

Diaqua[5,5'-dicarboxy-2,2'-(propane-1,3-diyl)bis(1*H*-imidazole-4-carboxylato)]nickel(II) dihydrate

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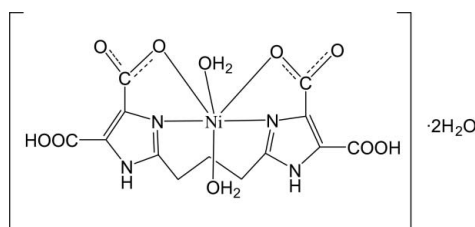
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; disorder in main residue; R factor = 0.040; wR factor = 0.098; data-to-parameter ratio = 12.5.

In the title complex, $[\text{Ni}(\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_8)(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$, the Ni^{2+} cation is six-coordinated by two N atoms and two O atoms from the tetradentate anion in equatorial positions and by two water O atoms in axial positions, leading to a distorted octahedral environment. The central C atom of the propane-diyl unit is disordered over two sites in a 0.531 (6):0.469 (6) ratio. In the crystal, adjacent molecules are linked through $\text{O}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen-bonding interactions into a three-dimensional network.

Related literature

For background to complexes based on 1*H*-imidazole-4,5-dicarboxylic acid, see: Baures *et al.* (2002); Sun & Yang (2007).



Experimental

Crystal data

 $[\text{Ni}(\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_8)(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$
 $M_r = 481.02$

 Triclinic, $P\bar{1}$
 $a = 8.9852$ (18) Å

 $b = 9.4392$ (19) Å

 $c = 12.538$ (3) Å

 $\alpha = 108.81$ (3)°

 $\beta = 92.34$ (3)°

 $\gamma = 116.18$ (3)°

 $V = 882.1$ (5) Å³
 $Z = 2$

 Mo $K\alpha$ radiation

 $\mu = 1.18$ mm⁻¹
 $T = 293$ K

 $0.21 \times 0.18 \times 0.15$ mm

Data collection

Rigaku Saturn diffractometer
Absorption correction: multi-scan
(*CrystalClear*; Rigaku/MS, 2006)

 $T_{\min} = 0.790$, $T_{\max} = 0.843$

9532 measured reflections
3451 independent reflections
3037 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.098$
 $S = 1.02$

3451 reflections

275 parameters

H-atom parameters constrained

 $\Delta\rho_{\max} = 0.79$ e Å⁻³
 $\Delta\rho_{\min} = -0.49$ e Å⁻³
Table 1

Selected bond lengths (Å).

Ni1—O5	2.0514 (18)	Ni1—O10	2.078 (2)
Ni1—N1	2.060 (2)	Ni1—O9	2.093 (2)
Ni1—N3	2.072 (2)	Ni1—O1	2.128 (2)

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H} \cdots A$	$D-\text{H}$	$\text{H} \cdots A$	$D \cdots A$	$D-\text{H} \cdots A$
O3—H3···O2	0.89	1.60	2.485 (3)	176
O7—H7···O6	0.89	1.62	2.501 (3)	171
O12—H12B···O4	0.85	2.57	3.279 (3)	142
N2—H2···O12 ⁱ	0.86	1.95	2.802 (3)	171
N4—H4···O11 ⁱⁱ	0.86	1.87	2.721 (3)	170
O10—H10A···O3 ⁱⁱⁱ	0.85	2.01	2.853 (3)	171
O9—H9A···O8 ⁱⁱⁱ	0.85	1.93	2.781 (3)	176
O9—H9A···O7 ⁱⁱⁱ	0.85	2.64	3.157 (3)	121
O11—H11B···O8 ⁱⁱⁱ	0.85	2.37	2.884 (3)	120
O9—H9B···O6 ^{iv}	0.85	1.91	2.762 (3)	175
O10—H10B···O4 ^v	0.85	1.84	2.667 (3)	165
O12—H12A···O1 ^v	0.85	2.26	3.063 (4)	159
O12—H12B···O10 ^v	0.85	2.62	3.198 (4)	126
O11—H11A···O5 ^{vi}	0.85	1.96	2.762 (3)	157
O11—H11B···O9 ^{vii}	0.85	2.34	3.100 (3)	148

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

Data collection: *CrystalClear* (Rigaku/MS, 2006); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: WM2496).

References

- Baures, P.-W., Rush, J.-R., Wiznycia, A.-V., Desper, J., Helfrich, B.-A. & Beatty, A.-M. (2002). *Cryst. Growth Des.* **6**, 653–664.
Rigaku/MS (2006). *CrystalClear*. Rigaku/MS Inc., The Woodlands, Texas, USA, and Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
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supplementary materials

Acta Cryst. (2011). E67, m988 [doi:10.1107/S1600536811024391]

Diaqua[5,5'-dicarboxy-2,2'-(propane-1,3-diyl)bis(1*H*-imidazole-4-carboxylato)]nickel(II) dihydrate

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Comment

Numerous compounds with metal-organic framework structures constructed from 1*H*-imidazole-4,5-dicarboxylic acid or its derivatives have been synthesized (Baures *et al.*, 2002; Sun & Yang, 2007). To further explore frameworks with new structures, we used 2,2'-(1,3-propanediyl)bis-1*H*-imidazole-4,5-dicarboxylic acid (H₆pbide) which has both N-donor and O-donor sites for self-assembly with various metal cations. As a metal source we have used NiCl₂ and have obtained the title complex [Ni(H₄pbide)(H₂O)₂]₂·2H₂O (H₆pbide = 2,2'-(1,3-propanediyl)bis-1*H*-imidazole-4,5-dicarboxylic acid), or [Ni(C₁₃H₁₀N₄O₈)(H₂O)₂]₂·2H₂O.

As shown in Figure 1, the Ni²⁺ cation is in a distorted octahedral coordination environment defined by atoms N1, N3, O1, O5 from the tetradentate H₄pbide²⁻ anion in equatorial positions and by atoms O9, O10 from water molecules in axial positions. The two imidazole rings are nearly co-planar, with a dihedral angle between the two least-square planes N1, C5, N2, C3, C2 and N3, C12, C10, N4, C9 of 6.8 (2) °. Intramolecular O—H··O hydrogen bonds between the carboxyl/carboxylate groups stabilize the molecular configuration. O—H··O and N—H··O hydrogen bonds between the water molecules and carboxylate O atoms and between imidazole groups and carboxylate O atoms of adjacent molecules consolidate the crystal packing.

Experimental

A mixture of NiCl₂ (0.05 mmol), 2,2'-(1,3-propanediyl)bis-1*H*-imidazole-4,5-dicarboxylic (0.05 mmol), methanol (2 ml) and water (2 ml) was placed in a 25 ml Teflon-lined stainless steel vessel and heated at 393 K for 48 h, then cooled to room temperature. Light-green crystals were obtained from the filtrate and dried in air.

Refinement

The disordered central C atom C7 of the propanediyl unit has been modelled by splitting it into two combined parts (C7 and C7A; ratio 0.531 (6):0.469 (6)). Hydrogen atoms except for those associated with O12 were positioned geometrically and refined as riding atoms, with C—H = 0.97 Å, N—H = 0.86 Å and O—H = 0.85 (H₂O) and 0.89 (—COOH) Å, and with U_{iso}(H) = 1.2 U_{eq}(C,N,O). Although water H atoms associated with O12 were located in the difference Fourier map (modelled with an O—H distance constrained to 0.85 Å, and with U_{iso}(H) = 1.2 U_{eq}(O)), it appears likely, both from the hydrogen bonding scheme and the symmetry-relation of adjacent O12 water molecules *via* inversion centres, that the H atoms of this water molecule are disordered. Nevertheless, the finally obtained model is plausible and we eventually kept these H atoms for refinement.

Figures

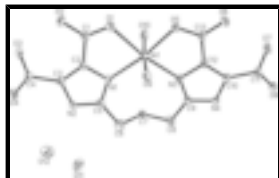


Fig. 1. View of the title complex, showing the labelling of the atoms. Displacement ellipsoids are displayed at the 30% probability level. H atoms are omitted for clarity; only one part of the central C atom of the propane-1,3-diy unit is shown.

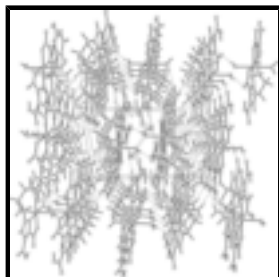


Fig. 2. View of the crystal packing of the title complex, showing the three-dimensional structure stabilized by hydrogen bonds (dashed lines).

Diaqua[5,5'-dicarboxy-2,2'-(propane-1,3-diy)bis(1H-imidazole-4-carboxylato)]nickel(II) dihydrate

Crystal data

$[\text{Ni}(\text{C}_{13}\text{H}_{10}\text{N}_4\text{O}_8)(\text{H}_2\text{O})_2] \cdot 2\text{H}_2\text{O}$

$M_r = 481.02$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 8.9852\ (18)\ \text{\AA}$

$b = 9.4392\ (19)\ \text{\AA}$

$c = 12.538\ (3)\ \text{\AA}$

$\alpha = 108.81\ (3)^\circ$

$\beta = 92.34\ (3)^\circ$

$\gamma = 116.18\ (3)^\circ$

$V = 882.1\ (5)\ \text{\AA}^3$

$Z = 2$

$F(000) = 496$

$D_x = 1.811\ \text{Mg m}^{-3}$

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

Cell parameters from 2450 reflections

$\theta = 2.6\text{--}27.9^\circ$

$\mu = 1.18\ \text{mm}^{-1}$

$T = 293\ \text{K}$

Prism, green

$0.21 \times 0.18 \times 0.15\ \text{mm}$

Data collection

Rigaku Saturn
diffractometer

Radiation source: fine-focus sealed tube
graphite

Detector resolution: $28.5714\ \text{pixels mm}^{-1}$

ω scans

Absorption correction: multi-scan
(*CrystalClear*; Rigaku/MSO, 2006)

$T_{\min} = 0.790$, $T_{\max} = 0.843$

9532 measured reflections

3451 independent reflections

3037 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.025$

$\theta_{\max} = 26.0^\circ$, $\theta_{\min} = 2.6^\circ$

$h = -11 \rightarrow 10$

$k = -11 \rightarrow 11$

$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.040$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.098$	H-atom parameters constrained
$S = 1.02$	$w = 1/[\sigma^2(F_o^2) + (0.056P)^2 + 0.3821P]$
3451 reflections	where $P = (F_o^2 + 2F_c^2)/3$
275 parameters	$(\Delta/\sigma)_{\max} < 0.001$
0 restraints	$\Delta\rho_{\max} = 0.79 \text{ e } \text{\AA}^{-3}$
	$\Delta\rho_{\min} = -0.49 \text{ e } \text{\AA}^{-3}$

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.

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	-0.42402 (4)	0.90838 (4)	0.72525 (3)	0.02527 (13)	
N1	-0.3010 (3)	0.8092 (3)	0.79563 (19)	0.0263 (5)	
N2	-0.1769 (3)	0.6933 (3)	0.8643 (2)	0.0316 (5)	
H2	-0.1639	0.6220	0.8872	0.038*	
N3	-0.6835 (3)	0.7484 (3)	0.69036 (17)	0.0230 (5)	
N4	-0.9581 (3)	0.5817 (3)	0.65436 (18)	0.0251 (5)	
H4	-1.0542	0.4986	0.6509	0.030*	
O1	-0.1678 (2)	1.1022 (3)	0.75887 (18)	0.0361 (5)	
O2	0.0976 (2)	1.1730 (3)	0.8274 (2)	0.0443 (5)	
O3	0.2406 (2)	1.0420 (3)	0.90408 (18)	0.0382 (5)	
H3	0.1934	1.0939	0.8789	0.046*	
O4	0.1688 (3)	0.8133 (3)	0.94778 (18)	0.0394 (5)	
O5	-0.5025 (2)	1.0349 (2)	0.65068 (17)	0.0319 (4)	
O6	-0.7326 (2)	1.0223 (3)	0.56576 (19)	0.0371 (5)	
O7	-1.0474 (2)	0.8392 (3)	0.5275 (2)	0.0451 (6)	
H7	-0.9373	0.9087	0.5364	0.054*	
O8	-1.2265 (2)	0.6084 (2)	0.55412 (17)	0.0356 (5)	
O9	-0.4159 (2)	0.7760 (2)	0.55768 (16)	0.0303 (4)	

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H9A	-0.3629	0.7202	0.5567	0.036*	
H9B	-0.3671	0.8430	0.5235	0.036*	
O10	-0.4382 (2)	1.0567 (3)	0.88393 (17)	0.0436 (5)	
H10A	-0.5282	1.0618	0.8968	0.052*	
H10B	-0.3653	1.0951	0.9453	0.052*	
O11	-0.2803 (3)	0.3396 (3)	0.6349 (2)	0.0513 (6)	
H11A	-0.3282	0.2375	0.6319	0.062*	
H11B	-0.3368	0.3486	0.5839	0.062*	
O12	0.1580 (4)	0.5672 (3)	1.0849 (3)	0.0723 (8)	
H12A	0.1773	0.6568	1.1416	0.087*	
H12B	0.2033	0.6225	1.0429	0.087*	
C1	-0.0641 (3)	1.0721 (4)	0.8012 (2)	0.0301 (6)	
C2	-0.1280 (3)	0.9137 (3)	0.8225 (2)	0.0247 (5)	
C3	-0.0494 (3)	0.8432 (3)	0.8655 (2)	0.0260 (6)	
C4	0.1325 (3)	0.9006 (3)	0.9095 (2)	0.0279 (6)	
C5	-0.3264 (3)	0.6761 (4)	0.8214 (3)	0.0331 (6)	
C6	-0.4936 (4)	0.5266 (5)	0.8043 (4)	0.0640 (10)	
H6BC	-0.4708	0.4323	0.7944	0.077*	0.531 (6)
H6BD	-0.5280	0.5511	0.8775	0.077*	0.531 (6)
H6AA	-0.4784	0.4641	0.8480	0.077*	0.469 (6)
H6AB	-0.5309	0.4519	0.7234	0.077*	0.469 (6)
C7	-0.6258 (7)	0.5718 (7)	0.8422 (5)	0.0250 (14)	0.469 (6)
H7A	-0.5750	0.6952	0.8718	0.030*	0.469 (6)
H7B	-0.6568	0.5367	0.9063	0.030*	0.469 (6)
C8	-0.7859 (4)	0.5000 (4)	0.7560 (3)	0.0435 (8)	
H8BC	-0.8907	0.3927	0.7314	0.052*	0.531 (6)
H8BD	-0.7651	0.5553	0.8391	0.052*	0.531 (6)
H8AA	-0.8817	0.4600	0.7918	0.052*	0.469 (6)
H8AB	-0.7941	0.4006	0.6950	0.052*	0.469 (6)
C9	-0.8044 (3)	0.6107 (3)	0.7005 (2)	0.0241 (5)	
C10	-0.9358 (3)	0.7068 (3)	0.6140 (2)	0.0242 (5)	
C11	-1.0812 (3)	0.7141 (3)	0.5620 (2)	0.0284 (6)	
C12	-0.7641 (3)	0.8093 (3)	0.6366 (2)	0.0234 (5)	
C13	-0.6606 (3)	0.9664 (3)	0.6158 (2)	0.0274 (6)	
C7A	-0.6330 (8)	0.4635 (9)	0.7229 (8)	0.0640 (10)	0.531 (6)
H7AA	-0.6791	0.3406	0.6893	0.077*	0.531 (6)
H7AB	-0.5961	0.5056	0.6625	0.077*	0.531 (6)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01820 (19)	0.0280 (2)	0.0328 (2)	0.01094 (15)	0.00339 (14)	0.01571 (15)
N1	0.0189 (11)	0.0294 (12)	0.0302 (12)	0.0123 (10)	0.0013 (9)	0.0103 (9)
N2	0.0277 (12)	0.0314 (12)	0.0435 (14)	0.0188 (11)	0.0040 (10)	0.0174 (11)
N3	0.0191 (11)	0.0269 (11)	0.0259 (11)	0.0117 (9)	0.0059 (9)	0.0126 (9)
N4	0.0183 (11)	0.0232 (11)	0.0323 (12)	0.0076 (9)	0.0048 (9)	0.0121 (9)
O1	0.0262 (10)	0.0364 (11)	0.0517 (13)	0.0140 (9)	0.0055 (9)	0.0255 (10)
O2	0.0227 (11)	0.0410 (12)	0.0694 (15)	0.0095 (10)	0.0035 (10)	0.0302 (11)

O3	0.0232 (10)	0.0449 (12)	0.0467 (12)	0.0179 (10)	0.0009 (9)	0.0159 (10)
O4	0.0331 (11)	0.0454 (12)	0.0407 (12)	0.0250 (10)	-0.0046 (9)	0.0101 (10)
O5	0.0209 (10)	0.0324 (10)	0.0471 (12)	0.0105 (8)	0.0052 (8)	0.0241 (9)
O6	0.0275 (10)	0.0453 (12)	0.0551 (13)	0.0196 (10)	0.0099 (9)	0.0358 (10)
O7	0.0218 (10)	0.0520 (13)	0.0728 (16)	0.0158 (10)	0.0044 (10)	0.0407 (12)
O8	0.0208 (10)	0.0348 (11)	0.0493 (13)	0.0116 (9)	0.0028 (9)	0.0168 (9)
O9	0.0265 (10)	0.0386 (11)	0.0373 (11)	0.0191 (9)	0.0108 (8)	0.0226 (9)
O10	0.0279 (11)	0.0621 (14)	0.0340 (11)	0.0262 (11)	0.0004 (9)	0.0040 (10)
O11	0.0313 (12)	0.0441 (13)	0.0710 (16)	0.0043 (10)	0.0005 (11)	0.0341 (12)
O12	0.090 (2)	0.0575 (16)	0.081 (2)	0.0379 (16)	0.0068 (16)	0.0390 (15)
C1	0.0230 (14)	0.0337 (15)	0.0339 (15)	0.0145 (12)	0.0059 (11)	0.0118 (12)
C2	0.0190 (13)	0.0310 (14)	0.0239 (13)	0.0137 (11)	0.0032 (10)	0.0079 (11)
C3	0.0234 (14)	0.0290 (14)	0.0260 (13)	0.0149 (12)	0.0040 (10)	0.0075 (11)
C4	0.0246 (14)	0.0332 (15)	0.0230 (13)	0.0167 (13)	0.0023 (10)	0.0034 (11)
C5	0.0249 (14)	0.0325 (15)	0.0454 (17)	0.0158 (13)	0.0070 (12)	0.0159 (13)
C6	0.0307 (16)	0.0442 (18)	0.118 (3)	0.0155 (15)	0.0163 (18)	0.036 (2)
C7	0.023 (3)	0.029 (3)	0.030 (3)	0.013 (2)	0.006 (2)	0.019 (2)
C8	0.0361 (18)	0.0466 (19)	0.061 (2)	0.0205 (15)	0.0116 (15)	0.0347 (17)
C9	0.0217 (13)	0.0252 (13)	0.0263 (13)	0.0117 (11)	0.0074 (10)	0.0101 (11)
C10	0.0195 (13)	0.0275 (13)	0.0244 (12)	0.0112 (11)	0.0037 (10)	0.0087 (10)
C11	0.0232 (14)	0.0309 (14)	0.0310 (14)	0.0141 (12)	0.0028 (11)	0.0103 (11)
C12	0.0218 (13)	0.0256 (13)	0.0273 (13)	0.0145 (11)	0.0062 (10)	0.0108 (10)
C13	0.0206 (13)	0.0312 (14)	0.0328 (14)	0.0131 (12)	0.0049 (11)	0.0142 (12)
C7A	0.0307 (16)	0.0442 (18)	0.118 (3)	0.0155 (15)	0.0163 (18)	0.036 (2)

Geometric parameters (Å, °)

Ni1—O5	2.0514 (18)	O11—H11A	0.8504
Ni1—N1	2.060 (2)	O11—H11B	0.8499
Ni1—N3	2.072 (2)	O12—H12A	0.8500
Ni1—O10	2.078 (2)	O12—H12B	0.8499
Ni1—O9	2.093 (2)	C1—C2	1.466 (4)
Ni1—O1	2.128 (2)	C2—C3	1.358 (4)
N1—C5	1.323 (4)	C3—C4	1.491 (4)
N1—C2	1.376 (3)	C5—C6	1.484 (4)
N2—C5	1.346 (3)	C6—C7A	1.346 (8)
N2—C3	1.368 (4)	C6—C7	1.477 (6)
N2—H2	0.8600	C6—H6BC	0.9700
N3—C9	1.325 (3)	C6—H6BD	0.9700
N3—C12	1.374 (3)	C6—H6AA	0.9702
N4—C9	1.348 (3)	C6—H6AB	0.9698
N4—C10	1.369 (3)	C7—C8	1.496 (6)
N4—H4	0.8600	C7—H7A	0.9700
O1—C1	1.234 (3)	C7—H7B	0.9700
O2—C1	1.290 (3)	C8—C9	1.489 (4)
O3—C4	1.284 (4)	C8—C7A	1.596 (7)
O3—H3	0.8899	C8—H8BC	0.9700
O4—C4	1.222 (3)	C8—H8BD	0.9700
O5—C13	1.258 (3)	C8—H8AA	0.9699

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O6—C13	1.254 (3)	C8—H8AB	0.9702
O7—C11	1.303 (3)	C10—C12	1.366 (4)
O7—H7	0.8901	C10—C11	1.475 (3)
O8—C11	1.219 (3)	C12—C13	1.478 (4)
O9—H9A	0.8499	C7A—H6AB	0.9711
O9—H9B	0.8499	C7A—H8AB	1.2792
O10—H10A	0.8497	C7A—H7AA	0.9700
O10—H10B	0.8499	C7A—H7AB	0.9700
O5—Ni1—N1	169.24 (8)	C5—C6—H6BD	105.7
O5—Ni1—N3	81.61 (8)	H6BC—C6—H6BD	106.1
N1—Ni1—N3	108.79 (9)	C7A—C6—H6AA	123.7
O5—Ni1—O10	88.48 (9)	C7—C6—H6AA	108.3
N1—Ni1—O10	94.21 (9)	C5—C6—H6AA	108.1
N3—Ni1—O10	89.72 (9)	C7—C6—H6AB	109.8
O5—Ni1—O9	85.09 (8)	C5—C6—H6AB	108.8
N1—Ni1—O9	92.00 (8)	H6BD—C6—H6AB	144.7
N3—Ni1—O9	89.98 (9)	H6AA—C6—H6AB	107.7
O10—Ni1—O9	173.54 (8)	C6—C7—C8	118.4 (4)
O5—Ni1—O1	89.84 (8)	C6—C7—H7A	107.7
N1—Ni1—O1	79.91 (8)	C8—C7—H7A	107.7
N3—Ni1—O1	170.90 (8)	C6—C7—H7B	107.7
O10—Ni1—O1	86.91 (9)	C8—C7—H7B	107.7
O9—Ni1—O1	92.42 (9)	H7A—C7—H7B	107.1
C5—N1—C2	106.1 (2)	C9—C8—C7	118.5 (3)
C5—N1—Ni1	143.02 (19)	C9—C8—C7A	111.2 (4)
C2—N1—Ni1	110.77 (17)	C7—C8—C7A	57.7 (4)
C5—N2—C3	108.5 (2)	C9—C8—H8BC	109.4
C5—N2—H2	125.8	C7—C8—H8BC	131.9
C3—N2—H2	125.8	C7A—C8—H8BC	109.4
C9—N3—C12	106.5 (2)	C9—C8—H8BD	109.4
C9—N3—Ni1	145.05 (18)	C7A—C8—H8BD	109.4
C12—N3—Ni1	108.42 (16)	H8BC—C8—H8BD	108.0
C9—N4—C10	108.6 (2)	C9—C8—H8AA	108.2
C9—N4—H4	125.7	C7—C8—H8AA	108.8
C10—N4—H4	125.7	C7A—C8—H8AA	139.8
C1—O1—Ni1	113.46 (18)	C9—C8—H8AB	107.3
C4—O3—H3	113.8	C7—C8—H8AB	106.4
C13—O5—Ni1	115.03 (17)	H8BC—C8—H8AB	60.8
C11—O7—H7	114.9	H8BD—C8—H8AB	143.2
Ni1—O9—H9A	112.4	H8AA—C8—H8AB	107.1
Ni1—O9—H9B	111.7	N3—C9—N4	110.0 (2)
H9A—O9—H9B	107.0	N3—C9—C8	128.3 (2)
Ni1—O10—H10A	122.8	N4—C9—C8	121.7 (2)
Ni1—O10—H10B	122.2	C12—C10—N4	105.5 (2)
H10A—O10—H10B	113.1	C12—C10—C11	132.8 (2)
H11A—O11—H11B	110.1	N4—C10—C11	121.7 (2)
H12A—O12—H12B	93.0	O8—C11—O7	121.9 (2)
O1—C1—O2	123.1 (3)	O8—C11—C10	120.8 (2)
O1—C1—C2	118.3 (2)	O7—C11—C10	117.3 (2)

O2—C1—C2	118.6 (2)	C10—C12—N3	109.5 (2)
C3—C2—N1	109.7 (2)	C10—C12—C13	131.6 (2)
C3—C2—C1	132.8 (2)	N3—C12—C13	118.9 (2)
N1—C2—C1	117.5 (2)	O6—C13—O5	124.5 (2)
C2—C3—N2	105.5 (2)	O6—C13—C12	119.5 (2)
C2—C3—C4	132.7 (3)	O5—C13—C12	116.0 (2)
N2—C3—C4	121.7 (2)	C6—C7A—C8	120.2 (6)
O4—C4—O3	124.9 (3)	C8—C7A—H6AB	165.8
O4—C4—C3	119.3 (3)	C6—C7A—H8AB	149.0
O3—C4—C3	115.8 (2)	H6AB—C7A—H8AB	151.6
N1—C5—N2	110.2 (2)	C6—C7A—H7AA	107.3
N1—C5—C6	125.8 (3)	C8—C7A—H7AA	107.3
N2—C5—C6	124.0 (3)	H6AB—C7A—H7AA	77.9
C7A—C6—C7	63.7 (4)	H8AB—C7A—H7AA	73.9
C7A—C6—C5	126.5 (5)	C6—C7A—H7AB	107.3
C7—C6—C5	113.9 (3)	C8—C7A—H7AB	107.3
C7A—C6—H6BC	105.7	H6AB—C7A—H7AB	83.1
C7—C6—H6BC	136.7	H8AB—C7A—H7AB	101.6
C5—C6—H6BC	105.7	H7AA—C7A—H7AB	106.9
C7A—C6—H6BD	105.7		
N3—Ni1—N1—C5	5.0 (3)	Ni1—N1—C5—N2	177.0 (2)
O10—Ni1—N1—C5	96.1 (3)	C2—N1—C5—C6	-178.3 (3)
O9—Ni1—N1—C5	-85.7 (3)	Ni1—N1—C5—C6	-1.9 (6)
O1—Ni1—N1—C5	-177.8 (3)	C3—N2—C5—N1	-0.5 (3)
O5—Ni1—N1—C2	16.6 (5)	C3—N2—C5—C6	178.4 (3)
N3—Ni1—N1—C2	-178.70 (16)	N1—C5—C6—C7A	29.0 (7)
O10—Ni1—N1—C2	-87.56 (18)	N2—C5—C6—C7A	-149.8 (5)
O9—Ni1—N1—C2	90.65 (18)	N1—C5—C6—C7	-45.1 (6)
O1—Ni1—N1—C2	-1.46 (16)	N2—C5—C6—C7	136.1 (4)
O5—Ni1—N3—C9	-177.6 (3)	C7A—C6—C7—C8	2.0 (5)
N1—Ni1—N3—C9	5.2 (3)	C5—C6—C7—C8	122.5 (4)
O10—Ni1—N3—C9	-89.1 (3)	C6—C7—C8—C9	-100.1 (5)
O9—Ni1—N3—C9	97.3 (3)	C6—C7—C8—C7A	-1.8 (4)
O5—Ni1—N3—C12	1.02 (16)	C12—N3—C9—N4	0.5 (3)
N1—Ni1—N3—C12	-176.13 (15)	Ni1—N3—C9—N4	179.1 (2)
O10—Ni1—N3—C12	89.52 (17)	C12—N3—C9—C8	-177.8 (3)
O9—Ni1—N3—C12	-84.02 (16)	Ni1—N3—C9—C8	0.9 (5)
O5—Ni1—O1—C1	-175.7 (2)	C10—N4—C9—N3	-0.7 (3)
N1—Ni1—O1—C1	1.0 (2)	C10—N4—C9—C8	177.7 (2)
O10—Ni1—O1—C1	95.8 (2)	C7—C8—C9—N3	21.0 (5)
O9—Ni1—O1—C1	-90.7 (2)	C7A—C8—C9—N3	-42.8 (5)
N1—Ni1—O5—C13	163.9 (4)	C7—C8—C9—N4	-157.1 (3)
N3—Ni1—O5—C13	-1.47 (19)	C7A—C8—C9—N4	139.1 (4)
O10—Ni1—O5—C13	-91.4 (2)	C9—N4—C10—C12	0.6 (3)
O9—Ni1—O5—C13	89.2 (2)	C9—N4—C10—C11	-177.8 (2)
O1—Ni1—O5—C13	-178.32 (19)	C12—C10—C11—O8	-177.5 (3)
Ni1—O1—C1—O2	179.6 (2)	N4—C10—C11—O8	0.3 (4)
Ni1—O1—C1—C2	-0.2 (3)	C12—C10—C11—O7	1.2 (4)
C5—N1—C2—C3	-0.4 (3)	N4—C10—C11—O7	179.0 (2)

supplementary materials

Ni1—N1—C2—C3	-178.14 (17)	N4—C10—C12—N3	-0.3 (3)
C5—N1—C2—C1	179.5 (2)	C11—C10—C12—N3	177.8 (3)
Ni1—N1—C2—C1	1.8 (3)	N4—C10—C12—C13	-178.8 (3)
O1—C1—C2—C3	178.9 (3)	C11—C10—C12—C13	-0.7 (5)
O2—C1—C2—C3	-1.0 (5)	C9—N3—C12—C10	-0.1 (3)
O1—C1—C2—N1	-1.1 (4)	Ni1—N3—C12—C10	-179.28 (17)
O2—C1—C2—N1	179.0 (2)	C9—N3—C12—C13	178.6 (2)
N1—C2—C3—N2	0.1 (3)	Ni1—N3—C12—C13	-0.6 (3)
C1—C2—C3—N2	-179.9 (3)	Ni1—O5—C13—O6	-178.4 (2)
N1—C2—C3—C4	-178.8 (3)	Ni1—O5—C13—C12	1.5 (3)
C1—C2—C3—C4	1.2 (5)	C10—C12—C13—O6	-2.3 (4)
C5—N2—C3—C2	0.2 (3)	N3—C12—C13—O6	179.3 (2)
C5—N2—C3—C4	179.3 (2)	C10—C12—C13—O5	177.7 (3)
C2—C3—C4—O4	177.4 (3)	N3—C12—C13—O5	-0.6 (4)
N2—C3—C4—O4	-1.4 (4)	C7—C6—C7A—C8	-1.9 (5)
C2—C3—C4—O3	-2.4 (4)	C5—C6—C7A—C8	-103.3 (6)
N2—C3—C4—O3	178.7 (2)	C9—C8—C7A—C6	113.1 (6)
C2—N1—C5—N2	0.6 (3)	C7—C8—C7A—C6	2.0 (5)

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3 \cdots O2	0.89	1.60	2.485 (3)	176
O7—H7 \cdots O6	0.89	1.62	2.501 (3)	171
O12—H12B \cdots O4	0.85	2.57	3.279 (3)	142
N2—H2 \cdots O12 ⁱ	0.86	1.95	2.802 (3)	171
N4—H4 \cdots O11 ⁱⁱ	0.86	1.87	2.721 (3)	170
O10—H10A \cdots O3 ⁱⁱ	0.85	2.01	2.853 (3)	171
O9—H9A \cdots O8 ⁱⁱⁱ	0.85	1.93	2.781 (3)	176
O9—H9A \cdots O7 ⁱⁱⁱ	0.85	2.64	3.157 (3)	121
O11—H11B \cdots O8 ⁱⁱⁱ	0.85	2.37	2.884 (3)	120
O9—H9B \cdots O6 ^{iv}	0.85	1.91	2.762 (3)	175
O10—H10B \cdots O4 ^v	0.85	1.84	2.667 (3)	165
O12—H12A \cdots O1 ^v	0.85	2.26	3.063 (4)	159
O12—H12B \cdots O10 ^v	0.85	2.62	3.198 (4)	126
O11—H11A \cdots O5 ^{vi}	0.85	1.96	2.762 (3)	157
O11—H11B \cdots O9 ^{vii}	0.85	2.34	3.100 (3)	148

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

Fig. 1

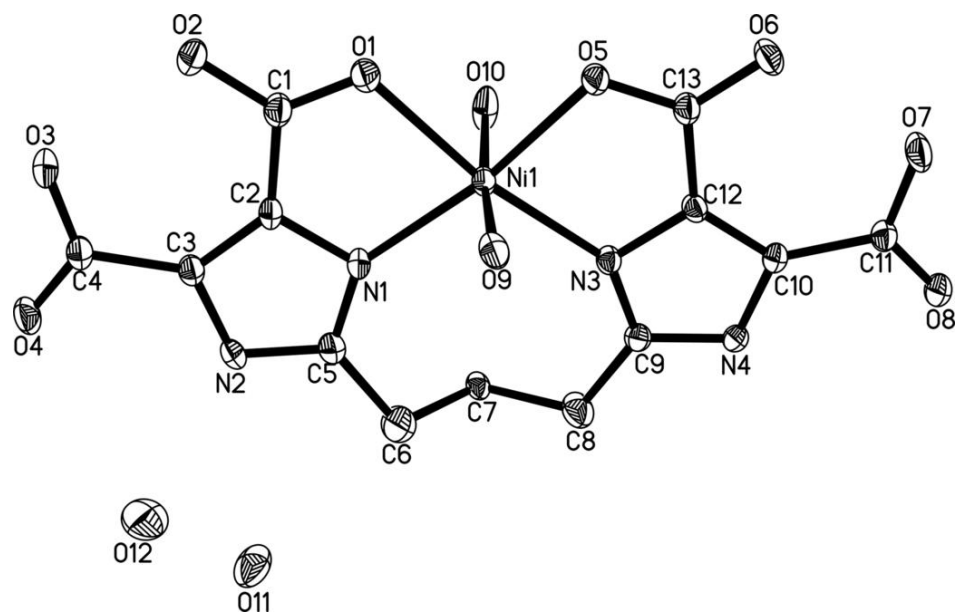


Fig. 2

