

Bis(guanidinium) bis(4-hydroxypyridine-2,6-dicarboxylato- κ^3O^2,N,O^6)nickel-ate(II) dihydrate

Hossein Aghabozorg,^{a*} Elham Motyeian,^a Jafar Attar Gharamaleki,^a Janet Soleimannejad,^b Mohammad Ghadermazi^c and Elizabeth Spey Sharon^d

^aFaculty of Chemistry, Teacher Training University, Tehran, Iran, ^bFaculty of Science, Department of Chemistry, Ilam University, Iran, ^cDepartment of Chemistry, Faculty of Science, University of Kurdistan, Sanandaj, Iran, and ^dDepartment of Chemistry, Sheffield University, Sheffield S3 7HF, England

Correspondence e-mail: haghabozorg@yahoo.com

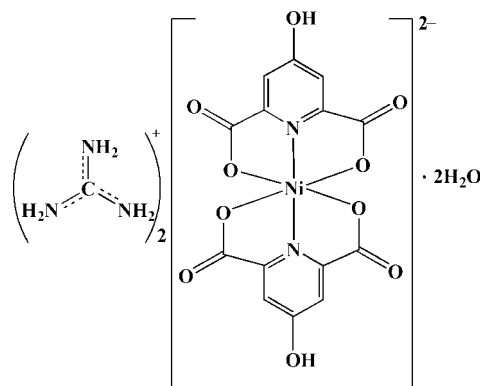
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Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(C-C) = 0.001$ Å; R factor = 0.026; wR factor = 0.076; data-to-parameter ratio = 31.4.

The reaction of nickel(II) nitrate hexahydrate, guanidine (G) and 4-hydroxypyridine-2,6-dicarboxylic acid (hypydcH₂) in a 1:2:2 molar ratio in aqueous solution resulted in the formation of the title compound, (CH₅N₃)₂[Ni(C₇H₃NO₅)₂].2H₂O or (GH)₂[Ni(hypydc)₂].2H₂O. The six donor atoms of the two 4-hydroxypyridine-2,6-dicarboxylate or (hypydc)²⁻ ligands form a distorted octahedral arrangement around the Ni^{II} centre. Considerable C—O... π stacking interactions between the CO groups of carboxylate fragments and the pyridine rings of (hypydc)²⁻ with a distance of 3.3212 (8) Å are observed. In the crystal structure, a wide range of noncovalent interactions consisting of hydrogen bonding (of the types O—H...O and N—H...O), ion pairing, and π - π [centroid-centroid distance 3.8037 (5) Å], N—H... π and C—O... π stacking interactions connect the various components into a supramolecular structure.

Related literature

For related literature, see: Aghabozorg, Attar Gharamaleki *et al.* (2007a, 2007b); Aghabozorg, Daneshvar *et al.* (2007).



Experimental

Crystal data

(CH₅N₃)₂[Ni(C₇H₃NO₅)₂].2H₂O
 $M_r = 577.13$
 Triclinic, $P\bar{1}$
 $a = 8.9253$ (6) Å
 $b = 9.9060$ (6) Å
 $c = 13.2186$ (9) Å
 $\alpha = 101.415$ (3)°
 $\beta = 103.099$ (3)°

$\gamma = 91.938$ (3)°
 $V = 1111.99$ (13) Å³
 $Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.96$ mm⁻¹
 $T = 150$ (2) K
 $0.50 \times 0.32 \times 0.15$ mm

Data collection

Bruker SMART 1000 diffractometer
 Absorption correction: multi-scan (SADABS; Bruker, 1998)
 $T_{min} = 0.647$, $T_{max} = 0.870$

46516 measured reflections
 10497 independent reflections
 9650 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.019$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.076$
 $S = 1.06$
 10497 reflections

334 parameters
 H-atom parameters constrained
 $\Delta\rho_{max} = 0.56$ e Å⁻³
 $\Delta\rho_{min} = -0.61$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ni1—N2	1.9665 (6)	Ni1—O10	2.1387 (6)
Ni1—N1	1.9700 (6)	Ni1—O6	2.1477 (6)
Ni1—O1	2.1088 (6)	Ni1—O5	2.2149 (6)
N2—Ni1—N1	171.30 (3)	O1—Ni1—O10	93.41 (3)
O1—Ni1—O5	154.97 (2)	O6—Ni1—O5	91.30 (2)
O10—Ni1—O6	154.87 (2)		

Table 2

Hydrogen-bond geometry (Å, °).

Cg1 is the centroid of the N1/C2—C6 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O3—H3C...O6 ⁱ	0.90	1.71	2.5901 (8)	166
O8—H8...O5 ⁱⁱ	0.90	1.84	2.7057 (9)	160
O11—H11A...O9 ⁱⁱⁱ	0.90	1.86	2.7106 (9)	156
O11—H11B...O2 ^{iv}	0.90	1.88	2.7464 (9)	161
O12—H12B...O11 ⁱⁱ	0.90	2.15	3.0425 (12)	172
O12—H12A...O5	0.90	2.15	3.0244 (13)	164

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O12–H12A \cdots O4	0.90	2.64	3.3823 (12)	141
N3–H3A \cdots O4 ^v	0.90	2.15	2.9307 (10)	144
N3–H3B \cdots O10	0.90	2.07	2.8817 (10)	149
N4–H4A \cdots O4 ^v	0.90	1.97	2.8072 (11)	154
N4–H4B \cdots O11 ^{vi}	0.90	2.06	2.9161 (10)	159
N5–H5A \cdots O10	0.90	2.19	2.9887 (10)	148
N5–H5B \cdots O2 ⁱⁱ	0.90	1.98	2.8656 (10)	169
N6–H6A \cdots O7 ^{viii}	0.90	2.28	3.0178 (11)	139
N6–H6A \cdots O1	0.90	2.49	3.0038 (9)	117
N6–H6B \cdots O3 ^{vii}	0.90	2.55	3.2320 (11)	133
N7–H7A \cdots O9 ⁱⁱⁱ	0.90	2.01	2.8999 (10)	172
N7–H7B \cdots O12 ^{ix}	0.90	1.93	2.8282 (13)	176
N8–H8A \cdots O7 ^{viii}	0.90	1.94	2.7993 (10)	158
N8–H8B \cdots O11	0.90	1.99	2.8847 (10)	174
N5–H5A \cdots Cg1	0.90	3.47	3.362 (7)	75

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2005) and *Mercury* (Version 1.4.2; Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: OM2189).

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supplementary materials

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Comment

The non-covalent interactions such as ion pairing, hydrogen bonding and π - π stacking are observed in these ionic compounds. The importance of weak hydrogen bonds in the context of crystal engineering, molecular recognition and supramolecular chemistry has been well recognized in recent years. Recently, we have defined a plan to prepare water soluble proton transfer compounds as novel self assembled systems that can function as suitable ligands in the synthesis of metal complexes. In this regard, we have reported cases in which proton transfers from pyridine-2,6-dicarboxylic acid, pydcH₂, and benzene-1,2,4,5-tetracarboxylic acid, btcH₄, to propane-1,3-diamine (pn) and 1,10-phenanthroline, (phen), resulted in the formation of novel self-assembled (pnH₂)(pydc)(pydcH₂)·2.5H₂O, (pnH₂)₂(btc)·2H₂O and (phenH)₄(btcH₃)₂(btcH₂) systems, respectively. The resulting compounds with some remaining sites as electron donors can coordinate to metallic ions (Aghabozorg, Attar Gharamaleki *et al.*, 2007a,b; Aghabozorg, Daneshvar *et al.*, 2007).

The molecular structure of the title compound is presented in Fig. 1. The Ni^{II} atom is six-coordinated by two 4-hydroxypyridine-2,6-dicarboxylate, or (hypydc)²⁻, groups, *i.e.* each (hypydc)²⁻ is coordinated through one pyridine N atom and two carboxylate O atoms (Table 1). N1 and N2 atoms of the two (hypydc)²⁻ fragments occupy the axial positions, while atoms O1, O5, O6 and O10 form the equatorial plane [with Ni—O distances ranging from 2.1088 (6) to 2.2150 (6) Å]. The N1—Ni1—N2 angle [171.30 (3)°] deviates from linearity. Therefore, the coordination around Ni^{II} is distorted octahedral. The O5—Ni1—O6 and O1—Ni1—O10 angles are equal to 91.30 (2) and 93.41 (3)°, respectively. On the other hand, O1—Ni1—O6—C8 and O10—Ni1—O5—C7 torsion angles are 93.20 (5) and 92.27 (5) Å, respectively indicating that two (hypydc)²⁻ units are almost perpendicular to each other.

A noticeable feature of the title compound is the presence of N—H \cdots π stacking interactions between N—H group of guanidinium ions with aromatic rings of (hypydc)²⁻ units. The H \cdots π distance (measured to the centre of phenyl ring) is 3.475 Å for N5—H5A \cdots Cg1 [Cg1 is the centroid of N1/C2—C6 ring]. There is also π \cdots π stacking interaction between two aromatic rings of (hypydc)²⁻ units, with distance of 3.8037 (5) Å [-x, 1 - y, -z] (Fig. 2).

Also a considerable C—O \cdots π stacking interactions between CO groups of carboxylate fragments with aromatic rings of 4-hydroxypyridine-2,6-dicarboxylate with distances of 3.321 (8) Å for C8—O7 \cdots Cg2 (-x, 1 - y, 1 - z) [Cg2 is the centroid for N2/C9—C13 ring] are observed in the prepared compound (Fig. 3). In the crystal structure, a wide range of non-covalent interactions consisting of hydrogen bonding (of the type of O—H \cdots O and N—H \cdots O with D \cdots A ranging from 2.5901 (8) Å to 3.3823 (12) Å), ion pairing, π \cdots π , N—H \cdots π and C—O \cdots π stacking connect the various components into a supramolecular structure (Table 2, Figs. 4 and 5).

Experimental

An aqueous solution of sodium hydroxide (80 mg, 2 mmol) was added to guanidine hydrochloride (200 mg, 2 mmol) in a 1:1 molar ratio. The resulting suspension was stirred for 1 h and filtered. An aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (290 mg, 1 mmol) and 4-hydroxypyridine-2,6-dicarboxylic (360 mg, 2 mmol) acid was added to the filtered solution in a 1:2 molar ratio, and the reaction mixture was heated to boiling point for 2 h. Green crystals were obtained from the solution after two days at room temperature.

Refinement

Hydrogen atoms were positioned geometrically and refined with a riding model with $\text{O}-\text{H} = 0.95 \text{ \AA}$, and with $U(\text{H})$ constrained to be 1.2 times U_{eq} of the carrier atom.

Figures

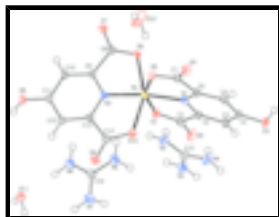


Fig. 1. The structure of the title compound showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

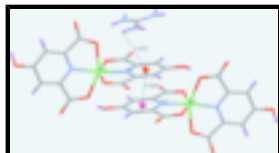


Fig. 2. $\pi \cdots \pi$ Stacking interaction between two aromatic rings of $(\text{hypydc})^{2-}$ units, with distance of $3.8037(5) \text{ \AA}$ $[-x, 1 - y, -z]$; $\text{N}-\text{H} \cdots \pi$ stacking interaction between $\text{N}-\text{H}$ groups of guanidinium ions with aromatic rings of $(\text{hypydc})^{2-}$ units. The $\text{H} \cdots \pi$ distance (measured to the centre of phenyl ring) is 2.96 \AA for $\text{N5}-\text{H5A} \cdots \text{Cg1}$ [Cg1 is the centroid of $\text{N1}/\text{C2}-\text{C6}$ ring].

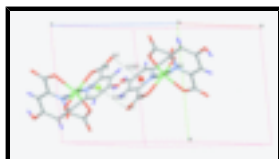


Fig. 3. $\text{C}-\text{O} \cdots \pi$ stacking interactions between CO groups of carboxylate fragments with aromatic rings of 4-hydroxypyridine-2,6-dicarboxylate with distances of $3.321(8) \text{ \AA}$ for $\text{C8}-\text{O7} \cdots \text{Cg2}$ $(-x, 1 - y, 1 - z)$ [Cg2 is the centroid for $\text{N2}/\text{C9}-\text{C13}$ ring].

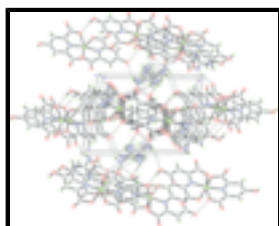


Fig. 4. A layered packing diagram. The space between the two layers of $[\text{Ni}(\text{hypydc})_2]^{2-}$ fragments is filled with a layer of $(\text{GH})^+$ cations and water molecules.

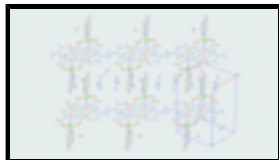


Fig. 5. The crystal packing of the title compound view down the a axis; hydrogen bonds are shown as dashed lines.

Bis(guanidinium) bis(4-hydroxypyridine-2,6-dicarboxylato- κ^3O^2,N,O^6)nickelate(II) dihydrate

Crystal data

$(CH_6N_3)_2[Ni(C_7H_3NO_5)_2] \cdot 2H_2O$	$Z = 2$
$M_r = 577.13$	$F_{000} = 596$
Triclinic, $P\bar{1}$	$D_x = 1.724 \text{ Mg m}^{-3}$
$a = 8.9253 (6) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 9.9060 (6) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$c = 13.2186 (9) \text{ \AA}$	Cell parameters from 9699 reflections
$\alpha = 101.415 (3)^\circ$	$\theta = 2.4\text{--}36.3^\circ$
$\beta = 103.099 (3)^\circ$	$\mu = 0.96 \text{ mm}^{-1}$
$\gamma = 91.938 (3)^\circ$	$T = 150 (2) \text{ K}$
$V = 1111.99 (13) \text{ \AA}^3$	Block, green
	$0.50 \times 0.32 \times 0.15 \text{ mm}$

Data collection

Bruker SMART 1000 diffractometer	10497 independent reflections
Radiation source: fine-focus sealed tube	9650 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.019$
Detector resolution: 8.3 pixels mm^{-1}	$\theta_{\text{max}} = 36.4^\circ$
$T = 296(2) \text{ K}$	$\theta_{\text{min}} = 1.6^\circ$
ω scans	$h = -14 \rightarrow 11$
Absorption correction: multi-scan (SADABS; Bruker, 1998)	$k = -16 \rightarrow 16$
$T_{\text{min}} = 0.647$, $T_{\text{max}} = 0.870$	$l = -21 \rightarrow 21$
46516 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
$R[F^2 > 2\sigma(F^2)] = 0.026$	H-atom parameters constrained
$wR(F^2) = 0.076$	$w = 1/[\sigma^2(F_o^2) + (0.043P)^2 + 0.2702P]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
10497 reflections	$(\Delta/\sigma)_{\text{max}} = 0.002$
334 parameters	$\Delta\rho_{\text{max}} = 0.56 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.61 \text{ e \AA}^{-3}$
	Extinction correction: none

supplementary materials

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.173117 (11)	0.423258 (10)	0.259400 (7)	0.01287 (3)
O1	-0.00784 (7)	0.27245 (6)	0.24384 (5)	0.01774 (10)
O2	-0.16765 (9)	0.11004 (7)	0.12138 (5)	0.02439 (13)
O3	-0.02586 (9)	0.20971 (7)	-0.21698 (5)	0.02167 (12)
H3C	-0.0206	0.2745	-0.2554	0.026*
O4	0.35691 (8)	0.60277 (7)	0.04763 (5)	0.02381 (12)
O5	0.31707 (7)	0.56247 (6)	0.20082 (5)	0.01687 (10)
O6	0.05225 (7)	0.59263 (6)	0.32052 (4)	0.01635 (10)
O7	0.02582 (8)	0.72029 (7)	0.47531 (5)	0.02065 (11)
O8	0.37838 (8)	0.46857 (7)	0.73456 (5)	0.02054 (11)
H8	0.4719	0.4367	0.7525	0.025*
O9	0.51375 (8)	0.19318 (7)	0.39007 (5)	0.02143 (11)
O10	0.34554 (7)	0.27853 (6)	0.26981 (5)	0.01768 (10)
O11	0.32536 (8)	-0.04310 (7)	0.73709 (5)	0.02032 (11)
H11A	0.3814	-0.1076	0.7089	0.024*
H11B	0.2653	-0.0814	0.7719	0.024*
O12	0.37899 (13)	0.87354 (12)	0.25296 (8)	0.0491 (3)
H12B	0.4704	0.9157	0.2539	0.059*
H12A	0.3664	0.7820	0.2257	0.059*
N1	0.09970 (7)	0.36856 (6)	0.10372 (5)	0.01309 (10)
N2	0.25270 (7)	0.44832 (6)	0.41390 (5)	0.01274 (10)
N3	0.50285 (9)	0.28895 (8)	0.10335 (6)	0.02072 (13)
H3A	0.5659	0.3475	0.0847	0.025*
H3B	0.4860	0.3064	0.1691	0.025*
N4	0.43549 (11)	0.16824 (9)	-0.06920 (7)	0.02808 (17)
H4A	0.5014	0.2288	-0.0833	0.034*
H4B	0.3907	0.0927	-0.1182	0.034*
N5	0.32885 (10)	0.09767 (8)	0.05716 (6)	0.02313 (14)
H5A	0.3226	0.1189	0.1254	0.028*
H5B	0.2719	0.0285	0.0071	0.028*
N6	0.12908 (10)	0.08178 (8)	0.38427 (6)	0.02258 (13)
H6A	0.0636	0.1481	0.3920	0.027*
H6B	0.1274	0.0351	0.3182	0.027*

N7	0.29526 (10)	-0.06930 (9)	0.45012 (7)	0.02577 (15)
H7A	0.3483	-0.1044	0.5041	0.031*
H7B	0.3174	-0.0873	0.3859	0.031*
N8	0.18342 (10)	0.08088 (8)	0.56283 (6)	0.02222 (13)
H8A	0.1141	0.1442	0.5680	0.027*
H8B	0.2214	0.0388	0.6166	0.027*
C1	-0.06666 (9)	0.20926 (8)	0.14912 (6)	0.01563 (12)
C2	-0.00601 (8)	0.26094 (7)	0.06391 (6)	0.01391 (11)
C3	-0.04990 (9)	0.20506 (8)	-0.04397 (6)	0.01656 (12)
H3	-0.1226	0.1295	-0.0705	0.020*
C4	0.01756 (9)	0.26469 (8)	-0.11267 (6)	0.01546 (12)
C5	0.12882 (9)	0.37751 (8)	-0.06979 (6)	0.01465 (11)
H5	0.1754	0.4190	-0.1134	0.018*
C6	0.16685 (8)	0.42490 (7)	0.03947 (5)	0.01292 (11)
C7	0.28988 (9)	0.53963 (8)	0.09859 (6)	0.01487 (11)
C8	0.08025 (9)	0.62575 (7)	0.42266 (6)	0.01421 (11)
C9	0.19209 (8)	0.53834 (7)	0.47982 (5)	0.01287 (11)
C10	0.23152 (9)	0.54827 (8)	0.58878 (6)	0.01447 (11)
H10	0.1879	0.6108	0.6338	0.017*
C11	0.33960 (9)	0.46069 (8)	0.62872 (6)	0.01443 (11)
C12	0.40380 (9)	0.36772 (8)	0.55896 (6)	0.01472 (11)
H12	0.4767	0.3100	0.5843	0.018*
C13	0.35558 (8)	0.36443 (7)	0.45134 (6)	0.01300 (11)
C14	0.41057 (9)	0.26960 (7)	0.36476 (6)	0.01460 (11)
C15	0.42237 (9)	0.18398 (8)	0.03028 (6)	0.01729 (12)
C16	0.20223 (9)	0.02991 (8)	0.46651 (7)	0.01741 (12)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.01507 (5)	0.01471 (4)	0.00908 (4)	0.00167 (3)	0.00287 (3)	0.00302 (3)
O1	0.0216 (3)	0.0205 (2)	0.0116 (2)	-0.0011 (2)	0.00473 (19)	0.00417 (18)
O2	0.0293 (3)	0.0251 (3)	0.0181 (3)	-0.0102 (2)	0.0079 (2)	0.0024 (2)
O3	0.0347 (3)	0.0192 (2)	0.0091 (2)	-0.0019 (2)	0.0017 (2)	0.00284 (18)
O4	0.0263 (3)	0.0261 (3)	0.0201 (3)	-0.0075 (2)	0.0076 (2)	0.0064 (2)
O5	0.0173 (2)	0.0194 (2)	0.0125 (2)	-0.00028 (18)	0.00219 (18)	0.00193 (18)
O6	0.0193 (2)	0.0184 (2)	0.0119 (2)	0.00462 (19)	0.00323 (18)	0.00461 (18)
O7	0.0252 (3)	0.0201 (3)	0.0179 (2)	0.0094 (2)	0.0069 (2)	0.0034 (2)
O8	0.0218 (3)	0.0283 (3)	0.0092 (2)	0.0049 (2)	-0.00023 (19)	0.0026 (2)
O9	0.0243 (3)	0.0229 (3)	0.0208 (3)	0.0117 (2)	0.0086 (2)	0.0079 (2)
O10	0.0230 (3)	0.0196 (2)	0.0121 (2)	0.0061 (2)	0.00636 (19)	0.00398 (18)
O11	0.0262 (3)	0.0188 (2)	0.0177 (2)	0.0029 (2)	0.0082 (2)	0.0044 (2)
O12	0.0487 (5)	0.0521 (6)	0.0417 (5)	-0.0196 (5)	0.0255 (4)	-0.0149 (4)
N1	0.0141 (2)	0.0150 (2)	0.0107 (2)	0.00126 (19)	0.00302 (18)	0.00398 (18)
N2	0.0140 (2)	0.0139 (2)	0.0106 (2)	0.00212 (18)	0.00304 (18)	0.00285 (18)
N3	0.0222 (3)	0.0198 (3)	0.0177 (3)	-0.0040 (2)	0.0059 (2)	-0.0021 (2)
N4	0.0392 (4)	0.0245 (3)	0.0186 (3)	-0.0094 (3)	0.0127 (3)	-0.0046 (3)
N5	0.0268 (3)	0.0208 (3)	0.0212 (3)	-0.0058 (3)	0.0068 (3)	0.0031 (2)

supplementary materials

N6	0.0266 (3)	0.0242 (3)	0.0192 (3)	0.0068 (3)	0.0045 (3)	0.0103 (3)
N7	0.0300 (4)	0.0283 (4)	0.0263 (4)	0.0142 (3)	0.0130 (3)	0.0135 (3)
N8	0.0262 (3)	0.0229 (3)	0.0187 (3)	0.0076 (3)	0.0047 (3)	0.0068 (2)
C1	0.0180 (3)	0.0167 (3)	0.0136 (3)	0.0009 (2)	0.0053 (2)	0.0047 (2)
C2	0.0154 (3)	0.0152 (3)	0.0115 (3)	0.0008 (2)	0.0029 (2)	0.0041 (2)
C3	0.0202 (3)	0.0167 (3)	0.0118 (3)	-0.0015 (2)	0.0020 (2)	0.0035 (2)
C4	0.0205 (3)	0.0156 (3)	0.0098 (2)	0.0018 (2)	0.0020 (2)	0.0034 (2)
C5	0.0179 (3)	0.0161 (3)	0.0109 (2)	0.0018 (2)	0.0038 (2)	0.0046 (2)
C6	0.0137 (3)	0.0148 (3)	0.0109 (2)	0.0017 (2)	0.0030 (2)	0.0041 (2)
C7	0.0148 (3)	0.0157 (3)	0.0144 (3)	0.0010 (2)	0.0036 (2)	0.0036 (2)
C8	0.0150 (3)	0.0149 (3)	0.0135 (3)	0.0021 (2)	0.0036 (2)	0.0043 (2)
C9	0.0140 (3)	0.0136 (2)	0.0109 (2)	0.0013 (2)	0.0028 (2)	0.0023 (2)
C10	0.0159 (3)	0.0160 (3)	0.0106 (2)	0.0012 (2)	0.0024 (2)	0.0016 (2)
C11	0.0151 (3)	0.0171 (3)	0.0098 (2)	-0.0002 (2)	0.0010 (2)	0.0023 (2)
C12	0.0154 (3)	0.0163 (3)	0.0122 (3)	0.0022 (2)	0.0016 (2)	0.0040 (2)
C13	0.0140 (3)	0.0137 (3)	0.0117 (2)	0.0017 (2)	0.0033 (2)	0.0032 (2)
C14	0.0168 (3)	0.0146 (3)	0.0140 (3)	0.0027 (2)	0.0059 (2)	0.0039 (2)
C15	0.0180 (3)	0.0152 (3)	0.0180 (3)	0.0007 (2)	0.0051 (2)	0.0011 (2)
C16	0.0171 (3)	0.0176 (3)	0.0197 (3)	0.0023 (2)	0.0051 (2)	0.0082 (2)

Geometric parameters (Å, °)

Ni1—N2	1.9665 (6)	N4—H4A	0.9000
Ni1—N1	1.9700 (6)	N4—H4B	0.9000
Ni1—O1	2.1088 (6)	N5—C15	1.3267 (11)
Ni1—O10	2.1387 (6)	N5—H5A	0.9002
Ni1—O6	2.1477 (6)	N5—H5B	0.9000
Ni1—O5	2.2149 (6)	N6—C16	1.3394 (10)
O1—C1	1.2668 (9)	N6—H6A	0.9000
O2—C1	1.2492 (10)	N6—H6B	0.9001
O3—C4	1.3394 (9)	N7—C16	1.3247 (11)
O3—H3C	0.9000	N7—H7A	0.9000
O4—C7	1.2357 (9)	N7—H7B	0.8999
O5—C7	1.2895 (9)	N8—C16	1.3238 (11)
O6—C8	1.2880 (9)	N8—H8A	0.9000
O7—C8	1.2343 (10)	N8—H8B	0.9002
O8—C11	1.3485 (9)	C1—C2	1.5198 (10)
O8—H8	0.9000	C2—C3	1.3832 (10)
O9—C14	1.2413 (9)	C3—C4	1.4044 (11)
O10—C14	1.2796 (9)	C3—H3	0.9300
O11—H11A	0.9000	C4—C5	1.4055 (11)
O11—H11B	0.9001	C5—C6	1.3857 (10)
O12—H12B	0.9000	C5—H5	0.9300
O12—H12A	0.9000	C6—C7	1.5111 (10)
N1—C6	1.3371 (9)	C8—C9	1.5141 (10)
N1—C2	1.3374 (9)	C9—C10	1.3856 (10)
N2—C9	1.3363 (9)	C10—C11	1.4032 (11)
N2—C13	1.3368 (9)	C10—H10	0.9300
N3—C15	1.3296 (10)	C11—C12	1.4021 (11)

N3—H3A	0.9001	C12—C13	1.3833 (10)
N3—H3B	0.9001	C12—H12	0.9300
N4—C15	1.3256 (11)	C13—C14	1.5143 (10)
N2—Ni1—N1	171.30 (3)	O2—C1—C2	118.69 (7)
O1—Ni1—O5	154.97 (2)	O1—C1—C2	115.64 (6)
O10—Ni1—O6	154.87 (2)	N1—C2—C3	121.56 (7)
N2—Ni1—O1	96.84 (2)	N1—C2—C1	112.83 (6)
N1—Ni1—O1	78.70 (2)	C3—C2—C1	125.60 (7)
N2—Ni1—O10	77.95 (2)	C2—C3—C4	118.69 (7)
N1—Ni1—O10	94.76 (2)	C2—C3—H3	120.7
O1—Ni1—O10	93.41 (3)	C4—C3—H3	120.7
N2—Ni1—O6	77.41 (2)	O3—C4—C3	118.15 (7)
N1—Ni1—O6	110.20 (2)	O3—C4—C5	122.66 (7)
O1—Ni1—O6	94.31 (2)	C3—C4—C5	119.18 (7)
N2—Ni1—O5	108.19 (2)	C6—C5—C4	117.89 (6)
N1—Ni1—O5	76.46 (2)	C6—C5—H5	121.1
O10—Ni1—O5	91.73 (2)	C4—C5—H5	121.1
O6—Ni1—O5	91.30 (2)	N1—C6—C5	122.25 (7)
C1—O1—Ni1	114.35 (5)	N1—C6—C7	113.16 (6)
C4—O3—H3C	111.0	C5—C6—C7	124.55 (6)
C7—O5—Ni1	113.28 (5)	O4—C7—O5	125.12 (7)
C8—O6—Ni1	114.63 (5)	O4—C7—C6	119.22 (7)
C11—O8—H8	109.2	O5—C7—C6	115.66 (6)
C14—O10—Ni1	114.35 (5)	O7—C8—O6	126.10 (7)
H11A—O11—H11B	109.4	O7—C8—C9	119.17 (7)
H12B—O12—H12A	115.5	O6—C8—C9	114.73 (6)
C6—N1—C2	120.41 (6)	N2—C9—C10	121.93 (7)
C6—N1—Ni1	121.23 (5)	N2—C9—C8	112.93 (6)
C2—N1—Ni1	117.81 (5)	C10—C9—C8	125.14 (7)
C9—N2—C13	120.78 (6)	C9—C10—C11	117.64 (7)
C9—N2—Ni1	119.82 (5)	C9—C10—H10	121.2
C13—N2—Ni1	119.03 (5)	C11—C10—H10	121.2
C15—N3—H3A	119.6	O8—C11—C12	121.73 (7)
C15—N3—H3B	119.6	O8—C11—C10	118.30 (7)
H3A—N3—H3B	120.4	C12—C11—C10	119.96 (6)
C15—N4—H4A	117.6	C13—C12—C11	118.05 (7)
C15—N4—H4B	120.5	C13—C12—H12	121.0
H4A—N4—H4B	121.3	C11—C12—H12	121.0
C15—N5—H5A	115.0	N2—C13—C12	121.62 (7)
C15—N5—H5B	119.8	N2—C13—C14	113.12 (6)
H5A—N5—H5B	125.0	C12—C13—C14	125.25 (7)
C16—N6—H6A	121.8	O9—C14—O10	125.71 (7)
C16—N6—H6B	118.1	O9—C14—C13	119.11 (7)
H6A—N6—H6B	118.4	O10—C14—C13	115.17 (6)
C16—N7—H7A	121.3	N4—C15—N5	120.87 (8)
C16—N7—H7B	116.5	N4—C15—N3	119.19 (8)
H7A—N7—H7B	121.1	N5—C15—N3	119.93 (8)
C16—N8—H8A	116.9	N8—C16—N7	121.25 (8)
C16—N8—H8B	119.8	N8—C16—N6	119.57 (8)

supplementary materials

H8A—N8—H8B	121.8	N7—C16—N6	119.16 (8)
O2—C1—O1	125.67 (7)		
N2—Ni1—O1—C1	-165.80 (6)	O2—C1—C2—C3	-1.87 (12)
N1—Ni1—O1—C1	6.63 (6)	O1—C1—C2—C3	177.90 (8)
O10—Ni1—O1—C1	-87.54 (6)	N1—C2—C3—C4	-0.79 (12)
O6—Ni1—O1—C1	116.39 (6)	C1—C2—C3—C4	-179.78 (7)
O5—Ni1—O1—C1	13.95 (10)	C2—C3—C4—O3	-179.99 (7)
N2—Ni1—O5—C7	170.16 (5)	C2—C3—C4—C5	0.95 (12)
N1—Ni1—O5—C7	-2.20 (5)	O3—C4—C5—C6	-179.04 (7)
O1—Ni1—O5—C7	-9.58 (9)	C3—C4—C5—C6	-0.02 (11)
O10—Ni1—O5—C7	92.27 (5)	C2—N1—C6—C5	1.36 (11)
O6—Ni1—O5—C7	-112.67 (5)	Ni1—N1—C6—C5	172.68 (5)
N2—Ni1—O6—C8	-2.86 (5)	C2—N1—C6—C7	-176.55 (6)
N1—Ni1—O6—C8	172.73 (5)	Ni1—N1—C6—C7	-5.23 (8)
O1—Ni1—O6—C8	93.20 (5)	C4—C5—C6—N1	-1.14 (11)
O10—Ni1—O6—C8	-14.34 (9)	C4—C5—C6—C7	176.52 (7)
O5—Ni1—O6—C8	-111.22 (5)	Ni1—O5—C7—O4	-179.06 (7)
N2—Ni1—O10—C14	3.50 (5)	Ni1—O5—C7—C6	0.27 (8)
N1—Ni1—O10—C14	-171.70 (6)	N1—C6—C7—O4	-177.72 (7)
O1—Ni1—O10—C14	-92.77 (6)	C5—C6—C7—O4	4.43 (12)
O6—Ni1—O10—C14	14.95 (9)	N1—C6—C7—O5	2.91 (10)
O5—Ni1—O10—C14	111.74 (6)	C5—C6—C7—O5	-174.94 (7)
N2—Ni1—N1—C6	-119.19 (16)	Ni1—O6—C8—O7	179.06 (7)
O1—Ni1—N1—C6	-179.02 (6)	Ni1—O6—C8—C9	-0.37 (8)
O10—Ni1—N1—C6	-86.48 (6)	C13—N2—C9—C10	-0.51 (11)
O6—Ni1—N1—C6	90.51 (6)	Ni1—N2—C9—C10	172.42 (5)
O5—Ni1—N1—C6	4.16 (6)	C13—N2—C9—C8	178.98 (6)
N2—Ni1—N1—C2	52.35 (19)	Ni1—N2—C9—C8	-8.09 (8)
O1—Ni1—N1—C2	-7.48 (6)	O7—C8—C9—N2	-174.29 (7)
O10—Ni1—N1—C2	85.06 (6)	O6—C8—C9—N2	5.18 (9)
O6—Ni1—N1—C2	-97.95 (6)	O7—C8—C9—C10	5.17 (11)
O5—Ni1—N1—C2	175.70 (6)	O6—C8—C9—C10	-175.36 (7)
N1—Ni1—N2—C9	-145.37 (15)	N2—C9—C10—C11	0.58 (11)
O1—Ni1—N2—C9	-86.74 (6)	C8—C9—C10—C11	-178.84 (7)
O10—Ni1—N2—C9	-178.78 (6)	C9—C10—C11—O8	-179.59 (7)
O6—Ni1—N2—C9	6.18 (5)	C9—C10—C11—C12	0.16 (11)
O5—Ni1—N2—C9	93.38 (6)	O8—C11—C12—C13	178.81 (7)
N1—Ni1—N2—C13	27.7 (2)	C10—C11—C12—C13	-0.94 (11)
O1—Ni1—N2—C13	86.32 (6)	C9—N2—C13—C12	-0.33 (11)
O10—Ni1—N2—C13	-5.72 (5)	Ni1—N2—C13—C12	-173.32 (5)
O6—Ni1—N2—C13	179.23 (6)	C9—N2—C13—C14	179.79 (6)
O5—Ni1—N2—C13	-93.57 (6)	Ni1—N2—C13—C14	6.80 (8)
Ni1—O1—C1—O2	174.96 (7)	C11—C12—C13—N2	1.04 (11)
Ni1—O1—C1—C2	-4.79 (9)	C11—C12—C13—C14	-179.09 (7)
C6—N1—C2—C3	-0.36 (11)	Ni1—O10—C14—O9	-179.76 (7)
Ni1—N1—C2—C3	-171.97 (6)	Ni1—O10—C14—C13	-1.05 (8)
C6—N1—C2—C1	178.76 (6)	N2—C13—C14—O9	175.34 (7)
Ni1—N1—C2—C1	7.15 (8)	C12—C13—C14—O9	-4.54 (11)
O2—C1—C2—N1	179.06 (7)	N2—C13—C14—O10	-3.46 (9)

O1—C1—C2—N1 -1.17 (10) C12—C13—C14—O10 176.66 (7)

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3C...O6 ⁱ	0.90	1.71	2.5901 (8)	166
O8—H8...O5 ⁱⁱ	0.90	1.84	2.7057 (9)	160
O11—H11A...O9 ⁱⁱⁱ	0.90	1.86	2.7106 (9)	156
O11—H11B...O2 ^{iv}	0.90	1.88	2.7464 (9)	161
O12—H12B...O11 ⁱⁱ	0.90	2.15	3.0425 (12)	172
O12—H12A...O5	0.90	2.15	3.0244 (13)	164
O12—H12A...O4	0.90	2.64	3.3823 (12)	141
N3—H3A...O4 ^v	0.90	2.15	2.9307 (10)	144
N3—H3B...O10	0.90	2.07	2.8817 (10)	149
N4—H4A...O4 ^v	0.90	1.97	2.8072 (11)	154
N4—H4B...O11 ^{vi}	0.90	2.06	2.9161 (10)	159
N5—H5A...O10	0.90	2.19	2.9887 (10)	148
N5—H5B...O2 ^{vii}	0.90	1.98	2.8656 (10)	169
N6—H6A...O7 ^{viii}	0.90	2.28	3.0178 (11)	139
N6—H6A...O1	0.90	2.49	3.0038 (9)	117
N6—H6B...O3 ^{vii}	0.90	2.55	3.2320 (11)	133
N7—H7A...O9 ⁱⁱⁱ	0.90	2.01	2.8999 (10)	172
N7—H7B...O12 ^{ix}	0.90	1.93	2.8282 (13)	176
N8—H8A...O7 ^{viii}	0.90	1.94	2.7993 (10)	158
N8—H8B...O11	0.90	1.99	2.8847 (10)	174
N5—H5A...Cg1(N1/C2—C6)	0.90	3.47	3.362 (7)	75

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

Fig. 1

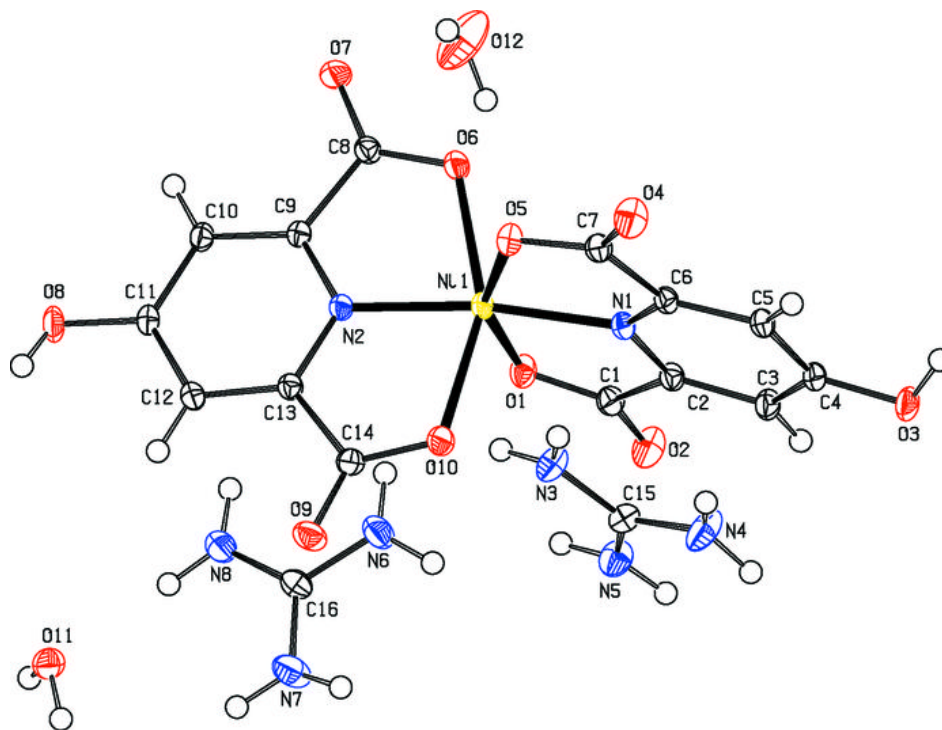


Fig. 2

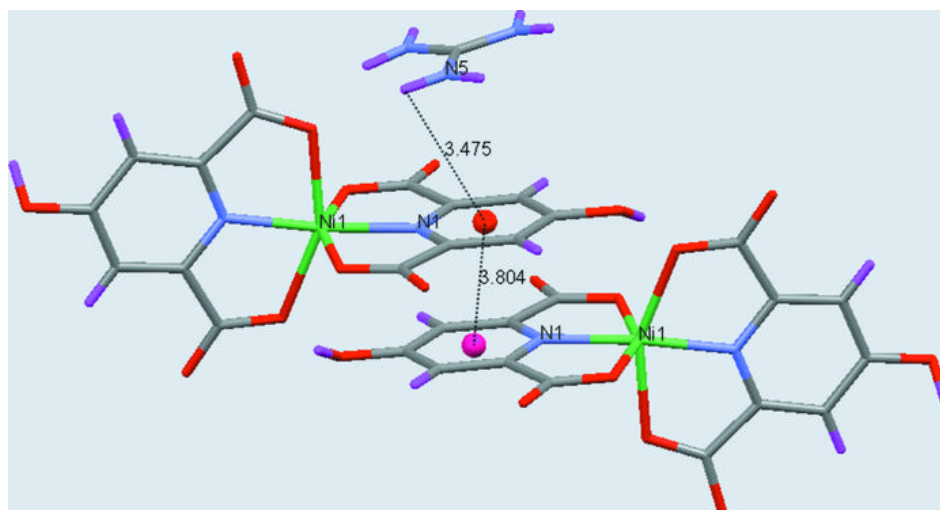


Fig. 3

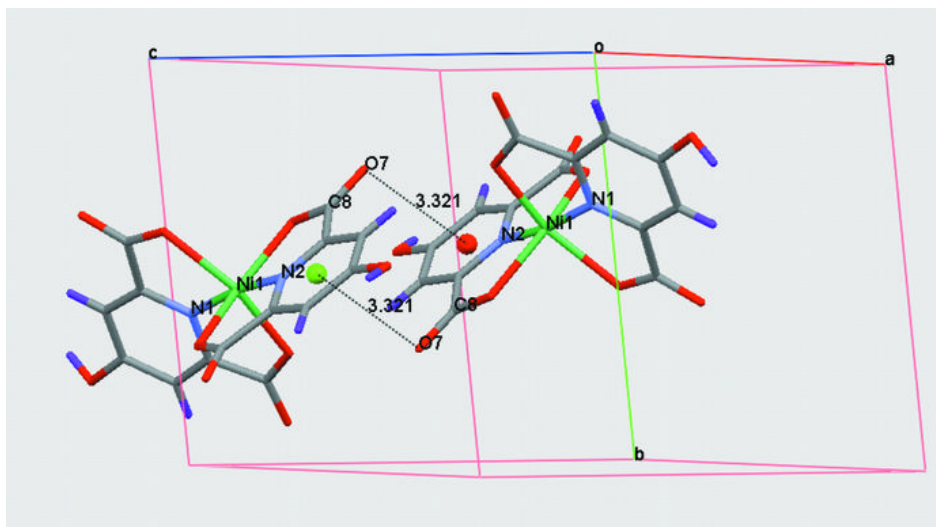


Fig. 4

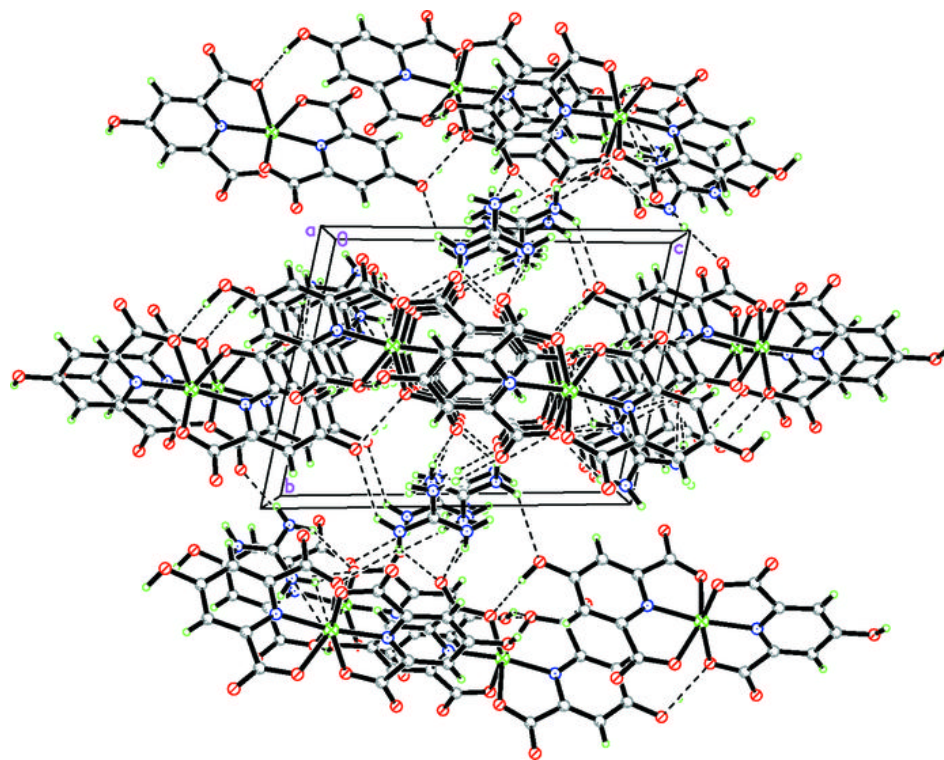


Fig. 5

