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# (Pyridine-2,6-dicarboxylato-$\kappa^3O,N,O'$)(2,2′:6′,2″-terpyridine-$\kappa^3N,N',N''$)nickel(II) dimethylformamide monosolvate monohydrate

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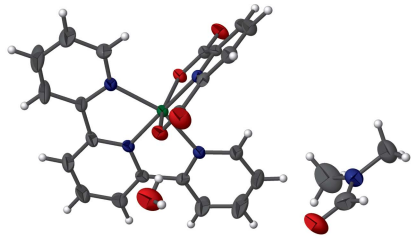
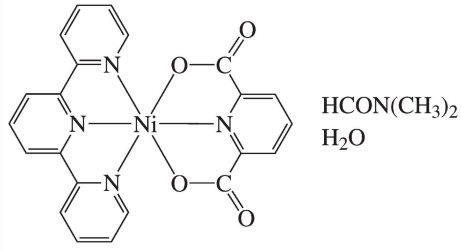
**Structural data**: full structural data are available from iucrdata.iucr.org

In the title complex, $[Ni(C_7H_3NO_4)(C_{15}H_{11}N_3)]\cdot C_3H_7NO\cdot H_2O$, the $Ni^{II}$ ion is six-coordinated within an octahedral geometry defined by three N atoms of the 2,2′:6′,2″-terpyridine ligand, and two O atoms and the N atom of the pyridine-2,6-dicarboxylate di-anion. In the crystal, the complex molecules are stacked in columns parallel to the *a* axis being connected by $\pi$–$\pi$ stacking [closest inter-centroid separation between pyridyl rings = 3.669 (3) Å]. The connections between columns and solvent molecules to sustain a three-dimensional architecture are of the type water-O—H···O(carbonyl) and pyridyl-, methyl-C—H···O(carbonyl).

**3D view**



**Chemical scheme**




## Structure description

With reference to the title complex, $[Ni(dipic)(terpy)]\cdot C_3H_7NO\cdot H_2O$ (dipic = pyridine-2,6-dicarboxylate; terpy = 2,2′:6′,2"-terpyridine), the crystal structures of related $Ni^{II}$ complexes $[Ni(dipic)(H_2O)_2]$ (Liu *et al.*, 2006), [Ni(dipic)(1,10-phenanthroline)($H_2O$)]·$H_2O$ (Ramadevi *et al.*, 2006) and $[NiCl(terpy)(H_2O)_2]Cl\cdot H_2O$ (Cortés *et al.*, 1985) have been determined previously.

In the title complex, the central $Ni^{II}$ ion is six-coordinated in a distorted octahedral coordination geometry defined by three N atoms from the tridentate terpy ligand, and two O atoms and the N atom from the dipic di-anion (Fig. 1). The tight O—Ni—N and N—Ni—N chelating angles of O—Ni1—N1 = 78.07 (10) and 78.18 (11)°, and N—Ni1—N = 78.25 (11) and 78.67 (11)° contribute to the distortion of the octahedron. The apical N1—Ni1—N3, N2—Ni1—N4 and O1—Ni1—O3 bond angles are 177.95 (12), 156.92 (10) and 156.26 (9)°, respectively. The Ni—N bonds [1.963 (2)-2.091 (3) Å] are slightly shorter than the Ni—O bonds [2.126 (2) and 2.131 (2) Å]. The two outer pyridyl rings of the

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O6—H6$A$···O2$^{i}$ | 0.71 (5) | 2.21 (5) | 2.907 (5) | 172 (5) |
| O6—H6$B$···O4 | 0.74 (6) | 2.14 (6) | 2.881 (5) | 175 (7) |
| C2—H2···O2$^{ii}$ | 0.94 | 2.49 | 3.254 (4) | 138 |
| C8—H8···O5$^{iii}$ | 0.94 | 2.47 | 3.133 (5) | 128 |
| C9—H9···O2$^{iv}$ | 0.94 | 2.55 | 3.465 (5) | 163 |
| C25—H25$C$···O4$^{v}$ | 0.97 | 2.45 | 3.361 (6) | 157 |

Symmetry codes: (i) $x+1, y, z+1$; (ii) $-x, -y, -z$; (iii) $x, y, z-1$; (iv) $x+1, y, z$; (v) $x-1, y, z$.

terpy ligand are located approximately parallel to the central pyridyl ring, making dihedral angles of 4.7 (3) and 2.3 (3)°. The dihedral angle between the least-squares planes of dipic and terpy ligands is 83.23 (3)°.

In the crystal, the complex molecules are stacked in columns parallel to the *a* axis. Within the columns, numerous intermolecular $\pi$–$\pi$ interactions between adjacent six-membered rings are present. For *Cg*1 (the centroid of ring N2/C8–C12) and *Cg*2$^{i}$ [the centroid of ring N3/C13–C17; symmetry code: (i) $x, \frac{1}{2}-y, -\frac{1}{2}+z$], the centroid-centroid distance is 3.669 (3) Å and the dihedral angle between the ring planes is 9.6 (2)° (Spek, 2009). The complex and solvent molecules display intermolecular O—H···O and C—H···O hydrogen bonds (Table 1) to stabilize the three-dimensional packing.

## Synthesis and crystallization

To a solution of $Ni(CH_3CO_2)_2{\cdot}4H_2O$ (0.2605 g, 1.047 mmol) in MeOH (20 ml) were added pyridine-2,6-dicarboxylic acid (0.1750 g, 1.047 mmol) and 2,2′:6′,2"-terpyridine (0.2444 g, 1.048 mmol), followed by stirring for 1 h at room temperature. The formed precipitate was separated by filtration, washed with MeOH and acetone, and dried at 323 K, to give a pale-green powder (0.3580 g). Green crystals suitable for X-ray analysis were obtained by the slow evaporation of its *N*,*N*-dimethylformamide solution at 333 K.

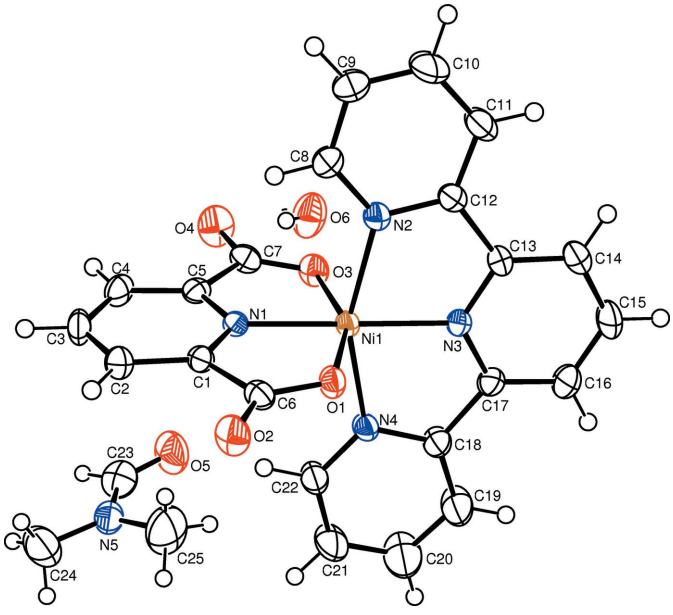



**Figure 1**
The molecular structure of the title compound showing the atom labelling and displacement ellipsoids drawn at the 50% probability level for non-H atoms.

**Table 2**
Experimental details.

| | |
|---|---|
| Crystal data | |
| Chemical formula | $[Ni(C_7H_3NO_4)(C_{15}H_{11}N_3)]{\cdot}C_3H_7NO{\cdot}H2O$ |
| $M_r$ | 548.19 |
| Crystal system, space group | Monoclinic, $P2_1/c$ |
| Temperature (K) | 223 |
| $a, b, c$ (Å) | 8.6188 (4), 27.5899 (13), 10.7559 (5) |
| $\beta$ (°) | 111.3813 (11) |
| $V$ (Å$^3$) | 2381.62 (19) |
| $Z$ | 4 |
| Radiation type | Mo $K\alpha$ |
| $\mu$ (mm$^{-1}$) | 0.87 |
| Crystal size (mm) | 0.16 × 0.13 × 0.09 |
| Data collection | |
| Diffractometer | PHOTON 100 CMOS detector |
| Absorption correction | Multi-scan (*SADABS*; Bruker, 2016) |
| $T_{min}$, $T_{max}$ | 0.683, 0.745 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 66113, 4729, 3085 |
| $R_{int}$ | 0.176 |
| Refinement | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.051, 0.105, 1.04 |
| No. of reflections | 4729 |
| No. of parameters | 344 |
| H-atom treatment | H atoms treated by a mixture of independent and constrained refinement |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.42, −0.39 |

Computer programs: *APEX2* and *SAINT* (Bruker, 2016), *SHELXL2014* (Sheldrick, 2015) and *ORTEP-3 for Windows* (Farrugia, 1997).

## Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The highest peak (0.42 e Å$^{-3}$) and the deepest hole (−0.39 e Å$^{-3}$) in the final difference Fourier map are located 0.88 Å and 0.29 Å, respectively, from the C20 atom.

## Acknowledgements

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## Funding information

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# full crystallographic data

*IUCrData* (2019). **4**, x191035 [https://doi.org/10.1107/S2414314619010356]

## (Pyridine-2,6-dicarboxylato-$\kappa^3O,N,O'$)(2,2′:6′,2″- terpyridine-$\kappa^3N,N',N''$)nickel(II) dimethylformamide monosolvate monohydrate

**Kwang Ha**

**(Pyridine-2,6-dicarboxylato-$\kappa^3O,N,O'$)(2,2′:6′,2″-terpyridine-$\kappa^3N,N',N''$)nickel(II) dimethylformamide monosolvate monohydrate**

*Crystal data*

$[Ni(C_7H_3NO_4)(C_{15}H_{11}N_3)]\cdot C_3H_7NO\cdot H2O$
$M_r$ = 548.19
Monoclinic, $P2_1/c$
$a$ = 8.6188 (4) Å
$b$ = 27.5899 (13) Å
$c$ = 10.7559 (5) Å
$\beta$ = 111.3813 (11)°
$V$ = 2381.62 (19) Å$^3$
$Z$ = 4
$F(000)$ = 1136
$D_x$ = 1.529 Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda$ = 0.71073 Å
Cell parameters from 7834 reflections
$\theta$ = 2.5–25.4°
$\mu$ = 0.87 mm$^{-1}$
$T$ = 223 K
Block, green
0.16 × 0.13 × 0.09 mm

*Data collection*

PHOTON 100 CMOS detector diffractometer
Radiation source: sealed tube
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (SADABS; Bruker, 2016)
$T_{min}$ = 0.683, $T_{max}$ = 0.745
66113 measured reflections
4729 independent reflections
3085 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.176
$\theta_{max}$ = 26.1°, $\theta_{min}$ = 2.2°
$h$ = −10→10
$k$ = −34→34
$l$ = −13→13

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.105
$S$ = 1.04
4729 reflections
344 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0327P)^2 + 2.9447P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.42 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.39 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**. Hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms: C—H = 0.94 Å (CH) or 0.97 Å ($CH_3$), and $U_{iso}$(H) = 1.2$U_{eq}$(C) or 1.5$U_{eq}$(methyl C). The H atoms of the solvent water molecule were localized from Fourier difference maps and refined with isotropic thermal parameters.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Ni1 | 0.36206 (5) | 0.16002 (2) | 0.23583 (4) | 0.02137 (13) |
| O1 | 0.1553 (3) | 0.14429 (8) | 0.0586 (2) | 0.0267 (6) |
| O2 | −0.0024 (3) | 0.08186 (9) | −0.0495 (2) | 0.0378 (6) |
| O3 | 0.5679 (3) | 0.14403 (9) | 0.4142 (2) | 0.0309 (6) |
| O4 | 0.7196 (3) | 0.08116 (10) | 0.5247 (3) | 0.0467 (7) |
| N1 | 0.3587 (3) | 0.08889 (9) | 0.2374 (3) | 0.0203 (6) |
| N2 | 0.5267 (3) | 0.17374 (10) | 0.1390 (3) | 0.0260 (7) |
| N3 | 0.3713 (3) | 0.23164 (9) | 0.2408 (3) | 0.0233 (6) |
| N4 | 0.2007 (3) | 0.17652 (10) | 0.3353 (3) | 0.0259 (7) |
| C1 | 0.2379 (4) | 0.06562 (12) | 0.1423 (3) | 0.0224 (8) |
| C2 | 0.2282 (5) | 0.01548 (13) | 0.1436 (4) | 0.0304 (9) |
| H2 | 0.1413 | −0.0011 | 0.0780 | 0.037* |
| C3 | 0.3494 (5) | −0.00932 (12) | 0.2437 (4) | 0.0347 (9) |
| H3 | 0.3457 | −0.0433 | 0.2467 | 0.042* |
| C4 | 0.4770 (5) | 0.01570 (13) | 0.3402 (4) | 0.0313 (9) |
| H4 | 0.5614 | −0.0011 | 0.4076 | 0.038* |
| C5 | 0.4770 (4) | 0.06553 (12) | 0.3350 (3) | 0.0239 (8) |
| C6 | 0.1188 (4) | 0.09963 (13) | 0.0402 (3) | 0.0262 (8) |
| C7 | 0.6005 (4) | 0.09928 (14) | 0.4347 (4) | 0.0295 (8) |
| C8 | 0.6049 (5) | 0.14092 (14) | 0.0920 (4) | 0.0349 (9) |
| H8 | 0.5753 | 0.1081 | 0.0923 | 0.042* |
| C9 | 0.7263 (6) | 0.15281 (16) | 0.0435 (5) | 0.0611 (14) |
| H9 | 0.7804 | 0.1288 | 0.0121 | 0.073* |
| C10 | 0.7662 (7) | 0.20063 (18) | 0.0422 (7) | 0.099 (2) |
| H10 | 0.8502 | 0.2099 | 0.0106 | 0.119* |
| C11 | 0.6846 (6) | 0.23548 (16) | 0.0869 (6) | 0.0767 (18) |
| H11 | 0.7097 | 0.2685 | 0.0837 | 0.092* |
| C12 | 0.5658 (4) | 0.22089 (13) | 0.1361 (4) | 0.0328 (9) |
| C13 | 0.4719 (4) | 0.25468 (12) | 0.1902 (4) | 0.0303 (9) |
| C14 | 0.4840 (5) | 0.30440 (14) | 0.1940 (4) | 0.0451 (11) |
| H14 | 0.5530 | 0.3206 | 0.1571 | 0.054* |
| C15 | 0.3911 (5) | 0.33003 (13) | 0.2541 (5) | 0.0506 (12) |
| H15 | 0.3992 | 0.3640 | 0.2599 | 0.061* |
| C16 | 0.2876 (5) | 0.30606 (14) | 0.3051 (4) | 0.0423 (10) |
| H16 | 0.2230 | 0.3233 | 0.3441 | 0.051* |
| C17 | 0.2804 (4) | 0.25613 (12) | 0.2978 (3) | 0.0273 (8) |

| | | | | |
|---|---|---|---|---|
| C18 | 0.1788 (5) | 0.22411 (13) | 0.3493 (4) | 0.0311 (9) |
| C19 | 0.0730 (7) | 0.24084 (16) | 0.4088 (6) | 0.0727 (17) |
| H19 | 0.0593 | 0.2742 | 0.4188 | 0.087* |
| C20 | −0.0130 (8) | 0.20715 (19) | 0.4536 (7) | 0.100 (2) |
| H20 | −0.0847 | 0.2177 | 0.4962 | 0.120* |
| C21 | 0.0047 (6) | 0.15893 (17) | 0.4370 (5) | 0.0616 (14) |
| H21 | −0.0564 | 0.1359 | 0.4647 | 0.074* |
| C22 | 0.1139 (5) | 0.14506 (14) | 0.3787 (4) | 0.0364 (10) |
| H22 | 0.1290 | 0.1118 | 0.3685 | 0.044* |
| O5 | 0.4038 (4) | 0.05868 (11) | 0.8998 (3) | 0.0635 (9) |
| N5 | 0.1913 (4) | 0.01358 (12) | 0.7603 (3) | 0.0400 (8) |
| C23 | 0.3260 (6) | 0.02115 (17) | 0.8683 (4) | 0.0503 (11) |
| H23 | 0.3651 | −0.0053 | 0.9265 | 0.060* |
| C24 | 0.1119 (6) | −0.03242 (17) | 0.7291 (5) | 0.0701 (15) |
| H24A | −0.0072 | −0.0284 | 0.7054 | 0.105* |
| H24B | 0.1553 | −0.0536 | 0.8060 | 0.105* |
| H24C | 0.1336 | −0.0466 | 0.6544 | 0.105* |
| C25 | 0.1256 (7) | 0.05288 (19) | 0.6690 (6) | 0.0858 (18) |
| H25A | 0.1672 | 0.0507 | 0.5967 | 0.129* |
| H25B | 0.1602 | 0.0834 | 0.7156 | 0.129* |
| H25C | 0.0049 | 0.0511 | 0.6331 | 0.129* |
| O6 | 0.8679 (5) | 0.15110 (13) | 0.7334 (5) | 0.0590 (10) |
| H6A | 0.896 (6) | 0.1358 (18) | 0.790 (5) | 0.052 (19)* |
| H6B | 0.825 (8) | 0.133 (2) | 0.681 (6) | 0.10 (3)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Ni1 | 0.0231 (2) | 0.0176 (2) | 0.0246 (2) | −0.0026 (2) | 0.01005 (17) | −0.0023 (2) |
| O1 | 0.0277 (13) | 0.0196 (13) | 0.0297 (14) | −0.0020 (10) | 0.0067 (11) | −0.0014 (10) |
| O2 | 0.0318 (15) | 0.0330 (16) | 0.0351 (15) | −0.0064 (12) | −0.0038 (13) | −0.0066 (12) |
| O3 | 0.0301 (14) | 0.0295 (15) | 0.0282 (14) | −0.0047 (11) | 0.0048 (12) | −0.0050 (11) |
| O4 | 0.0410 (17) | 0.0473 (18) | 0.0350 (16) | 0.0014 (14) | −0.0061 (14) | 0.0063 (14) |
| N1 | 0.0212 (14) | 0.0200 (14) | 0.0211 (14) | 0.0003 (13) | 0.0096 (12) | 0.0015 (13) |
| N2 | 0.0278 (16) | 0.0220 (17) | 0.0313 (17) | −0.0016 (12) | 0.0145 (14) | −0.0019 (13) |
| N3 | 0.0244 (15) | 0.0189 (14) | 0.0280 (15) | −0.0009 (13) | 0.0112 (13) | −0.0031 (13) |
| N4 | 0.0280 (16) | 0.0218 (16) | 0.0306 (17) | −0.0042 (13) | 0.0141 (14) | −0.0042 (13) |
| C1 | 0.0236 (18) | 0.0212 (19) | 0.0246 (19) | −0.0027 (15) | 0.0113 (16) | −0.0056 (15) |
| C2 | 0.033 (2) | 0.024 (2) | 0.035 (2) | −0.0027 (17) | 0.0129 (18) | −0.0049 (17) |
| C3 | 0.047 (2) | 0.0163 (18) | 0.046 (2) | 0.0005 (19) | 0.023 (2) | 0.0017 (19) |
| C4 | 0.034 (2) | 0.028 (2) | 0.032 (2) | 0.0094 (17) | 0.0125 (18) | 0.0100 (17) |
| C5 | 0.0254 (19) | 0.027 (2) | 0.0228 (19) | 0.0034 (15) | 0.0130 (16) | 0.0051 (15) |
| C6 | 0.027 (2) | 0.026 (2) | 0.028 (2) | −0.0055 (16) | 0.0120 (17) | −0.0041 (16) |
| C7 | 0.029 (2) | 0.034 (2) | 0.026 (2) | −0.0038 (18) | 0.0104 (18) | 0.0014 (18) |
| C8 | 0.039 (2) | 0.028 (2) | 0.045 (2) | 0.0015 (18) | 0.024 (2) | −0.0037 (18) |
| C9 | 0.074 (3) | 0.039 (3) | 0.104 (4) | 0.003 (2) | 0.072 (3) | −0.006 (3) |
| C10 | 0.120 (5) | 0.043 (3) | 0.205 (7) | −0.008 (3) | 0.143 (5) | −0.007 (4) |
| C11 | 0.095 (4) | 0.028 (3) | 0.157 (5) | −0.010 (3) | 0.106 (4) | −0.006 (3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C12 | 0.034 (2) | 0.024 (2) | 0.048 (2) | −0.0033 (17) | 0.026 (2) | −0.0026 (18) |
| C13 | 0.031 (2) | 0.0197 (19) | 0.043 (2) | −0.0033 (16) | 0.0162 (19) | 0.0010 (17) |
| C14 | 0.050 (3) | 0.026 (2) | 0.073 (3) | −0.0043 (19) | 0.039 (3) | 0.005 (2) |
| C15 | 0.062 (3) | 0.018 (2) | 0.084 (4) | −0.005 (2) | 0.041 (3) | −0.003 (2) |
| C16 | 0.050 (3) | 0.024 (2) | 0.064 (3) | 0.0024 (19) | 0.033 (2) | −0.008 (2) |
| C17 | 0.027 (2) | 0.023 (2) | 0.032 (2) | 0.0006 (15) | 0.0116 (17) | −0.0040 (16) |
| C18 | 0.040 (2) | 0.025 (2) | 0.036 (2) | −0.0011 (17) | 0.0229 (19) | −0.0053 (17) |
| C19 | 0.103 (4) | 0.031 (3) | 0.132 (5) | 0.002 (3) | 0.100 (4) | −0.005 (3) |
| C20 | 0.141 (5) | 0.049 (3) | 0.184 (7) | 0.005 (3) | 0.146 (6) | −0.002 (4) |
| C21 | 0.081 (3) | 0.038 (3) | 0.101 (4) | −0.007 (3) | 0.075 (3) | −0.003 (3) |
| C22 | 0.047 (2) | 0.025 (2) | 0.048 (3) | −0.0044 (18) | 0.030 (2) | −0.0031 (17) |
| O5 | 0.068 (2) | 0.046 (2) | 0.068 (2) | −0.0134 (17) | 0.0142 (18) | −0.0164 (17) |
| N5 | 0.041 (2) | 0.0323 (19) | 0.045 (2) | 0.0012 (16) | 0.0135 (18) | −0.0004 (16) |
| C23 | 0.061 (3) | 0.052 (3) | 0.041 (3) | 0.003 (2) | 0.022 (2) | −0.003 (2) |
| C24 | 0.071 (4) | 0.057 (3) | 0.090 (4) | −0.021 (3) | 0.039 (3) | −0.014 (3) |
| C25 | 0.067 (4) | 0.065 (4) | 0.099 (5) | 0.012 (3) | 0.000 (3) | 0.017 (3) |
| O6 | 0.063 (2) | 0.046 (2) | 0.053 (2) | 0.009 (2) | 0.0028 (18) | 0.003 (2) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Ni1—N1 | 1.963 (2) | C11—C12 | 1.373 (5) |
| Ni1—N3 | 1.978 (3) | C11—H11 | 0.9400 |
| Ni1—N2 | 2.078 (3) | C12—C13 | 1.486 (5) |
| Ni1—N4 | 2.091 (3) | C13—C14 | 1.375 (5) |
| Ni1—O1 | 2.126 (2) | C14—C15 | 1.391 (5) |
| Ni1—O3 | 2.131 (2) | C14—H14 | 0.9400 |
| O1—C6 | 1.269 (4) | C15—C16 | 1.375 (5) |
| O2—C6 | 1.236 (4) | C15—H15 | 0.9400 |
| O3—C7 | 1.268 (4) | C16—C17 | 1.380 (5) |
| O4—C7 | 1.232 (4) | C16—H16 | 0.9400 |
| N1—C1 | 1.329 (4) | C17—C18 | 1.485 (5) |
| N1—C5 | 1.333 (4) | C18—C19 | 1.372 (5) |
| N2—C8 | 1.333 (4) | C19—C20 | 1.380 (6) |
| N2—C12 | 1.347 (4) | C19—H19 | 0.9400 |
| N3—C17 | 1.340 (4) | C20—C21 | 1.358 (6) |
| N3—C13 | 1.340 (4) | C20—H20 | 0.9400 |
| N4—C22 | 1.336 (4) | C21—C22 | 1.362 (5) |
| N4—C18 | 1.343 (4) | C21—H21 | 0.9400 |
| C1—C2 | 1.386 (5) | C22—H22 | 0.9400 |
| C1—C6 | 1.523 (5) | O5—C23 | 1.213 (5) |
| C2—C3 | 1.377 (5) | N5—C23 | 1.326 (5) |
| C2—H2 | 0.9400 | N5—C24 | 1.423 (5) |
| C3—C4 | 1.390 (5) | N5—C25 | 1.433 (6) |
| C3—H3 | 0.9400 | C23—H23 | 0.9400 |
| C4—C5 | 1.376 (5) | C24—H24A | 0.9700 |
| C4—H4 | 0.9400 | C24—H24B | 0.9700 |
| C5—C7 | 1.523 (5) | C24—H24C | 0.9700 |
| C8—C9 | 1.369 (5) | C25—H25A | 0.9700 |

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| C8—H8 | 0.9400 | C25—H25B | 0.9700 |
| C9—C10 | 1.365 (6) | C25—H25C | 0.9700 |
| C9—H9 | 0.9400 | O6—H6A | 0.71 (5) |
| C10—C11 | 1.377 (6) | O6—H6B | 0.74 (6) |
| C10—H10 | 0.9400 | | |

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| N1—Ni1—N3 | 177.95 (12) | C9—C10—H10 | 119.7 |
| N1—Ni1—N2 | 101.62 (11) | C11—C10—H10 | 119.7 |
| N3—Ni1—N2 | 78.67 (11) | C12—C11—C10 | 118.5 (4) |
| N1—Ni1—N4 | 101.44 (11) | C12—C11—H11 | 120.7 |
| N3—Ni1—N4 | 78.25 (11) | C10—C11—H11 | 120.7 |
| N2—Ni1—N4 | 156.92 (10) | N2—C12—C11 | 121.4 (3) |
| N1—Ni1—O1 | 78.07 (10) | N2—C12—C13 | 114.8 (3) |
| N3—Ni1—O1 | 103.93 (10) | C11—C12—C13 | 123.8 (3) |
| N2—Ni1—O1 | 95.16 (10) | N3—C13—C14 | 120.9 (3) |
| N4—Ni1—O1 | 90.40 (10) | N3—C13—C12 | 112.8 (3) |
| N1—Ni1—O3 | 78.18 (11) | C14—C13—C12 | 126.3 (3) |
| N3—Ni1—O3 | 99.81 (11) | C13—C14—C15 | 118.1 (3) |
| N2—Ni1—O3 | 89.59 (10) | C13—C14—H14 | 121.0 |
| N4—Ni1—O3 | 94.29 (10) | C15—C14—H14 | 121.0 |
| O1—Ni1—O3 | 156.26 (9) | C16—C15—C14 | 120.5 (3) |
| C6—O1—Ni1 | 114.7 (2) | C16—C15—H15 | 119.7 |
| C7—O3—Ni1 | 114.7 (2) | C14—C15—H15 | 119.7 |
| C1—N1—C5 | 122.2 (3) | C15—C16—C17 | 118.7 (3) |
| C1—N1—Ni1 | 119.1 (2) | C15—C16—H16 | 120.7 |
| C5—N1—Ni1 | 118.7 (2) | C17—C16—H16 | 120.7 |
| C8—N2—C12 | 118.8 (3) | N3—C17—C16 | 120.5 (3) |
| C8—N2—Ni1 | 126.7 (2) | N3—C17—C18 | 113.1 (3) |
| C12—N2—Ni1 | 114.2 (2) | C16—C17—C18 | 126.4 (3) |
| C17—N3—C13 | 121.3 (3) | N4—C18—C19 | 121.7 (3) |
| C17—N3—Ni1 | 119.4 (2) | N4—C18—C17 | 114.4 (3) |
| C13—N3—Ni1 | 119.2 (2) | C19—C18—C17 | 123.8 (3) |
| C22—N4—C18 | 118.5 (3) | C18—C19—C20 | 118.0 (4) |
| C22—N4—Ni1 | 126.8 (2) | C18—C19—H19 | 121.0 |
| C18—N4—Ni1 | 114.6 (2) | C20—C19—H19 | 121.0 |
| N1—C1—C2 | 120.5 (3) | C21—C20—C19 | 120.9 (4) |
| N1—C1—C6 | 113.0 (3) | C21—C20—H20 | 119.5 |
| C2—C1—C6 | 126.5 (3) | C19—C20—H20 | 119.5 |
| C3—C2—C1 | 118.2 (3) | C20—C21—C22 | 117.7 (4) |
| C3—C2—H2 | 120.9 | C20—C21—H21 | 121.1 |
| C1—C2—H2 | 120.9 | C22—C21—H21 | 121.1 |
| C2—C3—C4 | 120.3 (3) | N4—C22—C21 | 123.2 (4) |
| C2—C3—H3 | 119.8 | N4—C22—H22 | 118.4 |
| C4—C3—H3 | 119.8 | C21—C22—H22 | 118.4 |
| C5—C4—C3 | 118.5 (3) | C23—N5—C24 | 122.6 (4) |
| C5—C4—H4 | 120.7 | C23—N5—C25 | 118.8 (4) |
| C3—C4—H4 | 120.7 | C24—N5—C25 | 118.5 (4) |
| N1—C5—C4 | 120.3 (3) | O5—C23—N5 | 126.7 (5) |

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| N1—C5—C7 | 113.4 (3) | O5—C23—H23 | 116.7 |
| C4—C5—C7 | 126.4 (3) | N5—C23—H23 | 116.7 |
| O2—C6—O1 | 126.7 (3) | N5—C24—H24A | 109.5 |
| O2—C6—C1 | 118.3 (3) | N5—C24—H24B | 109.5 |
| O1—C6—C1 | 115.0 (3) | H24A—C24—H24B | 109.5 |
| O4—C7—O3 | 126.9 (3) | N5—C24—H24C | 109.5 |
| O4—C7—C5 | 118.3 (3) | H24A—C24—H24C | 109.5 |
| O3—C7—C5 | 114.8 (3) | H24B—C24—H24C | 109.5 |
| N2—C8—C9 | 122.9 (4) | N5—C25—H25A | 109.5 |
| N2—C8—H8 | 118.5 | N5—C25—H25B | 109.5 |
| C9—C8—H8 | 118.5 | H25A—C25—H25B | 109.5 |
| C10—C9—C8 | 117.8 (4) | N5—C25—H25C | 109.5 |
| C10—C9—H9 | 121.1 | H25A—C25—H25C | 109.5 |
| C8—C9—H9 | 121.1 | H25B—C25—H25C | 109.5 |
| C9—C10—C11 | 120.6 (4) | H6A—O6—H6B | 100 (6) |

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| C5—N1—C1—C2 | 1.9 (5) | C10—C11—C12—C13 | 178.5 (5) |
| Ni1—N1—C1—C2 | −177.4 (2) | C17—N3—C13—C14 | −0.6 (6) |
| C5—N1—C1—C6 | −179.0 (3) | Ni1—N3—C13—C14 | −178.8 (3) |
| Ni1—N1—C1—C6 | 1.7 (3) | C17—N3—C13—C12 | 178.0 (3) |
| N1—C1—C2—C3 | −1.8 (5) | Ni1—N3—C13—C12 | −0.3 (4) |
| C6—C1—C2—C3 | 179.2 (3) | N2—C12—C13—N3 | 4.1 (5) |
| C1—C2—C3—C4 | 0.1 (5) | C11—C12—C13—N3 | −175.6 (4) |
| C2—C3—C4—C5 | 1.5 (5) | N2—C12—C13—C14 | −177.4 (4) |
| C1—N1—C5—C4 | −0.2 (5) | C11—C12—C13—C14 | 2.9 (7) |
| Ni1—N1—C5—C4 | 179.1 (2) | N3—C13—C14—C15 | 1.1 (6) |
| C1—N1—C5—C7 | −178.8 (3) | C12—C13—C14—C15 | −177.2 (4) |
| Ni1—N1—C5—C7 | 0.5 (3) | C13—C14—C15—C16 | −1.5 (7) |
| C3—C4—C5—N1 | −1.5 (5) | C14—C15—C16—C17 | 1.3 (7) |
| C3—C4—C5—C7 | 176.9 (3) | C13—N3—C17—C16 | 0.4 (5) |
| Ni1—O1—C6—O2 | 174.4 (3) | Ni1—N3—C17—C16 | 178.6 (3) |
| Ni1—O1—C6—C1 | −4.7 (3) | C13—N3—C17—C18 | −179.3 (3) |
| N1—C1—C6—O2 | −177.0 (3) | Ni1—N3—C17—C18 | −1.0 (4) |
| C2—C1—C6—O2 | 2.1 (5) | C15—C16—C17—N3 | −0.7 (6) |
| N1—C1—C6—O1 | 2.2 (4) | C15—C16—C17—C18 | 178.9 (4) |
| C2—C1—C6—O1 | −178.7 (3) | C22—N4—C18—C19 | 1.3 (6) |
| Ni1—O3—C7—O4 | 174.3 (3) | Ni1—N4—C18—C19 | 178.0 (4) |
| Ni1—O3—C7—C5 | −5.4 (3) | C22—N4—C18—C17 | −179.9 (3) |
| N1—C5—C7—O4 | −176.2 (3) | Ni1—N4—C18—C17 | −3.1 (4) |
| C4—C5—C7—O4 | 5.3 (5) | N3—C17—C18—N4 | 2.7 (5) |
| N1—C5—C7—O3 | 3.4 (4) | C16—C17—C18—N4 | −176.9 (4) |
| C4—C5—C7—O3 | −175.0 (3) | N3—C17—C18—C19 | −178.4 (4) |
| C12—N2—C8—C9 | 1.5 (6) | C16—C17—C18—C19 | 2.0 (7) |
| Ni1—N2—C8—C9 | −172.1 (3) | N4—C18—C19—C20 | −0.6 (8) |
| N2—C8—C9—C10 | −0.8 (8) | C17—C18—C19—C20 | −179.3 (5) |
| C8—C9—C10—C11 | −0.9 (9) | C18—C19—C20—C21 | −1.2 (10) |
| C9—C10—C11—C12 | 1.8 (10) | C19—C20—C21—C22 | 2.1 (10) |
| C8—N2—C12—C11 | −0.4 (6) | C18—N4—C22—C21 | −0.3 (6) |

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|---|---|---|---|
| Ni1—N2—C12—C11 | 173.9 (4) | Ni1—N4—C22—C21 | −176.6 (3) |
| C8—N2—C12—C13 | 179.8 (3) | C20—C21—C22—N4 | −1.4 (8) |
| Ni1—N2—C12—C13 | −5.8 (4) | C24—N5—C23—O5 | 177.5 (4) |
| C10—C11—C12—N2 | −1.2 (8) | C25—N5—C23—O5 | −0.7 (7) |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O6—H6*A*···O2$^{i}$ | 0.71 (5) | 2.21 (5) | 2.907 (5) | 172 (5) |
| O6—H6*B*···O4 | 0.74 (6) | 2.14 (6) | 2.881 (5) | 175 (7) |
| C2—H2···O2$^{ii}$ | 0.94 | 2.49 | 3.254 (4) | 138 |
| C8—H8···O5$^{iii}$ | 0.94 | 2.47 | 3.133 (5) | 128 |
| C9—H9···O2$^{iv}$ | 0.94 | 2.55 | 3.465 (5) | 163 |
| C25—H25*C*···O4$^{v}$ | 0.97 | 2.45 | 3.361 (6) | 157 |

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