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Poly[diaqua(μ_2-1,3-di-4-pyridylpropane-κ^2N:N')(μ_2-thiophene-2,5-dicarboxylato-κ^2O:O')nickel(II)]: a two-dimensional bilayered coordination polymer

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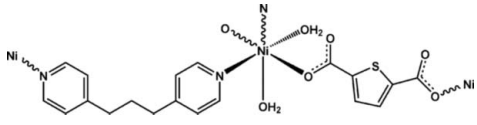
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.005 Å; R factor = 0.042; wR factor = 0.096; data-to-parameter ratio = 16.2.

The hydrothermally prepared title compound, $[Ni(C_6H_2O_4S)(C_{13}H_{14}N_2)(H_2O)_2]_n$, is an Ni polymer based on thiophene-2,5-dicarboxylate dianions (tda^{2-}) and 1,3-di-4-pyridylpropane (bpp) ligands. Each Ni atom is coordinated by two carboxylate O atoms from two independent tda^{2-} groups along the a direction, two N atoms from two bpp ligands along the b direction, and two aqua O atoms, in a distorted octahedral geometry. This leads to a two-dimensional grid-type bilayer assembly running parallel to the (001) plane, in which the bilayer is formed through intermolecular O—H···O hydrogen bonds.

Related literature

For related literature, see: Biradha *et al.* (2002); Bourne *et al.* (2001); Carlucci *et al.* (2000, 2002); Chen *et al.* (2006, 1999, 1998); Deng *et al.* (2006); Eddaoudi *et al.* (2002); Fu *et al.* (2003); Konar *et al.* (2004); Lou *et al.* (2006); Luan *et al.* (2005); Pan *et al.* (2001); Plater *et al.* (2000); Wang *et al.* (2005); Wu *et al.* (2005); Zhang *et al.* (2006, 2003).



Experimental

Crystal data

$[Ni(C_6H_2O_4S)(C_{13}H_{14}N_2)(H_2O)_2]$
M_r = 463.14
Monoclinic, $P2_1/c$
a = 11.024 (2) Å
b = 11.828 (2) Å
c = 16.780 (6) Å
β = 113.94 (2)°
V = 1999.7 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.11 mm^{-1}
T = 298 (2) K
0.30 × 0.25 × 0.18 mm

Data collection

Rigaku R-AXIS RAPID IP area-detector diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.731, T_{max} = 0.825
7838 measured reflections
4504 independent reflections
3211 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.042
$wR(F^2)$ = 0.096
S = 1.05
4504 reflections
278 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.71 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Table 1
Selected bond lengths (Å).

Ni1—O6^{i}	2.0245 (18)	Ni1—O1	2.114 (2)
Ni1—O3	2.0466 (17)	Ni1—N2^{ii}	2.115 (2)
Ni1—N1	2.111 (3)	Ni1—O2	2.126 (2)

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1A···O4	0.83 (4)	1.98 (4)	2.695 (3)	144 (3)
O1—H1B···O5^{i}	0.82 (4)	1.92 (4)	2.690 (3)	156 (4)
O2—H2B···O4^{iii}	0.89 (5)	1.81 (5)	2.706 (3)	174 (4)

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

Data collection: *RAPID-AUTO* (Rigaku, 2001); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97* and *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SK3112).

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supplementary materials

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Poly[diaqua(μ_2-1,3-di-4-pyridylpropane-κ^2N:N')(μ_2-thiophene-2,5-dicarboxylato-κ^2O:O')nickel(II)]: a two-dimensional bilayered coordination polymer

K.-F. Han, D. Wang and Z.-M. Wang

Comment

As an important structural unit, linear bipyridyl ligands such as 4,4'-bipyridine (Wang *et al.*, 2005; Chen *et al.*, 2006; Lou *et al.*, 2006) and 4,4'-bipyridyl with rigid or flexible spacers (Plater *et al.*, 2000; Biradha *et al.*, 2002; Fu *et al.*, 2003; Wu *et al.*, 2005) have been extensively employed to construct novel metal–organic coordination polymers with intriguing structural topologies and unexpected properties with potential applications as functional materials. The compound 1,3-di-4-pyridylpropane (bpp) is a bipyridine-type ligand with a flexible –$CH_2CH_2CH_2$– spacer, and a number of metal–bpp coordination polymers have been reported (Carlucci *et al.*, 2000, 2002; Pan *et al.*, 2001; Luan *et al.*, 2005). Thiophene-2,5-dicarboxylic acid (H_2tda), which is similar to other dicarboxylic acids, such as benzene-1,3-dicarboxylic acid (Bourne *et al.*, 2001; Zhang *et al.*, 2003; Konar *et al.*, 2004), shows diverse coordination modes and can act as a mono-, bi-, tri- or tetradentate ligand (Chen *et al.*, 1998, 1999; Eddaoudi *et al.*, 2002; Zhang *et al.*, 2006; Deng *et al.*, 2006). However, metal coordination polymers based on mixed bpp and thiophene-2,5-dicarboxylate dianions (tda^{2-}) ligands, to our knowledge, have not been reported to date. We report here the title new nickel(II) polymeric compound, $[Ni(tda)(bpp)(H_2O)_2]_n$, (I), with a two-dimensional grid-type bilayer structure, obtained *via* hydrothermal synthesis.

The Ni atom of (I) has a distorted octahedral geometry (Fig. 1) defined by two O atoms from two carboxylate groups of two independent tda ligands along the *a* direction, two N atoms from two bpp ligands along the *b* direction, and two aqua O atoms (Table 1). Both carboxylate groups of the tda ligand coordinate to Ni in a monodentate *syn* fashion, with an angle of 11.54 (11)° between the carboxylate planes. The C—O bond distances in both carboxylate groups are almost equivalent, consistent with its delocalized state. The shortest Ni···Ni distance bridged by a tda ligand is 11.024 (4) Å. The bpp ligand is in a *trans–gauche* conformation and acts as a μ_2-bridge linking two Ni centres, with an Ni···Ni separation of 11.828 (5) Å. The angle between the two pyridyl planes is 72.83 (16)°. The twist in the bpp ligand occurs at C7; the C3—C6—C7—C8 torsion angle is 73.2 (4)°. Two water molecules coordinate to the Ni atom in a *cis* fashion, with O1—Ni1—O2 = 82.05 (11)°.

As shown in Figs. 2 and 3, the Ni atoms are interlinked into a one-dimensional chain by the tda ligands along the *a* direction and this chain is propagated along the *b* direction by coordination between the Ni atoms and the flexible bpp ligands, to generate a two-dimensional grid-type layer 1 running parallel to the (001) plane. Two tda and two bpp ligands link four Ni atoms forming an Ni_4 grid with dimensions of 11.024 × 11.828 $Å^2$, which is the basic building unit for the whole two-dimensional network of (I) (Fig. 4). Based on layer 1, layers 2, 3 and 4 can also be produced *via* symmetry operations ($-x$, $1/2 + y$, $1/2 - z$), ($-x$, $-y$, $-z$) and (x, $1/2 - y$, $1/2 + z$), respectively (Fig. 2). As shown in Fig. 3, all Ni atoms in the same layer are coplanar, and the respective distances between planes 1 and 2, planes 2 and 3, and planes 3 and 4 are 1.570 (2), 6.098 (1), and 1.570 (2) Å, respectively.

In the structure of (I), there are two types of hydrogen bonds (Table 2), namely intramolecular O1—H1A···O4 and O1—H1B···$O5^i$ hydrogen bonds [symmetry code: (i) $-1 + x, y, z$], and intermolecular hydrogen bonds between the O2 atoms

of the coordinated water molecules and the uncoordinated carboxylate $O4^{ii}$ atoms, O2—H2B···$O4^{ii}$ (Fig. 3) [symmetry code: (ii) $1 - x$, $1/2 + y$, $1/2 - z$], leading to a two-dimensional hydrogen-bonding bilayer architecture between polymeric layers 1 and 2. The bilayer structure is also parallel to the (001) plane. There seems to be no obvious interaction between the bilayer structures, but the grid bilayers stack closely in an offset way. Additionally, there is a contact between O2—H2A and π ring $(N2/C11/C10/C9/C13/C12)^{iii}$ [symmetry code: (iii) $1 - x$, $-1/2 + y$, $1/2 - z$], and the distance between atom H2A and the centroid of the π ring is 2.97 (5) Å.

Experimental

A mixture of $NiCl_2·6H_2O$ (0.060 g, 0.25 mmol) with Na_2tda (0.108 g, 0.5 mmol) and bpp (0.050 g, 0.25 mmol), in the molar ratio 1:2:1, and water (4 ml) was placed in a Parr Teflon-lined stainless steel vessel (25 ml). The sealed vessel was heated and held at 423 K for 24 h before the reaction mixture was cooled to room temperature at a rate of 2.5 K h^{-1}. The reaction yielded light-green crystals of (I) in a yield of *ca* 35% based on bpp. IR spectroscopic analysis (solid KBr disc, ν, cm^{-1}): 3430.3 (*m*), 1714.5 (*s*), 1611.3 (*s*), 1551.2 (*m*), 1529.0 (*m*), 1375.4 (*vs*), 1272.0 (*w*), 1221.3 (*s*), 1068.7 (*w*), 1019.4 (*w*), 835.0 (*w*), 772.2 (*s*), 523.2 (*w*), 474.8 (*m*).

Refinement

H atoms attached to O atoms were located in a difference Fourier map and refined with a global U_{iso}(H) value. The O—H distances are in the range 0.82 (4)–0.89 (5) Å. H atoms attached to C atoms were placed in geometrically idealized positions, with C_{sp3}—H = 0.97 Å and C_{sp2}—H = 0.93 Å, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C).

Figures

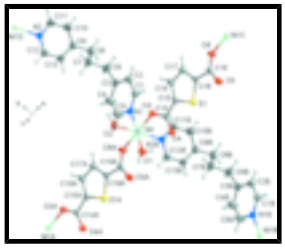


Fig. 1. A view of a fragment of the title compound, showing 50% probability displacement ellipsoids. [Symmetry codes: (A) −1 + *x*, *y*, *z*; (B) *x*, −1 + *y*, *z*; (C) 1 + *x*, *y*, *z*; (D) *x*, 1 + *y*, *z*.]

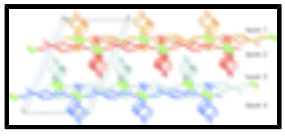


Fig. 2. The bilayer structure in (I), showing Ni atoms (green balls) linked by tda ligands along the *a* axis. H atoms attached to C atoms have been omitted.

Fig. 3. The crystal packing of complex (I), showing hydrogen-bonding interactions between the nearest layers along the *b* axis. Hydrogen bonds are shown as blue dotted lines, and H atoms attached to C atoms have been omitted. O atoms involved in hydrogen bonds are shown as balls and their colours are consistent with the corresponding colour of the layer.

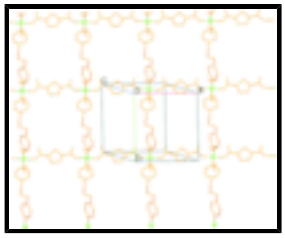


Fig. 4. A view of the two-dimensional network with grids.

Poly[diaqua(μ$_2$-1,3-di-4-pyridylpropane-κ^2*N*:*N*')(μ$_2$-thiophene- 2,5-dicarboxylato-κ^2*O*:*O*')nickel(II)]

Crystal data

$[Ni(C_6H_2O_4S)(C_{13}H_{14}N_2)(H_2O)_2]$	F_{000} = 960
M_r = 463.14	D_x = 1.538 Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2ybc	Cell parameters from 7838 reflections
a = 11.024 (2) Å	θ = 2.0–27.3º
b = 11.828 (2) Å	μ = 1.11 mm^{-1}
c = 16.780 (6) Å	T = 298 (2) K
β = 113.94 (2)º	Prism, light green
V = 1999.7 (9) Å^3	0.30 × 0.25 × 0.18 mm
Z = 4	

Data collection

Rigaku R-AXIS RAPID IP area-detector diffractometer	R_{int} = 0.033
ω scans	θ_{max} = 27.3º
Absorption correction: multi-scan (ABSCOR; Higashi, 1995)	θ_{min} = 2.0º
T_{min} = 0.731, T_{max} = 0.825	h = −14→14
7838 measured reflections	k = −14→15
4504 independent reflections	l = −21→21
3211 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0469P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.042	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.096	$\Delta\rho_{max}$ = 0.71 e Å^{-3}
S = 1.05	$\Delta\rho_{min}$ = −0.38 e Å^{-3}
4504 reflections	Extinction correction: none
278 parameters	

Special details

Experimental. IR spectroscopic analysis (solid KBr disc, ν, cm^{-1}): 3430.3 (*m*), 1714.5 (*s*), 1611.3 (*s*), 1551.2 (*m*), 1529.0 (*m*), 1375.4 (*versus*), 1272.0 (w), 1221.3 (*s*), 1068.7 (w), 1019.4 (w), 835.0 (w), 772.2 (*s*), 523.2 (w), 474.8 (*m*).

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($Å^2$)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.33294 (3)	−0.02984 (3)	0.19881 (2)	0.02540 (11)
S1	0.87336 (6)	−0.15078 (6)	0.26664 (5)	0.03019 (17)
O1	0.4077 (2)	−0.1171 (2)	0.31908 (14)	0.0365 (5)
O2	0.3718 (3)	0.1130 (2)	0.28245 (18)	0.0454 (6)
O3	0.52232 (16)	−0.01725 (17)	0.20610 (13)	0.0341 (5)
O4	0.61008 (19)	−0.17787 (18)	0.27715 (15)	0.0416 (5)
O5	1.15763 (19)	−0.17305 (19)	0.29222 (14)	0.0411 (5)
O6	1.14822 (17)	−0.03662 (19)	0.19681 (14)	0.0387 (5)
N1	0.2659 (2)	0.0805 (2)	0.09064 (16)	0.0332 (5)
N2	0.3041 (2)	0.8199 (2)	0.12500 (16)	0.0315 (5)
C1	0.3449 (3)	0.1259 (3)	0.0563 (2)	0.0435 (8)
H1	0.4321	0.1004	0.0766	0.052*
C2	0.3053 (3)	0.2080 (3)	−0.0070 (2)	0.0449 (8)
H2	0.3647	0.235	−0.0291	0.054*
C3	0.1783 (3)	0.2508 (2)	−0.03801 (18)	0.0342 (6)
C4	0.0960 (3)	0.2019 (3)	−0.0040 (2)	0.0554 (10)
H4	0.0082	0.2257	−0.0236	0.066*
C5	0.1413 (3)	0.1193 (3)	0.0581 (2)	0.0515 (9)
H5	0.0821	0.0883	0.0788	0.062*
C6	0.1313 (3)	0.3476 (3)	−0.1018 (2)	0.0428 (8)
H6A	0.0398	0.3347	−0.1417	0.051*
H6B	0.1846	0.3509	−0.1357	0.051*
C7	0.1418 (3)	0.4603 (3)	−0.0545 (2)	0.0396 (7)
H7A	0.0905	0.5168	−0.0966	0.048*
H7B	0.1029	0.4516	−0.0123	0.048*
C8	0.2833 (3)	0.5023 (3)	−0.0078 (2)	0.0446 (8)
H8A	0.3347	0.4464	0.0349	0.054*
H8B	0.3227	0.5108	−0.0497	0.054*
C9	0.2906 (3)	0.6137 (3)	0.0375 (2)	0.0371 (7)
C10	0.3346 (4)	0.7122 (3)	0.0135 (2)	0.0550 (10)
H10	0.3604	0.7116	−0.0328	0.066*
C11	0.3402 (4)	0.8112 (3)	0.0580 (2)	0.0492 (9)
H11	0.3709	0.8758	0.0406	0.059*
C12	0.2606 (3)	0.7246 (3)	0.14740 (19)	0.0371 (7)
H12	0.2343	0.7273	0.1935	0.045*

C13	0.2526 (3)	0.6234 (3)	0.1061 (2)	0.0389 (7)
H13	0.2211	0.5601	0.1246	0.047*
C14	0.6135 (2)	−0.0898 (2)	0.23658 (18)	0.0284 (6)
C15	0.7364 (2)	−0.0646 (2)	0.22304 (18)	0.0287 (6)
C16	0.7592 (3)	0.0253 (3)	0.1796 (2)	0.0380 (7)
H16	0.6972	0.0817	0.1528	0.046*
C17	0.8873 (3)	0.0227 (3)	0.1801 (2)	0.0386 (7)
H17	0.9186	0.0768	0.1529	0.046*
C18	0.9606 (2)	−0.0676 (2)	0.22476 (18)	0.0286 (6)
C19	1.1005 (2)	−0.0961 (3)	0.23969 (19)	0.0303 (6)
H1A	0.464 (4)	−0.161 (3)	0.317 (2)	0.059 (12)*
H1B	0.343 (4)	−0.144 (3)	0.324 (3)	0.069 (13)*
H2A	0.445 (5)	0.102 (4)	0.322 (3)	0.083 (16)*
H2B	0.382 (4)	0.183 (4)	0.266 (3)	0.085 (16)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01988 (15)	0.02479 (19)	0.0348 (2)	0.000 (14)	0.01443 (13)	0.00044 (16)
S1	0.0226 (3)	0.0324 (4)	0.0402 (4)	0.0004 (3)	0.0174 (3)	0.0007 (3)
O1	0.0275 (10)	0.0439 (13)	0.0416 (13)	0.0040 (10)	0.0175 (9)	0.0014 (10)
O2	0.0494 (14)	0.0348 (14)	0.0545 (16)	−0.0002 (12)	0.0237 (13)	−0.0069 (12)
O3	0.0218 (9)	0.0324 (11)	0.0518 (13)	0.0034 (8)	0.0187 (9)	0.0045 (9)
O4	0.0337 (10)	0.0354 (13)	0.0658 (15)	0.0067 (9)	0.0305 (11)	0.0123 (11)
O5	0.0303 (10)	0.0478 (14)	0.0504 (14)	0.0064 (10)	0.0216 (10)	0.0138 (11)
O6	0.0249 (9)	0.0482 (13)	0.0495 (13)	0.0020 (9)	0.0217 (9)	0.0123 (11)
N1	0.0315 (11)	0.0295 (13)	0.0415 (15)	−0.0009 (10)	0.0177 (11)	0.0032 (11)
N2	0.0318 (11)	0.0296 (14)	0.0341 (14)	−0.0034 (10)	0.0144 (10)	−0.0005 (10)
C1	0.0363 (15)	0.0387 (19)	0.063 (2)	0.0085 (14)	0.0278 (15)	0.0157 (16)
C2	0.0488 (17)	0.043 (2)	0.054 (2)	0.0008 (15)	0.0321 (16)	0.0083 (16)
C3	0.0424 (15)	0.0281 (16)	0.0284 (15)	−0.0014 (13)	0.0106 (13)	−0.0032 (12)
C4	0.0341 (16)	0.070 (3)	0.060 (2)	0.0114 (17)	0.0172 (16)	0.028 (2)
C5	0.0314 (15)	0.065 (2)	0.060 (2)	0.0019 (16)	0.0203 (15)	0.0244 (18)
C6	0.0574 (19)	0.0341 (18)	0.0304 (17)	−0.0026 (15)	0.0112 (14)	0.0007 (13)
C7	0.0492 (17)	0.0321 (17)	0.0312 (16)	0.0029 (14)	0.0098 (13)	−0.0008 (13)
C8	0.0506 (18)	0.0352 (19)	0.048 (2)	−0.0007 (14)	0.0202 (16)	−0.0095 (14)
C9	0.0383 (15)	0.0342 (17)	0.0359 (17)	−0.0013 (14)	0.0120 (13)	−0.0066 (14)
C10	0.086 (3)	0.046 (2)	0.052 (2)	−0.019 (2)	0.048 (2)	−0.0150 (18)
C11	0.075 (2)	0.0388 (19)	0.046 (2)	−0.0162 (18)	0.0363 (18)	−0.0032 (15)
C12	0.0421 (15)	0.0378 (18)	0.0349 (17)	−0.0024 (14)	0.0191 (13)	−0.0014 (14)
C13	0.0506 (17)	0.0303 (17)	0.0365 (17)	−0.0059 (14)	0.0186 (14)	0.0003 (13)
C14	0.0230 (12)	0.0306 (16)	0.0357 (16)	−0.0003 (12)	0.0160 (11)	−0.0054 (13)
C15	0.0208 (12)	0.0329 (16)	0.0347 (15)	−0.0005 (11)	0.0138 (11)	−0.0045 (12)
C16	0.0288 (13)	0.0400 (18)	0.0499 (19)	0.0076 (14)	0.0208 (13)	0.0091 (16)
C17	0.0296 (13)	0.0420 (18)	0.0512 (19)	0.0005 (14)	0.0238 (13)	0.0111 (16)
C18	0.0225 (11)	0.0329 (15)	0.0341 (15)	−0.0056 (11)	0.0153 (11)	−0.0052 (12)
C19	0.0238 (12)	0.0373 (17)	0.0345 (16)	−0.0035 (12)	0.0168 (11)	−0.0062 (13)

Geometric parameters (Å, °)

Ni1—O6^{i}	2.0245 (18)	C4—C5	1.366 (5)
Ni1—O3	2.0466 (17)	C4—H4	0.9300
Ni1—N1	2.111 (3)	C5—H5	0.9300
Ni1—O1	2.114 (2)	C6—C7	1.532 (4)
Ni1—N2^{ii}	2.115 (2)	C6—H6A	0.9700
Ni1—O2	2.126 (2)	C6—H6B	0.9700
S1—C18	1.713 (3)	C7—C8	1.518 (4)
S1—C15	1.720 (3)	C7—H7A	0.9700
O1—H1A	0.83 (4)	C7—H7B	0.9700
O1—H1B	0.82 (4)	C8—C9	1.506 (4)
O2—H2A	0.83 (5)	C8—H8A	0.9700
O2—H2B	0.89 (5)	C8—H8B	0.9700
O3—C14	1.262 (3)	C9—C13	1.381 (4)
O4—C14	1.253 (3)	C9—C10	1.384 (4)
O5—C19	1.246 (4)	C10—C11	1.377 (5)
O6—C19	1.264 (3)	C10—H10	0.9300
O6—Ni1^{iii}	2.0245 (18)	C11—H11	0.9300
N1—C5	1.337 (4)	C12—C13	1.368 (4)
N1—C1	1.337 (4)	C12—H12	0.9300
N2—C12	1.337 (4)	C13—H13	0.9300
N2—C11	1.340 (4)	C14—C15	1.492 (3)
N2—Ni1^{iv}	2.115 (2)	C15—C16	1.369 (4)
C1—C2	1.374 (4)	C16—C17	1.409 (4)
C1—H1	0.9300	C16—H16	0.9300
C2—C3	1.376 (4)	C17—C18	1.366 (4)
C2—H2	0.9300	C17—H17	0.9300
C3—C4	1.380 (4)	C18—C19	1.497 (3)
C3—C6	1.508 (4)		
O6^{i}—Ni1—O3	177.04 (9)	C3—C6—H6B	109.4
O6^{i}—Ni1—N1	90.64 (8)	C7—C6—H6B	109.4
O3—Ni1—N1	89.96 (8)	H6A—C6—H6B	108.0
O6^{i}—Ni1—O1	89.80 (9)	C8—C7—C6	113.5 (3)
O3—Ni1—O1	89.15 (9)	C8—C7—H7A	108.9
N1—Ni1—O1	171.03 (9)	C6—C7—H7A	108.9
O6^{i}—Ni1—N2^{ii}	92.62 (9)	C8—C7—H7B	108.9
O3—Ni1—N2^{ii}	90.20 (8)	C6—C7—H7B	108.9
N1—Ni1—N2^{ii}	95.69 (10)	H7A—C7—H7B	107.7
O1—Ni1—N2^{ii}	93.23 (9)	C9—C8—C7	112.4 (3)
O6^{i}—Ni1—O2	88.53 (9)	C9—C8—H8A	109.1
O3—Ni1—O2	88.59 (9)	C7—C8—H8A	109.1
N1—Ni1—O2	89.01 (11)	C9—C8—H8B	109.1
O1—Ni1—O2	82.05 (11)	C7—C8—H8B	109.1
N2^{ii}—Ni1—O2	175.15 (11)	H8A—C8—H8B	107.9

C18—S1—C15	91.57 (13)	C13—C9—C10	115.7 (3)
Ni1—O1—H1A	106 (3)	C13—C9—C8	121.4 (3)
Ni1—O1—H1B	106 (3)	C10—C9—C8	122.9 (3)
H1A—O1—H1B	118 (4)	C11—C10—C9	120.1 (3)
Ni1—O2—H2A	106 (3)	C11—C10—H10	119.9
Ni1—O2—H2B	124 (3)	C9—C10—H10	119.9
H2A—O2—H2B	101 (4)	N2—C11—C10	123.9 (3)
C14—O3—Ni1	126.91 (18)	N2—C11—H11	118.1
C19—O6—Ni1^{iii}	131.38 (19)	C10—C11—H11	118.1
C5—N1—C1	115.3 (3)	N2—C12—C13	123.5 (3)
C5—N1—Ni1	120.5 (2)	N2—C12—H12	118.2
C1—N1—Ni1	123.8 (2)	C13—C12—H12	118.2
C12—N2—C11	115.7 (3)	C12—C13—C9	121.1 (3)
C12—N2—Ni1^{iv}	122.0 (2)	C12—C13—H13	119.5
C11—N2—Ni1^{iv}	122.1 (2)	C9—C13—H13	119.5
N1—C1—C2	124.0 (3)	O4—C14—O3	126.2 (2)
N1—C1—H1	118.0	O4—C14—C15	118.6 (2)
C2—C1—H1	118.0	O3—C14—C15	115.2 (2)
C1—C2—C3	120.5 (3)	C16—C15—C14	127.7 (2)
C1—C2—H2	119.7	C16—C15—S1	111.56 (19)
C3—C2—H2	119.7	C14—C15—S1	120.8 (2)
C2—C3—C4	115.4 (3)	C15—C16—C17	112.4 (3)
C2—C3—C6	123.4 (3)	C15—C16—H16	123.8
C4—C3—C6	121.2 (3)	C17—C16—H16	123.8
C5—C4—C3	121.1 (3)	C18—C17—C16	112.8 (3)
C5—C4—H4	119.4	C18—C17—H17	123.6
C3—C4—H4	119.4	C16—C17—H17	123.6
N1—C5—C4	123.6 (3)	C17—C18—C19	127.4 (3)
N1—C5—H5	118.2	C17—C18—S1	111.65 (19)
C4—C5—H5	118.2	C19—C18—S1	120.9 (2)
C3—C6—C7	111.2 (2)	O5—C19—O6	127.0 (2)
C3—C6—H6A	109.4	O5—C19—C18	118.3 (2)
C7—C6—H6A	109.4	O6—C19—C18	114.7 (3)
N1—Ni1—O3—C14	−153.1 (2)	C12—N2—C11—C10	−0.1 (5)
O1—Ni1—O3—C14	35.8 (2)	Ni1^{iv}—N2—C11—C10	173.7 (3)
N2^{ii}—Ni1—O3—C14	−57.4 (2)	C9—C10—C11—N2	−0.5 (6)
O2—Ni1—O3—C14	117.9 (2)	C11—N2—C12—C13	0.2 (4)
O6^{i}—Ni1—N1—C5	4.9 (3)	Ni1^{iv}—N2—C12—C13	−173.6 (2)
O3—Ni1—N1—C5	−172.2 (3)	N2—C12—C13—C9	0.3 (5)
N2^{ii}—Ni1—N1—C5	97.6 (3)	C10—C9—C13—C12	−0.8 (5)
O2—Ni1—N1—C5	−83.6 (3)	C8—C9—C13—C12	179.5 (3)
O6^{i}—Ni1—N1—C1	177.3 (3)	Ni1—O3—C14—O4	−8.7 (4)
O3—Ni1—N1—C1	0.2 (3)	Ni1—O3—C14—C15	172.38 (17)
N2^{ii}—Ni1—N1—C1	−90.0 (3)	O4—C14—C15—C16	178.8 (3)
O2—Ni1—N1—C1	88.8 (3)	O3—C14—C15—C16	−2.2 (4)
C5—N1—C1—C2	1.0 (5)	O4—C14—C15—S1	−3.1 (4)
Ni1—N1—C1—C2	−171.8 (3)	O3—C14—C15—S1	175.9 (2)

N1—C1—C2—C3	1.4 (6)	C18—S1—C15—C16	−1.1 (2)
C1—C2—C3—C4	−2.8 (5)	C18—S1—C15—C14	−179.5 (2)
C1—C2—C3—C6	174.7 (3)	C14—C15—C16—C17	179.6 (3)
C2—C3—C4—C5	1.8 (5)	S1—C15—C16—C17	1.4 (4)
C6—C3—C4—C5	−175.7 (3)	C15—C16—C17—C18	−0.9 (4)
C1—N1—C5—C4	−2.0 (6)	C16—C17—C18—C19	−179.0 (3)
Ni1—N1—C5—C4	171.1 (3)	C16—C17—C18—S1	0.1 (4)
C3—C4—C5—N1	0.6 (6)	C15—S1—C18—C17	0.6 (2)
C2—C3—C6—C7	−95.4 (4)	C15—S1—C18—C19	179.7 (2)
C4—C3—C6—C7	81.8 (4)	Ni1^{iii}—O6—C19—O5	−4.8 (5)
C3—C6—C7—C8	73.2 (4)	Ni1^{iii}—O6—C19—C18	174.45 (18)
C6—C7—C8—C9	179.5 (3)	C17—C18—C19—O5	170.1 (3)
C7—C8—C9—C13	64.8 (4)	S1—C18—C19—O5	−8.9 (4)
C7—C8—C9—C10	−114.9 (4)	C17—C18—C19—O6	−9.3 (4)
C13—C9—C10—C11	0.9 (5)	S1—C18—C19—O6	171.7 (2)
C8—C9—C10—C11	−179.4 (3)		

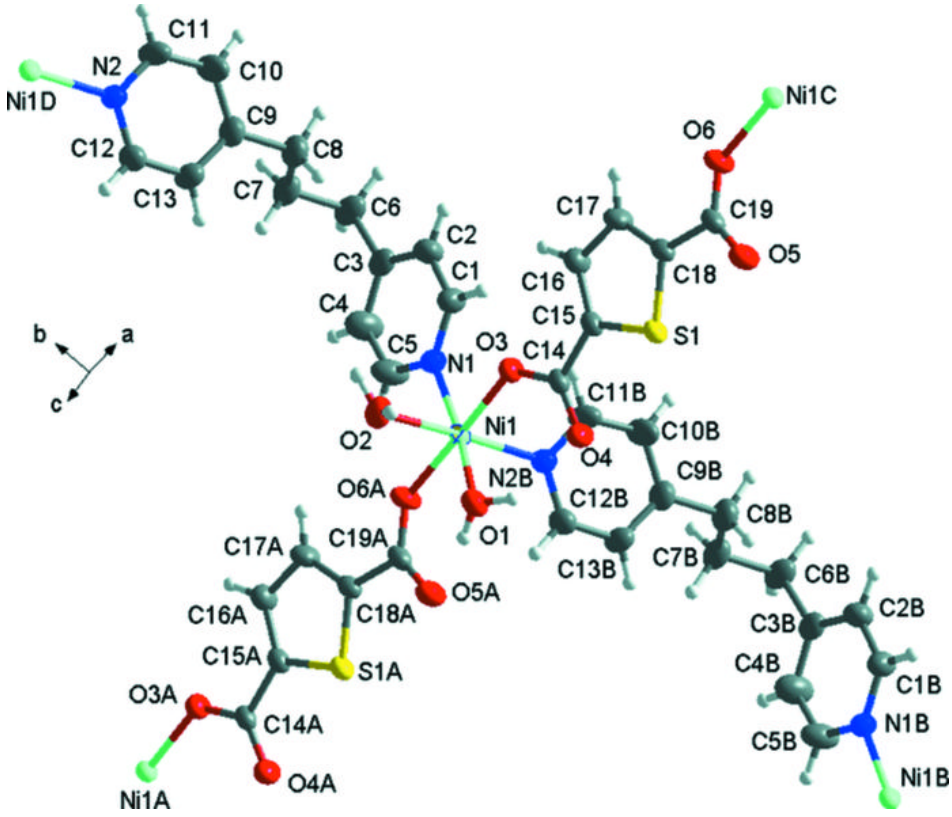
Symmetry codes: (i) *x*−1, *y*, *z*; (ii) *x*, *y*−1, *z*; (iii) *x*+1, *y*, *z*; (iv) *x*, *y*+1, *z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1A···O4	0.83 (4)	1.98 (4)	2.695 (3)	144 (3)
O1—H1B···O5^{i}	0.82 (4)	1.92 (4)	2.690 (3)	156 (4)
O2—H2B···O4^{v}	0.89 (5)	1.81 (5)	2.706 (3)	174 (4)

Symmetry codes: (i) *x*−1, *y*, *z*; (v) −*x*+1, *y*+1/2, −*z*+1/2.

Fig. 1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N2
C10
Ni1D
C9
C12
C8
C13
C7
C6
C2
C3
C1
C4
C5
N1
O3
C14
C11B
O2
Ni1
O4
C10B
O6A
N2B
C12B
C9B
C8B
C19A
O1
C17A
C7B
C6B
O5A
C16A
C18A
C3B
C2B
C15A
S1A
C4B
C1B
O3A
C14A
N1B
C5B
O4A
Ni1A
Ni1B
Ni1C
O6
C19
C17
O5
C18
C16
C15
S1
b
a
c

Fig. 2

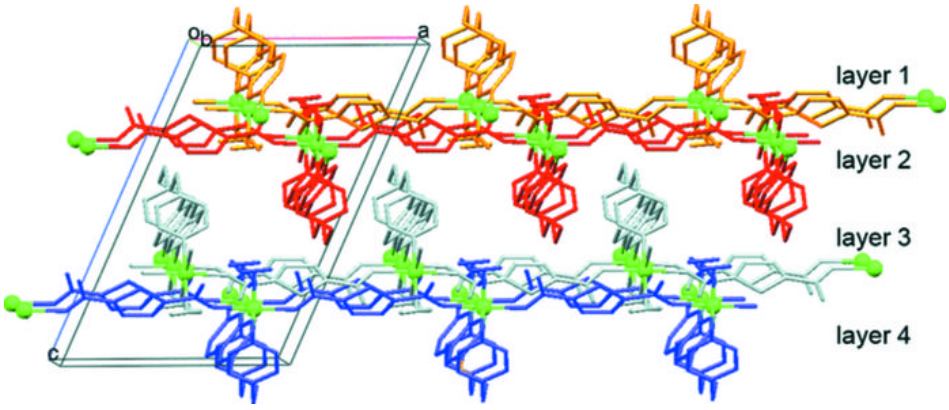

Fig. 3

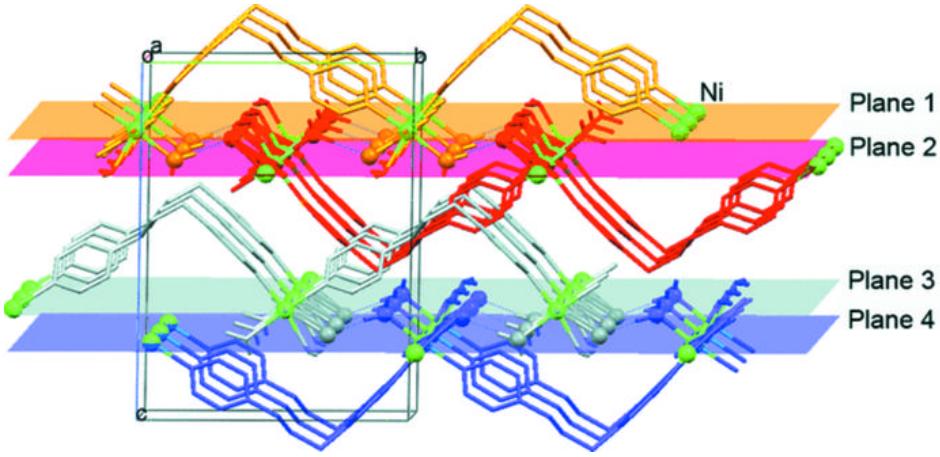

Fig. 4