Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

catena-Poly[[bis(di-4-pyridylamine-κN)-(terephthalato-$\kappa^2 O,O'$)nickel(II)]-μ-di-4-pyridylamine-$\kappa^2 N:N'$]

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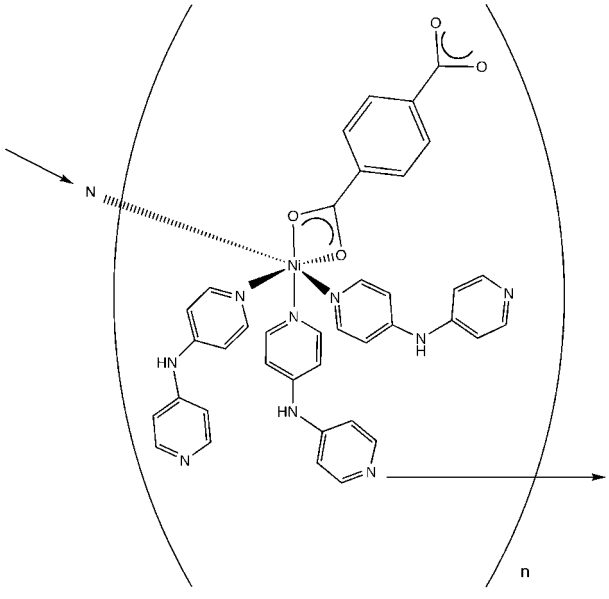
Received 16 October 2007; accepted 17 October 2007

Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.006 Å; R factor = 0.068; wR factor = 0.168; data-to-parameter ratio = 16.8.

In the title compound, $[Ni(C_8H_4O_4)(C_{10}H_9N_3)_3]_n$, an Ni^{II} atom with octahedral coordination is bound by one chelating terephthalate (tp) dianion, two monodentate di-4-pyridylamine (dpa) ligands, and two bridging dpa ligands. These link the Ni atoms into one-dimensional $[Ni(tp)(dpa)_3]_n$ coordination polymer chains that propagate along the *b*-axis direction. Interweaving pairs of chains stack in three dimensions *via* N—H···O hydrogen bonding.

Related literature

For related literature, see: Montney *et al.* (2007); Zapf *et al.* (1998).



Experimental

Crystal data

$[Ni(C_8H_4O_4)(C_{10}H_9N_3)_3]$
M_r = 735.42
Monoclinic, $P2_1/n$
a = 17.025 (3) Å
b = 11.048 (2) Å
c = 18.736 (4) Å
β = 110.281 (3)°
V = 3305.7 (11) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.65 mm^{-1}
T = 173 (2) K
0.38 × 0.14 × 0.08 mm

Data collection

Bruker SMART 1K diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.834, T_{max} = 0.950
39515 measured reflections
8097 independent reflections
4711 reflections with $I > 2\sigma(I)$
R_{int} = 0.118

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.068
$wR(F^2)$ = 0.168
S = 1.02
8097 reflections
481 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 1.12 e Å^{-3}
$\Delta\rho_{min}$ = −0.84 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2N···O4^{i}	0.99 (5)	1.83 (5)	2.793 (4)	164 (4)
N5—H5N···O3^{ii}	0.94 (5)	1.93 (5)	2.874 (5)	177 (4)
N8—H8N···O3^{iii}	0.91 (4)	1.93 (5)	2.841 (4)	179 (4)

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2003); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *CrystalMaker* (CrystalMaker Software, 2005); software used to prepare material for publication: *SHELXL97*.

We gratefully acknowledge Michigan State University for funding this work. MAB acknowledges the MSU Quality Fund Undergraduate Research Program for financial support. We thank Dr Richard Staples for crystallographic assistance.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2318).

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  doi:10.1107/S1600536807051112

supplementary materials

Acta Cryst. (2007). E**63**, m2780 [**doi:10.1107/S1600536807051112**]

catena-Poly[[bis(di-4-pyridylamine-κN)(terephthalato-$\kappa^2 O,O'$)nickel(II)]-μ-di-4-pyridylamine-$\kappa^2 N:N'$]

M. A. Braverman and R. L. LaDuca

Comment

In comparison to the large number of coordination polymers constructed from the rigid rod tethering ligand 4,4'-bipyridine, metal-organic materials based on 4,4'-dipyridylamine (dpa) are much rarer (Montney *et al.*, 2007). Prepared during continued attempts to develop this chemistry, the title compound possesses an asymmetric unit (Fig. 1) consisting of one nickel atom, one terephthalate (tp) dianion, and three crystallographically distinct dpa moieties. The nickel atom displays a $[NiN_4O_2]$ octahedral coordination sphere, with the *cis* O donor atoms belonging to a chelating carboxylate terminus of the tp ligand. Two of the N atom donors, disposed in a *cis* fashion, belong to different bridging dpa ligands. The other two N donors belong to crystallographically independent monodentate dpa lignds.

Extension of the structure along the *b* crystal direction reveals an 1-D chain coordination polymer of formulation $[Ni(tp)(dpa)_3]_n$, constructed by the linkage of adjacent Ni atoms through exobidentate dpa ligands (Fig. 2). Within the 1-D chain motif, the Ni–Ni through-ligand distance is 11.048 (2) Å, marking the *b* lattice parameter.

Each $[Ni(tp)(dpa)_3]_n$ chain is interwoven by another identical chain, related by the crystallographic 2_1 screw axis along *b* (Fig. 3). The double chain motifs are stabilized through N—H···O hydrogen bonding promoted by the central amine groups of the bridging dpa ligands. These one-dimensional subunits further aggregate into three dimensions *via* additional N—H···O hydrogen bonding patterns mediated by the pendant dpa ligands (Fig. 4).

Experimental

Nickel chloride hexahydrate and terephthalic acid were obtained commercially. Di-4-pyridylamine (dpa) was prepared *via* a published procedure (Zapf *et al.*, 1998). Nickel chloride hexahydrate (88 mg, 0.37 mmol), terephthalic acid (62 mg, 0.37 mmol) and dpa (127 mg, 0.74 mmol) were added to 10 ml H_2O in a 23 ml a Teflon-lined Parr acid digestion bomb. The pH was adjusted with 0.75 ml of 0.1 *M* NaOH and the bomb was sealed. The mixture was then heated under autogenous pressure at 393 K for 48 h., whereupon it was cooled slowly to 293 K. Small dark blue plates (76 mg, 42% yield based on dpa) of the title compound were produced.

Refinement

All H atoms bound to C atoms were placed in calculated positions, with C—H = 0.93 (2) Å and refined in riding mode with $U_{iso} = 1.2U_{eq}$(C). The H atoms bound to N within the dpa ligands were found *via* Fourier difference map and refined with $U_{iso} = 1.2U_{eq}$(N). The largest difference peak of 1.117 $e^-/Å^3$ was located 0.77 Å from H17.

Figures

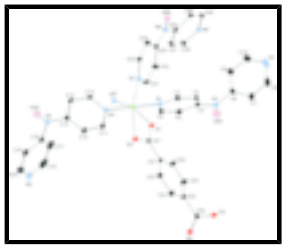

Fig. 1. Asymmetric unit of the title compound, showing 50% probability ellipsoids and partial atom numbering scheme. Color codes: light-blue N, yellow S, black C, pink H, green Ni.

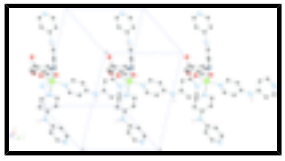

Fig. 2. A single $[Ni(tp)(dpa)_3]_n$ coordination polymer chain.

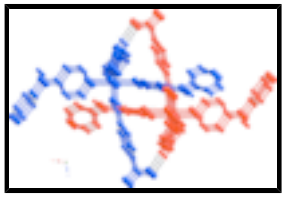

Fig. 3. Two interwoven $[Ni(tp)(dpa)_3]_n$ chains. Hydrogen bonding is shown as dashed lines.

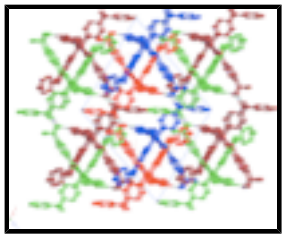

Fig. 4. Interaction of $[Ni(tp)(dpa)_3]_n$ double chain motifs through N—H···O hydrogen bonding, shown as gray lines.

catena-poly-[[(terephthalato-κ^2O:O)bis(di-4- pyridylamine-κN)nickel(II)]-μ-di-4-pyridylamine-κ^2N:N']

Crystal data

$[Ni(C_8H_4O_4)(C_{10}H_9N_3)_3]$	F_{000} = 1524
M_r = 735.42	D_x = 1.478 Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation λ = 0.71073 Å
Hall symbol: -P 2yn	Cell parameters from 39515 reflections
a = 17.025 (3) Å	θ = 1.4–28.5º
b = 11.048 (2) Å	μ = 0.65 mm^{-1}
c = 18.736 (4) Å	T = 173 (2) K
β = 110.281 (3)º	Plate, blue
V = 3305.7 (11) Å^3	0.38 × 0.14 × 0.08 mm
Z = 4	

Data collection

Bruker SMART 1K diffractometer	8097 independent reflections

Radiation source: fine-focus sealed tube	4711 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.118$
$T = 173(2)$ K	$\theta_{max} = 28.5°$
ω scans	$\theta_{min} = 1.4°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -22\rightarrow21$
$T_{min} = 0.834$, $T_{max} = 0.950$	$k = -14\rightarrow14$
39515 measured reflections	$l = -24\rightarrow24$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.068$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.168$	$w = 1/[\sigma^2(F_o^2) + (0.0719P)^2 + 3.6742P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} < 0.001$
8097 reflections	$\Delta\rho_{max} = 1.12$ e Å^{-3}
481 parameters	$\Delta\rho_{min} = -0.83$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Experimental. The small crystal width resulted in relatively weak diffraction and an R_{int} value in excess of 0.10 despite collection of 30 second frames. Nevertheless, refinement was satisfactory.

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Ni1	0.89296 (3)	0.64879 (4)	0.19611 (3)	0.01181 (14)
O1	0.90765 (17)	0.5489 (2)	0.29935 (15)	0.0182 (6)
O2	0.90374 (17)	0.7477 (2)	0.29665 (15)	0.0187 (6)
O3	0.78211 (18)	0.6437 (3)	0.61865 (15)	0.0265 (7)
O4	0.91737 (18)	0.6727 (3)	0.68384 (15)	0.0232 (7)
N1	0.7629 (2)	0.6457 (3)	0.17926 (18)	0.0170 (7)
N2	0.5155 (2)	0.6293 (3)	0.17493 (19)	0.0187 (8)

H2N	0.490 (3)	0.704 (5)	0.186 (3)	0.044 (15)*
N3	0.3284 (2)	0.3713 (4)	0.0703 (2)	0.0387 (11)
N4	1.0226 (2)	0.6513 (3)	0.21577 (18)	0.0153 (7)
N5	1.2732 (2)	0.7399 (4)	0.2528 (2)	0.0234 (8)
H5N	1.278 (3)	0.781 (4)	0.210 (3)	0.033 (13)*
N6	1.4651 (3)	0.7791 (6)	0.4648 (2)	0.0549 (15)
N7	0.8835 (2)	0.4967 (3)	0.12859 (18)	0.0142 (7)
N8	0.8390 (2)	0.1492 (3)	0.03052 (19)	0.0169 (7)
H8N	0.801 (3)	0.148 (4)	−0.017 (3)	0.026 (12)*
N9	0.8784 (2)	−0.1977 (3)	0.12899 (18)	0.0136 (7)
C1	0.7255 (2)	0.5395 (4)	0.1831 (2)	0.0176 (9)
H1	0.7564	0.4690	0.1864	0.021*
C2	0.6448 (2)	0.5283 (3)	0.1824 (2)	0.0166 (9)
H2	0.6227	0.4526	0.1862	0.020*
C3	0.5969 (2)	0.6323 (3)	0.1759 (2)	0.0150 (8)
C4	0.6360 (2)	0.7443 (4)	0.1748 (2)	0.0166 (9)
H4	0.6070	0.8163	0.1725	0.020*
C5	0.7172 (2)	0.7456 (3)	0.1770 (2)	0.0178 (9)
H5	0.7422	0.8204	0.1769	0.021*
C6	0.3238 (3)	0.4470 (5)	0.1237 (3)	0.0344 (12)
H6	0.2760	0.4440	0.1370	0.041*
C7	0.3849 (3)	0.5299 (4)	0.1610 (3)	0.0247 (10)
H7	0.3779	0.5804	0.1980	0.030*
C8	0.4569 (3)	0.5369 (4)	0.1424 (2)	0.0205 (9)
C9	0.4629 (3)	0.4571 (4)	0.0871 (2)	0.0284 (11)
H9	0.5101	0.4571	0.0729	0.034*
C10	0.3983 (3)	0.3783 (4)	0.0536 (3)	0.0345 (12)
H10	0.4036	0.3261	0.0166	0.041*
C11	1.0816 (2)	0.6437 (4)	0.2848 (2)	0.0202 (9)
H11	1.0646	0.6216	0.3251	0.024*
C12	1.1652 (3)	0.6660 (4)	0.3008 (2)	0.0223 (10)
H12	1.2031	0.6564	0.3500	0.027*
C13	1.1925 (2)	0.7032 (4)	0.2422 (2)	0.0170 (9)
C14	1.1316 (3)	0.7071 (4)	0.1691 (2)	0.0196 (9)
H14	1.1466	0.7277	0.1275	0.024*
C15	1.0502 (3)	0.6805 (3)	0.1592 (2)	0.0160 (9)
H15	1.0114	0.6828	0.1099	0.019*
C16	1.4283 (3)	0.6742 (6)	0.4430 (3)	0.0472 (16)
H16	1.4462	0.6090	0.4761	0.057*
C17	1.3634 (3)	0.6534 (5)	0.3728 (3)	0.0376 (12)
H17	1.3389	0.5774	0.3603	0.045*
C18	1.3377 (3)	0.7499 (4)	0.3236 (2)	0.0238 (10)
C19	1.3794 (3)	0.8621 (5)	0.3451 (3)	0.0342 (12)
H19	1.3654	0.9286	0.3128	0.041*
C20	1.4403 (3)	0.8694 (6)	0.4146 (3)	0.0489 (16)
H20	1.4671	0.9436	0.4285	0.059*
C21	0.8941 (2)	0.6499 (4)	0.4072 (2)	0.0157 (8)
C22	0.8732 (3)	0.7556 (4)	0.4357 (2)	0.0218 (9)
H22	0.8664	0.8268	0.4077	0.026*

C23	0.8625 (3)	0.7565 (4)	0.5055 (2)	0.0217 (9)
H23	0.8475	0.8282	0.5235	0.026*
C24	0.8736 (2)	0.6528 (4)	0.5489 (2)	0.0164 (8)
C25	0.8957 (3)	0.5464 (4)	0.5212 (2)	0.0233 (10)
H25	0.9048	0.4761	0.5502	0.028*
C26	0.9042 (3)	0.5447 (4)	0.4500 (2)	0.0207 (9)
H26	0.9169	0.4724	0.4309	0.025*
C27	0.9029 (2)	0.6480 (4)	0.3309 (2)	0.0138 (8)
C28	0.8570 (2)	0.6560 (4)	0.6235 (2)	0.0162 (8)
C31	0.9124 (3)	0.3975 (4)	0.1706 (2)	0.0192 (9)
H31	0.9433	0.4073	0.2220	0.023*
C32	0.8987 (3)	0.2815 (4)	0.1417 (2)	0.0200 (9)
H32	0.9175	0.2159	0.1743	0.024*
C33	0.8576 (2)	0.2617 (3)	0.0654 (2)	0.0154 (8)
C34	0.8301 (2)	0.3659 (3)	0.0207 (2)	0.0171 (9)
H34	0.8032	0.3584	−0.0316	0.020*
C35	0.8425 (3)	0.4797 (3)	0.0536 (2)	0.0157 (9)
C36	0.9312 (2)	−0.1059 (3)	0.1603 (2)	0.0163 (8)
H36	0.9755	−0.1210	0.2052	0.020*
C37	0.9237 (2)	0.0090 (3)	0.1299 (2)	0.0178 (9)
H37	0.9634	0.0679	0.1531	0.021*
C38	0.8561 (2)	0.0363 (3)	0.0640 (2)	0.0148 (8)
C39	0.8039 (2)	−0.0605 (4)	0.0296 (2)	0.0156 (8)
H39	0.7600	−0.0487	−0.0161	0.019*
C40	0.8171 (2)	−0.1734 (3)	0.0629 (2)	0.0151 (8)
H40	0.7816	−0.2362	0.0383	0.018*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0145 (3)	0.0100 (2)	0.0120 (2)	−0.0003 (2)	0.00601 (19)	−0.0002 (2)
O1	0.0243 (16)	0.0161 (15)	0.0179 (15)	0.0015 (12)	0.0118 (13)	−0.0024 (12)
O2	0.0253 (16)	0.0154 (15)	0.0184 (15)	−0.0014 (12)	0.0115 (13)	0.0008 (12)
O3	0.0186 (16)	0.0465 (19)	0.0155 (15)	−0.0040 (15)	0.0072 (12)	−0.0053 (14)
O4	0.0215 (16)	0.0316 (18)	0.0144 (15)	−0.0036 (13)	0.0036 (13)	0.0033 (12)
N1	0.0184 (18)	0.0145 (16)	0.0196 (18)	0.0000 (15)	0.0086 (15)	0.0005 (14)
N2	0.0139 (17)	0.021 (2)	0.0227 (19)	−0.0001 (14)	0.0087 (15)	−0.0023 (15)
N3	0.026 (2)	0.034 (3)	0.045 (3)	−0.0097 (19)	−0.002 (2)	0.007 (2)
N4	0.0202 (18)	0.0108 (15)	0.0146 (16)	0.0015 (14)	0.0057 (14)	0.0004 (14)
N5	0.0161 (19)	0.041 (2)	0.0141 (18)	−0.0029 (16)	0.0062 (16)	0.0051 (17)
N6	0.026 (3)	0.117 (5)	0.022 (2)	−0.021 (3)	0.010 (2)	0.005 (3)
N7	0.0145 (17)	0.0139 (17)	0.0146 (17)	0.0015 (13)	0.0058 (14)	−0.0001 (13)
N8	0.0219 (18)	0.0119 (16)	0.0141 (17)	−0.0014 (15)	0.0029 (15)	−0.0012 (15)
N9	0.0160 (18)	0.0104 (16)	0.0146 (17)	0.0006 (13)	0.0056 (14)	0.0013 (13)
C1	0.016 (2)	0.014 (2)	0.023 (2)	0.0036 (16)	0.0073 (18)	−0.0012 (17)
C2	0.017 (2)	0.012 (2)	0.022 (2)	−0.0012 (16)	0.0085 (18)	−0.0025 (16)
C3	0.015 (2)	0.019 (2)	0.0123 (19)	0.0008 (17)	0.0055 (16)	0.0020 (16)
C4	0.017 (2)	0.015 (2)	0.019 (2)	0.0069 (17)	0.0077 (18)	0.0011 (16)

C5	0.020 (2)	0.012 (2)	0.025 (2)	0.0002 (16)	0.0114 (19)	−0.0003 (17)
C6	0.019 (2)	0.040 (3)	0.041 (3)	−0.006 (2)	0.006 (2)	0.016 (3)
C7	0.014 (2)	0.030 (3)	0.030 (2)	0.0020 (18)	0.0075 (19)	0.009 (2)
C8	0.017 (2)	0.021 (2)	0.020 (2)	−0.0024 (17)	0.0013 (18)	0.0026 (17)
C9	0.022 (2)	0.034 (3)	0.025 (2)	−0.002 (2)	0.003 (2)	−0.001 (2)
C10	0.035 (3)	0.034 (3)	0.025 (3)	−0.002 (2)	−0.002 (2)	−0.001 (2)
C11	0.017 (2)	0.026 (2)	0.016 (2)	−0.0007 (19)	0.0054 (17)	0.0091 (18)
C12	0.017 (2)	0.034 (3)	0.015 (2)	−0.0015 (19)	0.0050 (18)	0.0043 (18)
C13	0.014 (2)	0.021 (2)	0.017 (2)	0.0014 (17)	0.0059 (17)	0.0039 (17)
C14	0.021 (2)	0.026 (2)	0.014 (2)	0.0011 (18)	0.0096 (18)	0.0007 (17)
C15	0.020 (2)	0.018 (2)	0.0088 (19)	0.0036 (16)	0.0032 (17)	−0.0012 (15)
C16	0.028 (3)	0.084 (5)	0.035 (3)	0.014 (3)	0.017 (3)	0.027 (3)
C17	0.025 (3)	0.059 (3)	0.032 (3)	0.006 (3)	0.014 (2)	0.020 (3)
C18	0.012 (2)	0.046 (3)	0.016 (2)	0.000 (2)	0.0077 (18)	0.002 (2)
C19	0.022 (2)	0.059 (3)	0.025 (2)	−0.002 (2)	0.013 (2)	0.004 (2)
C20	0.035 (3)	0.086 (5)	0.027 (3)	−0.024 (3)	0.012 (2)	−0.015 (3)
C21	0.016 (2)	0.021 (2)	0.0129 (19)	−0.0013 (18)	0.0088 (16)	−0.0002 (17)
C22	0.029 (2)	0.018 (2)	0.020 (2)	−0.0030 (19)	0.0115 (19)	0.0008 (17)
C23	0.031 (3)	0.016 (2)	0.025 (2)	−0.0008 (18)	0.017 (2)	−0.0022 (17)
C24	0.0128 (19)	0.026 (2)	0.0113 (19)	0.0012 (18)	0.0048 (16)	−0.0006 (17)
C25	0.033 (3)	0.022 (2)	0.016 (2)	0.0079 (19)	0.0102 (19)	0.0033 (18)
C26	0.030 (2)	0.020 (2)	0.016 (2)	0.0067 (19)	0.0119 (19)	0.0014 (17)
C27	0.0129 (19)	0.0157 (19)	0.0136 (19)	−0.0024 (17)	0.0059 (15)	−0.0004 (17)
C28	0.018 (2)	0.0130 (19)	0.017 (2)	0.0000 (17)	0.0054 (17)	0.0000 (17)
C31	0.027 (2)	0.019 (2)	0.011 (2)	0.0086 (18)	0.0068 (18)	−0.0002 (17)
C32	0.032 (3)	0.0091 (19)	0.016 (2)	0.0035 (17)	0.0051 (19)	0.0006 (16)
C33	0.017 (2)	0.013 (2)	0.017 (2)	−0.0007 (16)	0.0071 (18)	−0.0017 (16)
C34	0.023 (2)	0.015 (2)	0.0122 (19)	0.0026 (17)	0.0044 (17)	0.0016 (16)
C35	0.022 (2)	0.015 (2)	0.011 (2)	0.0010 (17)	0.0067 (17)	0.0003 (15)
C36	0.014 (2)	0.0149 (19)	0.017 (2)	0.0009 (16)	0.0016 (17)	0.0009 (16)
C37	0.014 (2)	0.014 (2)	0.023 (2)	−0.0025 (16)	0.0030 (18)	−0.0040 (17)
C38	0.020 (2)	0.012 (2)	0.015 (2)	0.0018 (16)	0.0091 (17)	−0.0012 (16)
C39	0.014 (2)	0.020 (2)	0.0107 (19)	−0.0014 (17)	0.0019 (16)	−0.0012 (16)
C40	0.014 (2)	0.012 (2)	0.019 (2)	−0.0020 (15)	0.0057 (17)	−0.0051 (15)

Geometric parameters (Å, °)

Ni1—N9^{i}	2.075 (3)	C9—C10	1.372 (6)
Ni1—N7	2.075 (3)	C9—H9	0.9300
Ni1—N4	2.108 (3)	C10—H10	0.9300
Ni1—N1	2.125 (3)	C11—C12	1.372 (6)
Ni1—O2	2.130 (3)	C11—H11	0.9300
Ni1—O1	2.165 (3)	C12—C13	1.395 (5)
Ni1—C27	2.472 (4)	C12—H12	0.9300
O1—C27	1.261 (4)	C13—C14	1.403 (5)
O2—C27	1.277 (4)	C14—C15	1.365 (5)
O3—C28	1.253 (5)	C14—H14	0.9300
O4—C28	1.250 (5)	C15—H15	0.9300
N1—C5	1.343 (5)	C16—C17	1.412 (7)

N1—C1	1.349 (5)	C16—H16	0.9300
N2—C3	1.379 (5)	C17—C18	1.378 (6)
N2—C8	1.410 (5)	C17—H17	0.9300
N2—H2N	0.99 (5)	C18—C19	1.416 (7)
N3—C6	1.327 (6)	C19—C20	1.357 (7)
N3—C10	1.334 (6)	C19—H19	0.9300
N4—C11	1.337 (5)	C20—H20	0.9300
N4—C15	1.340 (5)	C21—C22	1.382 (6)
N5—C13	1.379 (5)	C21—C26	1.389 (5)
N5—C18	1.403 (5)	C21—C27	1.487 (5)
N5—H5N	0.94 (5)	C22—C23	1.383 (6)
N6—C16	1.314 (8)	C22—H22	0.9300
N6—C20	1.334 (7)	C23—C24	1.379 (6)
N7—C31	1.341 (5)	C23—H23	0.9300
N7—C35	1.348 (5)	C24—C25	1.389 (6)
N8—C38	1.381 (5)	C24—C28	1.520 (5)
N8—C33	1.389 (5)	C25—C26	1.391 (5)
N8—H8N	0.91 (4)	C25—H25	0.9300
N9—C40	1.340 (5)	C26—H26	0.9300
N9—C36	1.348 (5)	C31—C32	1.379 (5)
N9—Ni1^{ii}	2.075 (3)	C31—H31	0.9300
C1—C2	1.375 (5)	C32—C33	1.374 (5)
C1—H1	0.9300	C32—H32	0.9300
C2—C3	1.390 (5)	C33—C34	1.406 (5)
C2—H2	0.9300	C34—C35	1.384 (5)
C3—C4	1.409 (5)	C34—H34	0.9300
C4—C5	1.368 (5)	C36—C37	1.378 (5)
C4—H4	0.9300	C36—H36	0.9300
C5—H5	0.9300	C37—C38	1.399 (5)
C6—C7	1.380 (6)	C37—H37	0.9300
C6—H6	0.9300	C38—C39	1.397 (5)
C7—C8	1.388 (6)	C39—C40	1.379 (5)
C7—H7	0.9300	C39—H39	0.9300
C8—C9	1.391 (6)	C40—H40	0.9300
N9^{i}—Ni1—N7	108.93 (12)	C13—C12—H12	120.5
N9^{i}—Ni1—N4	89.61 (13)	N5—C13—C12	124.1 (4)
N7—Ni1—N4	88.43 (12)	N5—C13—C14	119.6 (4)
N9^{i}—Ni1—N1	91.35 (13)	C12—C13—C14	116.3 (4)
N7—Ni1—N1	92.26 (13)	C15—C14—C13	119.9 (4)
N4—Ni1—N1	178.57 (13)	C15—C14—H14	120.1
N9^{i}—Ni1—O2	94.13 (11)	C13—C14—H14	120.1
N7—Ni1—O2	156.80 (11)	N4—C15—C14	124.2 (4)
N4—Ni1—O2	94.28 (11)	N4—C15—H15	117.9
N1—Ni1—O2	84.59 (12)	C14—C15—H15	117.9
N9^{i}—Ni1—O1	155.65 (11)	N6—C16—C17	124.6 (5)
N7—Ni1—O1	95.30 (11)	N6—C16—H16	117.7
N4—Ni1—O1	93.49 (11)	C17—C16—H16	117.7

N1—Ni1—O1	85.20 (11)	C18—C17—C16	117.5 (5)
O2—Ni1—O1	61.56 (10)	C18—C17—H17	121.3
N9^{i}—Ni1—C27	125.00 (13)	C16—C17—H17	121.3
N7—Ni1—C27	125.69 (13)	C17—C18—N5	122.3 (4)
N4—Ni1—C27	97.17 (12)	C17—C18—C19	118.4 (4)
N1—Ni1—C27	81.41 (12)	N5—C18—C19	119.3 (4)
O2—Ni1—C27	31.11 (11)	C20—C19—C18	117.8 (5)
O1—Ni1—C27	30.65 (11)	C20—C19—H19	121.1
C27—O1—Ni1	88.2 (2)	C18—C19—H19	121.1
C27—O2—Ni1	89.4 (2)	N6—C20—C19	125.6 (6)
C5—N1—C1	115.9 (3)	N6—C20—H20	117.2
C5—N1—Ni1	123.7 (3)	C19—C20—H20	117.2
C1—N1—Ni1	119.5 (3)	C22—C21—C26	118.8 (3)
C3—N2—C8	125.5 (3)	C22—C21—C27	120.5 (4)
C3—N2—H2N	119 (3)	C26—C21—C27	120.7 (4)
C8—N2—H2N	114 (3)	C21—C22—C23	120.6 (4)
C6—N3—C10	115.6 (4)	C21—C22—H22	119.7
C11—N4—C15	115.4 (3)	C23—C22—H22	119.7
C11—N4—Ni1	123.9 (3)	C24—C23—C22	121.0 (4)
C15—N4—Ni1	119.9 (3)	C24—C23—H23	119.5
C13—N5—C18	125.0 (3)	C22—C23—H23	119.5
C13—N5—H5N	113 (3)	C23—C24—C25	118.9 (4)
C18—N5—H5N	120 (3)	C23—C24—C28	119.4 (4)
C16—N6—C20	116.1 (5)	C25—C24—C28	121.6 (4)
C31—N7—C35	116.8 (3)	C24—C25—C26	120.1 (4)
C31—N7—Ni1	111.7 (2)	C24—C25—H25	119.9
C35—N7—Ni1	130.6 (3)	C26—C25—H25	119.9
C38—N8—C33	128.0 (3)	C21—C26—C25	120.6 (4)
C38—N8—H8N	114 (3)	C21—C26—H26	119.7
C33—N8—H8N	116 (3)	C25—C26—H26	119.7
C40—N9—C36	116.1 (3)	O1—C27—O2	120.0 (3)
C40—N9—Ni1^{ii}	127.9 (3)	O1—C27—C21	120.4 (3)
C36—N9—Ni1^{ii}	115.5 (3)	O2—C27—C21	119.6 (3)
N1—C1—C2	124.5 (4)	O1—C27—Ni1	61.11 (19)
N1—C1—H1	117.8	O2—C27—Ni1	59.51 (18)
C2—C1—H1	117.8	C21—C27—Ni1	170.9 (3)
C1—C2—C3	118.8 (4)	O4—C28—O3	125.4 (4)
C1—C2—H2	120.6	O4—C28—C24	118.5 (3)
C3—C2—H2	120.6	O3—C28—C24	116.1 (3)
N2—C3—C2	122.6 (4)	N7—C31—C32	123.5 (4)
N2—C3—C4	119.9 (3)	N7—C31—H31	118.3
C2—C3—C4	117.4 (3)	C32—C31—H31	118.3
C5—C4—C3	119.1 (4)	C33—C32—C31	120.8 (4)
C5—C4—H4	120.4	C33—C32—H32	119.6
C3—C4—H4	120.4	C31—C32—H32	119.6
N1—C5—C4	124.1 (4)	C32—C33—N8	125.7 (4)
N1—C5—H5	117.9	C32—C33—C34	115.7 (3)
C4—C5—H5	117.9	N8—C33—C34	118.5 (3)

N3—C6—C7	124.6 (5)	C35—C34—C33	120.7 (4)
N3—C6—H6	117.7	C35—C34—H34	119.7
C7—C6—H6	117.7	C33—C34—H34	119.7
C6—C7—C8	119.1 (5)	N7—C35—C34	122.4 (3)
C6—C7—H7	120.4	N9—C36—C37	124.2 (4)
C8—C7—H7	120.4	N9—C36—H36	117.9
C7—C8—C9	116.8 (4)	C37—C36—H36	117.9
C7—C8—N2	119.1 (4)	C36—C37—C38	119.5 (4)
C9—C8—N2	123.9 (4)	C36—C37—H37	120.2
C10—C9—C8	119.2 (4)	C38—C37—H37	120.2
C10—C9—H9	120.4	N8—C38—C39	118.8 (4)
C8—C9—H9	120.4	N8—C38—C37	125.1 (4)
N3—C10—C9	124.7 (5)	C39—C38—C37	116.1 (3)
N3—C10—H10	117.7	C40—C39—C38	120.4 (4)
C9—C10—H10	117.7	C40—C39—H39	119.8
N4—C11—C12	125.1 (4)	C38—C39—H39	119.8
N4—C11—H11	117.5	N9—C40—C39	123.5 (4)
C12—C11—H11	117.5	N9—C40—H40	118.2
C11—C12—C13	119.0 (4)	C39—C40—H40	118.2
C11—C12—H12	120.5		
$N9^{i}$—Ni1—O1—C27	1.4 (4)	N5—C13—C14—C15	−174.7 (4)
N7—Ni1—O1—C27	−173.1 (2)	C12—C13—C14—C15	2.9 (6)
N4—Ni1—O1—C27	98.2 (2)	C11—N4—C15—C14	−3.1 (6)
N1—Ni1—O1—C27	−81.2 (2)	Ni1—N4—C15—C14	167.0 (3)
O2—Ni1—O1—C27	5.2 (2)	C13—C14—C15—N4	0.8 (6)
$N9^{i}$—Ni1—O2—C27	173.3 (2)	C20—N6—C16—C17	−2.7 (8)
N7—Ni1—O2—C27	−0.8 (4)	N6—C16—C17—C18	0.7 (8)
N4—Ni1—O2—C27	−96.8 (2)	C16—C17—C18—N5	−179.3 (4)
N1—Ni1—O2—C27	82.3 (2)	C16—C17—C18—C19	1.9 (6)
O1—Ni1—O2—C27	−5.1 (2)	C13—N5—C18—C17	57.8 (6)
$N9^{i}$—Ni1—N1—C5	−38.6 (3)	C13—N5—C18—C19	−123.4 (5)
N7—Ni1—N1—C5	−147.6 (3)	C17—C18—C19—C20	−2.5 (6)
O2—Ni1—N1—C5	55.4 (3)	N5—C18—C19—C20	178.7 (4)
O1—Ni1—N1—C5	117.3 (3)	C16—N6—C20—C19	2.1 (8)
C27—Ni1—N1—C5	86.6 (3)	C18—C19—C20—N6	0.5 (8)
$N9^{i}$—Ni1—N1—C1	152.6 (3)	C26—C21—C22—C23	−0.1 (6)
N7—Ni1—N1—C1	43.6 (3)	C27—C21—C22—C23	177.9 (4)
O2—Ni1—N1—C1	−113.4 (3)	C21—C22—C23—C24	1.1 (7)
O1—Ni1—N1—C1	−51.6 (3)	C22—C23—C24—C25	−0.3 (6)
C27—Ni1—N1—C1	−82.2 (3)	C22—C23—C24—C28	−177.0 (4)
$N9^{i}$—Ni1—N4—C11	130.0 (3)	C23—C24—C25—C26	−1.5 (6)
N7—Ni1—N4—C11	−121.0 (3)	C28—C24—C25—C26	175.1 (4)
O2—Ni1—N4—C11	35.9 (3)	C22—C21—C26—C25	−1.7 (6)
O1—Ni1—N4—C11	−25.8 (3)	C27—C21—C26—C25	−179.7 (4)
C27—Ni1—N4—C11	4.7 (3)	C24—C25—C26—C21	2.5 (7)
$N9^{i}$—Ni1—N4—C15	−39.2 (3)	Ni1—O1—C27—O2	−8.8 (3)
N7—Ni1—N4—C15	69.8 (3)	Ni1—O1—C27—C21	169.6 (3)

O2—Ni1—N4—C15	−133.3 (3)	Ni1—O2—C27—O1	9.0 (4)
O1—Ni1—N4—C15	165.0 (3)	Ni1—O2—C27—C21	−169.5 (3)
C27—Ni1—N4—C15	−164.4 (3)	C22—C21—C27—O1	−167.8 (4)
N9^{i}—Ni1—N7—C31	164.7 (3)	C26—C21—C27—O1	10.2 (6)
N4—Ni1—N7—C31	75.6 (3)	C22—C21—C27—O2	10.7 (6)
N1—Ni1—N7—C31	−103.1 (3)	C26—C21—C27—O2	−171.3 (4)
O2—Ni1—N7—C31	−21.6 (5)	N9^{i}—Ni1—C27—O1	−179.3 (2)
O1—Ni1—N7—C31	−17.7 (3)	N7—Ni1—C27—O1	8.5 (3)
C27—Ni1—N7—C31	−22.1 (3)	N4—Ni1—C27—O1	−84.7 (2)
N9^{i}—Ni1—N7—C35	−27.1 (4)	N1—Ni1—C27—O1	95.1 (2)
N4—Ni1—N7—C35	−116.1 (3)	O2—Ni1—C27—O1	−171.1 (4)
N1—Ni1—N7—C35	65.1 (3)	N9^{i}—Ni1—C27—O2	−8.2 (3)
O2—Ni1—N7—C35	146.7 (3)	N7—Ni1—C27—O2	179.6 (2)
O1—Ni1—N7—C35	150.5 (3)	N4—Ni1—C27—O2	86.4 (2)
C27—Ni1—N7—C35	146.2 (3)	N1—Ni1—C27—O2	−93.8 (2)
C5—N1—C1—C2	2.1 (6)	O1—Ni1—C27—O2	171.1 (4)
Ni1—N1—C1—C2	171.7 (3)	C23—C24—C28—O4	−95.8 (5)
N1—C1—C2—C3	1.3 (6)	C25—C24—C28—O4	87.6 (5)
C8—N2—C3—C2	−34.4 (6)	C23—C24—C28—O3	82.8 (5)
C8—N2—C3—C4	149.3 (4)	C25—C24—C28—O3	−93.8 (5)
C1—C2—C3—N2	−179.9 (4)	C35—N7—C31—C32	−3.2 (6)
C1—C2—C3—C4	−3.5 (6)	Ni1—N7—C31—C32	166.8 (3)
N2—C3—C4—C5	179.0 (4)	N7—C31—C32—C33	3.7 (7)
C2—C3—C4—C5	2.5 (6)	C31—C32—C33—N8	−178.6 (4)
C1—N1—C5—C4	−3.2 (6)	C31—C32—C33—C34	−1.1 (6)
Ni1—N1—C5—C4	−172.3 (3)	C38—N8—C33—C32	1.0 (7)
C3—C4—C5—N1	0.9 (6)	C38—N8—C33—C34	−176.5 (4)
C10—N3—C6—C7	0.5 (7)	C32—C33—C34—C35	−1.8 (6)
N3—C6—C7—C8	0.1 (7)	N8—C33—C34—C35	176.0 (4)
C6—C7—C8—C9	−0.8 (6)	C31—N7—C35—C34	0.2 (6)
C6—C7—C8—N2	173.9 (4)	Ni1—N7—C35—C34	−167.5 (3)
C3—N2—C8—C7	164.6 (4)	C33—C34—C35—N7	2.3 (6)
C3—N2—C8—C9	−21.1 (6)	C40—N9—C36—C37	2.3 (6)
C7—C8—C9—C10	0.9 (6)	Ni1^{ii}—N9—C36—C37	−170.0 (3)
N2—C8—C9—C10	−173.5 (4)	N9—C36—C37—C38	2.4 (6)
C6—N3—C10—C9	−0.4 (7)	C33—N8—C38—C39	152.2 (4)
C8—C9—C10—N3	−0.3 (7)	C33—N8—C38—C37	−29.4 (6)
C15—N4—C11—C12	1.6 (6)	C36—C37—C38—N8	176.2 (4)
Ni1—N4—C11—C12	−168.0 (3)	C36—C37—C38—C39	−5.4 (6)
N4—C11—C12—C13	2.1 (7)	N8—C38—C39—C40	−177.5 (3)
C18—N5—C13—C12	−2.9 (7)	C37—C38—C39—C40	4.0 (6)
C18—N5—C13—C14	174.4 (4)	C36—N9—C40—C39	−3.8 (6)
C11—C12—C13—N5	173.2 (4)	Ni1^{ii}—N9—C40—C39	167.4 (3)
C11—C12—C13—C14	−4.2 (6)	C38—C39—C40—N9	0.7 (6)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2N···O4^{iii}	0.99 (5)	1.83 (5)	2.793 (4)	164 (4)
N5—H5N···O3^{iv}	0.94 (5)	1.93 (5)	2.874 (5)	177 (4)
N8—H8N···O3^{v}	0.91 (4)	1.93 (5)	2.841 (4)	179 (4)

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

Fig. 1

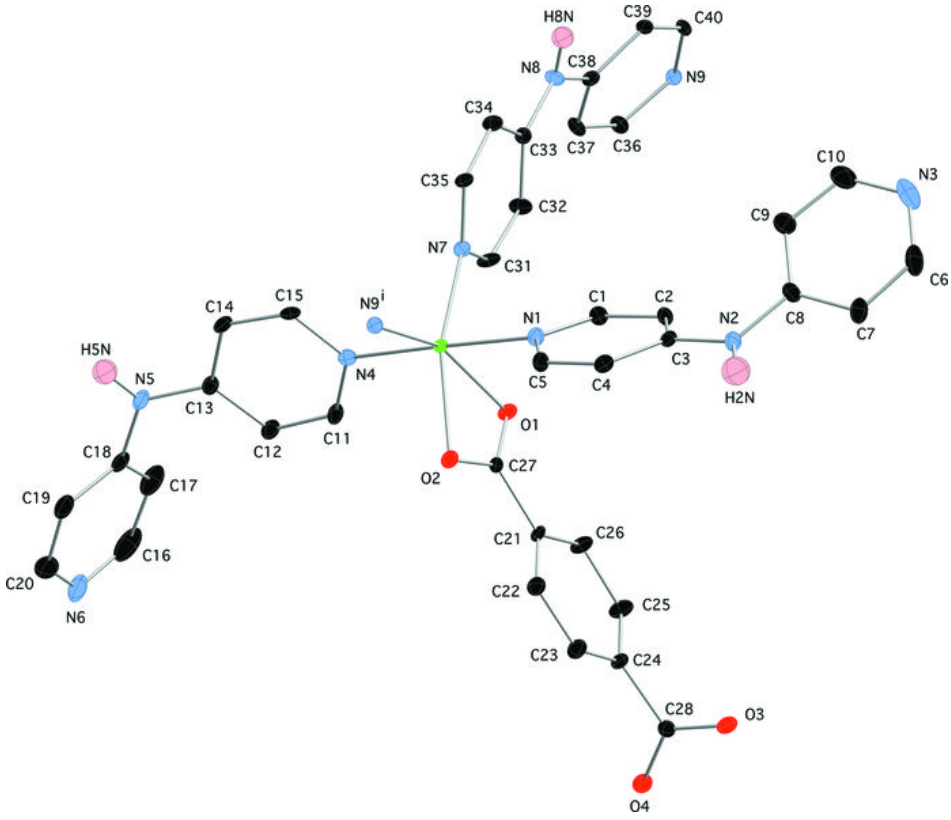
H8N
C39
C40
N8
C38
N9
C34
C33
C37
C36
C35
C32
C10
N3
C9
C6
N7
C31
C14
C15
N9i
N1
C1
C2
N2
C8
C7
H5N
N5
N4
C5
C4
C3
H2N
C13
O1
C18
C12
C11
O2
C27
C19
C17
C21
C26
C16
C22
C25
C20
N6
C23
C24
C28
O3
O4

Fig. 2

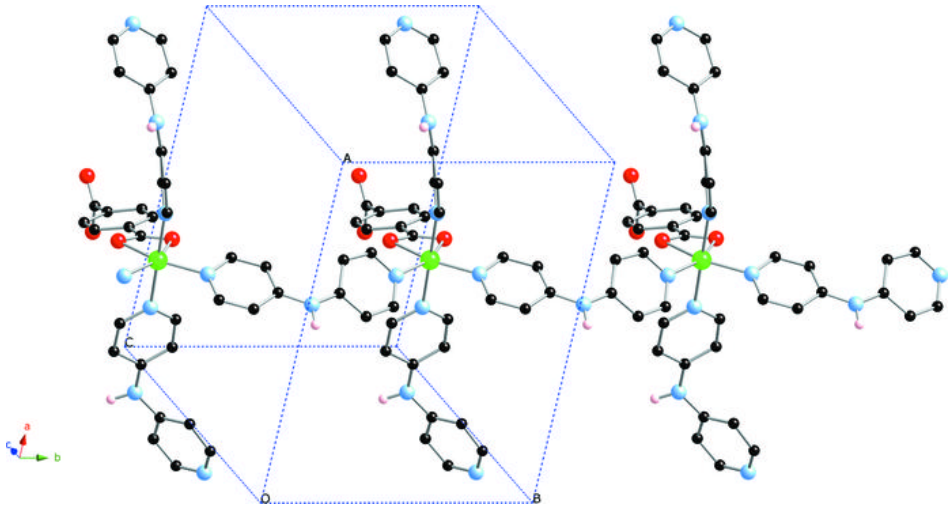

Fig. 3

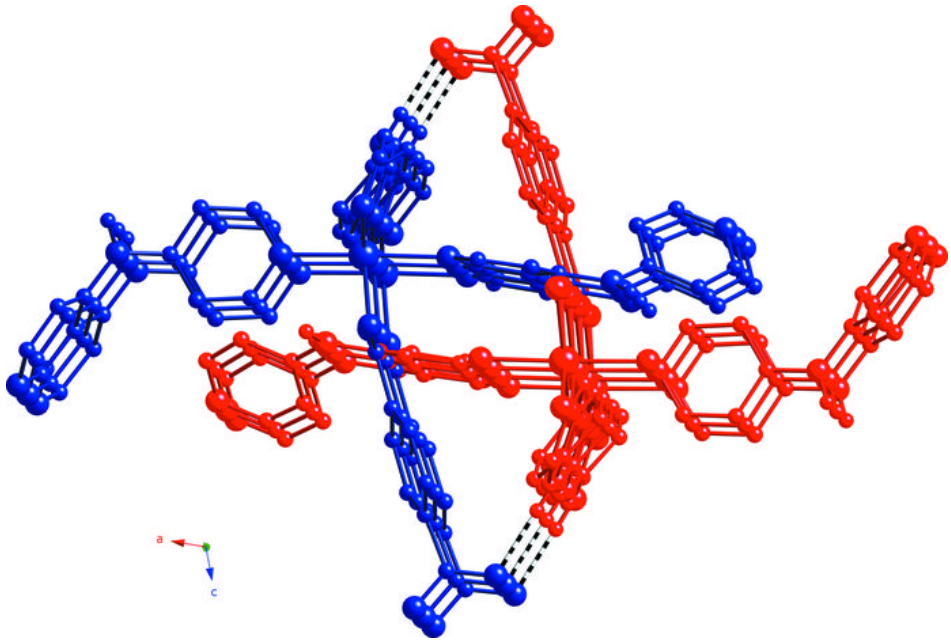

Fig. 4