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mer-Tris(1*H*-benzotriazole-κN)(pyridine-2,6-dicarboxylato-$\kappa^3 N,O,O'$)nickel(II)

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Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.036
wR factor = 0.094
Data-to-parameter ratio = 17.3

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

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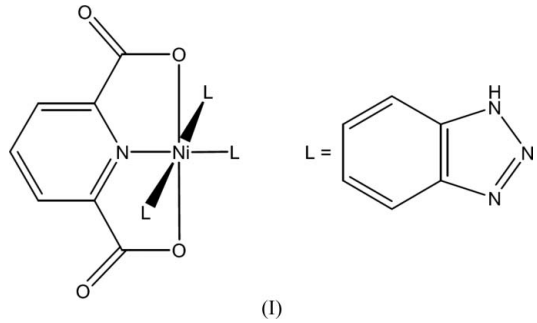
The title complex, $[Ni(C_7H_3NO_4)(C_6H_5N_3)_3]$, has been prepared hydrothermally. Three neutral monodentate benzotriazole ligands occupy meridional sites about the octahedrally coordinated nickel(II) cation. The remaining sites are occupied by the N and two O atoms of a tridentate pyridine-2,6-dicarboxylate dianion.

Comment

As part of our work on transition metal salts of pyridine-2,6-dicarboxylic acid (dipicolinic acid, dipicH_2) (Kumaresan *et al.*, 2004; Kumaresan & Ramadevi, 2005), we prepared the title compound, (I), from nickel(II) acetate, dipicolinic acid and benzotriazole (see *Experimental*).



(I)

The mononuclear complex contains an octahedrally coordinated nickel(II) cation. One N and two O atoms of a planar dipic^{2-} dianion occupy three coordination sites and the remaining three meridional sites are occupied by donor N atoms of identically coordinated benzotriazole ligands (Fig. 1). The molecule can be viewed as a four-bladed paddle wheel, with the Ni—O1 bond as axis and the four ligands, each nearly planar, as paddles.

The Cambridge Structural Database (CSD, Version 5.26, November 2004 update; Allen, 2002) contains results for nine complexes in which a nickel(II) cation is coordinated in a κ^3-N,O,O' fashion by a dipic^{2-} dianion. These compounds display Ni—N bond lengths in the narrow range 1.952–1.979 Å, more variable Ni—O distances of 2.092–2.182 Å and O—Ni—O angles of 154.4–156.5°. In the title complex (Table 1), the only non-typical feature of the Ni–dipic bonding is the Ni—N1 distance [1.992 (2) Å], which falls just outside the expected range. The difference in length between the Ni—O1 and Ni—O3 bonds of 0.068 (2) Å is not unusual. Here it is accompanied by differences in the conformations of the two chelate rings formed by the dipic^{2-} ligand. Both rings are envelopes with Ni at the flap; the N1—C5—C7—O3—Ni ring is the more puckered, with endocyclic torsion angles about Ni—O3 and Ni—N1 of −4.7 (1) and 4.8 (1)°, respectively. The corre-

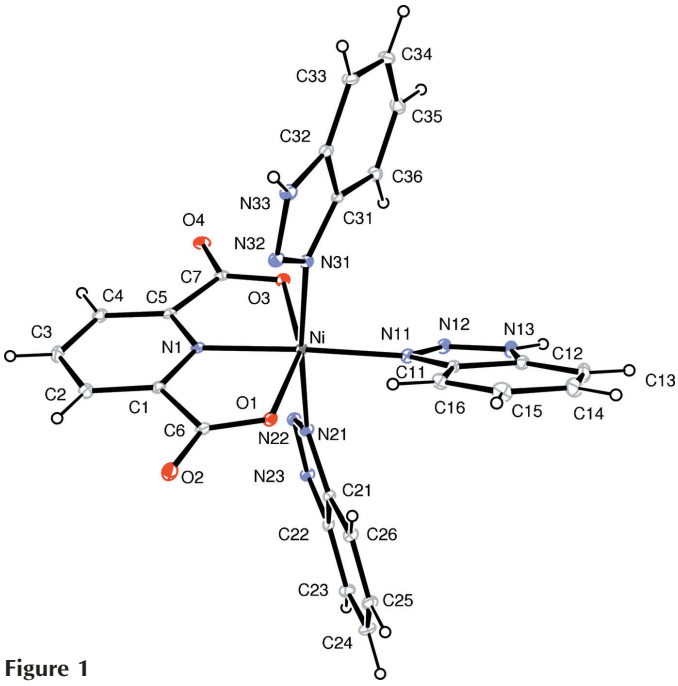


Figure 1
A view of the title molecule, with the atom-numbering scheme and 20% probability displacement ellipsoids.

sponding values for the N1—C1—C6—O1—Ni ring are only 1.3 (1) and −1.3 (1)°, respectively. We also note that the structurally characterized examples of nickel(II) bonded to neutral dipicH_2 and to monanionic dipicH^- have Ni—N and Ni—O bond lengths which fall in similar ranges to those found in Ni–dipic^{2-} complexes (Zhang *et al.*, 2003; Nathan & Mai, 2000).

Each benzotriazole ligand in (I) binds to the metal atom through a single unprotonated N atom. This is by far the most common form of coordination of the benzotriazole molecule to a metal, as a search of the CSD makes clear, but it has not previously been reported for nickel(II). However, a complex in which this ligand bridges two nickel(II) ions has been described (Meunier-Piret *et al.*, 1976). The mutually *trans* Ni—N21 and Ni—N31 bonds of 2.088 (2) and 2.079 (2) Å, respectively, are significantly longer than the Ni—N11 distance of 2.049 (2) Å, suggesting that the triazole N atom exerts a stronger *trans* influence than pyridine N. Corresponding bond lengths in the three triazole ligands agree well with each other (Table 2) and with values in benzotriazole ligands and free molecules from the CSD. Evidently, coordination has little effect on the character of the N—N bonds or on the slight tendency to bond alternation in the C_6 rings.

The mononuclear complexes are linked by N—H···O hydrogen bonds (Table 3). All three benzotriazole N—H bonds act as donors, two to the free carboxylate atoms O2 and O4, and one to the metal-coordinated atom O3 (Fig. 2). This may explain the lengthening of Ni—O3 by 0.068 (2) Å relative to Ni—O1.

The atomic U^{ij} values are moderately well reproduced by a TLS analysis (Schomaker & Trueblood, 1968): $R_2 = (\Sigma\Delta U^2/\Sigma U^2)^{\frac{1}{2}} = 0.20$. The worst discrepancy in the Hirshfeld (1976) rigid-bond test is $\Delta U = 0.004$ (11) Å^2 for C6—O1.

Experimental

A mixture of [Ni(CH$_3$CO$_2$)$_2$]·4H$_2$O (31 mg), dipicolinic acid (20 mg), benzotriazole (24 mg) and water (2.5 ml) in a mole ratio of 1.03:1:1.68:1.15 was homogenized for 30 min. It was then sealed in a 23 ml polyfluoroethylene-lined stainless steel bomb and kept at 423 K under autogenous pressure for 72 h. On cooling to room temperature at 10 K h^{-1}, blue crystals of (I) formed. These were collected by filtration, washed in de-ionized water and then in diethyl ether, and finally dried.

Crystal data

[Ni(C$_7$H$_3$NO$_4$)(C$_6$H$_5$N$_3$)$_3$]
M_r = 581.2
Monoclinic, $P2_1/c$
a = 9.8964 (1) Å
b = 10.3253 (1) Å
c = 26.0261 (4) Å
β = 98.971 (1)°
V = 2626.90 (6) Å^3
Z = 4
D_x = 1.47 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 15068 reflections
θ = 1–27°
μ = 0.79 mm^{-1}
T = 100 K
Needle, blue
0.56 × 0.18 × 0.18 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.731, T_{max} = 0.867
35667 measured reflections
6231 independent reflections
5149 reflections with $I > 2\sigma(I)$
R_{int} = 0.061
θ_{max} = 27.9°
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 12$
$l = -32 \rightarrow 34$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.036
$wR(F^2)$ = 0.094
S = 1.06
6231 reflections
361 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 1.0906P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.47 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni—N1	1.9922 (15)	O1—C6	1.265 (2)
Ni—N11	2.0489 (15)	O2—C6	1.245 (2)
Ni—N31	2.0788 (14)	O3—C7	1.270 (2)
Ni—N21	2.0879 (15)	O4—C7	1.246 (2)
Ni—O1	2.1124 (12)	C35—C36	1.375 (3)
Ni—O3	2.1802 (12)		
N1—Ni—N11	177.23 (6)	O1—Ni—O3	154.82 (5)
N31—Ni—N21	173.43 (6)		
O1—Ni—N11—N12	151.94 (13)	O1—Ni—N31—N32	−15.81 (13)
O1—Ni—N21—N22	149.03 (13)		

Table 2
Comparison of selected ligand bond lengths (Å).

Ligand	n = 1	n = 2	n = 3
Nn1—Nn2	1.310 (2)	1.311 (2)	1.318 (2)
Nn1—Cn1	1.373 (2)	1.379 (2)	1.379 (2)
Nn2—Nn3	1.334 (2)	1.339 (2)	1.336 (2)
Nn3—Cn2	1.361 (2)	1.360 (2)	1.355 (2)
Cn1—Cn2	1.393 (3)	1.395 (2)	1.395 (2)
Cn1—Cn6	1.406 (2)	1.408 (2)	1.407 (3)
Cn2—Cn3	1.404 (3)	1.404 (3)	1.403 (3)
Cn3—Cn4	1.369 (3)	1.369 (3)	1.373 (3)
Cn4—Cn5	1.413 (3)	1.412 (3)	1.417 (3)
Cn5—Cn6	1.375 (3)	1.379 (3)	1.375 (3)

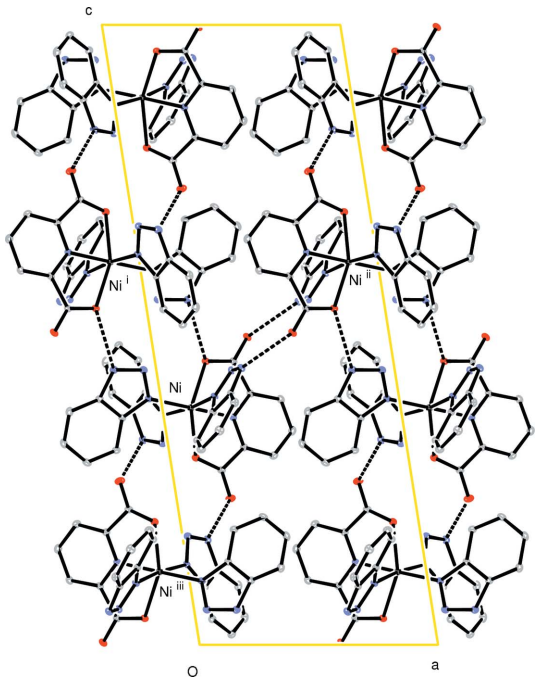


Figure 2
The unit-cell contents of (I), viewed in projection down *b*. Dotted lines represent hydrogen bonds. H atoms have been omitted. Symmetry codes are as defined in Table 3.

Table 3
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N13—H13···O3^{i}	0.86	1.96	2.7777 (19)	160
N23—H23···O4^{ii}	0.86	1.88	2.6612 (18)	151
N33—H33···O2^{iii}	0.86	1.78	2.617 (2)	165

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

The interpretation of the structure depends critically on the positioning of the H atoms and it is therefore important to note that all H atoms were unambiguously located in difference maps. In the final refinement, their positions were idealized geometrically and they then rode on their parent atoms, with C—H = 0.93 Å and N—H = 0.86 Å, and with U_{iso}(H) = 1.2U_{eq}(C or N).

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SORTAV* in *WinGX* (Farrugia, 1999); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX*.

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Hall symbol: -P 2ybc
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$b = 10.3253$ (1) Å
$c = 26.0261$ (4) Å
$\beta = 98.971$ (1)°
$V = 2626.90$ (6) Å^3
$Z = 4$
$F(000) = 1192$
$D_x = 1.47$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 15068 reflections
$\theta = 1$–27°
$\mu = 0.79$ mm^{-1}
$T = 100$ K
Needle, blue
0.56 × 0.18 × 0.18 mm

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Nonius KappaCCD diffractometer
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$T_{min} = 0.731$, $T_{max} = 0.867$
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5149 reflections with $I > 2\sigma(I)$
$R_{int} = 0.061$
$\theta_{max} = 27.9°$, $\theta_{min} = 1.6°$
$h = -13 \rightarrow 13$
$k = -13 \rightarrow 12$
$l = -32 \rightarrow 34$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.094$
$S = 1.06$
6231 reflections
361 parameters
0 restraints
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2 + 1.0906P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.43$ e Å^{-3}
$\Delta\rho_{min} = -0.47$ e Å^{-3}

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni	0.12095 (2)	0.09710 (2)	0.382311 (8)	0.01177 (8)

O1	0.10783 (12)	0.06269 (12)	0.30168 (5)	0.0153 (3)
O2	0.22625 (15)	0.09316 (13)	0.23589 (5)	0.0258 (3)
O3	0.21352 (12)	0.17539 (12)	0.45740 (5)	0.0151 (3)
O4	0.40362 (12)	0.27270 (12)	0.49653 (5)	0.0184 (3)
N1	0.29089 (14)	0.18225 (13)	0.36702 (6)	0.0126 (3)
N11	−0.05029 (15)	0.00120 (14)	0.39692 (5)	0.0147 (3)
N12	−0.05370 (15)	−0.04745 (15)	0.44320 (6)	0.0173 (3)
N13	−0.17786 (16)	−0.09760 (15)	0.44343 (6)	0.0186 (3)
H13	−0.204	−0.1341	0.4699	0.022*
N21	0.22638 (15)	−0.07625 (14)	0.40030 (6)	0.0145 (3)
N22	0.31645 (15)	−0.08786 (14)	0.44266 (6)	0.0153 (3)
N23	0.35794 (15)	−0.21138 (14)	0.44641 (6)	0.0160 (3)
H23	0.416	−0.2419	0.4715	0.019*
N31	0.00169 (14)	0.26337 (14)	0.37053 (5)	0.0141 (3)
N32	−0.02301 (15)	0.32273 (14)	0.32521 (6)	0.0170 (3)
N33	−0.10059 (16)	0.42614 (15)	0.33065 (6)	0.0188 (3)
H33	−0.13	0.4793	0.306	0.023*
C1	0.31712 (18)	0.17748 (16)	0.31845 (7)	0.0148 (4)
C2	0.43634 (19)	0.22958 (19)	0.30545 (7)	0.0210 (4)
H2	0.4532	0.2284	0.2713	0.025*
C3	0.5299 (2)	0.28356 (19)	0.34498 (8)	0.0236 (4)
H3	0.6111	0.3186	0.3374	0.028*
C4	0.50262 (18)	0.28541 (18)	0.39578 (7)	0.0193 (4)
H4	0.5651	0.3204	0.4226	0.023*
C5	0.37983 (18)	0.23371 (16)	0.40543 (7)	0.0141 (3)
C6	0.20750 (19)	0.10608 (16)	0.28182 (7)	0.0158 (4)
C7	0.33000 (17)	0.22710 (16)	0.45749 (7)	0.0135 (3)
C11	−0.17446 (18)	−0.01866 (17)	0.36617 (7)	0.0151 (4)
C12	−0.25780 (19)	−0.08346 (18)	0.39624 (7)	0.0182 (4)
C13	−0.3917 (2)	−0.1210 (2)	0.37571 (8)	0.0255 (4)
H13A	−0.4472	−0.1648	0.3956	0.031*
C14	−0.4361 (2)	−0.0897 (2)	0.32476 (8)	0.0271 (5)
H14	−0.5244	−0.1125	0.3098	0.033*
C15	−0.3520 (2)	−0.0238 (2)	0.29413 (8)	0.0262 (4)
H15	−0.3865	−0.0049	0.2596	0.031*
C16	−0.22077 (19)	0.01327 (19)	0.31388 (7)	0.0200 (4)
H16	−0.1657	0.057	0.2938	0.024*
C21	0.20973 (17)	−0.19459 (17)	0.37556 (7)	0.0143 (3)
C22	0.29633 (17)	−0.28227 (17)	0.40530 (7)	0.0156 (4)
C23	0.3065 (2)	−0.41260 (18)	0.39099 (8)	0.0212 (4)
H23A	0.3647	−0.4705	0.4109	0.025*
C24	0.2253 (2)	−0.44898 (19)	0.34581 (8)	0.0243 (4)
H24	0.2289	−0.5344	0.3347	0.029*
C25	0.1363 (2)	−0.36188 (19)	0.31540 (7)	0.0214 (4)
H25	0.0829	−0.3917	0.2851	0.026*
C26	0.12625 (19)	−0.23377 (18)	0.32936 (7)	0.0181 (4)
H26	0.0676	−0.1764	0.3093	0.022*
C31	−0.06213 (17)	0.32993 (16)	0.40595 (7)	0.0144 (3)

C32	−0.12705 (18)	0.43664 (18)	0.38003 (7)	0.0170 (4)
C33	−0.20051 (19)	0.52754 (18)	0.40474 (8)	0.0228 (4)
H33A	−0.2428	0.5987	0.3872	0.027*
C34	−0.2063 (2)	0.5053 (2)	0.45638 (8)	0.0259 (4)
H34	−0.2536	0.5631	0.4744	0.031*
C35	−0.1418 (2)	0.39635 (19)	0.48281 (8)	0.0238 (4)
H35	−0.1481	0.385	0.5178	0.029*
C36	−0.07033 (19)	0.30674 (18)	0.45864 (7)	0.0188 (4)
H36	−0.0297	0.2348	0.4762	0.023*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni	0.01316 (12)	0.01008 (12)	0.01152 (12)	−0.00039 (8)	0.00022 (8)	−0.00009 (8)
O1	0.0171 (6)	0.0140 (6)	0.0144 (6)	−0.0029 (5)	0.0012 (5)	−0.0006 (5)
O2	0.0342 (8)	0.0280 (8)	0.0161 (7)	−0.0136 (6)	0.0073 (6)	−0.0065 (6)
O3	0.0170 (6)	0.0146 (6)	0.0131 (6)	0.0001 (5)	0.0003 (5)	−0.0006 (5)
O4	0.0168 (6)	0.0192 (7)	0.0169 (6)	0.0037 (5)	−0.0048 (5)	−0.0056 (5)
N1	0.0147 (7)	0.0080 (7)	0.0145 (7)	0.0008 (5)	0.0005 (5)	−0.0006 (5)
N11	0.0161 (7)	0.0153 (7)	0.0123 (7)	−0.0005 (6)	0.0005 (6)	0.0018 (6)
N12	0.0188 (8)	0.0166 (8)	0.0158 (8)	−0.0018 (6)	0.0010 (6)	0.0014 (6)
N13	0.0197 (8)	0.0198 (8)	0.0165 (8)	−0.0035 (6)	0.0037 (6)	0.0041 (6)
N21	0.0144 (7)	0.0131 (7)	0.0151 (7)	−0.0004 (6)	−0.0006 (6)	−0.0011 (6)
N22	0.0148 (7)	0.0131 (7)	0.0172 (8)	0.0008 (6)	0.0004 (6)	0.0006 (6)
N23	0.0158 (7)	0.0136 (7)	0.0174 (8)	0.0026 (6)	−0.0013 (6)	0.0016 (6)
N31	0.0154 (7)	0.0134 (7)	0.0129 (7)	0.0005 (6)	0.0001 (6)	0.0011 (6)
N32	0.0193 (8)	0.0139 (8)	0.0171 (7)	0.0014 (6)	0.0006 (6)	0.0031 (6)
N33	0.0215 (8)	0.0148 (8)	0.0191 (8)	0.0037 (6)	0.0002 (6)	0.0053 (6)
C1	0.0183 (9)	0.0103 (8)	0.0158 (8)	0.0002 (7)	0.0026 (7)	0.0002 (7)
C2	0.0249 (10)	0.0202 (10)	0.0192 (9)	−0.0034 (8)	0.0073 (8)	−0.0020 (8)
C3	0.0206 (10)	0.0241 (10)	0.0274 (10)	−0.0088 (8)	0.0079 (8)	−0.0043 (8)
C4	0.0168 (9)	0.0175 (9)	0.0223 (10)	−0.0031 (7)	−0.0009 (7)	−0.0053 (8)
C5	0.0162 (8)	0.0083 (8)	0.0166 (9)	0.0018 (6)	−0.0011 (7)	−0.0016 (7)
C6	0.0213 (9)	0.0111 (8)	0.0147 (9)	−0.0008 (7)	0.0015 (7)	−0.0014 (7)
C7	0.0154 (8)	0.0089 (8)	0.0153 (8)	0.0046 (6)	−0.0005 (7)	−0.0001 (6)
C11	0.0161 (8)	0.0131 (8)	0.0158 (8)	0.0001 (7)	0.0015 (7)	−0.0020 (7)
C12	0.0201 (9)	0.0174 (9)	0.0172 (9)	−0.0007 (7)	0.0038 (7)	−0.0012 (7)
C13	0.0182 (9)	0.0302 (11)	0.0289 (11)	−0.0071 (8)	0.0064 (8)	−0.0021 (9)
C14	0.0152 (9)	0.0356 (12)	0.0289 (11)	−0.0026 (8)	−0.0015 (8)	−0.0074 (9)
C15	0.0241 (10)	0.0345 (12)	0.0177 (9)	0.0029 (9)	−0.0039 (8)	−0.0018 (9)
C16	0.0217 (9)	0.0229 (10)	0.0155 (9)	0.0019 (8)	0.0032 (7)	0.0002 (7)
C21	0.0155 (8)	0.0116 (8)	0.0161 (8)	−0.0004 (6)	0.0039 (7)	0.0002 (7)
C22	0.0140 (8)	0.0140 (9)	0.0190 (9)	−0.0015 (7)	0.0032 (7)	0.0015 (7)
C23	0.0233 (10)	0.0130 (9)	0.0273 (10)	0.0038 (7)	0.0042 (8)	0.0004 (8)
C24	0.0300 (11)	0.0122 (9)	0.0314 (11)	−0.0002 (8)	0.0072 (9)	−0.0048 (8)
C25	0.0256 (10)	0.0197 (10)	0.0188 (9)	−0.0050 (8)	0.0035 (7)	−0.0059 (8)
C26	0.0200 (9)	0.0162 (9)	0.0175 (9)	−0.0015 (7)	0.0011 (7)	−0.0001 (7)
C31	0.0121 (8)	0.0107 (8)	0.0200 (9)	−0.0012 (6)	0.0013 (7)	−0.0016 (7)

C32	0.0153 (8)	0.0140 (9)	0.0210 (9)	−0.0011 (7)	0.0004 (7)	0.0001 (7)
C33	0.0196 (9)	0.0135 (9)	0.0352 (11)	0.0029 (7)	0.0037 (8)	−0.0030 (8)
C34	0.0207 (10)	0.0215 (10)	0.0371 (12)	−0.0003 (8)	0.0099 (8)	−0.0114 (9)
C35	0.0223 (10)	0.0293 (11)	0.0208 (10)	−0.0034 (8)	0.0068 (8)	−0.0049 (8)
C36	0.0187 (9)	0.0192 (9)	0.0185 (9)	0.0002 (7)	0.0032 (7)	0.0008 (7)

Geometric parameters (Å, º)

Ni—N1	1.9922 (15)	N32—N33	1.336 (2)
Ni—N11	2.0489 (15)	N33—C32	1.355 (2)
Ni—N31	2.0788 (14)	N33—H33	0.86
Ni—N21	2.0879 (15)	C11—C12	1.393 (3)
Ni—O1	2.1124 (12)	C11—C16	1.406 (2)
Ni—O3	2.1802 (12)	C12—C13	1.404 (3)
O1—C6	1.265 (2)	C13—C14	1.369 (3)
O2—C6	1.245 (2)	C13—H13A	0.93
O3—C7	1.270 (2)	C14—C15	1.413 (3)
O4—C7	1.246 (2)	C14—H14	0.93
N1—C1	1.330 (2)	C15—C16	1.375 (3)
N1—C5	1.335 (2)	C15—H15	0.93
C1—C2	1.386 (3)	C16—H16	0.93
C1—C6	1.519 (2)	C21—C22	1.395 (2)
C2—C3	1.389 (3)	C21—C26	1.408 (2)
C2—H2	0.93	C22—C23	1.404 (3)
C3—C4	1.390 (3)	C23—C24	1.369 (3)
C3—H3	0.93	C23—H23A	0.93
C4—C5	1.386 (3)	C24—C25	1.412 (3)
C4—H4	0.93	C24—H24	0.93
C5—C7	1.514 (2)	C25—C26	1.379 (3)
N11—N12	1.310 (2)	C25—H25	0.93
N11—C11	1.373 (2)	C26—H26	0.93
N12—N13	1.334 (2)	C31—C32	1.395 (2)
N13—C12	1.361 (2)	C31—C36	1.407 (3)
N13—H13	0.86	C32—C33	1.403 (3)
N21—N22	1.311 (2)	C33—C34	1.373 (3)
N21—C21	1.379 (2)	C33—H33A	0.93
N22—N23	1.339 (2)	C34—C35	1.417 (3)
N23—C22	1.360 (2)	C34—H34	0.93
N23—H23	0.86	C35—C36	1.375 (3)
N31—N32	1.318 (2)	C35—H35	0.93
N31—C31	1.379 (2)	C36—H36	0.93
N1—Ni—N11	177.23 (6)	O1—C6—C1	116.21 (15)
N1—Ni—N31	94.80 (6)	O4—C7—O3	125.12 (16)
N11—Ni—N31	87.68 (6)	O4—C7—C5	118.81 (16)
N1—Ni—N21	90.87 (6)	O3—C7—C5	116.06 (14)
N11—Ni—N21	86.73 (6)	N11—C11—C12	107.38 (15)
N31—Ni—N21	173.43 (6)	N11—C11—C16	131.01 (17)

N1—Ni—O1	78.39 (5)	C12—C11—C16	121.61 (17)
N11—Ni—O1	100.29 (5)	N13—C12—C11	104.28 (16)
N31—Ni—O1	92.69 (5)	N13—C12—C13	134.03 (18)
N21—Ni—O1	91.70 (5)	C11—C12—C13	121.68 (17)
N1—Ni—O3	76.44 (5)	C14—C13—C12	116.40 (18)
N11—Ni—O3	104.89 (5)	C14—C13—H13A	121.8
N31—Ni—O3	88.60 (5)	C12—C13—H13A	121.8
N21—Ni—O3	89.51 (5)	C13—C14—C15	122.15 (18)
O1—Ni—O3	154.82 (5)	C13—C14—H14	118.9
C6—O1—Ni	114.54 (11)	C15—C14—H14	118.9
C7—O3—Ni	114.33 (11)	C16—C15—C14	121.87 (18)
C1—N1—C5	121.51 (15)	C16—C15—H15	119.1
C1—N1—Ni	117.99 (11)	C14—C15—H15	119.1
C5—N1—Ni	120.31 (12)	C15—C16—C11	116.30 (18)
N12—N11—C11	109.24 (14)	C15—C16—H16	121.8
N12—N11—Ni	119.77 (11)	C11—C16—H16	121.8
C11—N11—Ni	130.91 (12)	N21—C21—C22	107.32 (15)
N11—N12—N13	107.98 (14)	N21—C21—C26	131.67 (16)
N12—N13—C12	111.12 (15)	C22—C21—C26	121.01 (17)
N12—N13—H13	124.4	N23—C22—C21	104.39 (15)
C12—N13—H13	124.4	N23—C22—C23	133.06 (17)
N22—N21—C21	109.13 (14)	C21—C22—C23	122.55 (17)
N22—N21—Ni	121.17 (11)	C24—C23—C22	115.71 (17)
C21—N21—Ni	129.48 (11)	C24—C23—H23A	122.1
N21—N22—N23	108.00 (14)	C22—C23—H23A	122.1
N22—N23—C22	111.15 (14)	C23—C24—C25	122.55 (18)
N22—N23—H23	124.4	C23—C24—H24	118.7
C22—N23—H23	124.4	C25—C24—H24	118.7
N32—N31—C31	109.03 (14)	C26—C25—C24	121.83 (18)
N32—N31—Ni	122.54 (11)	C26—C25—H25	119.1
C31—N31—Ni	128.43 (12)	C24—C25—H25	119.1
N31—N32—N33	107.85 (14)	C25—C26—C21	116.34 (17)
N32—N33—C32	111.32 (15)	C25—C26—H26	121.8
N32—N33—H33	124.3	C21—C26—H26	121.8
C32—N33—H33	124.3	N31—C31—C32	107.14 (15)
N1—C1—C2	121.15 (16)	N31—C31—C36	131.97 (16)
N1—C1—C6	112.85 (15)	C32—C31—C36	120.90 (16)
C2—C1—C6	125.95 (16)	N33—C32—C31	104.65 (16)
C1—C2—C3	118.00 (17)	N33—C32—C33	132.73 (17)
C1—C2—H2	121	C31—C32—C33	122.62 (18)
C3—C2—H2	121	C34—C33—C32	116.12 (18)
C2—C3—C4	120.29 (17)	C34—C33—H33A	121.9
C2—C3—H3	119.9	C32—C33—H33A	121.9
C4—C3—H3	119.9	C33—C34—C35	121.57 (18)
C5—C4—C3	118.21 (17)	C33—C34—H34	119.2
C5—C4—H4	120.9	C35—C34—H34	119.2
C3—C4—H4	120.9	C36—C35—C34	122.46 (19)
N1—C5—C4	120.81 (16)	C36—C35—H35	118.8

N1—C5—C7	112.55 (15)	C34—C35—H35	118.8
C4—C5—C7	126.64 (16)	C35—C36—C31	116.32 (17)
O2—C6—O1	126.64 (16)	C35—C36—H36	121.8
O2—C6—C1	117.12 (16)	C31—C36—H36	121.8
N1—Ni—O1—C6	1.26 (12)	C3—C4—C5—C7	−179.49 (17)
N11—Ni—O1—C6	−176.26 (12)	Ni—O1—C6—O2	176.65 (15)
N31—Ni—O1—C6	95.61 (12)	Ni—O1—C6—C1	−1.33 (19)
N21—Ni—O1—C6	−89.28 (12)	N1—C1—C6—O2	−177.61 (16)
O3—Ni—O1—C6	3.19 (19)	C2—C1—C6—O2	−0.1 (3)
N1—Ni—O3—C7	−4.68 (11)	N1—C1—C6—O1	0.6 (2)
N11—Ni—O3—C7	172.82 (11)	C2—C1—C6—O1	178.12 (17)
N31—Ni—O3—C7	−99.96 (12)	Ni—O3—C7—O4	−176.72 (13)
N21—Ni—O3—C7	86.33 (12)	Ni—O3—C7—C5	3.96 (18)
O1—Ni—O3—C7	−6.62 (18)	N1—C5—C7—O4	−179.60 (15)
N31—Ni—N1—C1	−92.71 (13)	C4—C5—C7—O4	0.6 (3)
N21—Ni—N1—C1	90.61 (13)	N1—C5—C7—O3	−0.2 (2)
O1—Ni—N1—C1	−0.95 (12)	C4—C5—C7—O3	179.95 (17)
O3—Ni—N1—C1	179.90 (13)	N12—N11—C11—C12	0.1 (2)
N31—Ni—N1—C5	92.16 (13)	Ni—N11—C11—C12	−176.43 (12)
N21—Ni—N1—C5	−84.52 (13)	N12—N11—C11—C16	−178.86 (18)
O1—Ni—N1—C5	−176.08 (13)	Ni—N11—C11—C16	4.6 (3)
O3—Ni—N1—C5	4.77 (12)	N12—N13—C12—C11	−0.7 (2)
N31—Ni—N11—N12	−115.75 (13)	N12—N13—C12—C13	178.0 (2)
N21—Ni—N11—N12	60.80 (13)	N11—C11—C12—N13	0.3 (2)
O1—Ni—N11—N12	151.94 (13)	C16—C11—C12—N13	179.44 (16)
O3—Ni—N11—N12	−27.82 (14)	N11—C11—C12—C13	−178.55 (17)
N31—Ni—N11—C11	60.49 (16)	C16—C11—C12—C13	0.5 (3)
N21—Ni—N11—C11	−122.96 (16)	N13—C12—C13—C14	−179.0 (2)
O1—Ni—N11—C11	−31.82 (16)	C11—C12—C13—C14	−0.5 (3)
O3—Ni—N11—C11	148.42 (15)	C12—C13—C14—C15	0.4 (3)
C11—N11—N12—N13	−0.54 (19)	C13—C14—C15—C16	−0.3 (3)
Ni—N11—N12—N13	176.45 (11)	C14—C15—C16—C11	0.3 (3)
N11—N12—N13—C12	0.8 (2)	N11—C11—C16—C15	178.41 (19)
N1—Ni—N21—N22	70.61 (13)	C12—C11—C16—C15	−0.4 (3)
N11—Ni—N21—N22	−110.76 (13)	N22—N21—C21—C22	−0.18 (19)
O1—Ni—N21—N22	149.03 (13)	Ni—N21—C21—C22	−174.72 (12)
O3—Ni—N21—N22	−5.82 (13)	N22—N21—C21—C26	179.94 (18)
N1—Ni—N21—C21	−115.42 (15)	Ni—N21—C21—C26	5.4 (3)
N11—Ni—N21—C21	63.20 (15)	N22—N23—C22—C21	−1.28 (19)
O1—Ni—N21—C21	−37.01 (15)	N22—N23—C22—C23	178.84 (19)
O3—Ni—N21—C21	168.14 (15)	N21—C21—C22—N23	0.87 (19)
C21—N21—N22—N23	−0.61 (19)	C26—C21—C22—N23	−179.24 (16)
Ni—N21—N22—N23	174.46 (11)	N21—C21—C22—C23	−179.24 (17)
N21—N22—N23—C22	1.21 (19)	C26—C21—C22—C23	0.7 (3)
N1—Ni—N31—N32	62.76 (13)	N23—C22—C23—C24	179.59 (19)
N11—Ni—N31—N32	−116.01 (13)	C21—C22—C23—C24	−0.3 (3)
O1—Ni—N31—N32	−15.81 (13)	C22—C23—C24—C25	−0.2 (3)

O3—Ni—N31—N32	139.03 (13)	C23—C24—C25—C26	0.3 (3)
N1—Ni—N31—C31	−116.67 (15)	C24—C25—C26—C21	0.0 (3)
N11—Ni—N31—C31	64.56 (15)	N21—C21—C26—C25	179.34 (18)
O1—Ni—N31—C31	164.76 (14)	C22—C21—C26—C25	−0.5 (3)
O3—Ni—N31—C31	−40.40 (14)	N32—N31—C31—C32	−0.92 (19)
C31—N31—N32—N33	0.28 (19)	Ni—N31—C31—C32	178.57 (12)
Ni—N31—N32—N33	−179.25 (11)	N32—N31—C31—C36	178.63 (18)
N31—N32—N33—C32	0.5 (2)	Ni—N31—C31—C36	−1.9 (3)
C5—N1—C1—C2	−2.1 (3)	N32—N33—C32—C31	−1.0 (2)
Ni—N1—C1—C2	−177.12 (13)	N32—N33—C32—C33	178.98 (19)
C5—N1—C1—C6	175.63 (15)	N31—C31—C32—N33	1.17 (19)
Ni—N1—C1—C6	0.56 (19)	C36—C31—C32—N33	−178.44 (16)
N1—C1—C2—C3	1.9 (3)	N31—C31—C32—C33	−178.85 (16)
C6—C1—C2—C3	−175.43 (17)	C36—C31—C32—C33	1.5 (3)
C1—C2—C3—C4	−0.5 (3)	N33—C32—C33—C34	179.46 (19)
C2—C3—C4—C5	−0.8 (3)	C31—C32—C33—C34	−0.5 (3)
C1—N1—C5—C4	0.7 (3)	C32—C33—C34—C35	−0.2 (3)
Ni—N1—C5—C4	175.64 (13)	C33—C34—C35—C36	−0.1 (3)
C1—N1—C5—C7	−179.13 (15)	C34—C35—C36—C31	1.1 (3)
Ni—N1—C5—C7	−4.18 (19)	N31—C31—C36—C35	178.75 (18)
C3—C4—C5—N1	0.7 (3)	C32—C31—C36—C35	−1.8 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N13—H13···O3^{i}	0.86	1.96	2.7777 (19)	160
N23—H23···O4^{ii}	0.86	1.88	2.6612 (18)	151
N33—H33···O2^{iii}	0.86	1.78	2.617 (2)	165

Symmetry codes: (i) −*x*, −*y*, −*z*+1; (ii) −*x*+1, −*y*, −*z*+1; (iii) −*x*, *y*+1/2, −*z*+1/2.