyridyl ketone ligand (46.1 mg, 0.25 mmol). Suitable crystals of the title compound for X-ray analysis were obtained in a few weeks.

S3. Refinement

All H atoms attached to C atoms were fixed geometrically and treated as riding with C—H = 0.93 Å with $U_{iso}(H) = 1.2U_{eq}(C)$. Hydroxyl H atom for O2 were treated as riding on the parent atom with O—H = 0.82 Å and $U_{iso}(H) = 1.5U_{eq}(O)$. The hydroxyl H attached to O1 appears to be splitted on two positions. The coordinates of these two positions were initially refined with O—H restraints (0.85 Å) and $U_{iso}(H) = 1.5U_{eq}(O)$. Then in the last stage of refinement these disordered H atoms were treated as riding on the O atom.

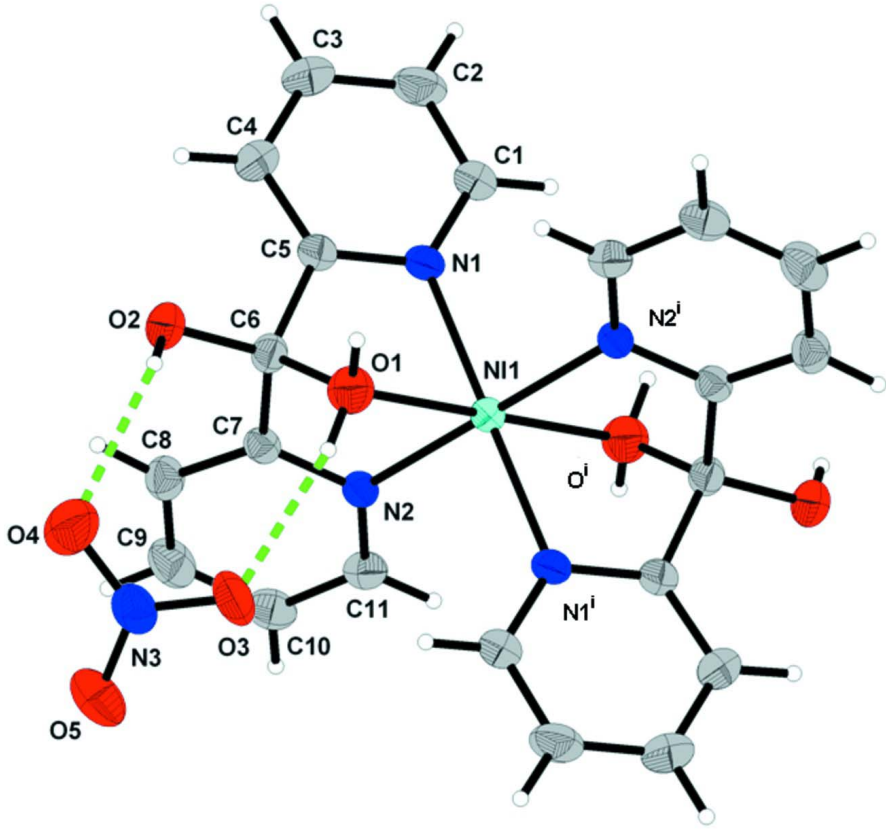

Figure 1

View of the title complex with the atom labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms are represented as small spheres of arbitrary radii and hydrogen bonds are shown as dashed lines. [Symmetry code: (i) 1 - *x*, 1 - *y*, 1 - *z*].

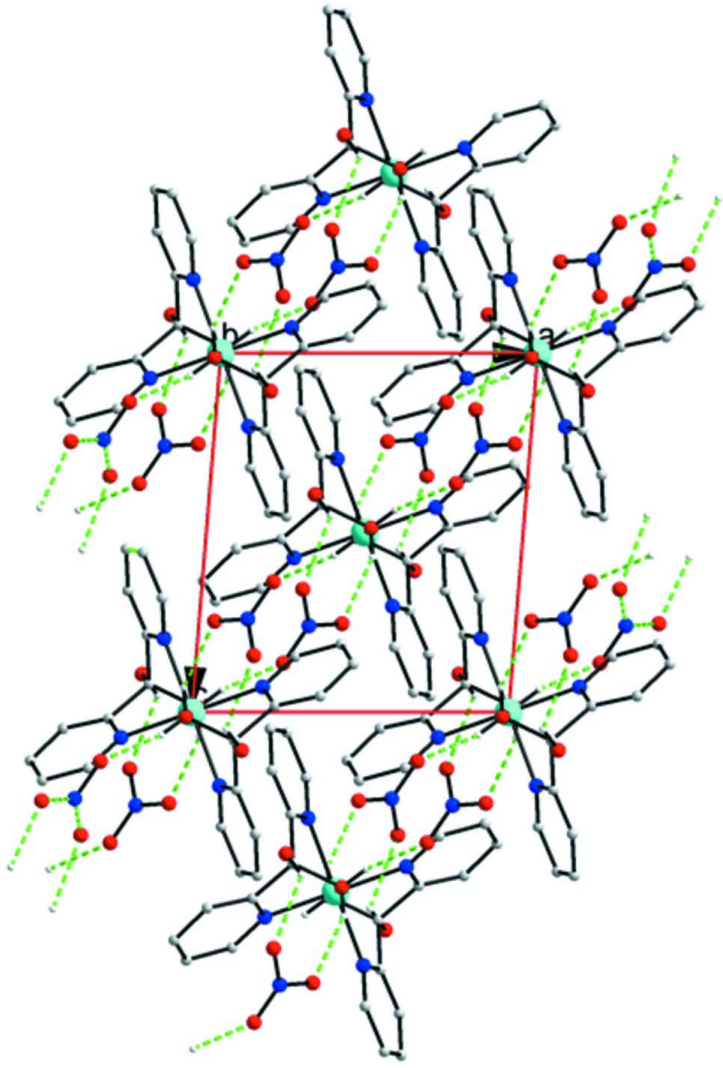

Figure 2

Packing view down the b axis. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bondings have been omitted for clarity.

Bis(di-2-pyridylmethanediol-κ^3N,O,N')nickel(II) dinitrate

Crystal data

$[Ni(C_{11}H_{10}N_2O_2)_2](NO_3)_2$
$M_r = 587.15$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 8.4077$ (9) Å
$b = 15.5098$ (16) Å
$c = 9.5556$ (10) Å
$\beta = 94.644$ (2)°
$V = 1242.0$ (2) Å^3
$Z = 2$
$F(000) = 604$
$D_x = 1.570$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2352 reflections
$\theta = 2.5$–25.6°
$\mu = 0.85$ mm^{-1}

T = 293 K
Plate, pale brown

0.20 × 0.10 × 0.03 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
7646 measured reflections
2442 independent reflections

1826 reflections with $I > 2\sigma(I)$
R_{int} = 0.057
θ_{max} = 26.0°, θ_{min} = 2.5°
h = −11→11
k = −20→12
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.135
S = 1.06
2442 reflections
179 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0755P)^2 + 0.0426P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.49 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 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.

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 (Å²)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
Ni1	0.5000	0.5000	0.5000	0.0334 (2)	
N1	0.3937 (3)	0.52480 (18)	0.2948 (3)	0.0389 (6)	
N2	0.2830 (3)	0.54084 (17)	0.5703 (3)	0.0347 (6)	
O1	0.5183 (3)	0.63487 (17)	0.4873 (2)	0.0574 (7)	
H1A	0.5905	0.6553	0.4370	0.086*	0.50
H1B	0.5305	0.6590	0.5688	0.086*	0.50
O2	0.3337 (3)	0.74355 (14)	0.3938 (3)	0.0539 (6)	
H2	0.3866	0.7720	0.4530	0.081*	
C1	0.3774 (4)	0.4731 (2)	0.1816 (4)	0.0478 (9)	
H1	0.4155	0.4169	0.1884	0.057*	
C2	0.3053 (5)	0.5019 (3)	0.0558 (4)	0.0639 (11)	
H2A	0.2927	0.4653	−0.0214	0.077*	
C3	0.2515 (5)	0.5865 (3)	0.0458 (4)	0.0685 (12)	
H3	0.2048	0.6076	−0.0389	0.082*	
C4	0.2677 (4)	0.6386 (3)	0.1615 (4)	0.0562 (10)	

H4	0.2310	0.6951	0.1573	0.067*
C5	0.3394 (4)	0.6055 (2)	0.2841 (3)	0.0394 (7)
C6	0.3583 (4)	0.6549 (2)	0.4213 (3)	0.0386 (7)
C7	0.2392 (3)	0.61766 (19)	0.5177 (3)	0.0353 (7)
C8	0.0989 (4)	0.6581 (2)	0.5451 (4)	0.0459 (8)
H8	0.0700	0.7112	0.5054	0.055*
C9	0.0030 (4)	0.6160 (3)	0.6345 (4)	0.0594 (10)
H9	−0.0919	0.6414	0.6569	0.071*
C10	0.0462 (4)	0.5378 (3)	0.6898 (4)	0.0521 (9)
H10	−0.0182	0.5097	0.7500	0.063*
C11	0.1873 (4)	0.5008 (2)	0.6552 (3)	0.0434 (8)
H11	0.2164	0.4470	0.6916	0.052*
N3	0.3476 (4)	0.7718 (2)	0.7595 (4)	0.0585 (8)
O3	0.4512 (4)	0.71600 (19)	0.7535 (3)	0.0755 (9)
O4	0.3188 (5)	0.8218 (2)	0.6577 (3)	0.1014 (12)
O5	0.2759 (4)	0.7785 (2)	0.8634 (4)	0.0834 (9)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0362 (3)	0.0326 (3)	0.0319 (3)	0.0023 (2)	0.0050 (2)	−0.0004 (2)
N1	0.0396 (15)	0.0451 (16)	0.0326 (15)	0.0016 (11)	0.0079 (11)	−0.0016 (11)
N2	0.0340 (13)	0.0360 (15)	0.0343 (14)	0.0020 (11)	0.0047 (11)	−0.0012 (11)
O1	0.0609 (16)	0.0526 (16)	0.0587 (16)	−0.0010 (12)	0.0049 (13)	−0.0001 (12)
O2	0.0675 (17)	0.0363 (13)	0.0578 (16)	0.0069 (12)	0.0054 (12)	0.0050 (11)
C1	0.054 (2)	0.050 (2)	0.040 (2)	0.0031 (16)	0.0081 (16)	−0.0051 (16)
C2	0.084 (3)	0.072 (3)	0.036 (2)	−0.001 (2)	0.0032 (19)	−0.0137 (19)
C3	0.087 (3)	0.079 (3)	0.038 (2)	0.011 (2)	−0.004 (2)	0.006 (2)
C4	0.072 (3)	0.054 (2)	0.043 (2)	0.0102 (19)	0.0005 (18)	0.0078 (17)
C5	0.0418 (18)	0.0411 (19)	0.0363 (17)	0.0017 (14)	0.0095 (14)	0.0007 (14)
C6	0.0390 (18)	0.0349 (18)	0.0422 (18)	0.0031 (14)	0.0059 (14)	0.0046 (14)
C7	0.0365 (16)	0.0357 (17)	0.0336 (16)	0.0002 (13)	0.0026 (13)	−0.0053 (13)
C8	0.0391 (18)	0.048 (2)	0.050 (2)	0.0069 (15)	−0.0001 (15)	−0.0015 (15)
C9	0.040 (2)	0.075 (3)	0.065 (2)	0.0062 (19)	0.0128 (18)	−0.010 (2)
C10	0.047 (2)	0.064 (2)	0.047 (2)	−0.0077 (18)	0.0155 (16)	−0.0005 (18)
C11	0.0485 (18)	0.0451 (19)	0.0370 (17)	−0.0049 (16)	0.0053 (14)	0.0002 (15)
N3	0.067 (2)	0.047 (2)	0.061 (2)	−0.0010 (16)	0.0000 (17)	−0.0192 (17)
O3	0.077 (2)	0.077 (2)	0.0714 (19)	0.0337 (16)	0.0032 (15)	−0.0251 (15)
O4	0.173 (4)	0.056 (2)	0.071 (2)	0.016 (2)	−0.014 (2)	−0.0052 (16)
O5	0.071 (2)	0.092 (2)	0.092 (2)	0.0066 (16)	0.0358 (18)	−0.0195 (18)

Geometric parameters (Å, º)

Ni1—N2	2.093 (2)	C2—H2A	0.9300
Ni1—N2^{i}	2.093 (2)	C3—C4	1.367 (5)
Ni1—O1	2.102 (3)	C3—H3	0.9300
Ni1—O1^{i}	2.102 (3)	C4—C5	1.372 (4)
Ni1—N1	2.123 (3)	C4—H4	0.9300

Ni1—N1^{i}	2.123 (3)	C5—C6	1.515 (4)
N1—C5	1.334 (4)	C6—C7	1.528 (4)
N1—C1	1.345 (4)	C7—C8	1.380 (4)
N2—C7	1.333 (4)	C8—C9	1.385 (5)
N2—C11	1.340 (4)	C8—H8	0.9300
O1—C6	1.472 (4)	C9—C10	1.360 (5)
O1—H1A	0.8650	C9—H9	0.9300
O1—H1B	0.8625	C10—C11	1.382 (5)
O2—C6	1.412 (4)	C10—H10	0.9300
O2—H2	0.8200	C11—H11	0.9300
C1—C2	1.377 (5)	N3—O5	1.206 (4)
C1—H1	0.9300	N3—O3	1.233 (4)
C2—C3	1.388 (5)	N3—O4	1.253 (4)

N2—Ni1—N2^{i}	180.0	C4—C3—C2	119.5 (4)
N2—Ni1—O1	77.70 (10)	C4—C3—H3	120.3
N2^{i}—Ni1—O1	102.30 (10)	C2—C3—H3	120.3
N2—Ni1—O1^{i}	102.30 (10)	C3—C4—C5	118.5 (4)
N2^{i}—Ni1—O1^{i}	77.70 (10)	C3—C4—H4	120.7
O1—Ni1—O1^{i}	180.0	C5—C4—H4	120.7
N2—Ni1—N1	85.93 (9)	N1—C5—C4	122.7 (3)
N2^{i}—Ni1—N1	94.07 (9)	N1—C5—C6	113.4 (3)
O1—Ni1—N1	78.10 (10)	C4—C5—C6	123.9 (3)
O1^{i}—Ni1—N1	101.90 (10)	O2—C6—O1	113.6 (2)
N2—Ni1—N1^{i}	94.07 (9)	O2—C6—C5	109.1 (3)
N2^{i}—Ni1—N1^{i}	85.93 (9)	O1—C6—C5	107.0 (2)
O1—Ni1—N1^{i}	101.90 (10)	O2—C6—C7	112.8 (2)
O1^{i}—Ni1—N1^{i}	78.10 (10)	O1—C6—C7	106.4 (2)
N1—Ni1—N1^{i}	180.000 (1)	C5—C6—C7	107.6 (2)
C5—N1—C1	119.1 (3)	N2—C7—C8	123.3 (3)
C5—N1—Ni1	110.9 (2)	N2—C7—C6	113.0 (2)
C1—N1—Ni1	130.0 (2)	C8—C7—C6	123.7 (3)
C7—N2—C11	118.7 (3)	C7—C8—C9	116.8 (3)
C7—N2—Ni1	111.76 (19)	C7—C8—H8	121.6
C11—N2—Ni1	129.5 (2)	C9—C8—H8	121.6
C6—O1—Ni1	99.56 (17)	C10—C9—C8	120.7 (3)
C6—O1—H1A	110.0	C10—C9—H9	119.7
Ni1—O1—H1A	117.0	C8—C9—H9	119.7
C6—O1—H1B	109.5	C9—C10—C11	119.0 (3)
Ni1—O1—H1B	112.6	C9—C10—H10	120.5
H1A—O1—H1B	107.8	C11—C10—H10	120.5
C6—O2—H2	109.5	N2—C11—C10	121.5 (3)
N1—C1—C2	121.2 (4)	N2—C11—H11	119.3
N1—C1—H1	119.4	C10—C11—H11	119.3
C2—C1—H1	119.4	O5—N3—O3	120.1 (4)
C1—C2—C3	119.0 (4)	O5—N3—O4	120.5 (4)

C1—C2—H2A	120.5	O3—N3—O4	119.4 (4)
C3—C2—H2A	120.5		

Symmetry code: (i) −*x*+1, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O4	0.82	2.22	2.810 (4)	129
O1—H1*B*···O3	0.86	2.13	2.933 (4)	155
O1—H1*A*···O5^{ii}	0.87	2.04	2.884 (4)	165

Symmetry code: (ii) *x*+1/2, −*y*+3/2, *z*−1/2.