

catena-Poly[[tetraaquanickel(II)]- μ_3 -benzene-1,3,5-tricarboxylato-3':1:2- κ^4 O¹:O³,O^{3'}:O⁵-[tetraaquanickel(II)]- μ_2 -benzene-1,3,5-tricarboxylato-2:3 κ^2 O¹:O³-[tetraaquanickel(II)]]

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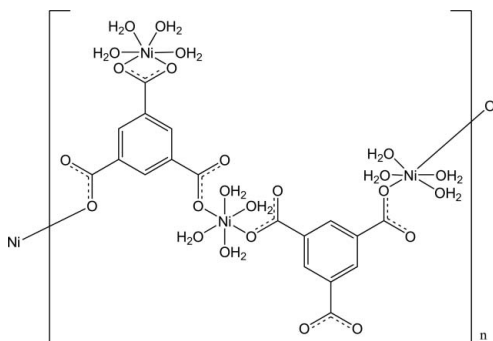
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Key indicators: single-crystal X-ray study; $T = 295$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.028; wR factor = 0.068; data-to-parameter ratio = 15.9.

The microwave solvothermal reaction of nickel nitrate with trimesic acid provided the title compound, $[\text{Ni}_3(\text{BTC})_2(\text{H}_2\text{O})_{12}]_n$ (BTC = benzene-1,3,5-tricarboxylate anion, $\text{C}_9\text{H}_3\text{O}_6$), which is a metal coordination polymer composed of one-dimensional zigzag chains. The crystal under investigation was ramecically twinned with an approximate twin domain ratio of 1:1. In the asymmetric unit, there are two types of Ni atoms. One of the NiO_6 groups (2 symmetry) is coordinated to only one carboxylate group and thus terminal, the other is bridging, forming the coordination polymer. The extended chains are connected by the organic BTC anions *via* μ_2 -linkages. O—H...O hydrogen bonds and π - π interactions between the chains [centroid-centroid distance 3.58 (1) Å] induce the complex to mimic a three-dimensional structure.

Related literature

For background information on the solvothermal synthesis of coordination polymers with organic carboxylate ligands, see: Kitagawa *et al.* (2004).



Experimental

Crystal data

$[\text{Ni}_3(\text{C}_9\text{H}_3\text{O}_6)_2(\text{H}_2\text{O})_{12}]$
 $M_r = 806.49$
Monoclinic, $C2$
 $a = 17.3394$ (10) Å
 $b = 12.8724$ (7) Å
 $c = 6.5462$ (3) Å
 $\beta = 111.609$ (2)°

$V = 1358.42$ (12) Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 2.17$ mm⁻¹
 $T = 295$ K
 $0.25 \times 0.18 \times 0.15$ mm

Data collection

Bruker APEXII CCD diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 2008)
 $T_{\min} = 0.613$, $T_{\max} = 0.737$

6798 measured reflections
3299 independent reflections
3156 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.046$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.068$
 $S = 1.07$
3299 reflections
208 parameters
1 restraint

H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.48$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.38$ e Å⁻³
Absolute structure: Flack (1983), 1531 Friedel pairs
Flack parameter: 0.549 (12)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O9—H9B...O10 ⁱ	0.87	1.90	2.767 (3)	172
O9—H9A...O12 ⁱⁱ	0.81	2.33	3.102 (3)	160
O6—H6B...O1 ⁱⁱⁱ	0.97	1.98	2.942 (3)	173
O6—H6A...O11 ^{iv}	0.85	1.83	2.683 (3)	173
O5—H5B...O12 ^{iv}	0.92	1.95	2.825 (3)	158
O5—H5A...O11	0.81	1.79	2.559 (3)	156
O4—H4C...O1 ⁱ	0.92	1.97	2.870 (3)	167
O4—H4B...O10	0.91	1.77	2.617 (3)	154
O3—H3B...O12 ^v	0.94	1.97	2.907 (3)	171
O3—H3A...O4 ^{vi}	0.94	2.03	2.917 (3)	156
O2—H2B...O5 ^{vii}	0.83	1.81	2.638 (3)	173
O2—H2A...O12 ^{viii}	0.85	2.02	2.861 (4)	171

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

Data collection: APEX2 (Bruker, 2008); cell refinement: SAINT (Bruker, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); 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: ZL2190).

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supplementary materials

Acta Cryst. (2009). E65, m625-m626 [doi:10.1107/S1600536809016729]

***catena*-Poly[[tetraaquanickel(II)]- μ_3 -benzene-1,3,5-tricarboxylato-3':1:2- $\kappa^4 O^1:O^3, O^3':O^5$ -
[tetraaquanickel(II)]- μ_2 -benzene-1,3,5-tricarboxylato-2:3 $\kappa^2 O^1:O^3$ -[tetraaquanickel(II)]]**

S.-C. Hsu, P.-H. Chiang, C.-H. Chang and C.-H. Lin

Comment

The synthesis of coordination polymers has been a subject of intense research owing to their interesting structural chemistry and potential applications in gas storage, separation, catalysis, magnetism, and luminescence. A large number of these materials have been synthesized by solvothermal reactions with organic carboxyl acids (Kitagawa *et al.* 2004). The coordination polymers commonly adopt three-dimensional, two-dimensional, and one-dimensional structures *via* employed metal ions as connectors and rigid or flexible organic ligands as linkers. As a further study of such a complex, we report here the structure of the title compound, a nickel coordination polymer with one dimensional zigzag chains.

The crystal structure analysis of the title compound reveals the structure to be composed of zigzag chains. The compound has a non-centrosymmetric $C2$ space group and the crystal under investigation was twinned with a Flack parameter of 0.549 (12). The asymmetric unit contains two types of NiO_6 groups (Fig. 1). The group of Ni1 is terminal and the metal atom is coordinated in a bidentate fashion to one carboxylate ligand and to four water oxygen atoms. The other nickel atom, Ni2, is coordinated in the axial positions by two monodentate carboxylate groups, and by four water molecules in the equatorial positions. All Ni–O bond lengths range from 2.021 (3) to 2.102 (3) Å. The BTC anions also have two types of coordination modes towards the NiO_6 groups. One of the BTC bridges between two Ni2 atoms *via* two of its carboxylate groups. The third carboxylate is protonated and not metal coordinated. The other BTC ligand bridges *via* two of its carboxylates between two Ni2 atoms. Its third carboxylate group coordinates to a Ni1 atom. The one-dimensional chains thus formed are further linked with each other by hydrogen bonds and π - π interactions to form a layered structure. Hydrogen bonding interactions between coordination waters are $O2-H2B\cdots O5^{ix}$, $O3-H3A\cdots O4^{viii}$, $O4-H4B\cdots O10$, $O4-H4C\cdots O1^{iii}$, $O5-H5A\cdots O11$, $O6-H6A\cdots O11^{vi}$, $O6-H6B\cdots O1^v$, and $O9-H9B\cdots O10^{iii}$ (Fig. 2). The uncoordinated carboxylate group is involved in hydrogen bonding *via* $O2-H2A\cdots O12^x$, $O3-H3B\cdots O12^{vii}$, $O5-H5B\cdots O12^{vi}$, and $O9-H9A\cdots O12^{iv}$ between nearby layers (Fig. 3, see table 1 for numerical values and symmetry operators). π - π stacking interactions are found between aromatic rings made up of C1 to C5, $C1^{ii}$ and $C5^{ii}$, and the ring defined by C2, C7, C9, C10, $C10^i$ and $C9^i$ (symmetry operators: (i) $-x+1, y, -z$; (ii) $-x+2, y, -z+1$). The centroid to centroid distance between $Cg1$ and $Cg2^{ix}$ defined by the two rings is 3.58 (1) Å. The rings are slipped against each other, and the approximate interplanar distance is 3.27 Å (as defined by the distance of carbon atom C4 and $Cg2^{ix}$ (symmetry operator: (ix) $1/2+x, -1/2+y, z$). These π - π interactions connect nearby layers with each other (Fig. 4).

Experimental

The title complex was obtained from the reaction of 1,3,5-benzenetricarboxylic acid ($C_9H_6O_6$, H_3BTC , 0.421 g, 2 mmol), $Ni(NO_3)_2 \cdot 6H_2O$ (0.8724 g, 3 mmol), ethanol (5.0 ml) and H_2O (5.0 ml) with pH value of 2.15. The reaction mixture was heated to 453 K for 20 minutes using a microwave output power of 400 W. The title compound in the form of green crystals was collected in a yield of 0.0979 g (12.2%, based on carboxylic acid reagent).

Refinement

The hydrogen atoms of benzene rings are placed in idealized positions and constrained to ride on their parent atoms, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. The hydrogen atoms of water molecules were found in difference Fourier maps and were refined using distance constraints with O—H = 0.81 to 0.96 Å with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{O})$. Friedel pairs were not merged prior to refinement. The value of the Flack parameter and its standard uncertainty were determined by full-matrix least-squares refinement using the TWIN/BASF commands in the *SHELXTL* program. It refined to 0.55 (1).

Figures

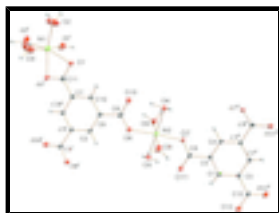


Fig. 1. A view of the title compound, showing 50% probability displacement ellipsoids. [symmetry codes: (i) $-x+1, y, -z$; (ii) $-x+2, y, -z+1$].

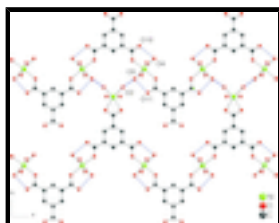


Fig. 2. The zigzag chains of the title compound with hydrogen bonding (blue dashed lines, H atoms are omitted).

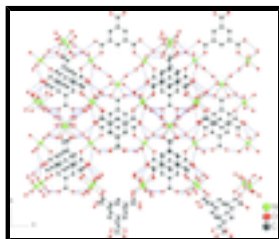


Fig. 3. The packing diagram of zigzag chains with hydrogen bonding (blue dashed lines, H atoms are omitted).

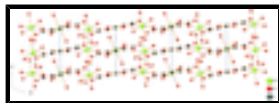


Fig. 4. The side view of the layers with the pi-pi interactions (blue dashed lines, H atoms are omitted).

catena-Poly[[tetraaquanickel(II)]- μ_3 -benzene-1,3,5-tricarboxylato- $3^1:1:2-\kappa^4 O^1:O^3, O^3^1:O^5$ - [tetraaquanickel(II)]- $\backslash\mu_2$ -benzene-1,3,5-tricarboxylato- $2:3\kappa^2 O^1:O^3$ -[tetraaquanickel(II)]]

Crystal data

$[\text{Ni}_3(\text{C}_9\text{H}_3\text{O}_6)_2(\text{H}_2\text{O})_{12}]$

$M_r = 806.49$

Monoclinic, $C2$

Hall symbol: $C 2y$

$a = 17.3394 (10) \text{ \AA}$

$F_{000} = 828$

$D_x = 1.972 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

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

Cell parameters from 4802 reflections

$\theta = 2.5\text{--}28.3^\circ$

$b = 12.8724 (7) \text{ \AA}$	$\mu = 2.17 \text{ mm}^{-1}$
$c = 6.5462 (3) \text{ \AA}$	$T = 295 \text{ K}$
$\beta = 111.609 (2)^\circ$	Columnar, light-blue
$V = 1358.42 (12) \text{ \AA}^3$	$0.25 \times 0.18 \times 0.15 \text{ mm}$
$Z = 2$	

Data collection

Bruker APEXII CCD diffractometer	3299 independent reflections
Radiation source: fine-focus sealed tube	3156 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.046$
$T = 295 \text{ K}$	$\theta_{\text{max}} = 28.4^\circ$
φ and ω scans	$\theta_{\text{min}} = 2.0^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 2008)	$h = -23 \rightarrow 22$
$T_{\text{min}} = 0.613$, $T_{\text{max}} = 0.737$	$k = -16 \rightarrow 17$
6798 measured reflections	$l = -7 \rightarrow 8$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.028$	$w = 1/[\sigma^2(F_o^2) + (0.0363P)^2]$
$wR(F^2) = 0.068$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{\text{max}} = 0.001$
3299 reflections	$\Delta\rho_{\text{max}} = 0.48 \text{ e \AA}^{-3}$
208 parameters	$\Delta\rho_{\text{min}} = -0.38 \text{ e \AA}^{-3}$
1 restraint	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1531 Friedel pairs
Secondary atom site location: difference Fourier map	Flack parameter: 0.549 (12)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. 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.

supplementary materials

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.5000	0.68238 (4)	0.0000	0.02554 (13)
Ni2	0.757745 (18)	-0.02765 (2)	0.22999 (5)	0.01825 (9)
O1	0.56460 (12)	0.54287 (15)	0.1157 (3)	0.0269 (4)
O2	0.58008 (19)	0.7828 (2)	0.1959 (5)	0.0659 (10)
H2A	0.5729	0.8177	0.2978	0.079*
H2B	0.6113	0.8141	0.1460	0.079*
O3	0.44433 (15)	0.68727 (18)	0.2333 (4)	0.0396 (5)
H3A	0.4101	0.6382	0.2657	0.047*
H3B	0.4382	0.7546	0.2822	0.047*
O4	0.83989 (12)	0.08047 (16)	0.4286 (3)	0.0259 (4)
H4B	0.8029	0.1274	0.4439	0.031*
H4C	0.8708	0.0577	0.5683	0.031*
O5	0.67707 (12)	-0.13068 (15)	0.0142 (3)	0.0229 (4)
H5A	0.7035	-0.1838	0.0246	0.028*
H5B	0.6543	-0.1191	-0.1354	0.028*
O6	0.77890 (12)	0.03467 (16)	-0.0377 (3)	0.0316 (5)
H6A	0.7595	0.0949	-0.0829	0.038*
H6B	0.8290	0.0322	-0.0698	0.038*
O7	0.85264 (11)	-0.12996 (14)	0.3010 (3)	0.0223 (4)
O8	0.65774 (12)	0.06587 (15)	0.1685 (3)	0.0237 (4)
O9	0.73419 (13)	-0.09194 (17)	0.4944 (3)	0.0299 (5)
H9A	0.6945	-0.0832	0.5292	0.036*
H9B	0.7453	-0.1563	0.5346	0.036*
O10	0.71601 (12)	0.21051 (15)	0.3445 (3)	0.0271 (4)
O11	0.78560 (12)	-0.27492 (14)	0.1508 (3)	0.0253 (4)
O12	0.93126 (13)	-0.61400 (16)	0.4291 (4)	0.0333 (5)
C1	0.92709 (16)	-0.3961 (2)	0.3927 (4)	0.0156 (5)
H1A	0.8781	-0.4324	0.3216	0.019*
C2	0.5000	0.1625 (3)	0.0000	0.0159 (7)
H2C	0.5000	0.0903	0.0000	0.019*
C3	1.0000	-0.4499 (3)	0.5000	0.0157 (7)
C4	1.0000	-0.2341 (3)	0.5000	0.0158 (6)
H4A	1.0000	-0.1618	0.5000	0.019*
C5	0.92667 (15)	-0.28782 (19)	0.3907 (4)	0.0149 (5)
C6	0.65536 (16)	0.1604 (2)	0.2156 (4)	0.0178 (5)
C7	0.5000	0.3778 (3)	0.0000	0.0163 (7)
C8	0.84852 (15)	-0.2270 (2)	0.2722 (4)	0.0159 (5)
C9	0.57403 (16)	0.2158 (2)	0.1077 (4)	0.0159 (5)
C10	0.57306 (15)	0.3237 (2)	0.1084 (4)	0.0167 (5)
H10A	0.6218	0.3601	0.1821	0.020*
C11	0.5000	0.4925 (3)	0.0000	0.0204 (8)
C12	1.0000	-0.5673 (3)	0.5000	0.0211 (8)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0250 (3)	0.0154 (2)	0.0335 (3)	0.000	0.0076 (2)	0.000
Ni2	0.01496 (14)	0.01230 (14)	0.02472 (16)	0.00137 (13)	0.00407 (11)	0.00049 (13)
O1	0.0201 (10)	0.0127 (9)	0.0360 (11)	-0.0018 (8)	-0.0037 (9)	-0.0020 (8)
O2	0.081 (2)	0.065 (2)	0.0751 (18)	-0.0546 (18)	0.0557 (17)	-0.0443 (17)
O3	0.0483 (14)	0.0264 (11)	0.0539 (13)	-0.0045 (11)	0.0305 (11)	-0.0004 (11)
O4	0.0207 (10)	0.0182 (10)	0.0317 (11)	0.0019 (8)	0.0013 (9)	-0.0023 (9)
O5	0.0204 (9)	0.0168 (10)	0.0260 (9)	0.0023 (7)	0.0019 (8)	-0.0001 (8)
O6	0.0284 (11)	0.0259 (11)	0.0450 (12)	0.0085 (9)	0.0187 (10)	0.0130 (9)
O7	0.0154 (9)	0.0131 (9)	0.0353 (11)	0.0028 (7)	0.0057 (8)	0.0000 (8)
O8	0.0203 (9)	0.0134 (9)	0.0345 (11)	0.0048 (7)	0.0068 (9)	-0.0024 (8)
O9	0.0294 (11)	0.0268 (11)	0.0337 (10)	0.0060 (9)	0.0120 (9)	0.0091 (8)
O10	0.0203 (10)	0.0203 (10)	0.0335 (10)	0.0044 (8)	0.0013 (9)	-0.0056 (8)
O11	0.0179 (9)	0.0163 (9)	0.0327 (10)	0.0029 (7)	-0.0014 (8)	-0.0047 (8)
O12	0.0333 (12)	0.0145 (10)	0.0376 (12)	-0.0044 (9)	-0.0040 (10)	0.0022 (9)
C1	0.0168 (12)	0.0127 (12)	0.0161 (12)	-0.0027 (10)	0.0045 (10)	-0.0025 (9)
C2	0.0224 (17)	0.0081 (16)	0.0183 (16)	0.000	0.0089 (14)	0.000
C3	0.0200 (17)	0.0096 (16)	0.0155 (16)	0.000	0.0039 (14)	0.000
C4	0.0202 (16)	0.0100 (15)	0.0184 (15)	0.000	0.0085 (13)	0.000
C5	0.0142 (11)	0.0137 (11)	0.0157 (11)	0.0025 (8)	0.0042 (9)	0.0000 (8)
C6	0.0193 (12)	0.0174 (13)	0.0171 (11)	0.0021 (10)	0.0073 (10)	0.0016 (9)
C7	0.0194 (17)	0.0130 (16)	0.0167 (16)	0.000	0.0068 (14)	0.000
C8	0.0159 (11)	0.0145 (12)	0.0187 (11)	0.0010 (9)	0.0081 (9)	-0.0004 (9)
C9	0.0183 (12)	0.0134 (11)	0.0178 (12)	0.0025 (9)	0.0087 (10)	0.0006 (9)
C10	0.0144 (11)	0.0156 (12)	0.0194 (12)	-0.0013 (9)	0.0052 (10)	0.0002 (9)
C11	0.0188 (16)	0.016 (2)	0.0235 (17)	0.000	0.0036 (14)	0.000
C12	0.029 (2)	0.0099 (17)	0.0175 (17)	0.000	0.0009 (15)	0.000

Geometric parameters (\AA , $^\circ$)

Ni1—O2 ⁱ	1.983 (3)	O9—H9A	0.8087
Ni1—O2	1.983 (3)	O9—H9B	0.8686
Ni1—O3 ⁱ	2.087 (2)	O10—C6	1.257 (3)
Ni1—O3	2.087 (2)	O11—C8	1.250 (3)
Ni1—O1 ⁱ	2.1043 (19)	O12—C12	1.261 (3)
Ni1—O1	2.1043 (19)	C1—C3	1.385 (3)
Ni1—C11	2.445 (4)	C1—C5	1.393 (4)
Ni2—O7	2.0235 (18)	C1—H1A	0.9300
Ni2—O8	2.026 (2)	C2—C9	1.396 (3)
Ni2—O5	2.0630 (19)	C2—C9 ⁱ	1.396 (3)
Ni2—O4	2.0716 (19)	C2—H2C	0.9300
Ni2—O6	2.0787 (19)	C3—C1 ⁱⁱ	1.385 (3)
Ni2—O9	2.090 (2)	C3—C12	1.512 (5)
O1—C11	1.275 (3)	C4—C5	1.392 (3)

supplementary materials

O2—H2A	0.8508	C4—C5 ⁱⁱ	1.392 (3)
O2—H2B	0.8329	C4—H4A	0.9300
O3—H3A	0.9431	C5—C8	1.509 (3)
O3—H3B	0.9439	C6—C9	1.504 (3)
O4—H4B	0.9132	C7—C10	1.390 (3)
O4—H4C	0.9216	C7—C10 ⁱ	1.390 (3)
O5—H5A	0.8116	C7—C11	1.476 (5)
O5—H5B	0.9233	C9—C10	1.390 (3)
O6—H6A	0.8533	C10—H10A	0.9300
O6—H6B	0.9664	C11—O1 ⁱ	1.275 (3)
O7—C8	1.261 (3)	C12—O12 ⁱⁱ	1.261 (3)
O8—C6	1.260 (3)		
O2 ⁱ —Ni1—O2	98.7 (2)	H5A—O5—H5B	103.5
O2 ⁱ —Ni1—O3 ⁱ	84.80 (10)	Ni2—O6—H6A	118.3
O2—Ni1—O3 ⁱ	92.94 (10)	Ni2—O6—H6B	128.5
O2 ⁱ —Ni1—O3	92.94 (10)	H6A—O6—H6B	103.1
O2—Ni1—O3	84.80 (10)	C8—O7—Ni2	127.85 (17)
O3 ⁱ —Ni1—O3	176.54 (13)	C6—O8—Ni2	128.92 (18)
O2 ⁱ —Ni1—O1 ⁱ	99.80 (12)	Ni2—O9—H9A	128.6
O2—Ni1—O1 ⁱ	160.42 (11)	Ni2—O9—H9B	122.6
O3 ⁱ —Ni1—O1 ⁱ	95.20 (9)	H9A—O9—H9B	99.5
O3—Ni1—O1 ⁱ	87.75 (9)	C3—C1—C5	120.4 (2)
O2 ⁱ —Ni1—O1	160.42 (11)	C3—C1—H1A	119.8
O2—Ni1—O1	99.80 (12)	C5—C1—H1A	119.8
O3 ⁱ —Ni1—O1	87.75 (9)	C9—C2—C9 ⁱ	121.2 (3)
O3—Ni1—O1	95.20 (9)	C9—C2—H2C	119.4
O1 ⁱ —Ni1—O1	62.84 (10)	C9 ⁱ —C2—H2C	119.4
O2 ⁱ —Ni1—C11	130.67 (11)	C1 ⁱⁱ —C3—C1	119.9 (3)
O2—Ni1—C11	130.67 (11)	C1 ⁱⁱ —C3—C12	120.03 (16)
O3 ⁱ —Ni1—C11	91.73 (7)	C1—C3—C12	120.03 (16)
O3—Ni1—C11	91.73 (7)	C5—C4—C5 ⁱⁱ	120.4 (3)
O1 ⁱ —Ni1—C11	31.42 (5)	C5—C4—H4A	119.8
O1—Ni1—C11	31.42 (5)	C5 ⁱⁱ —C4—H4A	119.8
O7—Ni2—O8	175.21 (9)	C4—C5—C1	119.4 (2)
O7—Ni2—O5	91.60 (7)	C4—C5—C8	118.9 (2)
O8—Ni2—O5	86.05 (8)	C1—C5—C8	121.6 (2)
O7—Ni2—O4	88.86 (8)	O10—C6—O8	124.4 (2)
O8—Ni2—O4	93.77 (8)	O10—C6—C9	118.7 (2)
O5—Ni2—O4	176.11 (9)	O8—C6—C9	116.9 (2)
O7—Ni2—O6	93.66 (8)	C10—C7—C10 ⁱ	119.9 (3)
O8—Ni2—O6	90.41 (8)	C10—C7—C11	120.07 (17)
O5—Ni2—O6	87.51 (8)	C10 ⁱ —C7—C11	120.07 (17)
O4—Ni2—O6	88.61 (8)	O11—C8—O7	124.9 (2)
O7—Ni2—O9	86.70 (8)	O11—C8—C5	118.6 (2)

O8—Ni2—O9	89.18 (8)	O7—C8—C5	116.5 (2)
O5—Ni2—O9	91.29 (8)	C10—C9—C2	118.9 (2)
O4—Ni2—O9	92.59 (8)	C10—C9—C6	118.9 (2)
O6—Ni2—O9	178.76 (9)	C2—C9—C6	122.2 (2)
C11—O1—Ni1	89.19 (17)	C9—C10—C7	120.6 (3)
Ni1—O2—H2A	125.6	C9—C10—H10A	119.7
Ni1—O2—H2B	117.6	C7—C10—H10A	119.7
H2A—O2—H2B	110.8	O1—C11—O1 ⁱ	118.8 (3)
Ni1—O3—H3A	130.1	O1—C11—C7	120.61 (16)
Ni1—O3—H3B	114.6	O1 ⁱ —C11—C7	120.61 (16)
H3A—O3—H3B	112.3	O1—C11—Ni1	59.39 (16)
Ni2—O4—H4B	99.5	O1 ⁱ —C11—Ni1	59.39 (16)
Ni2—O4—H4C	115.0	C7—C11—Ni1	180.0
H4B—O4—H4C	106.1	O12 ⁱⁱ —C12—O12	123.1 (4)
Ni2—O5—H5A	105.4	O12 ⁱⁱ —C12—C3	118.45 (18)
Ni2—O5—H5B	122.7	O12—C12—C3	118.45 (18)

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

Hydrogen-bond geometry (Å, °)

<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>
O9—H9B \cdots O10 ⁱⁱⁱ	0.87	1.90	2.767 (3)	172
O9—H9A \cdots O12 ^{iv}	0.81	2.33	3.102 (3)	160
O6—H6B \cdots O1 ^v	0.97	1.98	2.942 (3)	173
O6—H6A \cdots O11 ^{vi}	0.85	1.83	2.683 (3)	173
O5—H5B \cdots O12 ^{vi}	0.92	1.95	2.825 (3)	158
O5—H5A \cdots O11	0.81	1.79	2.559 (3)	156
O4—H4C \cdots O1 ⁱⁱⁱ	0.92	1.97	2.870 (3)	167
O4—H4B \cdots O10	0.91	1.77	2.617 (3)	154
O3—H3B \cdots O12 ^{vii}	0.94	1.97	2.907 (3)	171
O3—H3A \cdots O4 ^{viii}	0.94	2.03	2.917 (3)	156
O2—H2B \cdots O5 ^{ix}	0.83	1.81	2.638 (3)	173
O2—H2A \cdots O12 ^x	0.85	2.02	2.861 (4)	171

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

Fig. 1

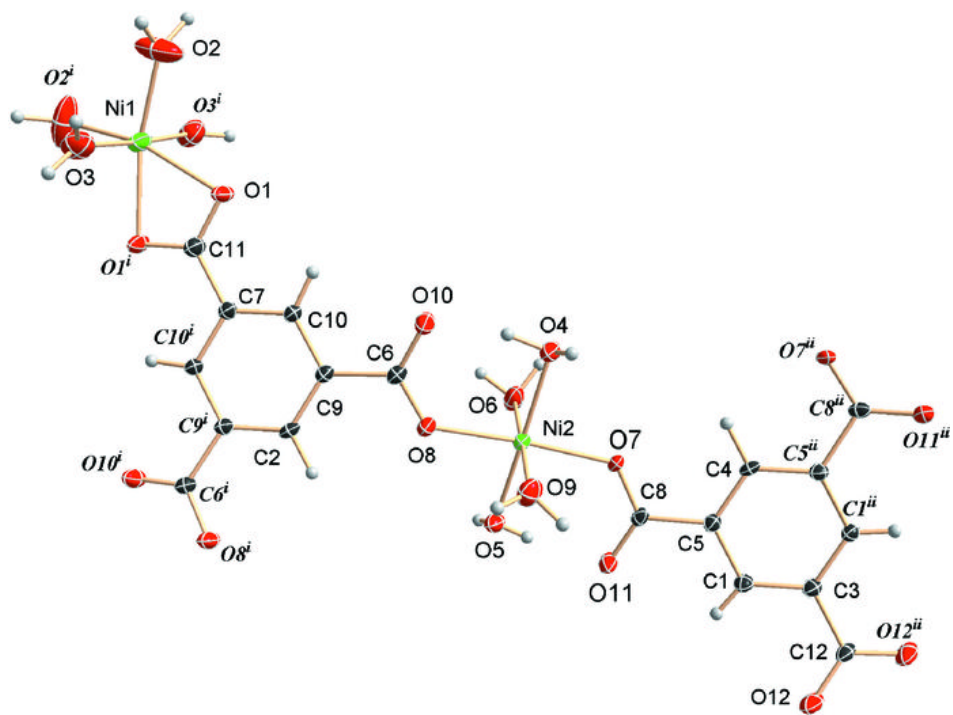


Fig. 2

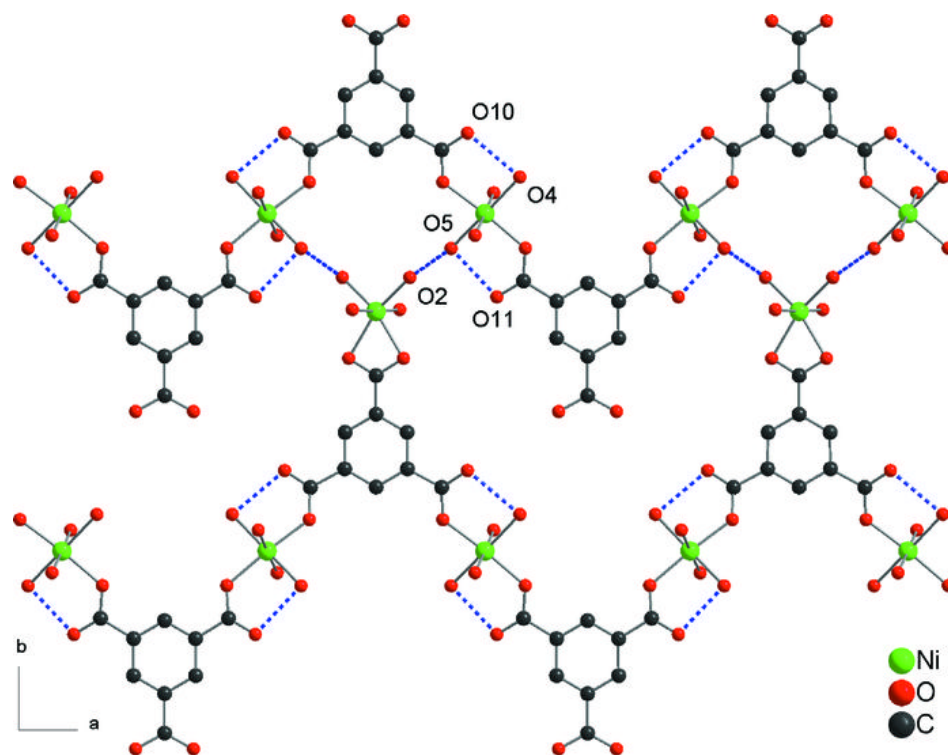


Fig. 3

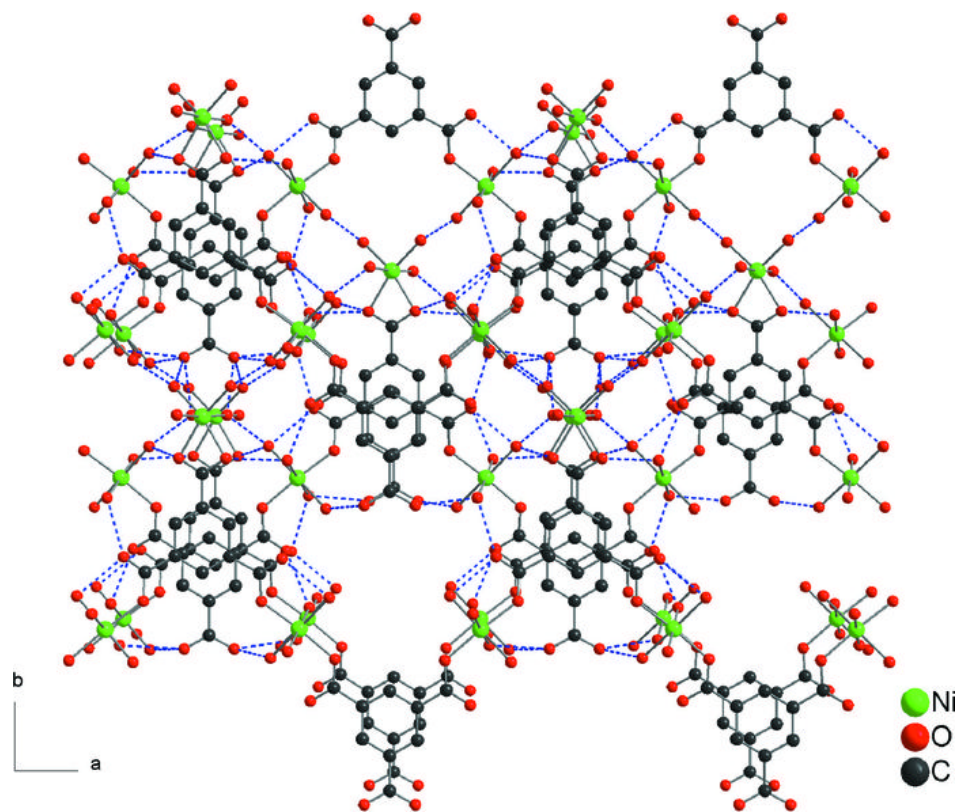


Fig. 4

