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Diaquabis(2,2'-bi-1*H*-imidazole- $\kappa^2N^3,N^{3'}$)nickel(II) bis(3-methylbenzoate) 3-methylbenzoic acid disolvate

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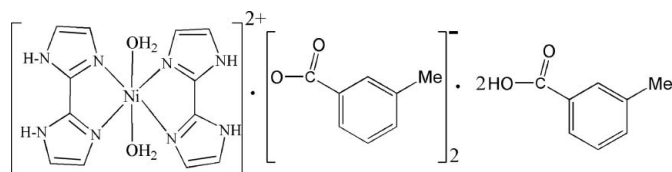
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 Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(C-C) = 0.008$ Å; H-atom completeness 87%; disorder in main residue; R factor = 0.091; wR factor = 0.269; data-to-parameter ratio = 15.4.

In the title compound, $[Ni(C_6H_6N_4)_2(H_2O)_2](C_8H_7O_2)_2 \cdot 2C_8H_8O_2$, the Ni^{II} atom (site symmetry $\bar{1}$) is coordinated by two *N,N'*-bidentate 2,2'-biimidazole ligands and two water molecules, resulting in a slightly distorted *trans*-NiO₂N₄ geometry for the metal ion. In the crystal, the components are linked by N—H...O and O—H...O hydrogen bonds, generating an infinite two-dimensional network running parallel to (100). The methyl group of the benzoic acid molecule is disordered over two sites in a 0.563 (17):0.437 (17) ratio.

Related literature

 For a related structure, see: Yang *et al.* (2009).


Experimental

Crystal data

$[Ni(C_6H_6N_4)_2(H_2O)_2](C_8H_7O_2)_2 \cdot 2C_8H_8O_2$
 $M_r = 905.60$
 Monoclinic, $C2/c$
 $a = 34.747$ (15) Å
 $b = 9.237$ (4) Å
 $c = 14.099$ (6) Å
 $\beta = 93.564$ (8)°

$V = 4516$ (3) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 0.50$ mm⁻¹
 $T = 296$ K
 $0.25 \times 0.19 \times 0.13$ mm

Data collection

Bruker SMART APEX CCD diffractometer
 Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
 $T_{min} = 0.886$, $T_{max} = 0.939$

12088 measured reflections
 4417 independent reflections
 2926 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.057$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.091$
 $wR(F^2) = 0.269$
 $S = 1.00$
 4417 reflections
 287 parameters
 12 restraints

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{max} = 2.27$ e Å⁻³
 $\Delta\rho_{min} = -0.39$ e Å⁻³

Table 1

Selected bond lengths (Å).

| | | | |
|--------|-----------|---------|-----------|
| Ni1—N1 | 2.092 (3) | Ni1—O1W | 2.105 (3) |
| Ni1—N4 | 2.097 (3) | | |

Table 2

Hydrogen-bond geometry (Å, °).

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|---------------------------|-------------|---------------|-----------------------|-------------------------|
| O4—H4...O2 ⁱ | 0.852 (8) | 1.759 (9) | 2.606 (4) | 172 (3) |
| O1W—H1WB...O3 | 0.849 (7) | 2.094 (10) | 2.897 (4) | 158 (2) |
| O1W—H1WA...O1 | 0.847 (7) | 1.819 (8) | 2.649 (3) | 166 (2) |
| N3—H3A...O2 ⁱⁱ | 0.890 (9) | 1.920 (12) | 2.763 (3) | 157 (2) |
| N2—H2A...O1 ⁱⁱ | 0.889 (8) | 1.854 (9) | 2.732 (3) | 169.4 (19) |

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); 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, 2009); software used to prepare material for publication: *PLATON*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5141).

References

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supplementary materials

Acta Cryst. (2009). E65, m1497 [doi:10.1107/S1600536809044705]

Diaquabis(2,2'-bi-1*H*-imidazole- $\kappa^2N^3,N^{3'}$)nickel(II) bis(3-methylbenzoate) 3-methylbenzoic acid disolvate

Z. Hui

Comment

2,2'-Biimidazole is an interesting ligand because it has two N sites and two –NH donors. Both N-donors having the stronger coordination ability and flexible coordination modes. Moreover, two –NH donors can interact with other hydrogen bonding acceptors *via* hydrogen bonds (Yang *et al.*, 2009). Herein, we report the title compound, (I).

In the symmetric unit of (I), Ni²⁺ having an inversion centre is coordinated by two water molecules occupied the axial sites and two 2,2'-biimidazole ligands through respective two N atoms occupied the equatorial plane, which results in a more regular octahedron (Ni1—N1 2.092 (3) Å; Ni1—N4 2.097 (3) Å; Ni1—O1W 2.105 (3) Å). Each water molecule interacts with 3-methyl-benzenecarboxylate and 3-methyl-benzenecarboxylic acid through O1W—H1WA··O1 and O1W—H1WA··O3 hydrogen bonds (Fig. 1). Adjacent units are linked together by two pairs of N2—H2A··O1 and N3—H3A··O1, and one O4—H4··O2 hydrogen bonds into an infinite two-dimensional network along the (100) direction (Fig. 2).

Experimental

NiSO₄·6H₂O (0.18 g, 0.70 mmol) was added into the aqueous solution (15 ml) including 3-methyl-benzenecarboxylic acid (0.14 g, 1.0 mmol) and NaOH (0.04 g, 1.0 mmol) and refluxed for 30 min. Then an ethanol solution (10 ml) containing 2,2'-biimidazole (0.08 g, 0.60 mmol) was slowly added with continuous stirring. The resulting solution was refluxed for 3 h, filtered and kept for crystallization. After nine days, green blocks of (I) were obtained.

Refinement

H atoms bonded to N atoms, carboxyl and water O atoms are located from the difference maps and refined isotropically with 0.89 (1) Å for N—H, 0.85 (1) Å for O—H and the distance H··H = 1.34 (1) Å from water molecule using *DFIX* commands, respectively. All the remaining H atoms were positioned geometrically with C—H = 0.93 Å (aromatic) and 0.96 Å (methyl) and were refined as riding with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (aromatic) and $1.5U_{\text{eq}}(\text{C})$ (methyl). The disordered methyl carbon was divided into two parts C22 and C22' with the anisotropic displacement parameters 0.102 and 0.117, respectively. H atoms bound to them are not added.

Figures

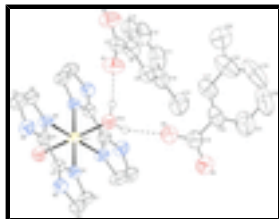


Fig. 1. Molecular structure of (I), showing displacement ellipsoids drawn at the 30% probability level. H-bonds are shown as dashed lines. Disordered part of C22' and H atoms not involved in the hydrogen bonds have been omitted for the clarity. Unlabeled atoms are related to labeled atoms by the symmetry transformation $1/2 - x, 1/2 - y, -z$.



Fig. 2. Part of the crystal structure of (I), showing the formation of the two-dimensional network along the (100) direction. Hydrogen bonds are shown as dashed lines. Disordered part of C22' and H atoms not involved in the hydrogen bonds have been omitted for the clarity.

Diaquabis(2,2'-bi-1*H*-imidazole- κ^2 N³,N^{3'})nickel(II) bis(3-methylbenzoate) 3-methylbenzoic acid disolvate

Crystal data

$[\text{Ni}(\text{C}_6\text{H}_6\text{N}_4)_2(\text{H}_2\text{O})_2](\text{C}_8\text{H}_7\text{O}_2)_2 \cdot 2\text{C}_8\text{H}_8\text{O}_2$

$M_r = 905.60$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 34.747\ (15)\ \text{\AA}$

$b = 9.237\ (4)\ \text{\AA}$

$c = 14.099\ (6)\ \text{\AA}$

$\beta = 93.564\ (8)^\circ$

$V = 4516\ (3)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1896$

$D_x = 1.332\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2285 reflections

$\theta = 2.3\text{--}22.7^\circ$

$\mu = 0.50\ \text{mm}^{-1}$

$T = 296\ \text{K}$

Block, green

$0.25 \times 0.19 \times 0.13\ \text{mm}$

Data collection

Bruker SMART APEX CCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 296\ \text{K}$

0.3° wide ω exposures scans

Absorption correction: multi-scan (SADABS; Bruker, 2001)

$T_{\text{min}} = 0.886, T_{\text{max}} = 0.939$

12088 measured reflections

4417 independent reflections

2926 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.057$

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

$\theta_{\text{min}} = 2.3^\circ$

$h = -41 \rightarrow 42$

$k = -11 \rightarrow 10$

$l = -12 \rightarrow 17$

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

| | |
|--|---|
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.091$ | H atoms treated by a mixture of independent and constrained refinement |
| $wR(F^2) = 0.269$ | $w = 1/[\sigma^2(F_o^2) + (0.1377P)^2 + 26.2495P]$ |
| $S = 1.00$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| 4417 reflections | $(\Delta/\sigma)_{\max} < 0.001$ |
| 287 parameters | $\Delta\rho_{\max} = 2.27 \text{ e } \text{\AA}^{-3}$ |
| 12 restraints | $\Delta\rho_{\min} = -0.39 \text{ e } \text{\AA}^{-3}$ |
| Primary atom site location: structure-invariant direct methods | Extinction correction: SHELXL97 (Sheldrick, 2008), $F_c^* = kF_c[1+0.001xF_c^2\lambda^3/\sin(2\theta)]^{-1/4}$ |
| | Extinction coefficient: 0.0013 (2) |

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 (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ | Occ. (<1) |
|------|--------------|--------------|--------------|----------------------------------|-----------|
| Ni1 | 0.2500 | 0.2500 | 0.0000 | 0.03434 (15) | |
| N1 | 0.23426 (8) | 0.0763 (3) | 0.08464 (19) | 0.0378 (7) | |
| N2 | 0.20745 (8) | 0.0135 (3) | 0.2167 (2) | 0.0439 (8) | |
| H2A | 0.1934 (3) | 0.014 (4) | 0.2673 (7) | 0.052 (11)* | |
| N3 | 0.18763 (9) | 0.3465 (3) | 0.2311 (2) | 0.0497 (8) | |
| H3A | 0.1819 (7) | 0.2986 (18) | 0.2832 (8) | 0.052 (4)* | |
| N4 | 0.21821 (9) | 0.3628 (3) | 0.0979 (2) | 0.0428 (8) | |
| O3 | 0.37232 (9) | 0.1134 (4) | 0.1108 (3) | 0.0818 (11) | |
| O4 | 0.40602 (10) | -0.0866 (4) | 0.1032 (3) | 0.0912 (13) | |
| H4 | 0.3851 (3) | -0.1337 (17) | 0.108 (2) | 0.040 (10)* | |
| O1W | 0.29960 (7) | 0.2675 (2) | 0.09288 (19) | 0.0485 (7) | |
| H1WA | 0.3112 (4) | 0.3481 (6) | 0.094 (2) | 0.024 (8)* | |
| H1WB | 0.3173 (3) | 0.2048 (8) | 0.090 (3) | 0.065 (13)* | |
| C1 | 0.23884 (11) | -0.0697 (4) | 0.0987 (3) | 0.0453 (10) | |
| H1 | 0.2515 | -0.1321 | 0.0593 | 0.054* | |
| C2 | 0.22193 (11) | -0.1089 (4) | 0.1793 (2) | 0.0455 (10) | |
| H2 | 0.2206 | -0.2019 | 0.2041 | 0.055* | |
| C3 | 0.21533 (10) | 0.1215 (4) | 0.1581 (2) | 0.0370 (8) | |
| C4 | 0.20634 (10) | 0.2754 (4) | 0.1646 (3) | 0.0406 (9) | |

supplementary materials

| | | | | | |
|------|--------------|--------------|---------------|-------------|------------|
| C5 | 0.18747 (12) | 0.4897 (4) | 0.2047 (3) | 0.0561 (11) | |
| H5 | 0.1767 | 0.5661 | 0.2368 | 0.067* | |
| C6 | 0.20573 (12) | 0.4988 (4) | 0.1241 (3) | 0.0563 (11) | |
| H6 | 0.2095 | 0.5839 | 0.0906 | 0.068* | |
| C15 | 0.40297 (13) | 0.0524 (5) | 0.1077 (3) | 0.0600 (12) | |
| C16 | 0.44042 (13) | 0.1300 (6) | 0.1130 (3) | 0.0694 (14) | |
| C17 | 0.44083 (15) | 0.2790 (6) | 0.1168 (3) | 0.0726 (15) | |
| H17 | 0.4175 | 0.3279 | 0.1184 | 0.087* | |
| C18 | 0.47472 (17) | 0.3594 (7) | 0.1183 (4) | 0.1015 (19) | |
| C19 | 0.5081 (2) | 0.2839 (10) | 0.1168 (6) | 0.144 (3) | |
| H19 | 0.5312 | 0.3347 | 0.1164 | 0.173* | |
| C20 | 0.50918 (19) | 0.1346 (10) | 0.1159 (6) | 0.138 (3) | |
| H20 | 0.5328 | 0.0868 | 0.1188 | 0.166* | |
| C21 | 0.47463 (5) | 0.05430 (17) | 0.11043 (11) | 0.116 (3) | |
| H21 | 0.4748 | -0.0461 | 0.1053 | 0.140* | |
| C22 | 0.47839 (5) | 0.50541 (17) | 0.12443 (11) | 0.102 (5)* | 0.437 (17) |
| C22' | 0.46819 (5) | 0.54041 (17) | 0.12053 (11) | 0.117 (4)* | 0.563 (17) |
| O1 | 0.32801 (5) | 0.53214 (17) | 0.11606 (11) | 0.0665 (9) | |
| O2 | 0.34258 (5) | 0.76257 (17) | 0.10071 (11) | 0.0758 (10) | |
| C7 | 0.34256 (5) | 0.63145 (17) | 0.07347 (11) | 0.0528 (11) | |
| C8 | 0.36146 (5) | 0.59948 (17) | -0.01813 (11) | 0.0536 (11) | |
| C9 | 0.37173 (5) | 0.45833 (17) | -0.04007 (11) | 0.0560 (11) | |
| H9 | 0.3662 | 0.3844 | 0.0017 | 0.067* | |
| C10 | 0.38992 (13) | 0.4239 (6) | -0.1220 (3) | 0.0663 (14) | |
| C11 | 0.39556 (13) | 0.5355 (7) | -0.1846 (3) | 0.0798 (17) | |
| H11 | 0.4069 | 0.5150 | -0.2411 | 0.096* | |
| C12 | 0.38518 (13) | 0.6747 (7) | -0.1668 (3) | 0.0777 (15) | |
| H12 | 0.3887 | 0.7467 | -0.2116 | 0.093* | |
| C13 | 0.36927 (13) | 0.7085 (5) | -0.0815 (3) | 0.0660 (13) | |
| H13 | 0.3639 | 0.8043 | -0.0670 | 0.079* | |
| C14 | 0.40365 (16) | 0.2721 (6) | -0.1383 (4) | 0.0880 (17) | |
| H14A | 0.4071 | 0.2582 | -0.2047 | 0.132* | |
| H14B | 0.3849 | 0.2044 | -0.1179 | 0.132* | |
| H14C | 0.4277 | 0.2566 | -0.1027 | 0.132* | |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| Ni1 | 0.0416 (3) | 0.0285 (3) | 0.0337 (3) | 0.0008 (3) | 0.0086 (2) | 0.0003 (2) |
| N1 | 0.0382 (15) | 0.0335 (14) | 0.0427 (15) | -0.0014 (12) | 0.0097 (12) | -0.0007 (12) |
| N2 | 0.0453 (16) | 0.0449 (16) | 0.0422 (15) | -0.0005 (13) | 0.0087 (13) | 0.0048 (13) |
| N3 | 0.0542 (17) | 0.0502 (16) | 0.0464 (16) | 0.0046 (14) | 0.0160 (13) | 0.0003 (14) |
| N4 | 0.0506 (16) | 0.0339 (14) | 0.0457 (15) | -0.0016 (13) | 0.0165 (13) | -0.0025 (12) |
| O3 | 0.0574 (18) | 0.069 (2) | 0.120 (3) | -0.0004 (16) | 0.0135 (18) | -0.0039 (19) |
| O4 | 0.070 (2) | 0.069 (2) | 0.135 (3) | 0.0079 (18) | 0.016 (2) | -0.008 (2) |
| O1W | 0.0504 (14) | 0.0431 (14) | 0.0523 (14) | -0.0011 (12) | 0.0068 (11) | 0.0002 (11) |
| C1 | 0.054 (2) | 0.0344 (17) | 0.0485 (19) | 0.0021 (16) | 0.0121 (16) | -0.0034 (15) |
| C2 | 0.060 (2) | 0.0359 (17) | 0.0407 (18) | -0.0001 (16) | 0.0068 (16) | 0.0080 (15) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| C3 | 0.0375 (17) | 0.0382 (17) | 0.0353 (16) | -0.0004 (14) | 0.0028 (13) | 0.0007 (14) |
| C4 | 0.0418 (18) | 0.0376 (18) | 0.0432 (18) | 0.0012 (14) | 0.0074 (14) | -0.0022 (14) |
| C5 | 0.067 (2) | 0.045 (2) | 0.058 (2) | 0.0105 (19) | 0.0118 (19) | -0.0050 (18) |
| C6 | 0.077 (3) | 0.0348 (18) | 0.059 (2) | 0.0029 (18) | 0.025 (2) | -0.0019 (17) |
| C15 | 0.058 (2) | 0.068 (3) | 0.055 (2) | 0.001 (2) | 0.0119 (19) | 0.001 (2) |
| C16 | 0.050 (2) | 0.105 (4) | 0.054 (2) | -0.007 (2) | 0.0080 (19) | -0.012 (2) |
| C17 | 0.068 (3) | 0.092 (3) | 0.057 (3) | -0.022 (3) | 0.005 (2) | -0.006 (2) |
| C18 | 0.095 (4) | 0.146 (5) | 0.065 (3) | -0.057 (3) | 0.020 (3) | -0.025 (3) |
| C19 | 0.076 (4) | 0.233 (8) | 0.126 (6) | -0.068 (5) | 0.022 (4) | -0.042 (5) |
| C20 | 0.053 (3) | 0.207 (8) | 0.153 (7) | 0.003 (5) | -0.001 (4) | -0.027 (7) |
| C21 | 0.077 (4) | 0.145 (6) | 0.128 (5) | 0.009 (4) | 0.010 (4) | -0.038 (5) |
| O1 | 0.0949 (19) | 0.0607 (16) | 0.0472 (14) | -0.0204 (15) | 0.0307 (14) | -0.0076 (13) |
| O2 | 0.101 (2) | 0.0515 (16) | 0.0805 (19) | -0.0076 (16) | 0.0458 (16) | -0.0024 (14) |
| C7 | 0.056 (2) | 0.054 (2) | 0.049 (2) | -0.0049 (19) | 0.0106 (17) | -0.0028 (18) |
| C8 | 0.054 (2) | 0.070 (2) | 0.0381 (18) | -0.005 (2) | 0.0124 (16) | 0.0022 (18) |
| C9 | 0.052 (2) | 0.068 (2) | 0.048 (2) | -0.003 (2) | 0.0063 (18) | -0.0046 (19) |
| C10 | 0.051 (2) | 0.094 (3) | 0.053 (2) | 0.000 (2) | 0.0013 (19) | -0.015 (2) |
| C11 | 0.057 (2) | 0.135 (4) | 0.049 (2) | 0.009 (3) | 0.0175 (19) | 0.006 (3) |
| C12 | 0.060 (3) | 0.118 (4) | 0.057 (2) | 0.003 (3) | 0.018 (2) | 0.027 (3) |
| C13 | 0.055 (2) | 0.081 (3) | 0.063 (2) | -0.001 (2) | 0.015 (2) | 0.020 (2) |
| C14 | 0.083 (3) | 0.102 (4) | 0.080 (3) | 0.015 (3) | 0.015 (3) | -0.038 (3) |

Geometric parameters (Å, °)

| | | | |
|----------------------|-----------|----------|------------|
| Ni1—Ni ⁱ | 2.092 (3) | C16—C21 | 1.381 (5) |
| Ni1—N1 | 2.092 (3) | C16—C17 | 1.378 (7) |
| Ni1—N4 ⁱ | 2.097 (3) | C17—C18 | 1.391 (7) |
| Ni1—N4 | 2.097 (3) | C17—H17 | 0.9300 |
| Ni1—O1W ⁱ | 2.105 (3) | C18—C19 | 1.354 (10) |
| Ni1—O1W | 2.105 (3) | C18—C22 | 1.357 (7) |
| N1—C3 | 1.328 (4) | C18—C22' | 1.688 (7) |
| N1—C1 | 1.371 (4) | C19—C20 | 1.380 (12) |
| N2—C3 | 1.335 (4) | C19—H19 | 0.9300 |
| N2—C2 | 1.357 (5) | C20—C21 | 1.409 (8) |
| N2—H2A | 0.889 (8) | C20—H20 | 0.9300 |
| N3—C4 | 1.345 (5) | C21—H21 | 0.9300 |
| N3—C5 | 1.374 (5) | O1—C7 | 1.2229 |
| N3—H3A | 0.890 (9) | O2—C7 | 1.2706 |
| N4—C4 | 1.325 (4) | C7—C8 | 1.5138 |
| N4—C6 | 1.387 (5) | C8—C13 | 1.384 (5) |
| O3—C15 | 1.208 (5) | C8—C9 | 1.3917 |
| O4—C15 | 1.290 (6) | C9—C10 | 1.388 (5) |
| O4—H4 | 0.852 (8) | C9—H9 | 0.9300 |
| O1W—H1WA | 0.847 (7) | C10—C11 | 1.379 (7) |
| O1W—H1WB | 0.849 (7) | C10—C14 | 1.503 (7) |
| C1—C2 | 1.362 (5) | C11—C12 | 1.362 (8) |
| C1—H1 | 0.9300 | C11—H11 | 0.9300 |
| C2—H2 | 0.9300 | C12—C13 | 1.391 (7) |

supplementary materials

| | | | |
|---------------------------------------|------------|--------------|-----------|
| C3—C4 | 1.460 (5) | C12—H12 | 0.9300 |
| C5—C6 | 1.338 (6) | C13—H13 | 0.9300 |
| C5—H5 | 0.9300 | C14—H14A | 0.9600 |
| C6—H6 | 0.9300 | C14—H14B | 0.9600 |
| C15—C16 | 1.483 (6) | C14—H14C | 0.9600 |
| N1 ⁱ —Ni1—N1 | 180.0 | O3—C15—C16 | 123.0 (4) |
| N1 ⁱ —Ni1—N4 ⁱ | 80.71 (11) | O4—C15—C16 | 114.2 (4) |
| N1—Ni1—N4 ⁱ | 99.29 (11) | C21—C16—C17 | 120.0 (4) |
| N1 ⁱ —Ni1—N4 | 99.29 (11) | C21—C16—C15 | 120.5 (4) |
| N1—Ni1—N4 | 80.71 (11) | C17—C16—C15 | 119.5 (4) |
| N4 ⁱ —Ni1—N4 | 180.0 | C16—C17—C18 | 122.7 (5) |
| N1 ⁱ —Ni1—O1W ⁱ | 86.39 (10) | C16—C17—H17 | 118.6 |
| N1—Ni1—O1W ⁱ | 93.61 (10) | C18—C17—H17 | 118.6 |
| N4 ⁱ —Ni1—O1W ⁱ | 89.82 (11) | C19—C18—C22 | 115.8 (5) |
| N4—Ni1—O1W ⁱ | 90.18 (11) | C19—C18—C17 | 116.7 (7) |
| N1 ⁱ —Ni1—O1W | 93.61 (10) | C22—C18—C17 | 127.4 (5) |
| N1—Ni1—O1W | 86.39 (10) | C19—C18—C22' | 128.8 (5) |
| N4 ⁱ —Ni1—O1W | 90.18 (11) | C22—C18—C22' | 13.21 (8) |
| N4—Ni1—O1W | 89.82 (11) | C17—C18—C22' | 114.5 (5) |
| O1W ⁱ —Ni1—O1W | 180.0 | C18—C19—C20 | 122.6 (7) |
| C3—N1—C1 | 104.8 (3) | C18—C19—H19 | 118.7 |
| C3—N1—Ni1 | 111.3 (2) | C20—C19—H19 | 118.7 |
| C1—N1—Ni1 | 143.6 (2) | C19—C20—C21 | 120.1 (6) |
| C3—N2—C2 | 106.7 (3) | C19—C20—H20 | 119.9 |
| C3—N2—H2A | 129 (2) | C21—C20—H20 | 119.9 |
| C2—N2—H2A | 124 (2) | C16—C21—C20 | 117.6 (4) |
| C4—N3—C5 | 106.0 (3) | C16—C21—H21 | 121.2 |
| C4—N3—H3A | 118.4 (13) | C20—C21—H21 | 121.2 |
| C5—N3—H3A | 134.8 (12) | O1—C7—O2 | 124.0 |
| C4—N4—C6 | 104.3 (3) | O1—C7—C8 | 119.1 |
| C4—N4—Ni1 | 111.4 (2) | O2—C7—C8 | 116.9 |
| C6—N4—Ni1 | 144.3 (2) | C13—C8—C9 | 118.4 (2) |
| C15—O4—H4 | 115.6 (12) | C13—C8—C7 | 121.4 (2) |
| Ni1—O1W—H1WA | 116.6 (14) | C9—C8—C7 | 120.2 |
| Ni1—O1W—H1WB | 119 (2) | C10—C9—C8 | 122.4 (2) |
| H1WA—O1W—H1WB | 104.7 (10) | C10—C9—H9 | 118.8 |
| C2—C1—N1 | 109.3 (3) | C8—C9—H9 | 118.8 |
| C2—C1—H1 | 125.4 | C11—C10—C9 | 116.8 (4) |
| N1—C1—H1 | 125.4 | C11—C10—C14 | 122.7 (4) |
| N2—C2—C1 | 107.0 (3) | C9—C10—C14 | 120.4 (4) |
| N2—C2—H2 | 126.5 | C12—C11—C10 | 122.6 (4) |
| C1—C2—H2 | 126.5 | C12—C11—H11 | 118.7 |
| N1—C3—N2 | 112.3 (3) | C10—C11—H11 | 118.7 |
| N1—C3—C4 | 118.2 (3) | C11—C12—C13 | 119.6 (5) |
| N2—C3—C4 | 129.5 (3) | C11—C12—H12 | 120.2 |
| N4—C4—N3 | 112.5 (3) | C13—C12—H12 | 120.2 |

| | | | |
|-----------|-----------|---------------|-----------|
| N4—C4—C3 | 118.1 (3) | C8—C13—C12 | 120.0 (4) |
| N3—C4—C3 | 129.4 (3) | C8—C13—H13 | 120.0 |
| C6—C5—N3 | 107.3 (3) | C12—C13—H13 | 120.0 |
| C6—C5—H5 | 126.4 | C10—C14—H14A | 109.5 |
| N3—C5—H5 | 126.4 | C10—C14—H14B | 109.5 |
| C5—C6—N4 | 110.0 (3) | H14A—C14—H14B | 109.5 |
| C5—C6—H6 | 125.0 | C10—C14—H14C | 109.5 |
| N4—C6—H6 | 125.0 | H14A—C14—H14C | 109.5 |
| O3—C15—O4 | 122.8 (4) | H14B—C14—H14C | 109.5 |

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

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|-----------|-------------|-------------|---------------|
| O4—H4 \cdots O2 ⁱⁱ | 0.852 (8) | 1.759 (9) | 2.606 (4) | 172 (3) |
| O1W—H1WB \cdots O3 | 0.849 (7) | 2.094 (10) | 2.897 (4) | 158 (2) |
| O1W—H1WA \cdots O1 | 0.847 (7) | 1.819 (8) | 2.649 (3) | 166 (2) |
| N3—H3A \cdots O2 ⁱⁱⁱ | 0.890 (9) | 1.920 (12) | 2.763 (3) | 157 (2) |
| N2—H2A \cdots O1 ⁱⁱⁱ | 0.889 (8) | 1.854 (9) | 2.732 (3) | 169.4 (19) |

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

Fig. 2

