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Piperazinediium bis(pyridine-2,6-dicarboxylato)nickelate(II) tetrahydrate

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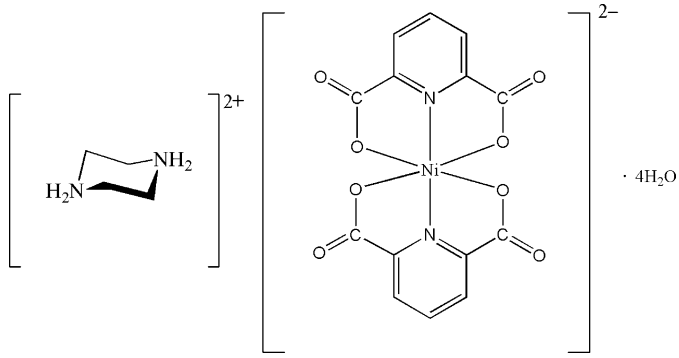
Key indicators: single-crystal X-ray study; T = 150 K; mean σ(C–C) = 0.003 Å; R factor = 0.038; wR factor = 0.094; data-to-parameter ratio = 16.1.

The reaction of nickel(II) nitrate hexahydrate with the proton-transfer compound piperazinediium pyridine-2,6-dicarboxylate, or (pipzH_2)(pydc) (in which pipz is piperazine and pydcH_2 is pyridine-2,6-dicarboxylic acid), in aqueous solution leads to the formation of the title compound, (pipzH_2)[Ni(pydc)$_2$]·4H_2O or ($C_4H_{12}N_2$)[Ni($C_7H_3NO_4$)$_2$]·4H_2O. The anion is a six-coordinate complex with a distorted octahedral geometry around Ni^{II}. The torsion angles show that the two $(pydc)^{2-}$ units are almost perpendicular to each other. Considerable π–π stacking interactions between two aromatic rings of $(pydc)^{2-}$, with distances of 3.4686 (14) and 3.5034 (14) Å, are observed. Extensive intermolecular O—H···O, N—H···O and C—H···O hydrogen bonding involving the $(pydc)^{2-}$ ligand, $(pipzH_2)^{2+}$ as counter-ion and uncoordinated water molecules connect the various components into a supramolecular structure.

Related literature

We have reported cases in which proton transfer from pyridine-2,6-dicarboxylic acid (pydcH_2) and benzene-1,2,4,5-tetracarboxylic acid (btcH_4) to piperazine (pipz) and 1,10-phenanthroline (phen) resulted in the formation of novel self-assembled (pipzH_2)(pydc) (Aghabozorg, Ghadermazi, Manteghi & Nakhjavan, 2006) and (phen$H$)$_4$(btcH_3)$_2$(btcH_2) (Aghabozorg, Ghadermazi & Attar Gharamaleki, 2006) systems, respectively. The resulting compounds, with some remaining sites as electron donors, can coordinate to many metallic ions (Aghabozorg, Ghasemikhah, Ghadermazi *et al.*, 2006; Aghabozorg, Ghasemikhah, Soleimannejad *et al.*, 2006).

For related literature, see: Aghabozorg, Aghajani & Sharif (2006); Aghabozorg, Zabihi *et al.* (2006).



Experimental

Crystal data

($C_4H_{12}N_2$)[Ni($C_7H_3NO_4$)$_2$]·4H_2O
M_r = 549.14
Monoclinic, $P2_1/n$
a = 7.9776 (11) Å
b = 13.2767 (19) Å
c = 21.054 (3) Å
β = 90.502 (2)°
V = 2229.8 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.94 mm^{-1}
T = 150 (2) K
0.18 × 0.15 × 0.07 mm

Data collection

Bruker SMART area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.849, T_{max} = 0.937
25180 measured reflections
5111 independent reflections
3612 reflections with $I > 2\sigma(I)$
R_{int} = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.094
S = 1.01
5111 reflections
318 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.42 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ni1—N2	1.9575 (19)	Ni1—O5	2.1340 (16)
Ni1—N1	1.9626 (19)	Ni1—O4	2.1400 (16)
Ni1—O8	2.1320 (16)	Ni1—O1	2.1429 (16)
N2—Ni1—N1	172.66 (8)	O8—Ni1—O1	87.00 (6)
O8—Ni1—O5	156.31 (6)	O4—Ni1—O1	155.72 (6)
O5—Ni1—O4	87.82 (6)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O9—H9B···O5^{i}	0.95	1.87	2.819 (2)	177
O9—H9A···O2^{ii}	0.95	1.90	2.828 (2)	166
O10—H10A···O7	0.95	1.99	2.927 (2)	167
O10—H10B···O9	0.95	1.90	2.846 (3)	173
O11—H11A···O6^{iii}	0.95	2.30	2.903 (2)	120
O11—H11A···O10^{iv}	0.95	2.37	3.124 (2)	136
O11—H11B···O3	0.95	1.88	2.834 (2)	177
O12—H12B···O8^{v}	0.95	1.83	2.781 (2)	177
O12—H12A···O11	0.95	1.92	2.844 (2)	164
N3—H3B···O2^{vi}	0.90	1.86	2.763 (3)	176
N3—H3B···O1^{vi}	0.90	2.58	3.161 (3)	123

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D—H···A	D—H	H···A	D···A	D—H···A
N3—H3A···O12	0.90	1.92	2.696 (2)	144
N4—H4B···O6^{vii}	0.90	1.86	2.754 (2)	170
N4—H4A···O3^{iii}	0.90	1.90	2.792 (3)	169
C15—H15A···O1^{vi}	0.99	2.58	3.204 (3)	121
C16—H16B···O10^{iv}	0.99	2.57	3.457 (3)	149
C17—H17B···O7^{iv}	0.99	2.39	3.184 (3)	137
C18—H18B···O11^{viii}	0.99	2.50	3.270 (3)	135

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2005); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BX2084).

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supplementary materials

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Piperazinediium bis(pyridine-2,6-dicarboxylato)nickelate(II) tetrahydrate

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Comment

The intermolecular binding forces in supramolecular systems may consist of ion pairing, hydrogen bonding, hydrophobic or hydrophilic, host guest, π-π stacking and donor-acceptor interactions. In order to develop new types of proton transfer compounds and hydrogen bonding systems, our research group has recently focused on one-pot synthesis of water soluble self-assembly systems that can function as suitable ligands in the synthesis of metal complexes.

Here, we report on the synthesis and X-ray crystal structure of the title compound, (I). The selected bond lengths, bond and torsion angles are given in Table 1 which are within normal ranges (Allen *et al.*, 1987). Accordingto the crystal structure of **(I)**, the Ni^{II} compound is composed of an anionic complex, $[Ni(pydc)_2]^{2-}$, piperazinediium as counter-ion, $(pipzH_2)^{2+}$, and four uncoordinated water molecules. Atoms N1 and N2 of the two $(pydc)^{2-}$ fragments occupy the axial positions, while atoms O1, O4, O5 and O8 form the equatorial plane. The N1—Ni1—N2 angle deviates slightly from linearity [172.66 (8)°]. Therefore, the coordination around Ni^{II} is distorted octahedral.

The O1—Ni1—O8 and O4—Ni1—O5 angles are equal to 87.00 (6) and 87.82 (6)°, respectively. On the other hand, O4—Ni1—O5—C8 and O5—Ni1—O4—C7 torsion angles are −92.26 (16)° and −84.08 (16)°, respectively indicating that two $(pydc)^{2-}$ units are almost perpendicular to each other (Table 1). Considerable π-π stacking interactions between two aromatic rings of $(pydc)^{2-}$, with distances of 3.4686 (14) Å and 3.5034 (14) Å are observed (Fig. 2) (Aghabozorg, Aghajani & Sharif, 2006; Aghabozorg, Zabihi *et al.*, 2006). In the crystal structure, the spaces between two layers of $[Ni(pydc)_2]^{2-}$ fragments are filled with layers of $(pipzH_2)^{2+}$ cations and water molecules (Fig. 3). The most important features of the crystal structure of **(I)** is the presence of a large number of O—H···O, N—H···O and C—H···O hydrogen bonds, with D···A distances ranging from 2.696 (3) to 3.457 (3) Å between $(pipzH_2)^{2+}$ and $[Ni(pydc)_2]^{2-}$ fragments and uncoordinated water molecules. (Table 2). Ion pairing and van der Waals interactions are also effective in the packing. These interactions result in the formation of a supramolecular structure (Fig. 4).

Experimental

The proton-transfer ion pair was prepared by a reaction between piperazine and pyridine-2,6-dicarboxylic acid. Starting with a 1:1 molar ratio of the reactants in THF, a puffy white precipitate was obtained. By recrystallization in an aqueous solution, pale-yellow crystals were obtained. A solution of $Ni(NO_3)_2{\cdot}6H_2O$ (145 mg, 0.5 mmol) in water (20 ml) was added to an aqueous solution of $(pipzH_2)(pydc)$ (253 mg, 1.0 mmol) in water (20 ml) in a 1:2 molar ratio. Green crystals of (I) suitable for X-ray characterization were obtained after a few days at room temperature.

Refinement

Hydrogen atoms were positioned geometrically and refined with a riding model (including torsional freedom for methyl groups), with C—H = 0.95–0.98 Å, and with U(H) constrained to be 1.2 (1.5 for methyl groups) times U_{eq} of the carrier atom.

Figures

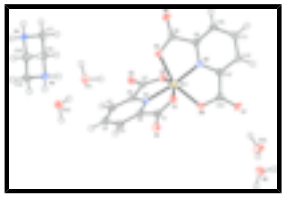

Fig. 1. The structure of (I), showing the atom-numbering scheme and displacements. Ellipsoids are drawn at the 50% probability level.

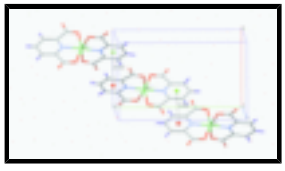

Fig. 2. π–π stacking interactions between two aromatic rings of (I). The average distances between the planes are 3.4686 (14) Å [symmetry operation (−*x*, −*y* + 1, −*z*)] and 3.5034 (14) Å [symmetry operation (−*x* + 1, −*y* + 2, −*z*)], respectively.

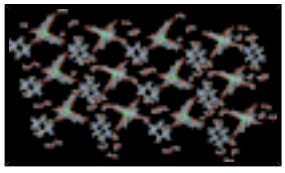

Fig. 3. The layered crystal-packing diagram of (I). The space between two layers of $[Ni(pydc)_2]^{2-}$ fragments is filled with a layer of $(pipzH_2)^{2+}$ cations and water molecules.

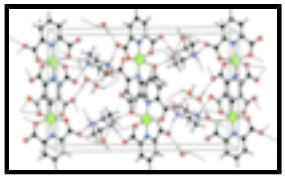

Fig. 4. The crystal packing of (I). Hydrogen bonds are shown as dashed lines.

Piperazinediium bis(pyridine-2,6-dicarboxylato)nickelate(II) tetrahydrate

Crystal data

$(C_4H_{12}N_2)[Ni(C_7H_3NO_4)_2]\cdot 4H_2O$	F_{000} = 1144
M_r = 549.14	D_x = 1.636 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
a = 7.9776 (11) Å	Cell parameters from 6417 reflections
b = 13.2767 (19) Å	θ = 2.5–27.0°
c = 21.054 (3) Å	μ = 0.94 mm^{-1}
β = 90.502 (2)°	T = 150 (2) K
V = 2229.8 (5) Å^3	Block, green
Z = 4	0.18 × 0.15 × 0.07 mm

Data collection

Bruker SMART area-detector diffractometer	5111 independent reflections
Radiation source: fine-focus sealed tube	3612 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.054$
Detector resolution: 100 pixels mm^{-1}	$\theta_{max} = 27.6°$
$T = 150(2)$ K	$\theta_{min} = 1.8°$
ω scans	$h = -10 \rightarrow 10$
Absorption correction: multi-scan (SADABS; Bruker, 1998)	$k = -17 \rightarrow 17$
$T_{min} = 0.849$, $T_{max} = 0.937$	$l = -27 \rightarrow 27$
25180 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.038$	H-atom parameters constrained
$wR(F^2) = 0.094$	$w = 1/[\sigma^2(F_o^2) + (0.0467P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
5111 reflections	$\Delta\rho_{max} = 0.36$ e $Å^{-3}$
318 parameters	$\Delta\rho_{min} = -0.42$ e $Å^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 $F^2 > 2\text{sigma}(F^2)$ 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 ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.23343 (4)	0.75474 (2)	0.007996 (14)	0.01605 (10)
O1	0.40312 (19)	0.70749 (12)	−0.06451 (8)	0.0202 (4)
O2	0.4609 (2)	0.57156 (12)	−0.12315 (8)	0.0223 (4)
O3	−0.0547 (2)	0.61563 (12)	0.14314 (8)	0.0218 (4)

O4	0.0453 (2)	0.73511 (11)	0.07875 (8)	0.0205 (4)
O5	0.4136 (2)	0.76423 (12)	0.08329 (8)	0.0214 (4)
O6	0.5285 (2)	0.87901 (13)	0.14854 (8)	0.0256 (4)
O7	0.0134 (2)	0.95380 (13)	−0.11768 (8)	0.0256 (4)
O8	0.07588 (19)	0.80978 (12)	−0.06660 (8)	0.0204 (4)
O9	0.0331 (2)	0.11768 (14)	0.32180 (9)	0.0364 (5)
H9B	0.0478	0.1686	0.3531	0.048 (9)*
H9A	−0.0006	0.0605	0.3456	0.077 (12)*
O10	0.7399 (2)	0.44110 (14)	0.71874 (9)	0.0328 (5)
H10A	0.6671	0.4377	0.6829	0.039*
H10B	0.6714	0.4158	0.7518	0.039*
O11	−0.0361 (2)	0.43955 (13)	0.21897 (8)	0.0304 (4)
H11A	0.0223	0.4592	0.2565	0.036*
H11B	−0.0404	0.4999	0.1947	0.036*
O12	0.1234 (2)	0.26988 (13)	0.16332 (9)	0.0291 (4)
H12B	0.0522	0.2448	0.1305	0.035*
H12A	0.0542	0.3246	0.1758	0.035*
N1	0.2149 (2)	0.60746 (14)	0.01186 (9)	0.0156 (4)
N2	0.2654 (2)	0.90052 (14)	0.01493 (9)	0.0152 (4)
N3	0.4462 (2)	0.27255 (15)	0.20231 (9)	0.0207 (5)
H3B	0.4720	0.3226	0.1753	0.025*
H3A	0.3530	0.2441	0.1860	0.025*
N4	0.7096 (2)	0.27635 (14)	0.29515 (9)	0.0195 (5)
H4B	0.8001	0.3024	0.3150	0.023*
H4A	0.6636	0.2288	0.3200	0.023*
C1	0.3960 (3)	0.61423 (18)	−0.07599 (11)	0.0176 (5)
C2	0.3014 (3)	0.55085 (17)	−0.02846 (11)	0.0159 (5)
C3	0.3007 (3)	0.44672 (18)	−0.02384 (11)	0.0192 (5)
H3	0.3609	0.4062	−0.0531	0.023*
C4	0.2093 (3)	0.40361 (18)	0.02486 (11)	0.0200 (5)
H4	0.2071	0.3325	0.0295	0.024*
C5	0.1213 (3)	0.46372 (17)	0.06671 (11)	0.0192 (5)
H5	0.0595	0.4345	0.1004	0.023*
C6	0.1251 (3)	0.56680 (17)	0.05859 (11)	0.0167 (5)
C7	0.0316 (3)	0.64473 (17)	0.09696 (11)	0.0176 (5)
C8	0.4416 (3)	0.85382 (18)	0.10199 (11)	0.0184 (5)
C9	0.3618 (3)	0.93598 (17)	0.06175 (11)	0.0164 (5)
C10	0.3872 (3)	1.03821 (17)	0.06906 (11)	0.0182 (5)
H10	0.4550	1.0635	0.1028	0.022*
C11	0.3114 (3)	1.10280 (18)	0.02607 (12)	0.0211 (5)
H11	0.3280	1.1734	0.0299	0.025*
C12	0.2111 (3)	1.06511 (17)	−0.02263 (11)	0.0185 (5)
H12	0.1590	1.1090	−0.0525	0.022*
C13	0.1889 (3)	0.96183 (17)	−0.02646 (11)	0.0164 (5)
C14	0.0830 (3)	0.90522 (18)	−0.07527 (11)	0.0178 (5)
C15	0.5776 (3)	0.19368 (18)	0.20308 (12)	0.0216 (5)
H15A	0.5970	0.1697	0.1592	0.026*
H15B	0.5393	0.1357	0.2288	0.026*
C16	0.4186 (3)	0.31777 (19)	0.26631 (11)	0.0223 (5)

H16A	0.3736	0.2661	0.2954	0.027*
H16B	0.3357	0.3730	0.2630	0.027*
C17	0.5813 (3)	0.35802 (18)	0.29238 (12)	0.0245 (6)
H17A	0.6217	0.4134	0.2650	0.029*
H17B	0.5635	0.3855	0.3355	0.029*
C18	0.7395 (3)	0.23442 (18)	0.23072 (12)	0.0206 (5)
H18A	0.8237	0.1798	0.2334	0.025*
H18B	0.7841	0.2878	0.2027	0.025*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01895 (16)	0.01449 (16)	0.01470 (17)	−0.00075 (13)	−0.00121 (11)	−0.00007 (13)
O1	0.0234 (9)	0.0173 (9)	0.0199 (9)	−0.0017 (7)	0.0036 (7)	−0.0006 (7)
O2	0.0268 (9)	0.0224 (9)	0.0176 (9)	0.0025 (7)	0.0040 (7)	−0.0021 (7)
O3	0.0284 (9)	0.0205 (9)	0.0164 (9)	0.0003 (7)	0.0051 (7)	0.0011 (7)
O4	0.0263 (9)	0.0180 (9)	0.0173 (9)	0.0015 (7)	0.0032 (7)	−0.0002 (7)
O5	0.0274 (9)	0.0177 (9)	0.0190 (9)	0.0029 (7)	−0.0055 (7)	0.0010 (7)
O6	0.0270 (9)	0.0275 (10)	0.0221 (10)	0.0057 (8)	−0.0125 (8)	−0.0034 (8)
O7	0.0295 (10)	0.0274 (10)	0.0197 (10)	−0.0041 (8)	−0.0115 (8)	0.0067 (8)
O8	0.0229 (9)	0.0189 (9)	0.0192 (10)	−0.0030 (7)	−0.0063 (7)	−0.0005 (7)
O9	0.0616 (13)	0.0251 (10)	0.0226 (11)	−0.0076 (9)	0.0043 (10)	−0.0009 (9)
O10	0.0251 (10)	0.0455 (12)	0.0277 (11)	−0.0005 (8)	−0.0042 (8)	−0.0036 (9)
O11	0.0461 (11)	0.0246 (10)	0.0204 (10)	−0.0028 (8)	−0.0056 (9)	0.0027 (8)
O12	0.0230 (9)	0.0279 (10)	0.0363 (11)	0.0005 (7)	−0.0109 (8)	−0.0049 (8)
N1	0.0179 (10)	0.0162 (10)	0.0125 (10)	−0.0002 (8)	−0.0020 (8)	−0.0006 (8)
N2	0.0145 (9)	0.0184 (10)	0.0126 (10)	−0.0002 (8)	−0.0014 (8)	−0.0009 (8)
N3	0.0185 (10)	0.0279 (12)	0.0157 (11)	−0.0053 (8)	−0.0028 (8)	0.0014 (9)
N4	0.0199 (10)	0.0206 (11)	0.0178 (11)	−0.0060 (8)	−0.0058 (9)	0.0004 (8)
C1	0.0147 (11)	0.0203 (13)	0.0179 (13)	0.0004 (9)	−0.0025 (10)	0.0014 (10)
C2	0.0134 (11)	0.0186 (12)	0.0156 (12)	−0.0010 (9)	−0.0018 (9)	−0.0023 (10)
C3	0.0171 (12)	0.0212 (12)	0.0193 (13)	0.0016 (10)	−0.0011 (10)	−0.0041 (10)
C4	0.0216 (12)	0.0161 (12)	0.0222 (14)	0.0019 (10)	−0.0024 (10)	0.0025 (10)
C5	0.0223 (12)	0.0196 (12)	0.0157 (13)	−0.0010 (10)	−0.0006 (10)	0.0031 (10)
C6	0.0158 (11)	0.0210 (12)	0.0132 (12)	−0.0004 (9)	−0.0023 (9)	0.0009 (10)
C7	0.0198 (12)	0.0180 (12)	0.0151 (13)	−0.0005 (10)	−0.0031 (10)	−0.0018 (10)
C8	0.0167 (12)	0.0224 (13)	0.0161 (13)	0.0019 (10)	−0.0001 (10)	0.0005 (10)
C9	0.0150 (11)	0.0202 (12)	0.0141 (12)	0.0024 (9)	−0.0002 (9)	−0.0019 (10)
C10	0.0179 (11)	0.0189 (12)	0.0179 (13)	−0.0011 (10)	−0.0038 (10)	−0.0041 (10)
C11	0.0207 (12)	0.0159 (12)	0.0266 (15)	−0.0006 (10)	0.0019 (11)	−0.0027 (10)
C12	0.0177 (12)	0.0196 (13)	0.0183 (13)	0.0016 (10)	0.0000 (10)	0.0049 (10)
C13	0.0160 (11)	0.0207 (12)	0.0125 (12)	−0.0010 (9)	0.0016 (9)	0.0020 (10)
C14	0.0157 (11)	0.0239 (13)	0.0138 (13)	−0.0011 (10)	0.0011 (9)	0.0008 (10)
C15	0.0244 (13)	0.0207 (13)	0.0199 (14)	−0.0019 (10)	0.0003 (11)	−0.0021 (11)
C16	0.0232 (13)	0.0267 (14)	0.0169 (13)	0.0012 (11)	0.0013 (10)	0.0003 (11)
C17	0.0310 (14)	0.0219 (13)	0.0205 (14)	0.0026 (11)	−0.0012 (11)	−0.0036 (11)
C18	0.0192 (12)	0.0227 (13)	0.0198 (13)	0.0002 (10)	0.0001 (10)	0.0002 (10)

Geometric parameters (Å, °)

Ni1—N2	1.9575 (19)	N4—C17	1.492 (3)
Ni1—N1	1.9626 (19)	N4—H4B	0.9000
Ni1—O8	2.1320 (16)	N4—H4A	0.9000
Ni1—O5	2.1340 (16)	C1—C2	1.514 (3)
Ni1—O4	2.1400 (16)	C2—C3	1.386 (3)
Ni1—O1	2.1429 (16)	C3—C4	1.387 (3)
O1—C1	1.263 (3)	C3—H3	0.9500
O2—C1	1.259 (3)	C4—C5	1.385 (3)
O3—C7	1.257 (3)	C4—H4	0.9500
O4—C7	1.265 (3)	C5—C6	1.380 (3)
O5—C8	1.272 (3)	C5—H5	0.9500
O6—C8	1.242 (3)	C6—C7	1.513 (3)
O7—C14	1.230 (3)	C8—C9	1.518 (3)
O8—C14	1.282 (3)	C9—C10	1.381 (3)
O9—H9B	0.9500	C10—C11	1.382 (3)
O9—H9A	0.9501	C10—H10	0.9500
O10—H10A	0.9501	C11—C12	1.388 (3)
O10—H10B	0.9499	C11—H11	0.9500
O11—H11A	0.9500	C12—C13	1.385 (3)
O11—H11B	0.9501	C12—H12	0.9500
O12—H12B	0.9500	C13—C14	1.523 (3)
O12—H12A	0.9499	C15—C18	1.512 (3)
N1—C2	1.331 (3)	C15—H15A	0.9900
N1—C6	1.336 (3)	C15—H15B	0.9900
N2—C9	1.331 (3)	C16—C17	1.503 (3)
N2—C13	1.336 (3)	C16—H16A	0.9900
N3—C15	1.481 (3)	C16—H16B	0.9900
N3—C16	1.493 (3)	C17—H17A	0.9900
N3—H3B	0.9001	C17—H17B	0.9900
N3—H3A	0.9000	C18—H18A	0.9900
N4—C18	1.487 (3)	C18—H18B	0.9900
N2—Ni1—N1	172.66 (8)	C6—C5—H5	120.6
N2—Ni1—O8	77.97 (7)	C4—C5—H5	120.6
N1—Ni1—O8	109.14 (7)	N1—C6—C5	120.3 (2)
N2—Ni1—O5	78.45 (7)	N1—C6—C7	112.8 (2)
N1—Ni1—O5	94.50 (7)	C5—C6—C7	126.9 (2)
O8—Ni1—O5	156.31 (6)	O3—C7—O4	125.1 (2)
N2—Ni1—O4	99.22 (7)	O3—C7—C6	118.6 (2)
N1—Ni1—O4	78.25 (7)	O4—C7—C6	116.3 (2)
O8—Ni1—O4	98.16 (6)	O6—C8—O5	126.3 (2)
O5—Ni1—O4	87.82 (6)	O6—C8—C9	118.4 (2)
N2—Ni1—O1	105.06 (7)	O5—C8—C9	115.3 (2)
N1—Ni1—O1	77.65 (7)	N2—C9—C10	120.9 (2)
O8—Ni1—O1	87.00 (6)	N2—C9—C8	113.3 (2)
O5—Ni1—O1	96.95 (6)	C10—C9—C8	125.7 (2)
O4—Ni1—O1	155.72 (6)	C9—C10—C11	118.3 (2)

C1—O1—Ni1	113.30 (14)	C9—C10—H10	120.9
C7—O4—Ni1	112.92 (14)	C11—C10—H10	120.9
C8—O5—Ni1	113.61 (14)	C10—C11—C12	120.4 (2)
C14—O8—Ni1	114.66 (14)	C10—C11—H11	119.8
H9B—O9—H9A	103.8	C12—C11—H11	119.8
H10A—O10—H10B	102.3	C13—C12—C11	118.2 (2)
H11A—O11—H11B	103.3	C13—C12—H12	120.9
H12B—O12—H12A	97.1	C11—C12—H12	120.9
C2—N1—C6	121.7 (2)	N2—C13—C12	120.5 (2)
C2—N1—Ni1	119.77 (15)	N2—C13—C14	112.8 (2)
C6—N1—Ni1	118.30 (15)	C12—C13—C14	126.7 (2)
C9—N2—C13	121.7 (2)	O7—C14—O8	127.0 (2)
C9—N2—Ni1	118.62 (15)	O7—C14—C13	118.4 (2)
C13—N2—Ni1	119.71 (15)	O8—C14—C13	114.6 (2)
C15—N3—C16	112.59 (18)	N3—C15—C18	110.69 (19)
C15—N3—H3B	111.3	N3—C15—H15A	109.5
C16—N3—H3B	108.0	C18—C15—H15A	109.5
C15—N3—H3A	106.8	N3—C15—H15B	109.5
C16—N3—H3A	112.7	C18—C15—H15B	109.5
H3B—N3—H3A	105.2	H15A—C15—H15B	108.1
C18—N4—C17	110.60 (18)	N3—C16—C17	109.8 (2)
C18—N4—H4B	115.7	N3—C16—H16A	109.7
C17—N4—H4B	106.6	C17—C16—H16A	109.7
C18—N4—H4A	109.6	N3—C16—H16B	109.7
C17—N4—H4A	104.4	C17—C16—H16B	109.7
H4B—N4—H4A	109.2	H16A—C16—H16B	108.2
O2—C1—O1	125.0 (2)	N4—C17—C16	110.2 (2)
O2—C1—C2	118.8 (2)	N4—C17—H17A	109.6
O1—C1—C2	116.1 (2)	C16—C17—H17A	109.6
N1—C2—C3	121.1 (2)	N4—C17—H17B	109.6
N1—C2—C1	111.8 (2)	C16—C17—H17B	109.6
C3—C2—C1	127.1 (2)	H17A—C17—H17B	108.1
C2—C3—C4	117.8 (2)	N4—C18—C15	109.97 (19)
C2—C3—H3	121.1	N4—C18—H18A	109.7
C4—C3—H3	121.1	C15—C18—H18A	109.7
C5—C4—C3	120.4 (2)	N4—C18—H18B	109.7
C5—C4—H4	119.8	C15—C18—H18B	109.7
C3—C4—H4	119.8	H18A—C18—H18B	108.2
C6—C5—C4	118.8 (2)		
N2—Ni1—O1—C1	−178.68 (15)	O1—C1—C2—C3	−167.5 (2)
N1—Ni1—O1—C1	8.35 (15)	N1—C2—C3—C4	−1.1 (3)
O8—Ni1—O1—C1	−101.99 (16)	C1—C2—C3—C4	177.8 (2)
O5—Ni1—O1—C1	101.46 (16)	C2—C3—C4—C5	0.5 (3)
O4—Ni1—O1—C1	1.3 (3)	C3—C4—C5—C6	0.6 (3)
N2—Ni1—O4—C7	−162.01 (16)	C2—N1—C6—C5	0.7 (3)
N1—Ni1—O4—C7	10.98 (16)	Ni1—N1—C6—C5	−173.99 (17)
O8—Ni1—O4—C7	118.95 (16)	C2—N1—C6—C7	−177.69 (19)
O5—Ni1—O4—C7	−84.08 (16)	Ni1—N1—C6—C7	7.6 (2)
O1—Ni1—O4—C7	18.0 (3)	C4—C5—C6—N1	−1.3 (3)

N2—Ni1—O5—C8	7.61 (16)	C4—C5—C6—C7	176.9 (2)
N1—Ni1—O5—C8	−170.29 (16)	Ni1—O4—C7—O3	170.98 (18)
O8—Ni1—O5—C8	13.2 (3)	Ni1—O4—C7—C6	−10.2 (2)
O4—Ni1—O5—C8	−92.26 (16)	N1—C6—C7—O3	−178.59 (19)
O1—Ni1—O5—C8	111.63 (16)	C5—C6—C7—O3	3.1 (4)
N2—Ni1—O8—C14	4.62 (15)	N1—C6—C7—O4	2.5 (3)
N1—Ni1—O8—C14	−177.30 (15)	C5—C6—C7—O4	−175.8 (2)
O5—Ni1—O8—C14	−1.0 (3)	Ni1—O5—C8—O6	172.99 (19)
O4—Ni1—O8—C14	102.37 (16)	Ni1—O5—C8—C9	−8.2 (2)
O1—Ni1—O8—C14	−101.48 (16)	C13—N2—C9—C10	−0.4 (3)
N2—Ni1—N1—C2	−114.2 (6)	Ni1—N2—C9—C10	−179.45 (17)
O8—Ni1—N1—C2	80.63 (17)	C13—N2—C9—C8	−177.99 (19)
O5—Ni1—N1—C2	−97.89 (17)	Ni1—N2—C9—C8	2.9 (2)
O4—Ni1—N1—C2	175.29 (18)	O6—C8—C9—N2	−177.1 (2)
O1—Ni1—N1—C2	−1.75 (16)	O5—C8—C9—N2	3.9 (3)
N2—Ni1—N1—C6	60.6 (6)	O6—C8—C9—C10	5.4 (3)
O8—Ni1—N1—C6	−104.56 (16)	O5—C8—C9—C10	−173.5 (2)
O5—Ni1—N1—C6	76.92 (16)	N2—C9—C10—C11	−0.7 (3)
O4—Ni1—N1—C6	−9.90 (16)	C8—C9—C10—C11	176.6 (2)
O1—Ni1—N1—C6	173.06 (17)	C9—C10—C11—C12	0.7 (3)
N1—Ni1—N2—C9	11.2 (7)	C10—C11—C12—C13	0.3 (3)
O8—Ni1—N2—C9	176.82 (17)	C9—N2—C13—C12	1.5 (3)
O5—Ni1—N2—C9	−5.48 (16)	Ni1—N2—C13—C12	−179.48 (17)
O4—Ni1—N2—C9	80.37 (16)	C9—N2—C13—C14	−179.07 (19)
O1—Ni1—N2—C9	−99.65 (16)	Ni1—N2—C13—C14	0.0 (2)
N1—Ni1—N2—C13	−167.9 (5)	C11—C12—C13—N2	−1.4 (3)
O8—Ni1—N2—C13	−2.27 (16)	C11—C12—C13—C14	179.2 (2)
O5—Ni1—N2—C13	175.44 (17)	Ni1—O8—C14—O7	174.76 (19)
O4—Ni1—N2—C13	−98.72 (16)	Ni1—O8—C14—C13	−5.8 (2)
O1—Ni1—N2—C13	81.26 (17)	N2—C13—C14—O7	−176.5 (2)
Ni1—O1—C1—O2	167.25 (18)	C12—C13—C14—O7	3.0 (3)
Ni1—O1—C1—C2	−12.8 (2)	N2—C13—C14—O8	4.1 (3)
C6—N1—C2—C3	0.5 (3)	C12—C13—C14—O8	−176.5 (2)
Ni1—N1—C2—C3	175.12 (16)	C16—N3—C15—C18	−55.1 (3)
C6—N1—C2—C1	−178.59 (19)	C15—N3—C16—C17	55.5 (3)
Ni1—N1—C2—C1	−4.0 (2)	C18—N4—C17—C16	59.7 (2)
O2—C1—C2—N1	−168.6 (2)	N3—C16—C17—N4	−57.0 (3)
O1—C1—C2—N1	11.5 (3)	C17—N4—C18—C15	−58.5 (2)
O2—C1—C2—C3	12.4 (3)	N3—C15—C18—N4	55.8 (3)

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O9—H9B···O5^{i}	0.95	1.87	2.819 (2)	177
O9—H9A···O2^{ii}	0.95	1.90	2.828 (2)	166
O10—H10A···O7	0.95	1.99	2.927 (2)	167
O10—H10B···O9	0.95	1.90	2.846 (3)	173
O11—H11A···O6^{iii}	0.95	2.30	2.903 (2)	120

O11—H11A···O10^{iv}	0.95	2.37	3.124 (2)	136
O11—H11B···O3	0.95	1.88	2.834 (2)	177
O12—H12B···O8^{v}	0.95	1.83	2.781 (2)	177
O12—H12A···O11	0.95	1.92	2.844 (2)	164
N3—H3B···O2^{vi}	0.90	1.86	2.763 (3)	176
N3—H3B···O1^{vi}	0.90	2.58	3.161 (3)	123
N3—H3A···O12	0.90	1.92	2.696 (2)	144
N4—H4B···O6^{vii}	0.90	1.86	2.754 (2)	170
N4—H4A···O3^{iii}	0.90	1.90	2.792 (3)	169
C15—H15A···O1^{vi}	0.99	2.58	3.204 (3)	121
C16—H16B···O10^{iv}	0.99	2.57	3.457 (3)	149
C17—H17B···O7^{iv}	0.99	2.39	3.184 (3)	137
C18—H18B···O11^{viii}	0.99	2.50	3.270 (3)	135

Symmetry codes: (i) *x*−1/2, −*y*+3/2, *z*−1/2; (ii) −*x*+1/2, *y*+1/2, −*z*−1/2; (iii) −*x*+1/2, *y*−1/2, −*z*+1/2; (iv) *x*+1/2, −*y*+3/2, *z*+1/2; (v) −*x*, −*y*+1, −*z*; (vi) −*x*+1, −*y*+1, −*z*; (vii) −*x*+3/2, *y*−1/2, −*z*+1/2; (viii) *x*+1, *y*, *z*.

Fig. 1

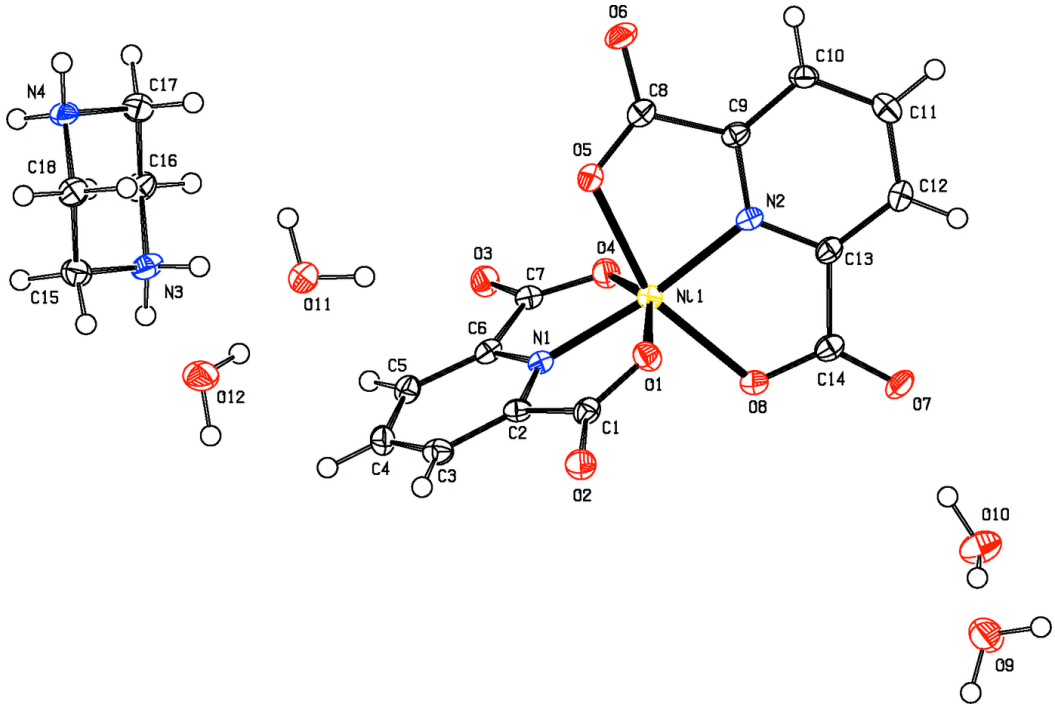
O6
C10
C8
C9
C11
O5
N2
C12
O3
O4
C7
C13
Ni1
C6
N1
O1
C5
O8
C14
O7
C2
C1
C4
C3
O2
O10
O9
N4
C17
C18
C16
C15
N3
O11
O12

Fig. 2

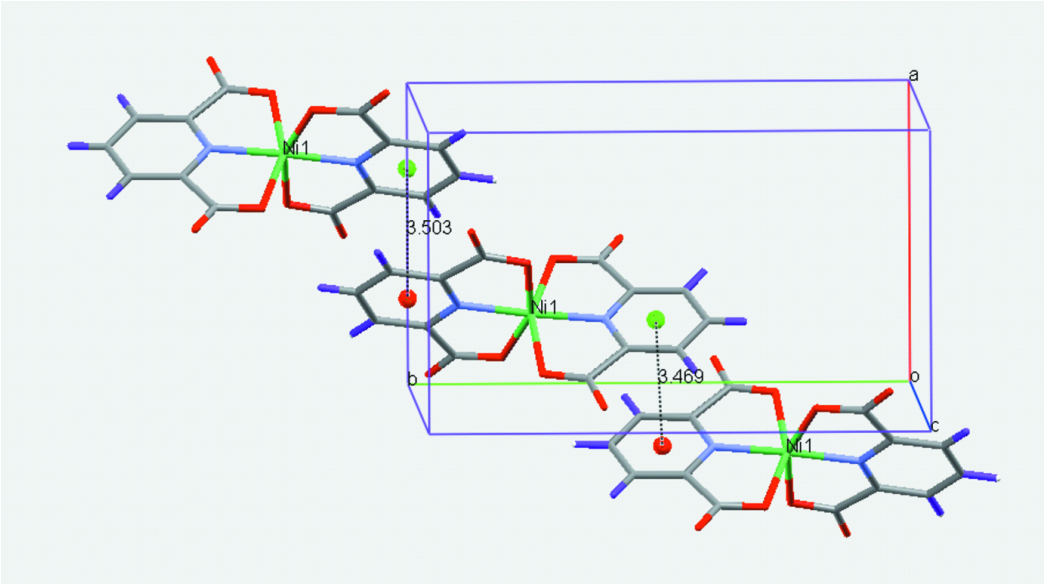

Fig. 3

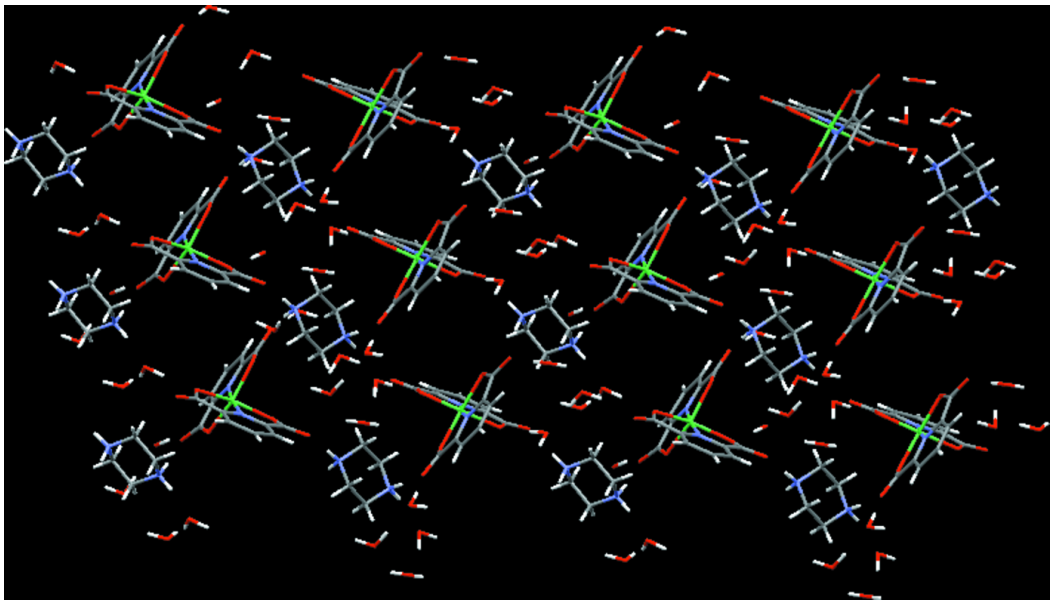

Fig. 4