

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Bis(dimethylmalonato- κ^2O,O')bis[4-(4-pyridylamino- κN^4)pyridinium]nickel(II) hexahydrate

Gregory A. Farnum and Robert L. LaDuca*

Lyman Briggs College, Department of Chemistry, Michigan State University, East Lansing, MI 48825, USA

Correspondence e-mail: laduca@msu.edu

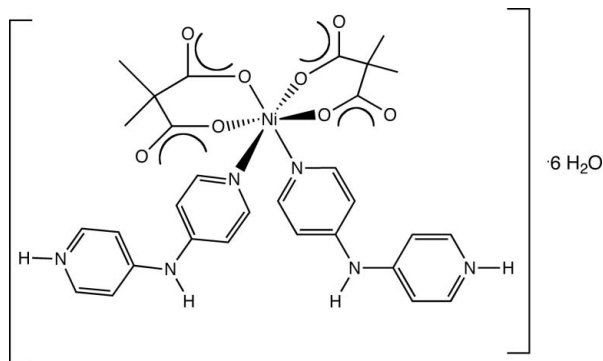
Received 30 October 2008; accepted 17 November 2008

 Key indicators: single-crystal X-ray study; $T = 173$ K; mean $\sigma(C-C) = 0.004$ Å; R factor = 0.054; wR factor = 0.163; data-to-parameter ratio = 16.3.

In the title compound, $[Ni(C_5H_6O_4)_2(C_{10}H_{10}N_3)_2] \cdot 6H_2O$, divalent nickel ions situated on the crystallographic twofold axis are octahedrally coordinated by four O atoms from two dimethylmalonate ligands in a 1,3-chelating mode and two N atoms from two protonated monodentate 4,4'-dipyridylamine molecules. The molecules link into chains *via* N—H...O hydrogen bonding mediated by protonated pyridyl groups. The chains form layer patterns *via* π - π stacking [centroid-centroid distance = 3.777 (2) Å]. Water molecule hexamers are generated from the unligated water molecules (three per asymmetric unit) by inversion centers at Wyckoff position *d*. These clusters are situated between the pseudolayers, providing hydrogen-bonding pathways that build up the three-dimensional structure.

Related literature

For 4,4'-dipyridylamine (dpa) coordination polymers, see: Martin *et al.* (2007). For cobalt and nickel malonate dpa coordination polymers, see: Montney *et al.* (2008).



Experimental

Crystal data

 $[Ni(C_5H_6O_4)_2(C_{10}H_{10}N_3)_2] \cdot 6H_2O$
 $M_r = 771.42$

 Monoclinic, $C2/c$
 $a = 18.428$ (4) Å

 $b = 8.0473$ (16) Å

 $c = 23.731$ (5) Å

 $\beta = 97.96$ (3)°

 $V = 3485.4$ (12) Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 0.63$ mm⁻¹
 $T = 173$ (2) K

 $0.30 \times 0.30 \times 0.10$ mm

Data collection

Bruker SMART 1K diffractometer

Absorption correction: multi-scan

(TWINABS; Sheldrick, 2007)

 $T_{min} = 0.833$, $T_{max} = 0.939$

49338 measured reflections

3998 independent reflections

 3222 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.079$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.163$
 $S = 1.09$

3998 reflections

246 parameters

10 restraints

H atoms treated by a mixture of independent and constrained refinement

 $\Delta\rho_{max} = 0.84$ e Å⁻³
 $\Delta\rho_{min} = -0.61$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

| $D-H \cdots A$ | $D-H$ | $H \cdots A$ | $D \cdots A$ | $D-H \cdots A$ |
|----------------------------|------------|--------------|--------------|----------------|
| $O1W-H1WA \cdots O3W^i$ | 0.85 | 1.96 | 2.811 (4) | 180 |
| $O1W-H1WB \cdots O2W$ | 0.840 (18) | 2.05 (2) | 2.870 (3) | 166 (4) |
| $O2W-H2WA \cdots O3$ | 0.840 (18) | 1.904 (19) | 2.741 (3) | 174 (4) |
| $O2W-H2WB \cdots O4^{ii}$ | 0.844 (18) | 1.95 (2) | 2.751 (3) | 158 (4) |
| $O3W-H3WA \cdots O1W$ | 0.85 | 1.90 | 2.754 (4) | 179 |
| $O3W-H3WB \cdots O3^{iii}$ | 0.85 | 1.94 | 2.793 (3) | 179 |
| $N2-H2N \cdots O2W^{iv}$ | 0.866 (18) | 2.16 (2) | 2.985 (3) | 158 (3) |
| $N3-H3N \cdots O2^v$ | 0.82 (4) | 1.86 (4) | 2.683 (3) | 176 (4) |

Symmetry codes: (i) $-x - \frac{1}{2}, -y + \frac{5}{2}, -z$; (ii) $-x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (iii) $-x - \frac{1}{2}, -y + \frac{3}{2}, -z$; (iv) $x + \frac{1}{2}, y + \frac{1}{2}, z$; (v) $x, -y + 2, z - \frac{1}{2}$.

Data collection: SMART (Bruker, 2006); cell refinement: SAINT-Plus (Bruker, 2006); data reduction: SAINT-Plus and CELL-NOW (Sheldrick, 2003); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: Crystal Maker (Palmer, 2007); software used to prepare material for publication: SHELXL97.

The authors gratefully acknowledge the donors of the American Chemical Society Petroleum Research Fund and Michigan State University for funding this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PK2132).

References

- Bruker (2006). SMART and SAINT-Plus. Bruker AXS Inc., Madison, Wisconsin, USA.
- Martin, D. P., Supkowski, R. M. & LaDuca, R. L. (2007). *Inorg. Chem.* **46**, 7917–7922.
- Montney, M. R., Supkowski, R. M. & LaDuca, R. L. (2008). *Polyhedron*, **27**, 2997–3003.
- Palmer, D. (2007). *Crystal Maker*. CrystalMaker Software, Bicester, Oxfordshire, England.
- Sheldrick, G. M. (2003). CELL-NOW. University of Göttingen, Germany.
- Sheldrick, G. M. (2007). TWINABS. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supplementary materials

Acta Cryst. (2008). E64, m1603 [doi:10.1107/S160053680803835X]

Bis(dimethylmalonato- κ^2O,O')bis[4-(4-pyridylamino- κN^4)pyridinium]nickel(II) hexahydrate

G. A. Farnum and R. L. LaDuca

Comment

The dipodal tethering ligand 4,4'-dipyridylamine (dpa) has proven beneficial for the construction of coordination polymer solids with novel topologies (Martin *et al.*, 2007). Isostructural cobalt and nickel malonate dpa coordination polymers possess a three-dimensional 4^46^6 sqp (square pyramidal) topology (Montney *et al.*, 2008). In an attempt to probe the effect of alkyl group substitution on coordination polymer structure by using dimethylmalonate, green crystals of the title compound were obtained.

The asymmetric unit of the title compound contains a nickel atom on a crystallographic two-fold axis, one dimethylmalonate dianion, one protonated Hdpa⁺ ligand and three water molecules of crystallization. Operation of the two-fold axis generates a neutral molecular complex, $\{[\text{Ni}(\text{dimethylmalonate})_2(\text{Hdpa})_2]\cdot 6\text{H}_2\text{O}\}$, in which the nickel atom is octahedrally coordinated (Fig. 1). The dimethylmalonate ligands bind in a 1,3-chelating fashion, each bridging two *cis* coordination sites. The Hdpa ligands are disposed in a *cis* fashion relative to each other.

Neighboring $[\text{Ni}(\text{dimethylmalonate})_2(\text{Hdpa})_2]$ molecules are connected into supramolecular chain patterns, parallel to the *c* crystal direction, through hydrogen bonding between the protonated pyridyl termini of the Hdpa ligands and unligated dimethylmalonate oxygen atoms. These chains interact *via* π - π stacking between protonated pyridyl rings to form supramolecular layers oriented parallel to the *bc* crystal planes (Fig. 2). The supramolecular layers interact with each other by hydrogen bonding patterns between the dpa central amine groups or dimethylmalonate carboxylate groups and water molecules of crystallization to form the three-dimensional structure of the title compound (Fig. 3). The unligated water molecules themselves form a hydrogen bonded hexameric cluster centered on a cyclic tetrameric unit, as seen in Fig. 1. The centroids of the clusters rest on crystallographic inversion centers (Wyckoff position d).

Experimental

All chemicals were obtained commercially. Nickel perchlorate hexahydrate (135 mg, 0.37 mmol) and dimethylmalonic acid (49 mg, 0.74 mmol) were dissolved in 3 ml water in a glass vial. A 1 ml aliquot of a 1:1 water-ethanol was carefully layered onto the aqueous solution, followed by 3 ml of an ethanolic solution of dpa (127 mg, 0.74 mmol). Green blocks of the title compound formed after 1 week.

Refinement

All H atoms bound to C atoms were placed in calculated positions, with C—H = 0.95 Å and refined in riding mode with $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$. The H atoms bound to O atoms were found *via* Fourier difference map, restrained at fixed positions or with O—H = 0.85 Å, and refined with $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{O})$. The H atoms bound to N atoms were found *via* Fourier difference map, restrained with N—H = 0.89 Å, and refined with $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{N})$.

Figures

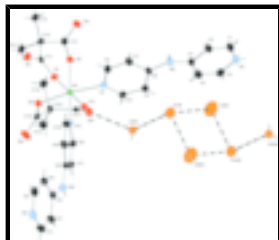


Fig. 1. A full molecular unit of the title compound, along with hydrogen bonded water molecule hexamer, showing 50% probability ellipsoids and the atom numbering scheme. Hydrogen atom positions are shown as gray sticks. Hydrogen bonding interactions are shown as dashed lines. Color codes: green Ni, light blue N, red O, black C. Symmetry codes: (i) $-x, y, -z + 1/2$; (ii) $-x - 1/2, -y + 5/2, -z$

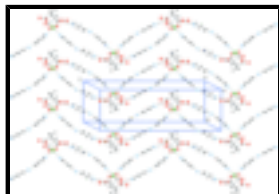


Fig. 2. A single supramolecular layer in the title compound, formed from π - π stacking of hydrogen-bonded $[\text{Ni}(\text{dimethylmalonate})_2(\text{Hdpa})_2]_n$ supramolecular chains. Hydrogen bonding is indicated as dashed lines.

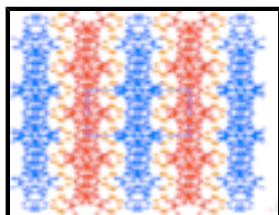


Fig. 3. Packing diagram illustrating the AB layer stacking pattern, which forms the 3-D crystal structure of the title compound through hydrogen bonding between water molecules of crystallization and the amine groups of the Hdpa ligands. Individual pseudolayers are shown in blue and red. The oxygen atoms of the water molecules of crystallization are shown in orange.

Bis(dimethylmalonato- κ^2O, O')bis[4-(4-pyridylamino- κN^4)pyridinium]nickel(II) hexahydrate

Crystal data

$[\text{Ni}(\text{C}_5\text{H}_6\text{O}_4)_2(\text{C}_{10}\text{H}_{10}\text{N}_3)_2] \cdot 6\text{H}_2\text{O}$

$M_r = 771.42$

Monoclinic, $C2/c$

Hall symbol: $-C\ 2yc$

$a = 18.428\ (4)\ \text{\AA}$

$b = 8.0473\ (16)\ \text{\AA}$

$c = 23.731\ (5)\ \text{\AA}$

$\beta = 97.96\ (3)^\circ$

$V = 3485.4\ (12)\ \text{\AA}^3$

$Z = 4$

$F_{000} = 1624$

$D_x = 1.470\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 49338 reflections

$\theta = 1.7\text{--}28.1^\circ$

$\mu = 0.63\ \text{mm}^{-1}$

$T = 173\ (2)\ \text{K}$

Block, green

$0.30 \times 0.30 \times 0.10\ \text{mm}$

Data collection

Bruker SMART 1K diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 173\ (2)\ \text{K}$

ω scans

Absorption correction: multi-scan

3998 independent reflections

3222 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.079$

$\theta_{\text{max}} = 28.1^\circ$

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

$h = -20 \rightarrow 24$

(TWINABS; Sheldrick, 2007)

$T_{\min} = 0.833$, $T_{\max} = 0.939$

49338 measured reflections

$k = -10 \rightarrow 0$

$l = -19 \rightarrow 31$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.054$

$wR(F^2) = 0.163$

$S = 1.09$

3998 reflections

246 parameters

10 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

$$w = 1/[\sigma^2(F_o^2) + (0.0996P)^2 + 4.676P]$$

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

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

$\Delta\rho_{\max} = 0.84 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\min} = -0.60 \text{ e } \text{\AA}^{-3}$

Extinction correction: none

Special details

Experimental. Reflection data were collected on a non-merohedrally twinned crystal. The twin law was determined with *CELL-NOW* (Sheldrick, 2003). The structure was solved and refined using reflections from only the major twin component, whose reflection file was generated using TWINABS (Sheldrick, 2007). Composite reflections belonging to both twin domains were omitted from the reflection list, causing the loss of 252 reflections from the major twin component data. The data set was still 99.9% complete to 2θ of 50° .

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 | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|---------------|-------------|--------------|----------------------------------|
| Ni1 | 0.0000 | 0.68844 (6) | 0.2500 | 0.01265 (17) |
| O1 | -0.10290 (10) | 0.6794 (2) | 0.20559 (8) | 0.0169 (4) |
| O1W | -0.18013 (13) | 1.0666 (3) | 0.04163 (11) | 0.0386 (6) |
| H1WA | -0.2030 | 1.1538 | 0.0492 | 0.046* |
| H1WB | -0.198 (2) | 0.986 (3) | 0.0576 (16) | 0.046* |
| O2 | -0.03894 (10) | 0.5158 (2) | 0.30453 (7) | 0.0163 (4) |
| O2W | -0.26118 (12) | 0.8279 (3) | 0.09768 (9) | 0.0270 (5) |
| H2WA | -0.2400 (19) | 0.746 (3) | 0.1144 (14) | 0.032* |

supplementary materials

| | | | | |
|------|---------------|------------|---------------|-------------|
| H2WB | -0.2807 (19) | 0.888 (4) | 0.1206 (13) | 0.032* |
| O3 | -0.20007 (10) | 0.5600 (3) | 0.15784 (8) | 0.0207 (4) |
| O3W | -0.2449 (2) | 1.1445 (4) | -0.06678 (12) | 0.0712 (11) |
| H3WA | -0.2253 | 1.1212 | -0.0331 | 0.085* |
| H3WB | -0.2620 | 1.0821 | -0.0944 | 0.085* |
| O4 | -0.14160 (11) | 0.4853 (3) | 0.34207 (8) | 0.0277 (5) |
| N1 | 0.02492 (12) | 0.8724 (3) | 0.19288 (9) | 0.0151 (5) |
| N2 | 0.08802 (13) | 1.1902 (3) | 0.06757 (10) | 0.0199 (5) |
| H2N | 0.1351 (10) | 1.203 (4) | 0.0737 (15) | 0.024* |
| N3 | 0.00229 (14) | 1.3886 (3) | -0.08748 (10) | 0.0231 (5) |
| H3N | -0.0118 (19) | 1.422 (5) | -0.1199 (16) | 0.028* |
| C1 | 0.07385 (18) | 1.3998 (4) | -0.06814 (12) | 0.0262 (7) |
| H1 | 0.1052 | 1.4516 | -0.0902 | 0.031* |
| C2 | 0.10115 (17) | 1.3359 (4) | -0.01648 (12) | 0.0236 (6) |
| H2 | 0.1508 | 1.3467 | -0.0031 | 0.028* |
| C3 | 0.05471 (16) | 1.2533 (4) | 0.01689 (11) | 0.0193 (6) |
| C4 | -0.01943 (16) | 1.2421 (4) | -0.00520 (12) | 0.0228 (6) |
| H4 | -0.0521 | 1.1883 | 0.0152 | 0.027* |
| C5 | -0.04357 (17) | 1.3111 (4) | -0.05712 (13) | 0.0251 (6) |
| H5 | -0.0930 | 1.3040 | -0.0716 | 0.030* |
| C6 | 0.09491 (14) | 0.9063 (4) | 0.18757 (11) | 0.0186 (6) |
| H6 | 0.1315 | 0.8551 | 0.2126 | 0.022* |
| C7 | 0.11574 (15) | 1.0124 (4) | 0.14740 (11) | 0.0193 (6) |
| H7 | 0.1651 | 1.0319 | 0.1457 | 0.023* |
| C8 | 0.06220 (15) | 1.0909 (3) | 0.10910 (11) | 0.0169 (5) |
| C9 | -0.01058 (15) | 1.0630 (4) | 0.11588 (11) | 0.0205 (6) |
| H9 | -0.0482 | 1.1167 | 0.0927 | 0.025* |
| C10 | -0.02595 (15) | 0.9540 (4) | 0.15780 (11) | 0.0193 (6) |
| H10 | -0.0749 | 0.9364 | 0.1618 | 0.023* |
| C11 | -0.14996 (13) | 0.5650 (3) | 0.19920 (10) | 0.0134 (5) |
| C12 | -0.14587 (14) | 0.4205 (3) | 0.24216 (11) | 0.0159 (5) |
| C13 | -0.22274 (15) | 0.3538 (4) | 0.24762 (12) | 0.0220 (6) |
| H13A | -0.2462 | 0.3181 | 0.2110 | 0.033* |
| H13B | -0.2513 | 0.4401 | 0.2618 | 0.033* |
| H13C | -0.2187 | 0.2615 | 0.2735 | 0.033* |
| C14 | -0.10114 (16) | 0.2814 (4) | 0.21810 (12) | 0.0211 (6) |
| H14A | -0.1258 | 0.2466 | 0.1817 | 0.032* |
| H14B | -0.0965 | 0.1887 | 0.2438 | 0.032* |
| H14C | -0.0533 | 0.3226 | 0.2138 | 0.032* |
| C15 | -0.10720 (14) | 0.4782 (3) | 0.30049 (11) | 0.0163 (5) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|--------------|-------------|
| Ni1 | 0.0109 (3) | 0.0145 (3) | 0.0122 (2) | 0.000 | 0.00056 (16) | 0.000 |
| O1 | 0.0145 (9) | 0.0167 (10) | 0.0186 (9) | -0.0025 (7) | -0.0008 (7) | 0.0019 (7) |
| O1W | 0.0325 (13) | 0.0370 (15) | 0.0459 (15) | -0.0012 (11) | 0.0042 (11) | 0.0057 (11) |
| O2 | 0.0152 (9) | 0.0195 (10) | 0.0137 (9) | -0.0010 (7) | -0.0003 (7) | 0.0010 (7) |

| | | | | | | |
|-----|-------------|-------------|-------------|--------------|--------------|--------------|
| O2W | 0.0282 (12) | 0.0304 (13) | 0.0228 (11) | 0.0086 (9) | 0.0044 (9) | 0.0049 (9) |
| O3 | 0.0183 (10) | 0.0239 (11) | 0.0180 (9) | -0.0021 (8) | -0.0049 (7) | -0.0008 (8) |
| O3W | 0.108 (3) | 0.062 (2) | 0.0338 (15) | 0.026 (2) | -0.0247 (16) | -0.0222 (14) |
| O4 | 0.0259 (11) | 0.0408 (14) | 0.0175 (10) | -0.0098 (10) | 0.0063 (8) | -0.0048 (9) |
| N1 | 0.0149 (10) | 0.0150 (11) | 0.0157 (10) | -0.0010 (9) | 0.0030 (8) | -0.0010 (9) |
| N2 | 0.0163 (11) | 0.0258 (13) | 0.0168 (11) | -0.0029 (10) | -0.0006 (9) | 0.0077 (9) |
| N3 | 0.0323 (14) | 0.0223 (13) | 0.0134 (11) | 0.0046 (11) | -0.0014 (10) | 0.0017 (10) |
| C1 | 0.0328 (16) | 0.0278 (17) | 0.0188 (13) | 0.0004 (13) | 0.0062 (11) | 0.0050 (12) |
| C2 | 0.0246 (14) | 0.0294 (16) | 0.0169 (13) | -0.0007 (12) | 0.0031 (11) | 0.0023 (11) |
| C3 | 0.0269 (15) | 0.0175 (14) | 0.0134 (12) | 0.0017 (11) | 0.0023 (10) | -0.0004 (10) |
| C4 | 0.0223 (14) | 0.0276 (16) | 0.0179 (13) | -0.0046 (12) | 0.0004 (11) | -0.0013 (12) |
| C5 | 0.0241 (15) | 0.0281 (16) | 0.0218 (14) | 0.0029 (12) | -0.0014 (11) | -0.0055 (12) |
| C6 | 0.0160 (13) | 0.0210 (15) | 0.0174 (12) | -0.0008 (11) | -0.0024 (10) | 0.0023 (10) |
| C7 | 0.0140 (12) | 0.0251 (15) | 0.0182 (13) | -0.0057 (11) | 0.0000 (10) | 0.0007 (11) |
| C8 | 0.0206 (13) | 0.0177 (14) | 0.0126 (11) | -0.0039 (10) | 0.0036 (10) | -0.0009 (10) |
| C9 | 0.0189 (13) | 0.0230 (15) | 0.0197 (13) | 0.0042 (11) | 0.0026 (10) | 0.0040 (11) |
| C10 | 0.0157 (12) | 0.0214 (15) | 0.0209 (13) | 0.0023 (11) | 0.0027 (10) | 0.0009 (11) |
| C11 | 0.0135 (12) | 0.0154 (13) | 0.0115 (11) | 0.0013 (10) | 0.0024 (9) | -0.0035 (9) |
| C12 | 0.0164 (12) | 0.0153 (13) | 0.0155 (12) | -0.0015 (10) | 0.0002 (9) | 0.0020 (10) |
| C13 | 0.0178 (13) | 0.0239 (15) | 0.0235 (14) | -0.0054 (11) | 0.0007 (11) | 0.0007 (11) |
| C14 | 0.0231 (14) | 0.0172 (14) | 0.0223 (14) | -0.0001 (11) | 0.0005 (11) | -0.0022 (11) |
| C15 | 0.0181 (13) | 0.0140 (13) | 0.0161 (12) | 0.0014 (10) | -0.0003 (10) | 0.0029 (10) |

Geometric parameters (Å, °)

| | | | |
|---------------------|-------------|----------|-----------|
| Ni1—O1 | 2.0392 (19) | C1—H1 | 0.9300 |
| Ni1—O1 ⁱ | 2.0392 (19) | C2—C3 | 1.410 (4) |
| Ni1—O2 ⁱ | 2.0920 (19) | C2—H2 | 0.9300 |
| Ni1—O2 | 2.0921 (19) | C3—C4 | 1.397 (4) |
| Ni1—N1 ⁱ | 2.100 (2) | C4—C5 | 1.368 (4) |
| Ni1—N1 | 2.100 (2) | C4—H4 | 0.9300 |
| O1—C11 | 1.259 (3) | C5—H5 | 0.9300 |
| O1W—H1WA | 0.8506 | C6—C7 | 1.373 (4) |
| O1W—H1WB | 0.840 (18) | C6—H6 | 0.9300 |
| O2—C15 | 1.284 (3) | C7—C8 | 1.396 (4) |
| O2W—H2WA | 0.840 (18) | C7—H7 | 0.9300 |
| O2W—H2WB | 0.844 (18) | C8—C9 | 1.391 (4) |
| O3—C11 | 1.252 (3) | C9—C10 | 1.385 (4) |
| O3W—H3WA | 0.8502 | C9—H9 | 0.9300 |
| O3W—H3WB | 0.8499 | C10—H10 | 0.9300 |
| O4—C15 | 1.246 (3) | C11—C12 | 1.541 (4) |
| N1—C10 | 1.337 (3) | C12—C13 | 1.537 (4) |
| N1—C6 | 1.341 (3) | C12—C15 | 1.538 (4) |
| N2—C3 | 1.370 (3) | C12—C14 | 1.545 (4) |
| N2—C8 | 1.402 (3) | C13—H13A | 0.9600 |
| N2—H2N | 0.866 (18) | C13—H13B | 0.9600 |
| N3—C1 | 1.338 (4) | C13—H13C | 0.9600 |
| N3—C5 | 1.338 (4) | C14—H14A | 0.9600 |

supplementary materials

| | | | |
|--------------------------------------|-------------|---------------|-----------|
| N3—H3N | 0.82 (4) | C14—H14B | 0.9600 |
| C1—C2 | 1.360 (4) | C14—H14C | 0.9600 |
| O1—Ni1—O1 ⁱ | 175.89 (10) | N3—C5—H5 | 119.2 |
| O1—Ni1—O2 ⁱ | 91.75 (7) | C4—C5—H5 | 119.2 |
| O1 ⁱ —Ni1—O2 ⁱ | 85.51 (7) | N1—C6—C7 | 123.8 (2) |
| O1—Ni1—O2 | 85.51 (7) | N1—C6—H6 | 118.1 |
| O1 ⁱ —Ni1—O2 | 91.75 (7) | C7—C6—H6 | 118.1 |
| O2 ⁱ —Ni1—O2 | 96.77 (11) | C6—C7—C8 | 119.5 (2) |
| O1—Ni1—N1 ⁱ | 95.05 (8) | C6—C7—H7 | 120.2 |
| O1 ⁱ —Ni1—N1 ⁱ | 87.85 (8) | C8—C7—H7 | 120.2 |
| O2 ⁱ —Ni1—N1 ⁱ | 172.54 (8) | C9—C8—C7 | 117.2 (2) |
| O2—Ni1—N1 ⁱ | 86.81 (8) | C9—C8—N2 | 126.8 (2) |
| O1—Ni1—N1 | 87.85 (8) | C7—C8—N2 | 115.9 (2) |
| O1 ⁱ —Ni1—N1 | 95.05 (8) | C10—C9—C8 | 118.8 (3) |
| O2 ⁱ —Ni1—N1 | 86.81 (8) | C10—C9—H9 | 120.6 |
| O2—Ni1—N1 | 172.54 (8) | C8—C9—H9 | 120.6 |
| N1 ⁱ —Ni1—N1 | 90.39 (12) | N1—C10—C9 | 124.3 (3) |
| C11—O1—Ni1 | 131.61 (17) | N1—C10—H10 | 117.9 |
| H1WA—O1W—H1WB | 108.1 | C9—C10—H10 | 117.9 |
| C15—O2—Ni1 | 121.78 (16) | O3—C11—O1 | 122.6 (2) |
| H2WA—O2W—H2WB | 111 (3) | O3—C11—C12 | 117.2 (2) |
| H3WA—O3W—H3WB | 131.1 | O1—C11—C12 | 120.1 (2) |
| C10—N1—C6 | 116.2 (2) | C13—C12—C15 | 110.3 (2) |
| C10—N1—Ni1 | 123.44 (18) | C13—C12—C11 | 111.0 (2) |
| C6—N1—Ni1 | 120.21 (18) | C15—C12—C11 | 110.0 (2) |
| C3—N2—C8 | 132.4 (2) | C13—C12—C14 | 108.9 (2) |
| C3—N2—H2N | 115 (2) | C15—C12—C14 | 110.3 (2) |
| C8—N2—H2N | 112 (2) | C11—C12—C14 | 106.4 (2) |
| C1—N3—C5 | 120.8 (3) | C12—C13—H13A | 109.5 |
| C1—N3—H3N | 118 (3) | C12—C13—H13B | 109.5 |
| C5—N3—H3N | 121 (3) | H13A—C13—H13B | 109.5 |
| N3—C1—C2 | 120.5 (3) | C12—C13—H13C | 109.5 |
| N3—C1—H1 | 119.7 | H13A—C13—H13C | 109.5 |
| C2—C1—H1 | 119.7 | H13B—C13—H13C | 109.5 |
| C1—C2—C3 | 120.5 (3) | C12—C14—H14A | 109.5 |
| C1—C2—H2 | 119.8 | C12—C14—H14B | 109.5 |
| C3—C2—H2 | 119.8 | H14A—C14—H14B | 109.5 |
| N2—C3—C4 | 127.0 (3) | C12—C14—H14C | 109.5 |
| N2—C3—C2 | 115.8 (3) | H14A—C14—H14C | 109.5 |
| C4—C3—C2 | 117.2 (3) | H14B—C14—H14C | 109.5 |
| C5—C4—C3 | 119.4 (3) | O4—C15—O2 | 122.0 (2) |
| C5—C4—H4 | 120.3 | O4—C15—C12 | 120.2 (2) |
| C3—C4—H4 | 120.3 | O2—C15—C12 | 117.7 (2) |
| N3—C5—C4 | 121.5 (3) | | |
| O1 ⁱ —Ni1—O1—C11 | 18.9 (2) | C3—C4—C5—N3 | 0.3 (5) |
| O2 ⁱ —Ni1—O1—C11 | 67.1 (2) | C10—N1—C6—C7 | -2.8 (4) |

| | | | |
|-----------------------------|------------|----------------|--------------|
| O2—Ni1—O1—C11 | -29.5 (2) | Ni1—N1—C6—C7 | 173.3 (2) |
| N1 ⁱ —Ni1—O1—C11 | -115.9 (2) | N1—C6—C7—C8 | -0.3 (4) |
| N1—Ni1—O1—C11 | 153.9 (2) | C6—C7—C8—C9 | 3.3 (4) |
| O1—Ni1—O2—C15 | -9.1 (2) | C6—C7—C8—N2 | -176.7 (3) |
| O1 ⁱ —Ni1—O2—C15 | 174.0 (2) | C3—N2—C8—C9 | -17.2 (5) |
| O2 ⁱ —Ni1—O2—C15 | -100.3 (2) | C3—N2—C8—C7 | 162.8 (3) |
| N1 ⁱ —Ni1—O2—C15 | 86.2 (2) | C7—C8—C9—C10 | -3.2 (4) |
| N1—Ni1—O2—C15 | 18.1 (7) | N2—C8—C9—C10 | 176.8 (3) |
| O1—Ni1—N1—C10 | 15.1 (2) | C6—N1—C10—C9 | 2.9 (4) |
| O1 ⁱ —Ni1—N1—C10 | -167.8 (2) | Ni1—N1—C10—C9 | -173.1 (2) |
| O2 ⁱ —Ni1—N1—C10 | 107.0 (2) | C8—C9—C10—N1 | 0.1 (4) |
| O2—Ni1—N1—C10 | -12.0 (7) | Ni1—O1—C11—O3 | -157.24 (19) |
| N1 ⁱ —Ni1—N1—C10 | -80.0 (2) | Ni1—O1—C11—C12 | 20.7 (3) |
| O1—Ni1—N1—C6 | -160.7 (2) | O3—C11—C12—C13 | -32.9 (3) |
| O1 ⁱ —Ni1—N1—C6 | 16.4 (2) | O1—C11—C12—C13 | 149.1 (2) |
| O2 ⁱ —Ni1—N1—C6 | -68.9 (2) | O3—C11—C12—C15 | -155.2 (2) |
| O2—Ni1—N1—C6 | 172.2 (5) | O1—C11—C12—C15 | 26.7 (3) |
| N1 ⁱ —Ni1—N1—C6 | 104.2 (2) | O3—C11—C12—C14 | 85.4 (3) |
| C5—N3—C1—C2 | -1.6 (5) | O1—C11—C12—C14 | -92.7 (3) |
| N3—C1—C2—C3 | 1.6 (5) | Ni1—O2—C15—O4 | -127.2 (2) |
| C8—N2—C3—C4 | 5.0 (5) | Ni1—O2—C15—C12 | 53.7 (3) |
| C8—N2—C3—C2 | -174.0 (3) | C13—C12—C15—O4 | -8.5 (4) |
| C1—C2—C3—N2 | 178.5 (3) | C11—C12—C15—O4 | 114.2 (3) |
| C1—C2—C3—C4 | -0.6 (4) | C14—C12—C15—O4 | -128.8 (3) |
| N2—C3—C4—C5 | -179.3 (3) | C13—C12—C15—O2 | 170.6 (2) |
| C2—C3—C4—C5 | -0.3 (4) | C11—C12—C15—O2 | -66.6 (3) |
| C1—N3—C5—C4 | 0.6 (5) | C14—C12—C15—O2 | 50.3 (3) |

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

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

| <i>D</i> —H \cdots <i>A</i> | <i>D</i> —H | H \cdots <i>A</i> | <i>D</i> \cdots <i>A</i> | <i>D</i> —H \cdots <i>A</i> |
|-------------------------------------|-------------|---------------------|----------------------------|-------------------------------|
| O1W—H1WA \cdots O3W ⁱⁱ | 0.85 | 1.96 | 2.811 (4) | 180 |
| O1W—H1WB \cdots O2W | 0.840 (18) | 2.05 (2) | 2.870 (3) | 166 (4) |
| O2W—H2WA \cdots O3 | 0.840 (18) | 1.904 (19) | 2.741 (3) | 174 (4) |
| O2W—H2WB \cdots O4 ⁱⁱⁱ | 0.844 (18) | 1.95 (2) | 2.751 (3) | 158 (4) |
| O3W—H3WA \cdots O1W | 0.85 | 1.90 | 2.754 (4) | 179 |
| O3W—H3WB \cdots O3 ^{iv} | 0.85 | 1.94 | 2.793 (3) | 179 |
| N2—H2N \cdots O2W ^v | 0.866 (18) | 2.16 (2) | 2.985 (3) | 158 (3) |
| N3—H3N \cdots O2 ^{vi} | 0.82 (4) | 1.86 (4) | 2.683 (3) | 176 (4) |

Symmetry codes: (ii) $-x-1/2, -y+5/2, -z$; (iii) $-x-1/2, y+1/2, -z+1/2$; (iv) $-x-1/2, -y+3/2, -z$; (v) $x+1/2, y+1/2, z$; (vi) $x, -y+2, z-1/2$.

Fig. 2

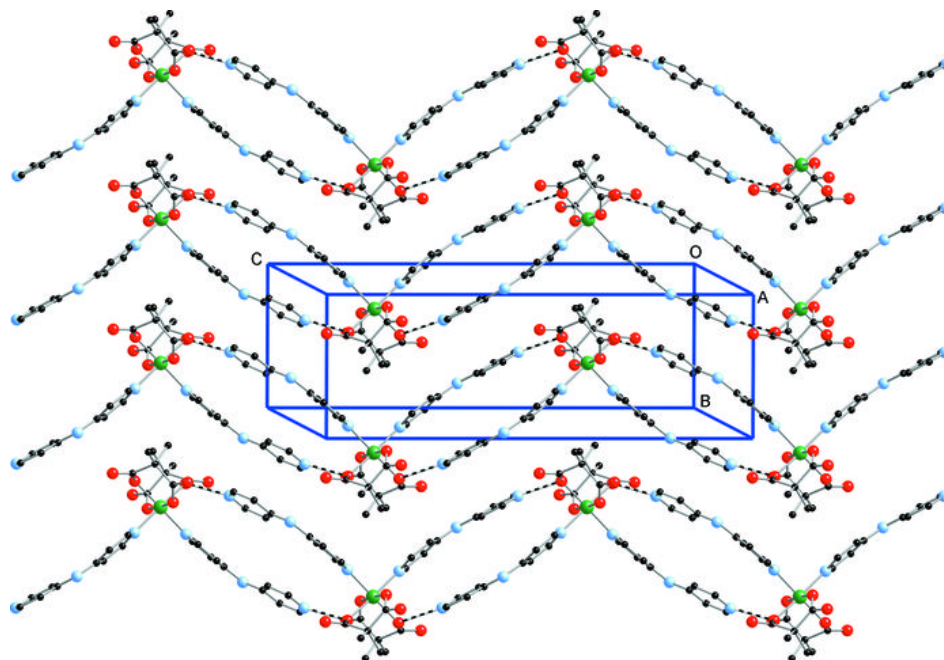


Fig. 3

