

Aqua(*N,N*-diethylethylenediamine- κ^2N,N')(pyridine-2,6-dicarboxylato- κ^3N,O,O')nickel(II) 2.5-hydrate

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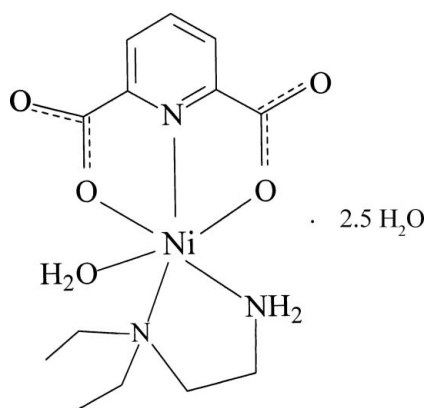
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Key indicators: single-crystal X-ray study; $T = 297$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; H-atom completeness 85%; disorder in main residue; R factor = 0.046; wR factor = 0.123; data-to-parameter ratio = 13.5.

In the title compound, $[\text{Ni}(\text{C}_7\text{H}_3\text{NO}_4)(\text{C}_6\text{H}_{16}\text{N}_2)(\text{H}_2\text{O})] \cdot 2.5\text{H}_2\text{O}$, the discrete neutral $[\text{Ni}(\text{dpc})(\text{dien})(\text{H}_2\text{O})]$ (dien is diethylethylenediamine and dpc is dipicolinate) complex lies on a mirror plane. The Ni^{II} ion is coordinated by the dpc ligand through the pyridine N atom and one O atom of each carboxylate group, an aqua ligand and two N atoms of the bidentate dien ligand, forming a distorted octahedral geometry. One of the C atoms of the ethylenediamine group is disordered across the mirror plane. The symmetry-independent ethyl group is disordered over two orientations with equal occupancy. The complex molecules are connected via $\text{O}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{O}$ intermolecular hydrogen-bonding interactions.

Related literature

For related literature, see: Altin *et al.* (2004); Chaigneau *et al.* (2004); Krilova *et al.* (2007); Liu *et al.* (2006); Ma *et al.* (2003); Nathan & Mai (2000); Okabe & Oya (2000); Park *et al.* (2007); Perry *et al.* (2004); Ramadevi *et al.* (2005); Ramezaniopour *et al.* (2005); Uçar *et al.* (2005, 2007); Zhang *et al.* (2003).



Experimental

Crystal data

$[\text{Ni}(\text{C}_7\text{H}_3\text{NO}_4)(\text{C}_6\text{H}_{16}\text{N}_2)(\text{H}_2\text{O})] \cdot 2.5\text{H}_2\text{O}$
 $M_r = 403.08$
 Orthorhombic, *Imcb*
 $a = 11.268$ (4) Å
 $b = 14.141$ (5) Å
 $c = 22.831$ (12) Å

$V = 3638$ (3) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 1.11$ mm⁻¹
 $T = 297$ (2) K
 $0.42 \times 0.30 \times 0.25$ mm

Data collection

Stoe IPDS 2 diffractometer
 Absorption correction: integration
 (*X-RED32*; Stoe & Cie, 2002)
 $T_{\text{min}} = 0.925$, $T_{\text{max}} = 0.974$

28305 measured reflections
 2120 independent reflections
 1926 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.123$
 $S = 1.18$
 2120 reflections
 157 parameters
 38 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.41$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.12$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

N1—Ni1	2.122 (3)	O1—Ni1	2.070 (2)
N2—Ni1	2.070 (3)	O2—Ni1	2.145 (2)
N3—Ni1	1.986 (3)	Ni1—O2 ⁱ	2.145 (2)
N3—Ni1—O1	89.57 (11)	N3—Ni1—O2	77.86 (5)
N3—Ni1—N2	92.73 (12)	O1—Ni1—O2	88.57 (5)
O1—Ni1—N2	177.70 (12)	N2—Ni1—O2	91.92 (5)
N3—Ni1—N1	176.55 (11)	N1—Ni1—O2	102.20 (5)
O1—Ni1—N1	93.88 (12)	O2 ⁱ —Ni1—O2	155.57 (10)
N2—Ni1—N1	83.83 (12)		

Symmetry code: (i) $-x, y, z$.

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
O5—H5 ⁱⁱ ···O4	0.862 (11)	1.789 (14)	2.644 (3)	171 (6)
N2—H2 ⁱⁱⁱ ···O3 ⁱⁱ	0.85 (3)	2.33 (3)	3.142 (3)	161 (3)
O1—H1A ⁱⁱⁱ ···O3 ⁱⁱⁱ	0.827 (10)	1.922 (12)	2.743 (2)	171 (2)

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

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2403).

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supplementary materials

Acta Cryst. (2007). E63, m2327-m2328 [doi:10.1107/S1600536807038196]

Aqua(*N,N*-diethylethylenediamine- κ^2N,N')(pyridine-2,6-dicarboxylato- κ^3N,O,O')nickel(II) 2.5-hydrate

I. Uçar, A. Bulut and C. Kazak

Comment

Pyridine-2,6-dicarboxylic acid, known as dipicolinic acid (H₂dpc), is a versatile ligand and it can function as a neutral, mono basic or dibasic tridentate chelating ligand (Nathan & Mai, 2000; Perry *et al.*, 2004). Having potential donor oxygen and nitrogen atoms, dipicolinic acid has attracted the scientist from the coordination chemistry and number of studies have been carried out with dipicolinate (dpc) ligand by both inorganic and bioinorganic chemists during the past few years (Krillova *et al.*, 2007). Dipicolinates commonly coordinate to transition metals by either carboxylate bridges between metal centres, to form polymeric (Ma *et al.*, 2003) or dimeric complexes (Ramezaniopour *et al.*, 2005), or tridentate (O, N, O') chelation to one metal ion (Okabe & Oya, 2000). The dipicolinate ligand with Ni^{II} ions commonly has one or two coordination modes. In one coordination mode, a single planar dpc ligand binds in the equatorial plane of a Ni^{II} cation and other ligands such as H₂O or pyridine based heterocycles occupy the remaining sites, thereby forming square pyramidal or octahedral coordination geometry (Liu *et al.*, 2006; Zhang *et al.*, 2003), or two planar dpc molecules coordinate perpendicularly generating a distorted octahedral coordination geometry (Park *et al.*, 2007). In our ongoing research on determination of further coordination modes of chelates of dipicolinic acid with biologically important transition metal ions, we have recently synthesized mixed-ligand metal(II) complexes of dipicolinic acid and their structures have been reported (Uçar *et al.*, 2005; Uçar *et al.*, 2007). As a continuation of these studies, we have now prepared and characterized a new Ni^{II} complex containing dipicolinate anion together with diethylethylenediamine (dien)ligand, namely [Ni(dien)(dpc)(H₂O)]·2.5H₂O.

The asymmetric unit of the title compound consists of one-half of a discrete neutral [Ni(dien)(dpc)(H₂O)] unit and 1.25 lattice water molecules. The [Ni(dien)(dpc)(H₂O)] unit lies across a mirror plane with atoms Ni1, N1, N2, N3, C4 and C5 on the mirror plane. Atom C6 is disordered over two positions across the mirror plane (Fig. 1). The H₂dpc is deprotonated during the reaction and acts as a tridentate ligand. The Ni^{II} ion is six-coordinated in a distorted octahedral geometry, with one N (N3) two O atoms of the tridentate dpc dianion and one N atom from the dien (N1) ligand composing the basal plane, and the aqua O atom and the other N atom (N2) of the dien ligand occupying the axial sites.

The fact that the Ni1—N_{dpc} [1.986 (3) Å] length is significantly shorter than Ni1—N_{dien} [2.070 (3) and 2.122 (3)] bond lengths indicates that atom N3 is the strongest site, because the two carboxylate groups in *ortho* positions enhance the basicity of this atom. The Ni1—N_{dpc}, Ni1—O_{dpc} [2.145 (2) Å] and Ni1—O_{aqua} [2.070 (2) Å] bond lengths in the title complex are slightly different from those observed in previously reported mixed-ligand nickel(II) dipicolinate complexes (Ramadevi *et al.*, 2005; Liu *et al.*, 2006; Park *et al.*, 2007). The dpc chelate angle is 77.79 (10)°, which is comparable to that found in other dipicolinate-metal complexes (Chaigneau *et al.*, 2004; Altin *et al.*, 2004).

The crystal packing is stabilized by intermolecular O—H...O and N—H...O hydrogen bonds, involving the oxygen atoms of coordinated and free water molecules (see Table 2 and Fig. 2).

Experimental

To an ethanol/water (30 ml, 1:1) containing NiCl₂·4H₂O (1 mmol) and disodium dipicolinate (1 mmol), dien (1 mmol) was added slowly with continuous stirring. The resulting solution was refluxed for 1 h and then filtered. The green filtrate was allowed to stand for about two weeks at room temperature, after which time light-green crystals of the title compound suitable for X-ray diffraction analysis were collected.

Refinement

Atoms Ni1, N1, N2, N3, C4 and C5 lie on the crystallographic mirror plane. Atom C6 is disordered across the mirror plane and as a result the occupancy factor for the disordered components were fixed at 0.50 each. The independent ethyl group is disordered over two orientations with equal occupancy. The corresponding N—C and C—C distances involving the disorder components were restrained to be equal. In the ethyl group, the components of the displacement parameters in the direction of the bond were restrained to be equal. The displacement parameters of atoms C22A, C23A, C22B, C23B and O4 were restrained to approximate isotropic behaviour. The N1—C6 distance was restrained to 1.45 (1) Å. H atoms of the coordinated water molecule were located in a difference map and refined with O—H and H···H distances restrained to 0.84 (1) and 1.37 (2) Å, respectively. H atoms on O5 and N2 were located in a difference map and refined freely. H atoms on O5 are disordered over two positions. H atoms on one of the free water molecules (O4) could not be located from the difference map. H atoms attached to C atoms were placed at calculated positions (C—H = 0.93–0.97 Å) and were allowed to ride on the parent atom [$U_{\text{iso}}(\text{H}) = 1.2\text{--}1.5U_{\text{eq}}(\text{C})$].

Figures

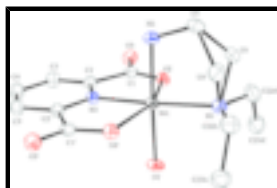


Fig. 1. The structure of [Ni(C₇H₃NO₄)(C₆H₁₆N₂)(H₂O)] complex in the title compound. Displacement ellipsoids are drawn at the 30% probability level. Atoms Ni1, N1, N2, N3, C4 and C5 lie on a crystallographic mirror plane. Only one component of the disordered ethyl group is shown. Hydrogen atoms have been omitted for clarity. Symmetry code: (i) $-x, y, z$.

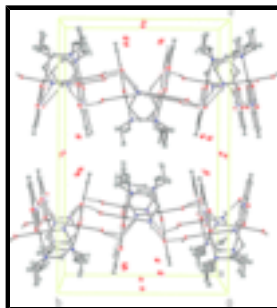


Fig. 2. The crystal packing of the title compound, viewed down the *a* axis. Hydrogen bonds are shown as dashed lines.

Aqua(*N,N*-diethylethylenediamine- κ^2N,N')(pyridine-2,6- λ dicarboxylato- κ^3N,O,O')nickel(II) 2.5-hydrate

Crystal data

[Ni(C₇H₃NO₄)(C₆H₁₆N₂)(H₂O)]·2.5H₂O

$F_{000} = 1672.0$

$M_r = 403.08$

Orthorhombic, *Imcb*

Hall symbol: -I 2a 2

$a = 11.268$ (4) Å

$b = 14.141$ (5) Å

$c = 22.831$ (12) Å

$V = 3638$ (3) Å³

$Z = 8$

$D_x = 1.457$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71069$ Å

Cell parameters from 1657 reflections

$\theta = 1.7$ – 27.2°

$\mu = 1.11$ mm⁻¹

$T = 297$ (2) K

Prism, light green

$0.42 \times 0.30 \times 0.25$ mm

Data collection

Stoe IPDS2
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

Detector resolution: 6.67 pixels mm⁻¹

$T = 297$ (2) K

ω scans

Absorption correction: integration
(X-RED32; Stoe & Cie, 2002)

$T_{\min} = 0.925$, $T_{\max} = 0.974$

28305 measured reflections

2120 independent reflections

1926 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.047$

$\theta_{\text{max}} = 27.2^\circ$

$\theta_{\text{min}} = 1.7^\circ$

$h = -14 \rightarrow 14$

$k = -18 \rightarrow 18$

$l = -29 \rightarrow 29$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.123$

$S = 1.18$

2120 reflections

157 parameters

38 restraints

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

H atoms treated by a mixture of
independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0761P)^2 + 2.2047P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.41$ e Å⁻³

$\Delta\rho_{\text{min}} = -1.12$ e Å⁻³

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.

supplementary materials

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
C1	0.2093 (2)	0.13012 (16)	0.29423 (11)	0.0402 (5)	
C2	0.10328 (19)	0.14295 (16)	0.33506 (10)	0.0392 (5)	
C3	0.1064 (2)	0.1627 (2)	0.39387 (11)	0.0523 (6)	
H3	0.1783	0.1694	0.4134	0.063*	
C4	0.0000	0.1726 (3)	0.42341 (17)	0.0602 (10)	
H4	0.0000	0.1859	0.4633	0.072*	
C5	0.0000	-0.0869 (3)	0.17882 (19)	0.0589 (10)	
H5A	0.0386	-0.1471	0.1830	0.071*	0.50
H5B	-0.0800	-0.0976	0.1659	0.071*	0.50
C6	0.0666 (6)	-0.0233 (4)	0.1345 (2)	0.0596 (14)	0.50
H6A	0.0663	-0.0538	0.0969	0.072*	0.50
H6B	0.1476	-0.0153	0.1466	0.072*	0.50
C22A	-0.1050 (6)	0.0632 (5)	0.1032 (3)	0.0673 (16)	0.50
H22A	-0.0730	0.0670	0.0638	0.081*	0.50
H22B	-0.1522	0.0059	0.1045	0.081*	0.50
C23A	-0.1689 (8)	0.1566 (5)	0.0959 (3)	0.0741 (18)	0.50
H23A	-0.1947	0.1790	0.1335	0.111*	0.50
H23B	-0.2366	0.1481	0.0709	0.111*	0.50
H23C	-0.1160	0.2020	0.0787	0.111*	0.50
C22B	-0.0951 (7)	0.1371 (5)	0.1028 (3)	0.0656 (16)	0.50
H22C	-0.1670	0.1319	0.1259	0.079*	0.50
H22D	-0.0677	0.2019	0.1060	0.079*	0.50
C23B	-0.1277 (10)	0.1164 (6)	0.0386 (3)	0.098 (3)	0.50
H23D	-0.0638	0.1362	0.0135	0.147*	0.50
H23E	-0.1985	0.1505	0.0284	0.147*	0.50
H23F	-0.1410	0.0499	0.0337	0.147*	0.50
N1	0.0000	0.0711 (2)	0.13202 (13)	0.0537 (8)	
N2	0.0000	-0.0374 (2)	0.23465 (14)	0.0428 (6)	
H2	0.061 (2)	-0.051 (2)	0.2546 (12)	0.043 (7)*	
N3	0.0000	0.13362 (19)	0.30763 (12)	0.0354 (5)	
O1	0.0000	0.25168 (16)	0.20606 (13)	0.0472 (6)	
H1A	0.0615 (9)	0.2816 (15)	0.1993 (13)	0.058 (8)*	
O2	0.18606 (15)	0.11705 (12)	0.24116 (8)	0.0433 (4)	
O3	0.31037 (14)	0.13235 (15)	0.31665 (8)	0.0520 (5)	
O4	0.3847 (3)	0.1075 (3)	0.43248 (15)	0.1158 (13)	
O5	0.2500	0.0000	0.5000	0.1026 (19)	
H5	0.294 (4)	0.030 (4)	0.4753 (19)	0.042 (14)*	0.50
Ni1	0.0000	0.10766 (2)	0.222149 (16)	0.03365 (18)	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0317 (11)	0.0375 (10)	0.0516 (12)	-0.0017 (9)	0.0012 (9)	0.0059 (10)
C2	0.0324 (11)	0.0397 (11)	0.0455 (11)	-0.0001 (8)	-0.0018 (9)	0.0030 (9)
C3	0.0415 (14)	0.0685 (17)	0.0470 (12)	-0.0032 (12)	-0.0069 (10)	-0.0014 (11)
C4	0.053 (2)	0.086 (3)	0.0423 (18)	0.000	0.000	-0.0039 (18)
C5	0.081 (3)	0.0297 (15)	0.066 (2)	0.000	0.000	-0.0072 (15)
C6	0.081 (4)	0.046 (3)	0.052 (3)	0.015 (3)	0.009 (3)	-0.010 (2)
C22A	0.081 (4)	0.058 (3)	0.063 (3)	0.002 (3)	-0.023 (3)	-0.014 (3)
C23A	0.087 (5)	0.065 (4)	0.070 (4)	0.013 (4)	-0.020 (4)	-0.003 (3)
C22B	0.085 (5)	0.060 (4)	0.051 (3)	0.010 (3)	-0.016 (3)	0.001 (3)
C23B	0.132 (7)	0.097 (5)	0.066 (4)	0.003 (5)	-0.035 (5)	0.005 (4)
N1	0.081 (2)	0.0355 (15)	0.0451 (15)	0.000	0.000	-0.0027 (12)
N2	0.0412 (15)	0.0309 (13)	0.0562 (17)	0.000	0.000	0.0047 (12)
N3	0.0299 (12)	0.0356 (12)	0.0408 (13)	0.000	0.000	0.0010 (10)
O1	0.0350 (12)	0.0284 (10)	0.0783 (16)	0.000	0.000	0.0055 (11)
O2	0.0358 (9)	0.0462 (9)	0.0480 (9)	0.0015 (7)	0.0037 (7)	-0.0003 (7)
O3	0.0303 (8)	0.0657 (11)	0.0601 (11)	-0.0043 (8)	-0.0018 (7)	0.0083 (9)
O4	0.086 (2)	0.175 (4)	0.0863 (19)	0.006 (2)	-0.0049 (17)	0.0427 (19)
O5	0.129 (6)	0.111 (5)	0.068 (4)	0.000	0.000	0.000
Ni1	0.0328 (3)	0.0287 (3)	0.0394 (3)	0.000	0.000	-0.00016 (13)

Geometric parameters (\AA , $^\circ$)

C1—O3	1.249 (3)	C23A—H23A	0.96
C1—O2	1.253 (3)	C23A—H23B	0.96
C1—C2	1.526 (3)	C23A—H23C	0.96
C2—N3	1.328 (3)	C22B—C23B	1.540 (8)
C2—C3	1.372 (3)	C22B—N1	1.570 (7)
C3—C4	1.382 (3)	C22B—H22C	0.97
C3—H3	0.93	C22B—H22D	0.97
C4—C3 ⁱ	1.382 (3)	C23B—H23D	0.96
C4—H4	0.93	C23B—H23E	0.96
C5—N2	1.455 (5)	C23B—H23F	0.96
C5—C6 ⁱ	1.548 (7)	N1—C22A ⁱ	1.358 (6)
C5—C6	1.548 (7)	N1—C6 ⁱ	1.533 (5)
C5—H5A	0.96	N1—C22B ⁱ	1.570 (7)
C5—H5B	0.96	N1—Ni1	2.122 (3)
C6—C22A ⁱ	1.481 (9)	N2—Ni1	2.070 (3)
C6—C6 ⁱ	1.501 (13)	N2—H2	0.85 (3)
C6—N1	1.533 (5)	N3—C2 ⁱ	1.328 (3)
C6—H6A	0.96	N3—Ni1	1.986 (3)
C6—H6B	0.96	O1—Ni1	2.070 (2)
C22A—N1	1.358 (6)	O1—H1A	0.827 (10)
C22A—C6 ⁱ	1.481 (9)	O2—Ni1	2.145 (2)

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C22A—C23A	1.514 (9)	O5—H5	0.862 (11)
C22A—H22A	0.97	Ni1—O2 ⁱ	2.145 (2)
C22A—H22B	0.97		
O3—C1—O2	126.2 (2)	N1—C22B—H22D	108.2
O3—C1—C2	117.4 (2)	H22A—C22B—H22D	133.1
O2—C1—C2	116.4 (2)	H22C—C22B—H22D	107.3
N3—C2—C3	120.2 (2)	C22B—C23B—H23D	109.5
N3—C2—C1	112.7 (2)	C22B—C23B—H23E	109.5
C3—C2—C1	127.0 (2)	H23D—C23B—H23E	109.5
C2—C3—C4	118.4 (2)	C22B—C23B—H23F	109.5
C2—C3—H3	120.8	H23D—C23B—H23F	109.5
C4—C3—H3	120.8	H23E—C23B—H23F	109.5
C3 ⁱ —C4—C3	120.2 (3)	C22A—N1—C6	111.9 (4)
C3 ⁱ —C4—H4	119.9	C22A—N1—C22B ⁱ	116.0 (5)
C3—C4—H4	119.9	C6—N1—C22B ⁱ	101.5 (4)
N2—C5—C6 ⁱ	107.0 (3)	C22A ⁱ —N1—C22B	116.0 (5)
N2—C5—C6	107.0 (3)	C6 ⁱ —N1—C22B	101.5 (4)
N2—C5—H5A	109.9	C22A—N1—Ni1	119.3 (3)
C6—C5—H5A	111.1	C22A ⁱ —N1—Ni1	119.3 (3)
N2—C5—H5B	110.1	C6—N1—Ni1	100.2 (2)
C6—C5—H5B	110.2	C6 ⁱ —N1—Ni1	100.2 (2)
H5A—C5—H5B	108.4	C22B ⁱ —N1—Ni1	105.5 (3)
N1—C6—C5	107.0 (4)	C22B—N1—Ni1	105.5 (3)
N1—C6—H6A	110.9	C5—N2—Ni1	110.9 (2)
C5—C6—H6A	108.8	C5—N2—H2	111.0 (19)
N1—C6—H6B	111.9	Ni1—N2—H2	108 (2)
C5—C6—H6B	109.9	C2—N3—C2 ⁱ	122.4 (3)
H6A—C6—H6B	108.3	C2—N3—Ni1	118.79 (14)
N1—C22A—C23A	113.3 (6)	C2 ⁱ —N3—Ni1	118.79 (14)
N1—C22A—H22A	96.9	Ni1—O1—H1A	122.5 (15)
C23A—C22A—H22A	91.5	C1—O2—Ni1	114.12 (15)
N1—C22A—H22B	122.2	N3—Ni1—O1	89.57 (11)
C23A—C22A—H22B	118.1	N3—Ni1—N2	92.73 (12)
H22A—C22A—H22B	106.1	O1—Ni1—N2	177.70 (12)
C22A—C23A—H23A	109.5	N3—Ni1—N1	176.55 (11)
C22A—C23A—H23B	109.5	O1—Ni1—N1	93.88 (12)
H23A—C23A—H23B	109.5	N2—Ni1—N1	83.83 (12)
C23A—C23A—H23C	109.5	N3—Ni1—O2 ⁱ	77.86 (5)
H23B—C23A—H23C	109.5	O1—Ni1—O2 ⁱ	88.57 (5)
H23B—C23A—H22C	119.6	N2—Ni1—O2 ⁱ	91.92 (5)
H23C—C23A—H22C	130.6	N1—Ni1—O2 ⁱ	102.20 (5)
C23B—C22B—N1	117.1 (6)	N3—Ni1—O2	77.86 (5)
C23B—C22B—H22C	107.7	O1—Ni1—O2	88.57 (5)
N1—C22B—H22C	107.0	N2—Ni1—O2	91.92 (5)
H22A—C22B—H22C	117.0	N1—Ni1—O2	102.20 (5)

C23B—C22B—H22D	109.2	O2 ⁱ —Ni1—O2	155.57 (10)
O3—C1—C2—N3	-176.1 (2)	C3—C2—N3—C2 ⁱ	0.1 (5)
O2—C1—C2—N3	3.0 (3)	C1—C2—N3—C2 ⁱ	-179.40 (19)
O3—C1—C2—C3	4.4 (4)	C3—C2—N3—Ni1	178.7 (2)
O2—C1—C2—C3	-176.5 (2)	C1—C2—N3—Ni1	-0.8 (3)
N3—C2—C3—C4	0.0 (5)	O3—C1—O2—Ni1	175.5 (2)
C1—C2—C3—C4	179.4 (3)	C2—C1—O2—Ni1	-3.5 (2)
C2—C3—C4—C3 ⁱ	-0.1 (6)	C2—N3—Ni1—O1	-89.3 (2)
N2—C5—C6—C22A ⁱ	-41.7 (17)	C2 ⁱ —N3—Ni1—O1	89.3 (2)
C6 ⁱ —C5—C6—C22A ⁱ	58.1 (17)	C2—N3—Ni1—N2	90.7 (2)
N2—C5—C6—C6 ⁱ	-99.78 (19)	C2 ⁱ —N3—Ni1—N2	-90.7 (2)
N2—C5—C6—N1	-58.8 (4)	C2—N3—Ni1—O2 ⁱ	-177.9 (2)
C6 ⁱ —C5—C6—N1	41.0 (4)	C2 ⁱ —N3—Ni1—O2 ⁱ	0.7 (2)
C6 ⁱ —C22A—N1—C22A ⁱ	99.5 (7)	C2—N3—Ni1—O2	-0.7 (2)
C23A—C22A—N1—C22A ⁱ	-106.9 (6)	C2 ⁱ —N3—Ni1—O2	177.9 (2)
C6 ⁱ —C22A—N1—C6	30.7 (4)	C5—N2—Ni1—N3	180.0
C23A—C22A—N1—C6	-175.6 (5)	C5—N2—Ni1—N1	0.0
C23A—C22A—N1—C6 ⁱ	153.6 (7)	C5—N2—Ni1—O2 ⁱ	102.07 (5)
C6 ⁱ —C22A—N1—C22B ⁱ	146.5 (5)	C5—N2—Ni1—O2	-102.07 (5)
C23A—C22A—N1—C22B ⁱ	-59.9 (7)	C22A—N1—Ni1—O1	-87.5 (4)
C6 ⁱ —C22A—N1—C22B	-165.6 (7)	C22A ⁱ —N1—Ni1—O1	87.5 (4)
C23A—C22A—N1—C22B	-11.9 (6)	C6—N1—Ni1—O1	150.2 (3)
C6 ⁱ —C22A—N1—Ni1	-85.6 (4)	C6 ⁱ —N1—Ni1—O1	-150.2 (3)
C23A—C22A—N1—Ni1	68.0 (7)	C22B ⁱ —N1—Ni1—O1	45.1 (3)
C22A ⁱ —C6—N1—C22A	114.6 (7)	C22B—N1—Ni1—O1	-45.1 (3)
C6 ⁱ —C6—N1—C22A	-31.7 (4)	C22A—N1—Ni1—N2	92.5 (4)
C5—C6—N1—C22A	-72.8 (5)	C22A ⁱ —N1—Ni1—N2	-92.5 (4)
C6 ⁱ —C6—N1—C22A ⁱ	-146.3 (4)	C6—N1—Ni1—N2	-29.8 (3)
C5—C6—N1—C22A ⁱ	172.6 (5)	C6 ⁱ —N1—Ni1—N2	29.8 (3)
C22A ⁱ —C6—N1—C6 ⁱ	146.3 (4)	C22B ⁱ —N1—Ni1—N2	-134.9 (3)
C5—C6—N1—C6 ⁱ	-41.1 (4)	C22B—N1—Ni1—N2	134.9 (3)
C22A ⁱ —C6—N1—C22B ⁱ	-9.7 (4)	C22A—N1—Ni1—O2 ⁱ	1.9 (4)
C6 ⁱ —C6—N1—C22B ⁱ	-155.9 (4)	C22A ⁱ —N1—Ni1—O2 ⁱ	176.9 (4)
C5—C6—N1—C22B ⁱ	163.0 (4)	C6—N1—Ni1—O2 ⁱ	-120.5 (3)
C22A ⁱ —C6—N1—C22B	92.7 (9)	C6 ⁱ —N1—Ni1—O2 ⁱ	-60.8 (3)
C6 ⁱ —C6—N1—C22B	-53.5 (7)	C22B ⁱ —N1—Ni1—O2 ⁱ	134.5 (3)
C5—C6—N1—C22B	-94.6 (8)	C22B—N1—Ni1—O2 ⁱ	44.3 (3)
C22A ⁱ —C6—N1—Ni1	-118.0 (3)	C22A—N1—Ni1—O2	-176.9 (4)
C6 ⁱ —C6—N1—Ni1	95.78 (15)	C22A ⁱ —N1—Ni1—O2	-1.9 (4)
C5—C6—N1—Ni1	54.7 (4)	C6—N1—Ni1—O2	60.8 (3)
C23B—C22B—N1—C22A	-54.3 (7)	C6 ⁱ —N1—Ni1—O2	120.5 (3)
C23B—C22B—N1—C22A ⁱ	54.2 (8)	C22B ⁱ —N1—Ni1—O2	-44.3 (3)

supplementary materials

C23B—C22B—N1—C6	-22.8 (12)	C22B—N1—Ni1—O2	-134.5 (3)
C23B—C22B—N1—C6 ⁱ	-67.2 (7)	C1—O2—Ni1—N3	2.43 (16)
C23B—C22B—N1—C22B ⁱ	83.7 (7)	C1—O2—Ni1—O1	92.30 (17)
C23B—C22B—N1—Ni1	-171.3 (6)	C1—O2—Ni1—N2	-89.94 (17)
C6 ⁱ —C5—N2—Ni1	-30.5 (3)	C1—O2—Ni1—N1	-174.04 (17)
C6—C5—N2—Ni1	30.5 (3)	C1—O2—Ni1—O2 ⁱ	8.9 (3)

Symmetry codes: (i) $-x, y, z$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O5—H5 \cdots O4	0.862 (11)	1.789 (14)	2.644 (3)	171 (6)
N2—H2 \cdots O3 ⁱⁱ	0.85 (3)	2.33 (3)	3.142 (3)	161 (3)
O1—H1A \cdots O3 ⁱⁱⁱ	0.827 (10)	1.922 (12)	2.743 (2)	171 (2)

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

Fig. 2

