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► **To cite this version:**

Ignacio Chi-Duran, Zouaoui Setifi, Fatima Setifi, Christian Jelsch, Bernd Morgenstern, et al.. Crystal structure and Hirshfeld surface analysis of tris(2,2'-bipyridine)nickel(II) bis(1,1,3,3-tetracyano-2-ethoxypropenide) dihydrate. *Acta crystallographica. Section E, Crystallographic communications*, International Union of Crystallography, 2019, 75 (6), pp.867-871. 10.1107/S2056989019006959 . hal-02355939

**HAL Id: hal-02355939**

**<https://hal.archives-ouvertes.fr/hal-02355939>**

Submitted on 8 Nov 2019

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# Crystal structure and Hirshfeld surface analysis of tris(2,2'-bipyridine)nickel(II) bis(1,1,3,3-tetracyano-2-ethoxypropenide) dihydrate

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Received 14 January 2019

Accepted 14 May 2019

Edited by J. T. Mague, Tulane University, USA

**Keywords:** crystal structure; polynitrile ligand; Hirshfeld surface analysis; hydrogen bonding.

**CCDC reference:** 1915961

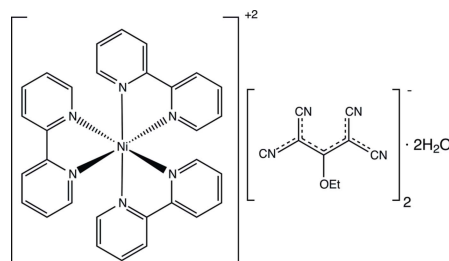
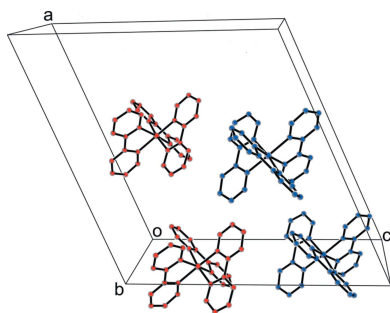
**Supporting information:** this article has supporting information at journals.iucr.org/e

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The title compound,  $[\text{Ni}(\text{C}_{10}\text{H}_8\text{N}_2)_3](\text{C}_9\text{H}_5\text{N}_4\text{O})_2 \cdot 2\text{H}_2\text{O}$ , crystallizes as a racemic mixture in the monoclinic space group  $C2/c$ . In the crystal, the 1,1,3,3-tetracyano-2-ethoxypropenide anions and the water molecules are linked by  $\text{O}-\text{H} \cdots \text{N}$  hydrogen bonds, forming chains running along the  $[010]$  direction. The bpy ligands of the cation are linked to the chain *via*  $\text{C}-\text{H} \cdots \pi(\text{cation})$  interactions involving the  $\text{CH}_3$  group. The intermolecular interactions were investigated by Hirshfeld surface analysis and two-dimensional fingerprint plots.

## 1. Chemical context

The use of polynitrile anions as ligands, either alone or in combination with neutral co-ligands, is a very promising and appealing strategy to obtain molecular architectures with different topologies and dimensionalities owing to their ability to coordinate and bridge metal ions in many different ways (Miyazaki *et al.*, 2003; Atmani *et al.*, 2008; Benmansour *et al.*, 2007, 2008; Yuste *et al.*, 2009; Gaamoune *et al.*, 2010; Addala *et al.*, 2015; Setifi *et al.*, 2010, 2013*a,b*, 2014*a,b*, 2015, 2016, 2017). The presence of several potentially coordinating nitrile groups, their rigidity and their electronic delocalization, allows the synthesis of original magnetic high-dimensional coordination polymers with transition-metal ions (Benmansour *et al.*, 2010).



In view of the possible roles of these versatile polynitrile ligands, we have been interested in using them in combination

**Table 1**  
Selected geometric parameters (Å, °).

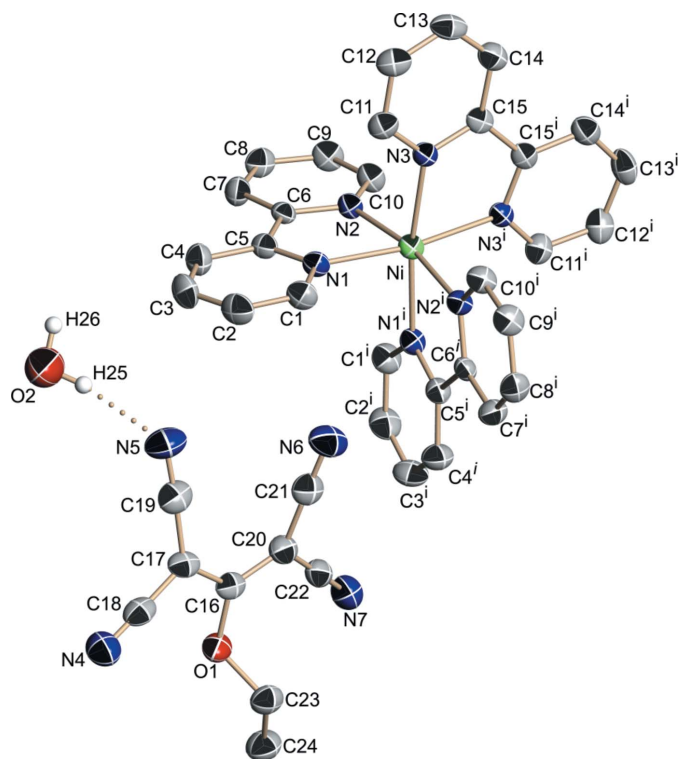
Ni—N2	2.077 (3)	Ni—N3	2.090 (3)
Ni—N1	2.088 (3)		
N1—Ni—N2	78.64 (12)	N2—Ni—N3	92.87 (11)
N1 <sup>i</sup> —Ni—N2	93.73 (11)	N1—Ni—N3	95.55 (11)
N1—Ni—N1 <sup>i</sup>	91.20 (16)	N2—Ni—N3 <sup>i</sup>	95.52 (11)
N1—Ni—N3 <sup>i</sup>	171.36 (11)	N3—Ni—N3 <sup>i</sup>	78.26 (16)
N2—Ni—N2 <sup>i</sup>	169.18 (16)		

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

with other chelating or bridging neutral co-ligands to explore their structural and electronic characteristics in the field of molecular materials exhibiting interesting magnetic exchange coupling. During the course of attempts to prepare such complexes with 2,2-dipyridyl, we isolated the title compound, whose structure is described herein along with the Hirshfeld surface analysis.

## 2. Structural commentary

The asymmetric unit of the title compound comprises a half of  $[\text{Ni}(\text{bpy})_3]^{2+}$  cation, one  $(\text{tnc}^{\text{oe}})^-$  anion and a solvent water molecule within the monoclinic  $C2/c$ -centred cell (Fig. 1). In addition, this compound crystallizes presenting  $\Delta$  and  $\Lambda$  chiral configurations and related to each other by inversion, forming a racemic mixture as illustrated in Fig. 2; this compound is



**Figure 1**  
Molecular structure of the title compound, showing the atom labeling and displacement ellipsoids drawn at the 50% probability level. Hydrogen atoms on the  $[\text{Ni}(\text{bpy})_3]^{2+}$  cation and  $(\text{tnc}^{\text{oe}})^-$  were omitted for clarity. Symmetry code: (i)  $1 - x, y, \frac{1}{2} - z$ .

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

Cg1 is the centroid of the N2/C6–C10 ring.

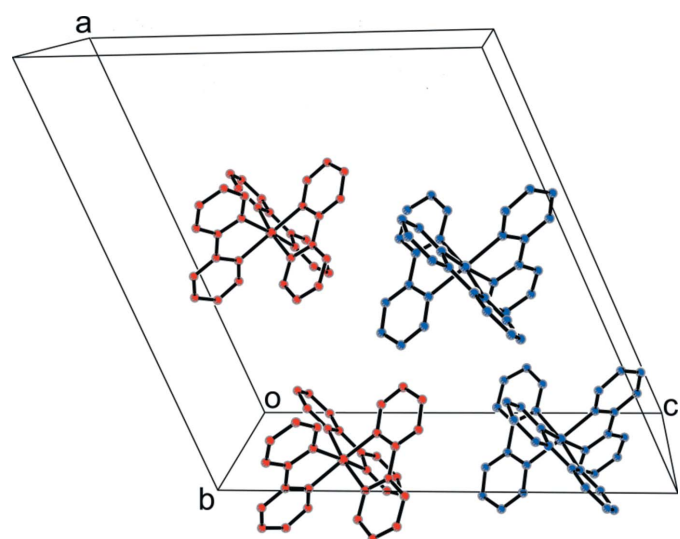
$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H25 $\cdots$ N5	0.86	2.11	2.945 (5)	164
O2—H26 $\cdots$ N4 <sup>ii</sup>	0.86	2.10	2.955 (5)	175
C24—H24A $\cdots$ Cg1 <sup>iii</sup>	0.98	3.01	3.921	156

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

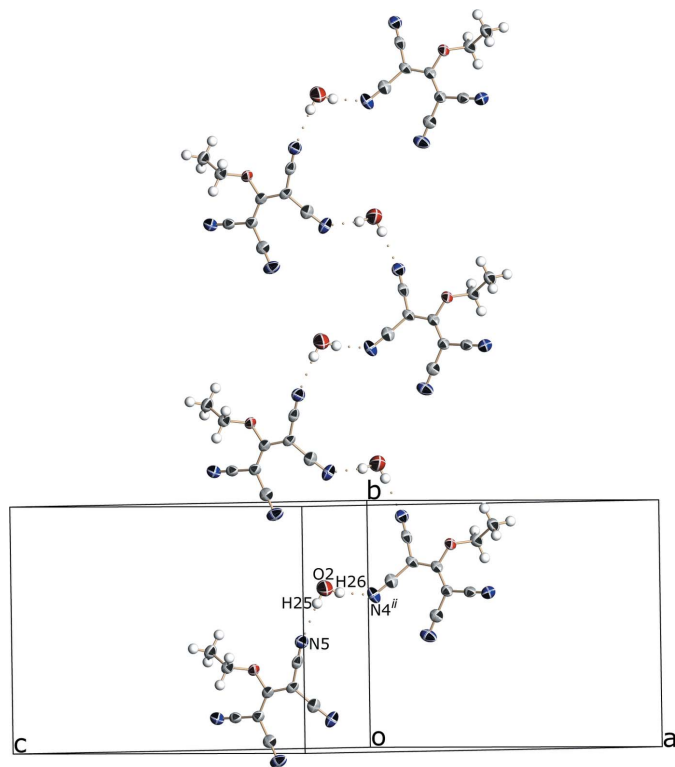
isostructural to  $\text{Fe}(\text{bpy})_3(\text{tnc}^{\text{oe}})_2(2\text{H}_2\text{O})$  (Setifi *et al.*, 2014c). The Ni atom is located on the Wyckoff position 4e on the twofold axis. The  $[\text{Ni}(\text{bpy})_3]^{2+}$  complex presents a slightly distorted octahedral geometry of  $C_2$  point-group symmetry (Table 1). The Ni—N bond lengths are very similar to each other, being in the range 2.077 (3)–2.090 (3) Å, which is in agreement with the Ni—N distances for other  $[\text{Ni}(\text{bpy})_3]^{2+}$  complexes reported in the literature (Freire *et al.*, 2000; Su *et al.*, 2007; Yang *et al.*, 1998). In addition, the Ni—N distances are slightly longer than the Fe—N bonds  $[\text{Fe}(\text{bpy})_3]^{2+}$  [1.971 (2)–1.972 (2) Å] because of the larger  $\text{Ni}^{2+}$  radius compared to  $\text{Fe}^{2+}$  in a low-spin configuration (Shannon & Prewitt, 1969). The distorted N—Ni—N angles of the chelating bipyridine ligands [78.26 (16)–78.64 (12)°] are significantly less than 90°, as is usually found for  $[\text{Ni}(\text{bpy})_3]^{2+}$  complexes (Freire *et al.*, 2000; Yang *et al.*, 1998).

## 3. Supramolecular features

As shown in Fig. 2, there are four  $[\text{Ni}(\text{bpy})_3]^{2+}$  cationic units within the unit cell of the compound, charge-balancing the 1,1,3,3-tetracyano-2-ethoxypropene anions. These, together with the hydration water, define planar and zigzag hydrogen-bonded chains, in which anions and water molecules alternate, running along the [010] direction, as shown in Fig. 3. The O(water)—H $\cdots$ N(cyano) hydrogen-bonding interactions

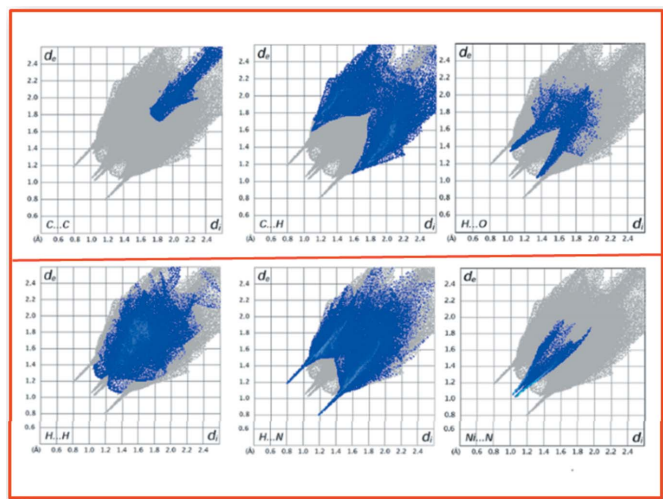


**Figure 2**  
Disposition of  $\Delta$  (red) and  $\Lambda$  (blue) stereoisomers in the unit cell.



**Figure 3**  
Partial crystal packing diagram showing the alternating zigzag  $(\text{tcnoet})^-$  water chains defined by  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bonds running along the [010] direction. Symmetry code: (ii)  $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ .

(Table 2) define the chain, with  $\text{H}\cdots\text{N}$  distances of 2.11 and 2.10 Å. Finally, a  $\text{C}-\text{H}\cdots\pi$  interaction between the  $\text{CH}_3$  group of the  $(\text{tcnoet})^-$  anion and the bpy ligand is observed, with a  $\text{H}\cdots$ centroid distance of 3.01 Å (Table 2).



**Figure 4**  
Hirshfeld surface fingerprint plot for the title compound showing the  $\text{C}\cdots\text{C}$ ,  $\text{C}\cdots\text{H}$ ,  $\text{H}\cdots\text{O}$ ,  $\text{H}\cdots\text{H}$ ,  $\text{H}\cdots\text{N}$  and  $\text{Ni}\cdots\text{N}$  contacts in detail.

**Table 3**

Nature of intermolecular contacts on the Hirshfeld surface by chemical type.

The top part of the table gives the contribution  $S_x$  of each chemical type  $X$  to the Hirshfeld surface. The chemical types are grouped as hydrophobic (C, Hc) and charged (N, Ho, O) atoms. The next part shows the percentage contributions  $C_{xy}$  of the actual contact types to the surface. The lower part of the table shows the  $E_{xy}$  contact enrichment ratios. The major  $C_{xy}$  contact types and the  $E_{xy}$  ratios much larger than unity (enriched contacts) are highlighted in bold. The hydrophobic Hc atoms bound to carbon are distinguished from the more polar Ho water hydrogen atoms.

Atom type	Ho	O	N	Hc	C
Surface (%)	5.3	4.5	16.5	38.0	35.7
Ho	0.0				
O	0.0	0.0			
Contacts (%)					
N	<b>5.0</b>	0.0	0.0		
Hc	4.7	6.1	<b>20.9</b>	7.5	
C	1.9	3.0	8.5	<b>27.8</b>	<b>14.7</b>
Ho	0.0				
O	0.0	0.0			
Enrichment					
N	<b>2.5</b>	0.0	0.0		
Hc	1.1	<b>1.8</b>	<b>1.6</b>	0.54	
C	0.47	0.92	0.7	1.06	1.2

#### 4. Hirshfeld surface analysis

The fingerprint plots (Fig. 4) of the intermolecular contacts were computed using program *CrystalExplorer* (McKinnon *et al.*, 2007; Wolff *et al.*, 2012). The short contacts spikes are due to the  $\text{N}\cdots\text{H}$  hydrogen bonds (outer spikes) and to the  $\text{Ni}\cdots\text{N}$  coordination bonds (inner spikes).

The proportions of the different contacts and their enrichment (Jelsch *et al.*, 2014; Table 3) were computed with program *MoProViewer* (Guillot *et al.*, 2014). The enrichment ratios  $E_{xy}$  are obtained from the actual contacts between the different chemical species ( $x, y$ ) and equi-probable proportions computed from the surface chemical content (Jelsch *et al.*, 2014). They allow contacts that are favored (over-represented) and which are likely to be the crystal driving force to be highlighted.

The Hirshfeld surface was computed for all the entities present in the crystal – the  $(\text{tcnoet})^-$  anion, the  $[\text{Ni}(\text{bpy})_3]^{2+}$  complex and the water molecule – in order to analyze the crystal contacts. Moieties not in contact with each other were selected in the crystal packing in order to obtain integral surfaces.

The nickel cation does not contribute to the molecular surface, as it is coordinated by six nitrogen atoms within the  $[\text{Ni}(\text{bpy})_3]^{2+}$  complex. Nearly three quarters of the Hirshfeld surface is of hydrophobic in nature, constituted by atoms C and Hc. The most abundant contact is of the  $\text{C}\cdots\text{Hc}$  type as a result of the extensive  $\text{C}-\text{H}\cdots\pi$  interactions involving the aromatic rings. The second major contact is  $\text{N}\cdots\text{Hc}$ , which is due to the abundance of the N and Hc chemical types and to the significant enrichment of this favorable weak hydrogen bond. The third major contact is of the  $\text{C}\cdots\text{C}$  type and is due

**Table 4**  
Experimental details.

Crystal data	
Chemical formula	[Ni(C <sub>10</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>3</sub> ](C <sub>9</sub> H <sub>5</sub> N <sub>4</sub> O) <sub>2</sub> ·2H <sub>2</sub> O
<i>M</i> <sub>r</sub>	933.63
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	162
<i>a</i> , <i>b</i> , <i>c</i> (Å)	20.345 (3), 12.439 (3), 19.575 (4)
$\beta$ (°)	112.800 (9)
<i>V</i> (Å <sup>3</sup> )	4566.8 (17)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.49
Crystal size (mm)	0.17 × 0.14 × 0.07
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2012)
<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub>	0.683, 0.745
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	22477, 4670, 2483
<i>R</i> <sub>int</sub>	0.108
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.627
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.061, 0.125, 1.00
No. of reflections	4670
No. of parameters	310
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$ , $\Delta\rho_{\text{min}}$ (e Å <sup>-3</sup> )	0.36, -0.40

Computer programs: *APEX2* and *SAINT* (Bruker, 2012), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015) and *pubCIF* (Westrip, 2010).

to stacking between the [Ni(bpy)<sub>3</sub>]<sup>2+</sup> aromatic rings and the C(C≡N)<sub>2</sub> group of the (tcnoet)<sup>-</sup> anion.

The other significantly over-represented contacts are the strong hydrogen bonds N··H—O (*E* = 2.5) between the water molecule and two nitrile groups. These are the hydrogen bonds with shortest distance *d*(N5··H25) = 2.11 Å and *d*(N4··H26) = 2.10 Å (Table 1). There is a deficit of strong hydrogen-bond donors compared to acceptors in this crystal structure. As a result, weak hydrogen bonds to H—C groups are formed. N··H—C weak hydrogen bonds occur and are slightly enriched. The oxygen atoms form only weak O··H—C hydrogen bonds, which are quite favored at *E* = 1.8. Globally there are two O—H··N strong hydrogen bonds, six C—H··N and two C—H··O weak hydrogen bonds (Table 2). The two major hydrophobic contacts, C··H<sub>c</sub> and C··C, are both slightly enriched. If all hydrophobic contacts (within C and H<sub>c</sub> atoms) are considered together, they are globally slightly under-represented with an enrichment ratio *E* = 0.92 because of the avoidance of the less favorable H<sub>c</sub>··H<sub>c</sub> contacts. All contacts between charged atoms (O, H<sub>o</sub>, N) are absent except for the attractive N··H<sub>o</sub> hydrogen bond. The cross hydrophilic/hydrophobic contacts are slightly over-represented at *E* = 1.16 because of the occurrence of many weak O··H<sub>c</sub> and N··H<sub>c</sub> hydrogen bonds, which result from an unbalanced number of strong hydrogen-bond acceptors *versus* donors.

## 5. Database survey

The Cambridge Structural Database (CSD, Version 5.39, update August 2018, Groom *et al.*, 2016) includes a few structures involving polycyanopropide counter-ions, of which only 16 entries are hexacyano derivatives and four have (tcnoet)<sup>-</sup> anions. There are no significant differences in C—N and C—C bond lengths between the hexacyano derivatives and (tcnoet)<sup>-</sup> anions. However, the C21—C20—C16—C17 torsion angles in (tcnoet)<sup>-</sup> anion (15.78°) are slightly smaller than the analogous torsion angle in other anions (16.32–21.68°). This difference can be explained by this compound and its isostructural structure featuring two hydrogen bonds, O2—H25··N5 and O2—H25··N4<sup>ii</sup>. These interactions orient the cyano groups toward to coplanarity with respect to other (tcnoet)<sup>-</sup> molecules that exhibit fewer hydrogen bonds. Finally, this compound has been used for the synthesis of low-dimensional metal–organic frameworks employing Mn<sup>II</sup>, Cu<sup>II</sup>, Co<sup>II</sup> and Fe<sup>II</sup> ions because the half cyano groups interact by hydrogen bonding with the metal aqua complexes, avoiding the formation of high-dimensional frameworks (Thétiot *et al.*, 2003).

## 6. Synthesis and crystallization

The title compound was synthesized solvothermally under autogenous pressure from a mixture of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (29 mg, 0.1 mmol), 2,2-dipyridyl (16 mg, 0.1 mmol) and K(tcnoet) (45 mg, 0.2 mmol) in water–ethanol (4:1 *v/v*, 20 cm<sup>-3</sup>). This mixture was sealed in a Teflon-lined autoclave and held at 423 K for three days, and then cooled to ambient temperature at a rate of 10 K h<sup>-1</sup> (yield: 54%). Light-green blocks of the title compound suitable for single-crystal X-ray diffraction were selected directly from the synthesized product.

## 7. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 4. All H atoms were located in difference-Fourier maps. C-bound H atoms were then treated as riding atoms: C—H = 0.95 Å (aromatic), 0.98 Å (CH<sub>3</sub>) or 0.99 Å (CH<sub>2</sub>), and with *U*<sub>iso</sub>(H) = *kU*<sub>eq</sub>(C), where *k* = 1.5 for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all others. H atoms bonded to the water O atom were permitted to ride at the positions located in the difference map, with *U*<sub>iso</sub>(H) = 1.5*U*<sub>eq</sub>(O).

## Funding information

FS gratefully acknowledges the Algerian DG-RSDT (Direction Générale de la Recherche Scientifique et du Développement Technologique) and Université Ferhat Abbas Sétif 1 for financial support. FH is supported by CONICYT through the Proyecto REDES ETAPA INICIAL, Convocatoria 2017 No. REDI 170423, and FONDECYT Regular 1181743. DPS

and FH are grateful for support from the Iniciativa Científica Milenio (ICM) through the Millennium Institute for Research in Optics (MIRO).

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## supporting information

*Acta Cryst.* (2019). E75, 867-871 [https://doi.org/10.1107/S2056989019006959]

## Crystal structure and Hirshfeld surface analysis of tris(2,2'-bipyridine)nickel(II) bis(1,1,3,3-tetracyano-2-ethoxypropenide) dihydrate

**Ignacio Chi-Duran, Zouaoui Setifi, Fatima Setifi, Christian Jelsch, Bernd Morgenstern, Andres Vega, Felipe Herrera, Dinesh Pratap Singh, Kaspar Hegetschweiler and Rabab Boyaala**

### Computing details

Data collection: *APEX2* (Bruker, 2012); cell refinement: *SAINT* (Bruker, 2012); data reduction: *SAINT* (Bruker, 2012); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

### Tris(2,2'-bipyridine)nickel(II) bis(1,1,3,3-tetracyano-2-ethoxypropenide) dihydrate

#### Crystal data

$[\text{Ni}(\text{C}_{10}\text{H}_8\text{N}_2)_3](\text{C}_9\text{H}_5\text{N}_4\text{O})_2 \cdot 2\text{H}_2\text{O}$

$M_r = 933.63$

Monoclinic, *C2/c*

$a = 20.345$  (3) Å

$b = 12.439$  (3) Å

$c = 19.575$  (4) Å

$\beta = 112.800$  (9)°

$V = 4566.8$  (17) Å<sup>3</sup>

$Z = 4$

$F(000) = 1936$

$D_x = 1.358$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 1400 reflections

$\theta = 2.5$ – $19.1$ °

$\mu = 0.49$  mm<sup>-1</sup>

$T = 162$  K

Block, light green

$0.17 \times 0.14 \times 0.07$  mm

#### Data collection

Bruker APEXII CCD  
diffractometer

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan  
(SADABS; Bruker, 2012)

$T_{\min} = 0.683$ ,  $T_{\max} = 0.745$

22477 measured reflections

4670 independent reflections

2483 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.108$

$\theta_{\max} = 26.5$ °,  $\theta_{\min} = 2.0$ °

$h = -25 \rightarrow 22$

$k = -12 \rightarrow 15$

$l = -24 \rightarrow 24$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.061$

$wR(F^2) = 0.125$

$S = 1.00$

4670 reflections

310 parameters

2 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent  
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0372P)^2 + 4.4221P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.36$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -0.39$  e Å<sup>-3</sup>

*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.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni	0.5000	0.13563 (5)	0.2500	0.0258 (2)
N1	0.44888 (16)	0.2530 (2)	0.28779 (16)	0.0277 (7)
N2	0.56997 (15)	0.1514 (2)	0.35984 (15)	0.0258 (7)
N3	0.44732 (16)	0.0053 (2)	0.27341 (15)	0.0251 (7)
C1	0.3878 (2)	0.3033 (3)	0.2479 (2)	0.0358 (10)
H1	0.3624	0.2810	0.1981	0.043*
C2	0.3600 (2)	0.3857 (3)	0.2755 (2)	0.0412 (11)
H2	0.3160	0.4185	0.2459	0.049*
C3	0.3976 (2)	0.4192 (3)	0.3472 (2)	0.0424 (11)
H3	0.3802	0.4766	0.3675	0.051*
C4	0.4604 (2)	0.3688 (3)	0.3890 (2)	0.0375 (10)
H4	0.4868	0.3911	0.4386	0.045*
C5	0.48510 (19)	0.2855 (3)	0.3585 (2)	0.0272 (9)
C6	0.55264 (19)	0.2279 (3)	0.3992 (2)	0.0250 (9)
C7	0.5973 (2)	0.2508 (3)	0.4718 (2)	0.0336 (10)
H7	0.5844	0.3045	0.4989	0.040*
C8	0.6604 (2)	0.1949 (3)	0.5044 (2)	0.0353 (10)
H8	0.6916	0.2097	0.5540	0.042*
C9	0.6777 (2)	0.1174 (3)	0.4641 (2)	0.0344 (10)
H9	0.7210	0.0784	0.4852	0.041*
C10	0.6310 (2)	0.0976 (3)	0.3927 (2)	0.0319 (10)
H10	0.6427	0.0430	0.3653	0.038*
C11	0.3952 (2)	0.0107 (3)	0.29930 (19)	0.0335 (10)
H11	0.3776	0.0795	0.3050	0.040*
C12	0.3661 (2)	-0.0790 (3)	0.3179 (2)	0.0380 (10)
H12	0.3289	-0.0720	0.3355	0.046*
C13	0.3915 (2)	-0.1782 (3)	0.3106 (2)	0.0391 (11)
H13	0.3732	-0.2411	0.3243	0.047*
C14	0.4440 (2)	-0.1851 (3)	0.2830 (2)	0.0354 (10)
H14	0.4618	-0.2533	0.2766	0.042*
C15	0.47114 (19)	-0.0920 (3)	0.26463 (18)	0.0273 (9)
N4	0.2358 (2)	0.9371 (3)	0.0957 (2)	0.0518 (10)
N5	0.25094 (19)	0.6205 (3)	0.1895 (2)	0.0578 (11)
N6	0.3282 (2)	0.4535 (3)	0.10158 (19)	0.0561 (11)
N7	0.5030 (2)	0.6277 (3)	0.07484 (19)	0.0488 (9)
O1	0.38199 (14)	0.8243 (2)	0.08018 (14)	0.0389 (7)
C16	0.3536 (2)	0.7331 (3)	0.0959 (2)	0.0341 (10)
C17	0.2966 (2)	0.7526 (3)	0.1182 (2)	0.0345 (10)
C18	0.2635 (2)	0.8550 (4)	0.1055 (2)	0.0385 (11)



C19	0.2720 (2)	0.6775 (4)	0.1570 (2)	0.0435 (11)
C20	0.3857 (2)	0.6355 (3)	0.0944 (2)	0.0378 (10)
C21	0.3536 (2)	0.5348 (4)	0.0987 (2)	0.0412 (11)
C22	0.4508 (2)	0.6307 (3)	0.0835 (2)	0.0379 (10)
C23	0.3802 (2)	0.8371 (3)	0.0057 (2)	0.0412 (11)
H23A	0.3362	0.8755	-0.0257	0.049*
H23B	0.3803	0.7657	-0.0166	0.049*
C24	0.4438 (2)	0.8993 (3)	0.0101 (2)	0.0489 (12)
H24A	0.4451	0.9676	0.0355	0.073*
H24B	0.4414	0.9136	-0.0400	0.073*
H24C	0.4870	0.8579	0.0377	0.073*
O2	0.2745 (2)	0.6530 (3)	0.3463 (2)	0.0829 (11)
H25	0.274 (3)	0.634 (4)	0.3041 (15)	0.099*
H26	0.271 (3)	0.592 (2)	0.365 (3)	0.099*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Ni	0.0223 (4)	0.0255 (4)	0.0259 (4)	0.000	0.0053 (3)	0.000
N1	0.0243 (18)	0.0273 (18)	0.0285 (19)	0.0033 (16)	0.0070 (16)	0.0031 (15)
N2	0.0226 (17)	0.0255 (18)	0.0262 (17)	0.0024 (16)	0.0059 (15)	0.0002 (15)
N3	0.0239 (18)	0.0253 (18)	0.0218 (17)	-0.0001 (16)	0.0040 (15)	0.0005 (14)
C1	0.030 (2)	0.036 (2)	0.037 (2)	0.007 (2)	0.008 (2)	0.005 (2)
C2	0.034 (2)	0.039 (3)	0.052 (3)	0.013 (2)	0.018 (2)	0.007 (2)
C3	0.041 (3)	0.036 (3)	0.053 (3)	0.011 (2)	0.022 (2)	-0.005 (2)
C4	0.039 (3)	0.038 (2)	0.037 (2)	0.005 (2)	0.015 (2)	-0.004 (2)
C5	0.024 (2)	0.026 (2)	0.033 (2)	0.0029 (19)	0.0130 (19)	0.0025 (19)
C6	0.028 (2)	0.020 (2)	0.027 (2)	-0.0019 (18)	0.0105 (19)	0.0012 (17)
C7	0.036 (3)	0.035 (2)	0.030 (2)	0.003 (2)	0.013 (2)	-0.003 (2)
C8	0.032 (2)	0.041 (3)	0.024 (2)	-0.004 (2)	0.002 (2)	-0.001 (2)
C9	0.022 (2)	0.039 (3)	0.032 (2)	0.004 (2)	-0.0004 (19)	0.003 (2)
C10	0.025 (2)	0.032 (2)	0.033 (2)	0.003 (2)	0.005 (2)	-0.0005 (19)
C11	0.029 (2)	0.039 (3)	0.031 (2)	0.003 (2)	0.008 (2)	0.005 (2)
C12	0.027 (2)	0.045 (3)	0.038 (3)	-0.001 (2)	0.009 (2)	0.009 (2)
C13	0.034 (3)	0.036 (3)	0.038 (3)	-0.011 (2)	0.003 (2)	0.008 (2)
C14	0.036 (3)	0.031 (2)	0.032 (2)	-0.003 (2)	0.005 (2)	-0.001 (2)
C15	0.023 (2)	0.029 (2)	0.020 (2)	-0.0042 (19)	-0.0026 (17)	-0.0011 (17)
N4	0.048 (3)	0.047 (3)	0.067 (3)	-0.006 (2)	0.030 (2)	-0.003 (2)
N5	0.055 (3)	0.067 (3)	0.056 (3)	-0.010 (2)	0.027 (2)	0.013 (2)
N6	0.065 (3)	0.044 (2)	0.046 (2)	-0.021 (2)	0.007 (2)	-0.002 (2)
N7	0.051 (2)	0.043 (2)	0.053 (2)	0.003 (2)	0.020 (2)	-0.0022 (19)
O1	0.0416 (17)	0.0363 (17)	0.0430 (17)	-0.0162 (14)	0.0211 (14)	-0.0076 (13)
C16	0.035 (3)	0.037 (3)	0.022 (2)	-0.015 (2)	0.003 (2)	-0.0040 (19)
C17	0.031 (2)	0.035 (3)	0.031 (2)	-0.015 (2)	0.005 (2)	0.000 (2)
C18	0.033 (3)	0.049 (3)	0.035 (2)	-0.016 (3)	0.014 (2)	-0.002 (2)
C19	0.034 (3)	0.054 (3)	0.038 (3)	-0.013 (2)	0.008 (2)	-0.004 (2)
C20	0.043 (3)	0.035 (2)	0.034 (2)	-0.009 (3)	0.013 (2)	-0.004 (2)
C21	0.041 (3)	0.047 (3)	0.027 (2)	-0.008 (3)	0.002 (2)	-0.003 (2)

C22	0.050 (3)	0.031 (2)	0.029 (2)	-0.004 (3)	0.011 (2)	-0.003 (2)
C23	0.043 (3)	0.045 (3)	0.030 (2)	-0.006 (2)	0.008 (2)	0.003 (2)
C24	0.050 (3)	0.052 (3)	0.048 (3)	-0.010 (2)	0.023 (2)	0.002 (2)
O2	0.112 (3)	0.070 (3)	0.078 (3)	-0.017 (3)	0.049 (3)	-0.009 (2)

*Geometric parameters (Å, °)*

Ni—N2	2.077 (3)	C11—C12	1.376 (5)
Ni—N2 <sup>i</sup>	2.077 (3)	C11—H11	0.9500
Ni—N1	2.088 (3)	C12—C13	1.366 (5)
Ni—N1 <sup>i</sup>	2.088 (3)	C12—H12	0.9500
Ni—N3	2.090 (3)	C13—C14	1.373 (5)
Ni—N3 <sup>i</sup>	2.090 (3)	C13—H13	0.9500
N1—C1	1.339 (4)	C14—C15	1.389 (5)
N1—C5	1.353 (4)	C14—H14	0.9500
N2—C10	1.335 (4)	C15—C15 <sup>i</sup>	1.493 (7)
N2—C6	1.354 (4)	N4—C18	1.146 (5)
N3—C15	1.339 (4)	N5—C19	1.141 (5)
N3—C11	1.343 (4)	N6—C21	1.146 (5)
C1—C2	1.379 (5)	N7—C22	1.139 (5)
C1—H1	0.9500	O1—C16	1.361 (4)
C2—C3	1.376 (5)	O1—C23	1.453 (4)
C2—H2	0.9500	C16—C20	1.384 (5)
C3—C4	1.373 (5)	C16—C17	1.409 (5)
C3—H3	0.9500	C17—C19	1.413 (5)
C4—C5	1.384 (5)	C17—C18	1.417 (6)
C4—H4	0.9500	C20—C22	1.422 (6)
C5—C6	1.479 (5)	C20—C21	1.431 (6)
C6—C7	1.388 (5)	C23—C24	1.482 (5)
C7—C8	1.381 (5)	C23—H23A	0.9900
C7—H7	0.9500	C23—H23B	0.9900
C8—C9	1.374 (5)	C24—H24A	0.9800
C8—H8	0.9500	C24—H24B	0.9800
C9—C10	1.374 (5)	C24—H24C	0.9800
C9—H9	0.9500	O2—H25	0.856 (10)
C10—H10	0.9500	O2—H26	0.860 (10)
N1—Ni—N2	78.64 (12)	C8—C9—C10	118.7 (4)
N1 <sup>i</sup> —Ni—N2	93.73 (11)	C8—C9—H9	120.7
N1 <sup>i</sup> —Ni—N2	93.73 (11)	C10—C9—H9	120.7
N2 <sup>i</sup> —Ni—N1 <sup>i</sup>	78.64 (12)	N2—C10—C9	123.2 (3)
N1—Ni—N1 <sup>i</sup>	91.20 (16)	N2—C10—H10	118.4
N1 <sup>i</sup> —Ni—N3	171.36 (11)	C9—C10—H10	118.4
N1—Ni—N3 <sup>i</sup>	171.36 (11)	N3—C11—C12	122.8 (4)
N2—Ni—N2 <sup>i</sup>	169.18 (16)	N3—C11—H11	118.6
N2—Ni—N3	92.87 (11)	C12—C11—H11	118.6
N2 <sup>i</sup> —Ni—N3	95.51 (11)	C13—C12—C11	119.1 (4)
N1—Ni—N3	95.55 (11)	C13—C12—H12	120.5

N2—Ni—N3 <sup>i</sup>	95.52 (11)	C11—C12—H12	120.5
N2 <sup>i</sup> —Ni—N3 <sup>i</sup>	92.87 (11)	C12—C13—C14	118.8 (4)
N1 <sup>i</sup> —Ni—N3 <sup>i</sup>	95.55 (11)	C12—C13—H13	120.6
N3—Ni—N3 <sup>i</sup>	78.26 (16)	C14—C13—H13	120.6
C1—N1—C5	118.2 (3)	C13—C14—C15	119.8 (4)
C1—N1—Ni	126.6 (3)	C13—C14—H14	120.1
C5—N1—Ni	115.0 (2)	C15—C14—H14	120.1
C10—N2—C6	118.5 (3)	N3—C15—C14	121.3 (3)
C10—N2—Ni	126.0 (2)	N3—C15—C15 <sup>i</sup>	115.3 (2)
C6—N2—Ni	115.5 (2)	C14—C15—C15 <sup>i</sup>	123.4 (2)
C15—N3—C11	118.2 (3)	C16—O1—C23	118.1 (3)
C15—N3—Ni	115.5 (2)	O1—C16—C20	118.7 (3)
C11—N3—Ni	126.2 (3)	O1—C16—C17	113.5 (4)
N1—C1—C2	123.2 (4)	C20—C16—C17	127.6 (4)
N1—C1—H1	118.4	C16—C17—C19	124.0 (4)
C2—C1—H1	118.4	C16—C17—C18	119.5 (3)
C3—C2—C1	118.3 (4)	C19—C17—C18	116.4 (4)
C3—C2—H2	120.8	N4—C18—C17	178.8 (4)
C1—C2—H2	120.8	N5—C19—C17	177.1 (5)
C4—C3—C2	119.4 (4)	C16—C20—C22	121.0 (4)
C4—C3—H3	120.3	C16—C20—C21	122.4 (4)
C2—C3—H3	120.3	C22—C20—C21	116.5 (4)
C3—C4—C5	119.5 (4)	N6—C21—C20	179.0 (5)
C3—C4—H4	120.2	N7—C22—C20	179.4 (5)
C5—C4—H4	120.2	O1—C23—C24	108.5 (3)
N1—C5—C4	121.4 (3)	O1—C23—H23A	110.0
N1—C5—C6	115.5 (3)	C24—C23—H23A	110.0
C4—C5—C6	123.1 (3)	O1—C23—H23B	110.0
N2—C6—C7	121.0 (3)	C24—C23—H23B	110.0
N2—C6—C5	115.2 (3)	H23A—C23—H23B	108.4
C7—C6—C5	123.7 (3)	C23—C24—H24A	109.5
C8—C7—C6	119.5 (3)	C23—C24—H24B	109.5
C8—C7—H7	120.3	H24A—C24—H24B	109.5
C6—C7—H7	120.3	C23—C24—H24C	109.5
C9—C8—C7	119.1 (4)	H24A—C24—H24C	109.5
C9—C8—H8	120.4	H24B—C24—H24C	109.5
C7—C8—H8	120.4	H25—O2—H26	102 (5)
C5—N1—C1—C2	-0.4 (5)	C3—C4—C5—C6	179.2 (3)
Ni—N1—C1—C2	-175.1 (3)	C10—N2—C6—C7	0.4 (5)
N1—C1—C2—C3	1.2 (6)	Ni—N2—C6—C7	-176.1 (3)
C1—C2—C3—C4	-1.1 (6)	C10—N2—C6—C5	178.7 (3)
C2—C3—C4—C5	0.2 (6)	Ni—N2—C6—C5	2.2 (4)
C1—N1—C5—C4	-0.5 (5)	N1—C5—C6—N2	1.1 (4)
Ni—N1—C5—C4	174.8 (3)	C4—C5—C6—N2	-177.5 (3)
C1—N1—C5—C6	-179.2 (3)	N1—C5—C6—C7	179.4 (3)

Ni—N1—C5—C6	-3.8 (4)	C4—C5—C6—C7	0.8 (5)
C3—C4—C5—N1	0.6 (5)	N2—C6—C7—C8	0.3 (5)

Symmetry code: (i)  $-x+1, y, -z+1/2$ .

#### Hydrogen-bond geometry ( $\text{\AA}, ^\circ$ )

$Cg1$  is the centroid of the N2/C6–C10 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H25 $\cdots$ N5	0.86	2.11	2.945 (5)	164
O2—H26 $\cdots$ N4 <sup>ii</sup>	0.86	2.10	2.955 (5)	175
C24—H24A $\cdots$ Cg1 <sup>iii</sup>	0.98	3.01	3.921	156

Symmetry codes: (ii)  $-x+1/2, y-1/2, -z+1/2$ ; (iii)  $-x+1/2, -y+3/2, -z$ .

#### Selected geometry parameters ( $\text{\AA}, ^\circ$ )

Ni-N1	2.088 (3)
Ni-N2	2.077 (3)
Ni-N3	2.090 (3)
N1-Ni-N2	78.64 (12)
N1-Ni-N3	95.55 (11)
N2-Ni-N3	92.87 (11)