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# Tris(2,2'-bipyridine)iron(II) bis(1,1,3,3-tetracyano-2-ethoxypropenide) dihydrate: chiral hydrogen-bonded frameworks interpenetrate in three dimensions

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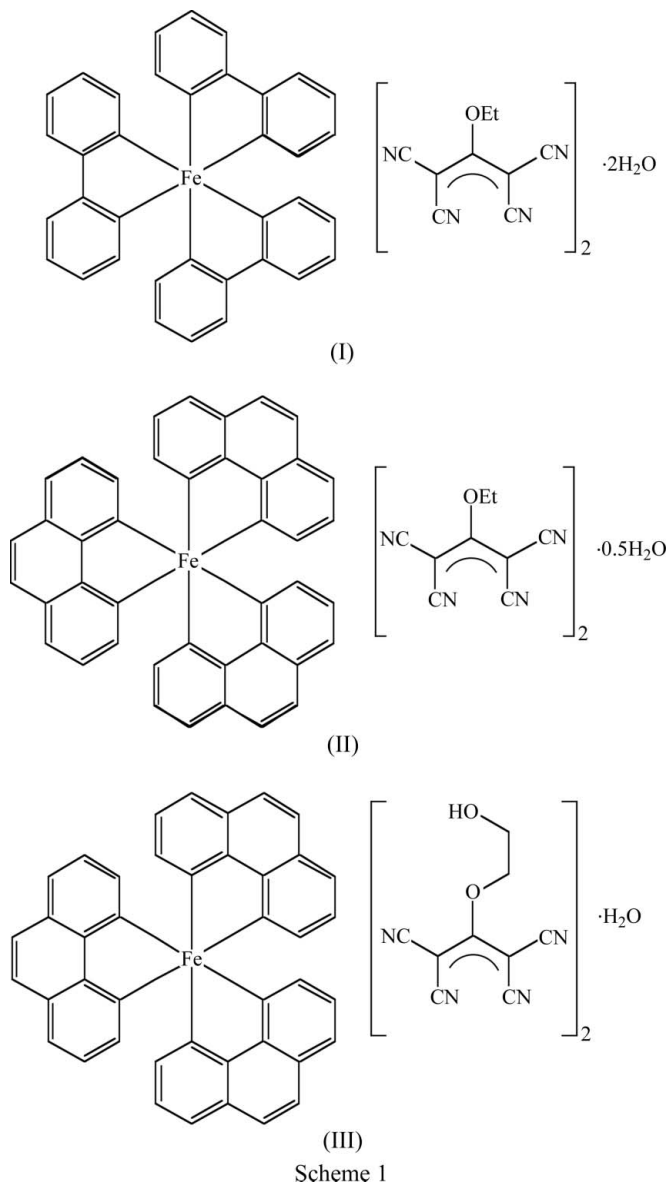
In the title compound,  $[\text{Fe}(\text{C}_{10}\text{H}_8\text{N}_2)_3](\text{C}_9\text{H}_5\text{N}_4\text{O})_2 \cdot 2\text{H}_2\text{O}$ , the chiral cations lie across twofold rotation axes in the space group  $C2/c$ . The anions and the water molecules are linked by two independent  $\text{O} \cdots \text{H} \cdots \text{N}$  hydrogen bonds to form  $C_2^2(8)$  chains, and these chains are linked by the cations *via*  $\text{C} \cdots \text{H} \cdots \text{N}$  and  $\text{C} \cdots \text{H} \cdots \text{O}$  hydrogen bonds to form two interpenetrating three-dimensional frameworks, each of which contains only one enantiomeric form of the chiral cation.

**Keywords:** crystal structure; hydrogen bonding; tris(2,2'-bipyridine)iron(II); 1,1,3,3-tetracyano-2-ethoxypropenide; interpenetrating chiral frameworks; polynitrile ligands; spin crossover (SCO) phenomenon.

## 1. Introduction

Organic polynitrile ligands have received considerable attention recently in the design of new molecular compounds exhibiting the spin crossover (SCO) phenomenon (Dupouy *et al.*, 2008, 2009; Benmansour *et al.*, 2010). Iron(II) complexes containing octahedral  $\text{FeN}_6$  coordination are amongst the most studied SCO compounds and in such materials, control over co-operative SCO behaviour is still of major interest in this field. Co-operativity is in fact responsible for steep transitions observed in the solid state and, in some cases, for hysteresis loops (Matouzenko *et al.*, 2004). Both strong interactions between metal centres and rigid supramolecular structures are required to achieve highly co-operative SCO

systems, and both hydrogen bonds and  $\pi$ - $\pi$  interactions are among the intermolecular interactions most commonly used for the construction of rigid systems (Halcrow, 2011), the potential significance of anion  $\cdots \pi$  interactions for SCO systems has recently been reported and evaluated (Quesada *et al.*, 2008; Kitchen *et al.*, 2009). Thus, the use of new families of polynitrile ligands with a tris-chelate complex cation is a particularly attractive way to better understand the role of noncovalent anion  $\cdots \pi$  interactions for the development and



synthesis of SCO materials (Ellingsworth *et al.*, 2013; Setifi, Domasevitch *et al.*, 2013). In a further exploration of low-spin iron(II) complexes offering the potential for this type of anion  $\cdots \pi$  interaction, we now report the synthesis and structure of the title compound,  $[\text{Fe}(\text{bipy})_3](\text{tcoet})_2 \cdot 2\text{H}_2\text{O}$ , (I), where bipy represents 2,2'-bipyridine and  $\text{tcoet}^-$  represents the 1,1,3,3-tetracyano-2-ethoxypropenide anion, and we compare the structure of (I) with those of related 1,10-phenanthroline complexes (II) (Setifi, Setifi *et al.*, 2013) and (III) (Setifi, Domasevitch *et al.*, 2013) (see Scheme 1).

**Table 1**  
Experimental details.

Crystal data	
Chemical formula	[Fe(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<sub>r</sub></i>	930.77
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	150
<i>a</i> , <i>b</i> , <i>c</i> (Å)	20.273 (4), 12.4463 (6), 19.4907 (16)
$\beta$ (°)	113.080 (9)
<i>V</i> (Å <sup>3</sup> )	4524.3 (9)
<i>Z</i>	4
Radiation type	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.40
Crystal size (mm)	0.16 × 0.10 × 0.05
Data collection	
Diffractometer	Bruker APEXII CCD diffractometer
Absorption correction	Multi-scan ( <i>SADABS</i> ; Sheldrick, 2003)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.842, 0.981
No. of measured, independent and observed [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] reflections	17754, 5991, 4305
<i>R<sub>int</sub></i>	0.072
( <i>sin</i> $\theta$ / $\lambda$ ) <sub>max</sub> (Å <sup>-1</sup> )	0.682
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>	0.065, 0.135, 1.09
No. of reflections	5991
No. of parameters	304
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$ , $\Delta\rho_{min}$ (e Å <sup>-3</sup> )	0.36, -0.45

Computer programs: *APEX2* (Bruker, 2009), *SAINT* (Bruker, 2009), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

## 2. Experimental

### 2.1. Synthesis and crystallization

The salt K(tcnoet) was prepared following the published method of Middleton *et al.* (1958). For the synthesis of compound (I), a solution containing iron(II) sulfate hepta-

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

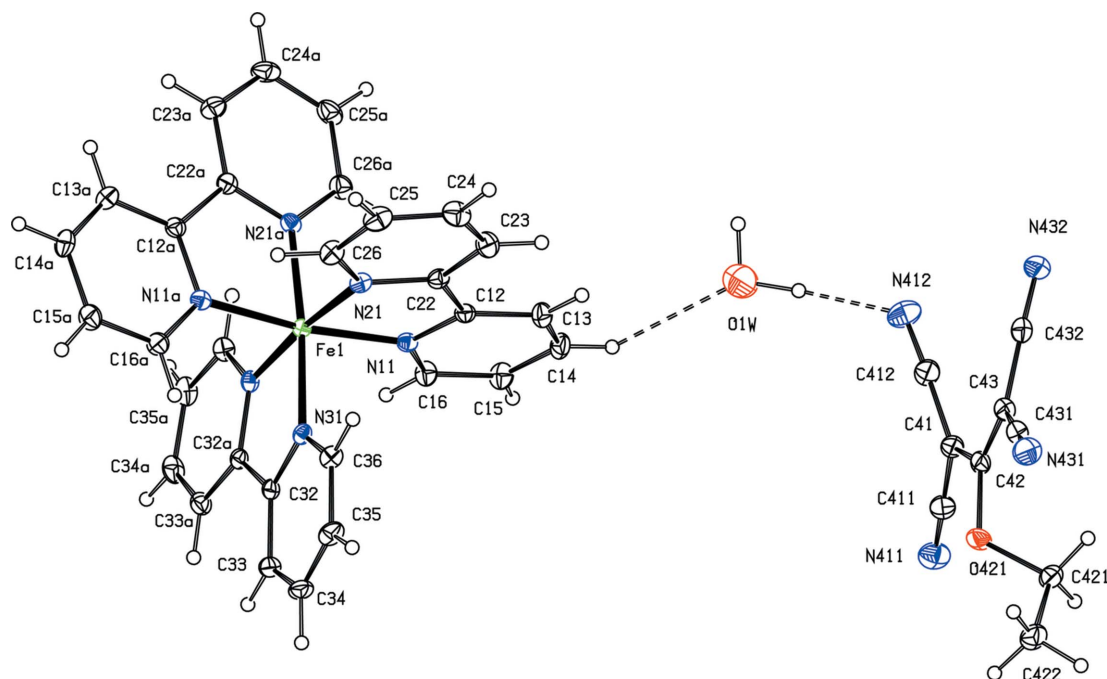
<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C14—H14...O1W	0.95	2.52	3.316 (4)	141
C15—H15...N432 <sup>i</sup>	0.95	2.50	3.296 (4)	142
C23—H23...N431 <sup>ii</sup>	0.95	2.59	3.439 (4)	148
C26—H26...Cg1 <sup>iii</sup>	0.95	2.91	3.697 (3)	141
O1W—H1A...N412	1.03	1.93	2.950 (4)	173
O1W—H1B...N411 <sup>iv</sup>	1.01	2.00	3.000 (4)	169

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

hydrate (28 mg, 0.1 mmol), 2,2'-bipyridine (15 mg, 0.1 mmol) and K(tcnoet) (45 mg, 0.2 mmol) in water (20 ml) was stirred in air for 5 min and then transferred to a Teflon-lined autoclave and heated at 433 K for 2 d. After cooling to ambient temperature, red crystals of compound (I) suitable for single-crystal X-ray diffraction were collected by filtration, washed with water and dried in air (yield 55%).

### 2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. All H atoms were located in difference maps and then treated as riding atoms. H atoms bonded to C atoms were treated as riding atoms in geometrically idealized positions, with C—H = 0.95 (aromatic), 0.98 (CH<sub>3</sub>) or 0.99 Å (CH<sub>2</sub>), and with  $U_{iso}(H) = kU_{eq}(C)$ , where  $k = 1.5$  for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 for all other H atoms bonded to C atoms. H atoms bonded to the water O atom were permitted to ride at the positions located in a difference map, with  $U_{iso}(H) =$



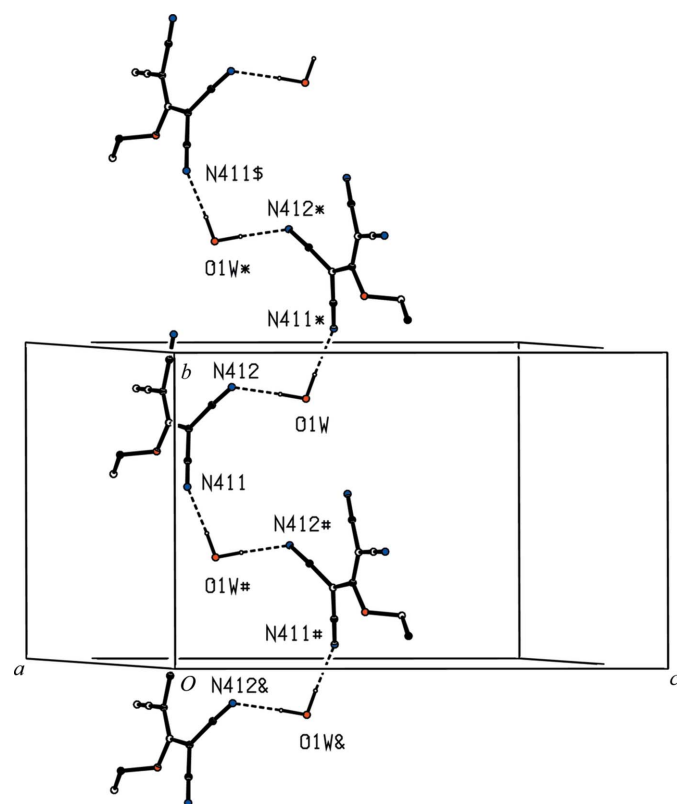
**Figure 1**

The independent components of compound (I), showing the atom-labelling scheme and the hydrogen bonds within the selected asymmetric unit. The cation has the  $\Delta$  configuration and the atoms with labels marked 'a' are at the symmetry position ( $-x + 1, y, -z + \frac{3}{2}$ ). Displacement ellipsoids are drawn at the 30% probability level.

$1.5U_{\text{eq}}(\text{O})$ , giving the O—H distances shown in Table 2. The low-angle reflection 110, which had been attenuated by the beam stop, was omitted from the refinements. No extinction correction was required. Examination of the refined structure using *PLATON* (Spek, 2009) showed the presence of four symmetry-related cavities per unit cell, each of volume  $27 \text{ \AA}^3$  and centred close to  $(0, \frac{1}{2}, \frac{1}{4})$ ,  $(0, \frac{1}{2}, \frac{3}{4})$ ,  $(\frac{1}{2}, 0, \frac{1}{4})$  and  $(\frac{1}{2}, 0, \frac{3}{4})$ . These cavities are too small to accommodate any solvent species and, consistent with this, application of the SQUEEZE procedure in *PLATON* (Spek, 2009) returned a count of zero additional electrons per unit cell.

### 3. Results and discussion

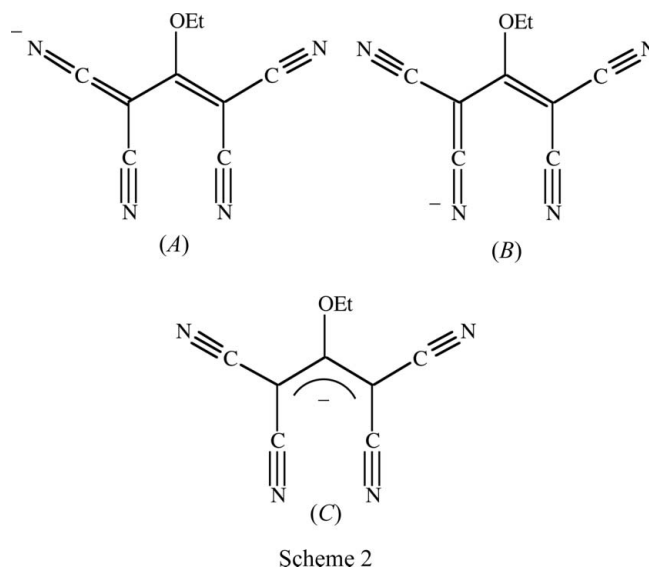
Compound (I) (Fig. 1) consists of  $[\text{Fe}(\text{bipy})_3]^{2+}$  cations lying across twofold rotation axes in the space group  $C2/c$ , together with 1,1,3,3-tetracyano-2-ethoxypropenide anions and water molecules, both occupying general positions, consistent with the overall stoichiometry  $[\text{Fe}(\text{bipy})_3](\text{tcnoet})_2 \cdot 2\text{H}_2\text{O}$ . The presence of three independent molecular components, one of them chiral, provides considerable flexibility in the selection of the asymmetric unit. The reference cation was selected to be one having the  $\Delta$  configuration and lying across the twofold



**Figure 2**  
Part of the crystal structure of compound (I), showing the formation of a  $C_2^2(8)$  hydrogen-bonded chain along  $[010]$  built from anions and water molecules. For the sake of clarity, the cations and H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (\*), a hash (#), a dollar sign (\$) or an ampersand (&) are at the symmetry positions  $(-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2})$ ,  $(-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2})$ ,  $(x, y + 1, z)$  and  $(x, y - 1, z)$ , respectively.

rotation axis along  $(\frac{1}{2}, y, \frac{3}{4})$ , and it was then possible to assemble a reasonably compact asymmetric unit in which the three independent components are linked by hydrogen bonds (Fig. 1 and Table 2). The centrosymmetric space group confirms that the compound crystallizes as a racemic mixture.

The three independent Fe—N distances (Table 3) are all closely similar, and they are similar also to the values found in compounds (II) and (III) (Scheme 1), and typical of those for low-spin  $\text{Fe}^{\text{II}}$  in octahedral  $\text{FeN}_6$  coordination (Orpen *et al.*, 1989). The bond distances in the anion (Table 3) provide a clear indication of an asymmetric electronic structure. Thus, the C41—C42 bond is longer than C42—C43, the C—CN distances involving atom C41 are shorter than those involving C43 and the C—N distances adjacent to C41 are marginally longer than those adjacent to C43. These observations taken together point to a significant contribution to the overall electronic structure of the anion by the asymmetric forms (A) and (B) (see Scheme 2), in addition to the symmetrical form (C). The shorter C—CN bonds and the longer C—N bonds involving atoms C411 and C412 are associated with the strong and nearly linear O—H $\cdots$ N hydrogen bonds which have atoms N411 and N412 as the acceptors (Table 3); by contrast, the N atoms at the other end of the anion, atoms N431 and N432, are involved only in the weaker C—H $\cdots$ N hydrogen bonds. As usually observed in anions of this type (Setifi, Domasevitch *et al.*, 2013; Setifi, Setifi *et al.*, 2013, 2014; Setifi, Lehchili *et al.*, 2014), the two  $-\text{C}(\text{CN})_2$  units in the anion of compound (I) are rotated, in conrotatory fashion, out of the plane of the central propenide fragment. The dihedral angles between the central  $\text{C}_3$  unit and the  $-\text{C}(\text{CN})_2$  units based on atoms C41 and C43 are  $13.9(4)$  and  $26.1(3)^\circ$ , respectively.



The independent components of compound (I) are linked by a combination of O—H $\cdots$ N, C—H $\cdots$ O and C—H $\cdots$ N hydrogen bonds (Table 2) to form two interpenetrating three-dimensional frameworks, whose formation is readily analysed in terms of simple substructural motifs (Ferguson *et al.*, 1998a,b; Gregson *et al.*, 2000); the anions and the water molecules together form chains, and these chains are linked by the

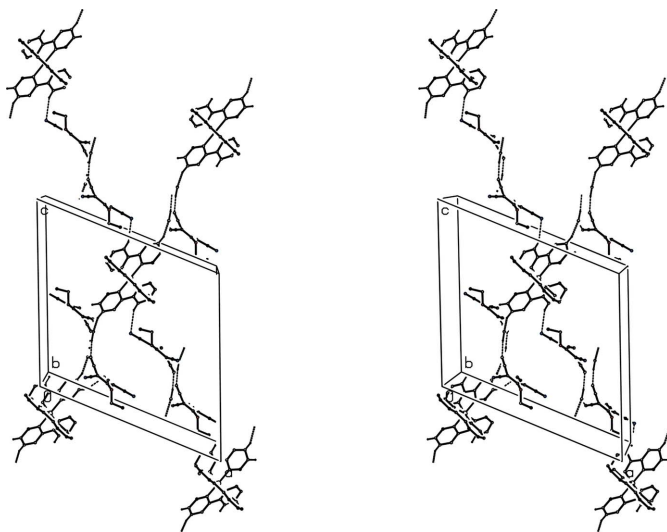
**Table 3**

Selected geometric parameters (Å, °).

Fe1—N11	1.9744 (19)	C43—C431	1.423 (4)
Fe1—N21	1.979 (2)	C43—C432	1.436 (4)
Fe1—N31	1.971 (2)	C411—N411	1.151 (4)
C41—C42	1.405 (4)	C412—N412	1.151 (4)
C41—C411	1.411 (4)	C431—N431	1.144 (4)
C41—C412	1.413 (4)	C432—N432	1.142 (4)
C42—C43	1.388 (4)		
C41—C42—C43—C431	167.2 (2)	C43—C42—C41—C411	169.1 (2)
C41—C42—C43—C432	−15.7 (4)	C43—C42—C41—C412	−15.5 (4)

cations. The reference water molecule is linked, *via* O—H···N hydrogen bonds, to the two anions at  $(x, y, z)$  and  $(-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2})$ , so generating a  $C_2^2(8)$  (Bernstein *et al.*, 1995) chain running parallel to the [010] direction and built from species related by the  $2_1$  screw axis along  $(\frac{1}{4}, y, \frac{1}{4})$  (Fig. 2). Four chains of this type pass through each unit cell built, respectively, from anions and water molecules related by the screw axes along  $(\frac{1}{4}, y, \frac{1}{4})$ ,  $(\frac{3}{4}, y, \frac{3}{4})$ ,  $(\frac{1}{4}, y, \frac{3}{4})$  and  $(\frac{3}{4}, y, \frac{1}{4})$ . Fragments of a similar  $C_2^2(8)$  chain are present in the structure of the related hemihydrate (II) (Setifi, Setifi *et al.*, 2013) (see Scheme 1). The chains in compound (II) involve only one of the two independent anions in this compound and they are not continuous, but are punctuated at random as only half of the water sites are occupied.

Each cation links four symmetry-related [010] chains by means of C—H···O hydrogen bonds. Thus the reference cation lying across the rotation axis along  $(\frac{1}{2}, y, \frac{3}{4})$  is directly linked to the [010] chains associated with the screw axes along  $(\frac{1}{4}, y, \frac{1}{4})$  and  $(\frac{3}{4}, y, \frac{3}{4})$  by means of the C—H···N hydrogen bond involving atom C15 as the donor, and to the chains associated with the screw axes along  $(\frac{3}{4}, y, \frac{1}{4})$  and  $(\frac{1}{4}, y, \frac{3}{4})$  by means of the C—H···N hydrogen bond involving atom C23 as the donor, so linking these chains into a continuous three-dimensional


**Figure 3**

A stereoview of part of the crystal structure of compound (I), showing how cations of  $\Delta$  configuration are linked to the water–anion chains along  $(\frac{1}{4}, y, \frac{1}{4})$ ,  $(\frac{3}{4}, y, \frac{1}{4})$ ,  $(\frac{1}{4}, y, \frac{3}{4})$  and  $(\frac{3}{4}, y, \frac{3}{4})$ . For the sake of clarity, H atoms not involved in the motifs shown have been omitted.

framework. Within this framework, all of the cations have the  $\Delta$  configuration, and the structure also contains a second framework, related to the first by inversion, in which all of the cations have the  $\Lambda$  configuration. The two frameworks are thus continuously interpenetrating in three dimensions, but there are no direction-specific interactions between the two inversion-related frameworks. In particular, the only C—H··· $\pi$  interaction (Table 3) lies within a cation.

The structure of compound (I) contains no  $\pi$ – $\pi$  stacking interactions. In this respect, (I) may be contrasted with the structure of monohydrate (III) (Setifi, Domasevitch *et al.*, 2013) (see Scheme 1), where the anion contains a 2-hydroxyethoxy substituent rather than the simple ethoxy substituent found in compounds (I) and (II) [although (III) was inadvertently named in the original report as a 2-hydroxyethyl derivative]. In the structure of compound (III), multiple  $\pi$ – $\pi$  stacking interactions links the cations into chains, along which cations of  $\Delta$  and  $\Lambda$  configurations alternate; however, significant  $\pi$ – $\pi$  stacking interactions are absent from the structure of compound (II). Also present in the structure of compound (III) are two rather short anion··· $\pi$  contacts within the selected asymmetric unit, and involving a single N atom and the pyridine rings of two different ligands, with N···(centroid) distances of 3.21 (3) and 3.418 (2) Å. By contrast, the shortest comparable N···(centroid) distance observed in compound (I) is much longer, at 3.835 (3) Å, between atom N432 in the reference anion and the centroid of the N11/C12–C16 ring (Fig. 3) at  $(x, -y + 2, z - \frac{1}{2})$ .

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Supporting information for this paper is available from the IUCr electronic archives (Reference: YF3061).

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## supplementary materials

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## Tris(2,2'-bipyridine)iron(II) bis(1,1,3,3-tetracyano-2-ethoxypropenide) dihydrate: chiral hydrogen-bonded frameworks interpenetrate in three dimensions

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### Computing details

Data collection: *APEX2* (Bruker, 2009); cell refinement: *APEX2* and *S SAINT* (Bruker, 2009); data reduction: *S SAINT* (Bruker, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008) and *PLATON* (Spek, 2009).

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

#### Crystal data

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

$M_r = 930.77$

Monoclinic, *C2/c*

Hall symbol: -C 2yc

$a = 20.273$  (4) Å

$b = 12.4463$  (6) Å

$c = 19.4907$  (16) Å

$\beta = 113.080$  (9)°

$V = 4524.3$  (9) Å<sup>3</sup>

$Z = 4$

$F(000) = 1928$

$D_x = 1.366$  Mg m<sup>-3</sup>

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

Cell parameters from 9124 reflections

$\theta = 3.3\text{--}34.8^\circ$

$\mu = 0.40$  mm<sup>-1</sup>

$T = 150$  K

Block, red

$0.16 \times 0.10 \times 0.05$  mm

#### Data collection

Bruker APEXII CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

$\varphi$  &  $\omega$  scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 2003)

$T_{\min} = 0.842$ ,  $T_{\max} = 0.981$

17754 measured reflections

5991 independent reflections

4305 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.072$

$\theta_{\max} = 29.0^\circ$ ,  $\theta_{\min} = 2.1^\circ$

$h = -27 \rightarrow 24$

$k = -16 \rightarrow 16$

$l = -26 \rightarrow 26$

#### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.065$

$wR(F^2) = 0.135$

$S = 1.09$

5991 reflections

304 parameters

0 restraints

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from

neighbouring sites

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0494P)^2 + 3.4815P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 0.36 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.45 \text{ e } \text{\AA}^{-3}$

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Fe1	0.5000	0.63612 (4)	0.7500	0.01652 (13)
N11	0.43186 (10)	0.64656 (16)	0.64498 (11)	0.0198 (4)
C12	0.44707 (12)	0.72318 (19)	0.60388 (13)	0.0209 (5)
C13	0.40172 (14)	0.7440 (2)	0.53006 (14)	0.0279 (6)
H13	0.4140	0.7972	0.5021	0.033*
C14	0.33899 (13)	0.6865 (2)	0.49812 (14)	0.0294 (6)
H14	0.3069	0.7005	0.4482	0.035*
C15	0.32346 (13)	0.6082 (2)	0.53967 (14)	0.0297 (6)
H15	0.2807	0.5672	0.5186	0.036*
C16	0.37092 (13)	0.5900 (2)	0.61239 (14)	0.0260 (6)
H16	0.3600	0.5354	0.6404	0.031*
N21	0.54926 (10)	0.74922 (16)	0.71649 (11)	0.0202 (4)
C22	0.51385 (12)	0.7822 (2)	0.64485 (13)	0.0213 (5)
C23	0.53931 (14)	0.8649 (2)	0.61423 (15)	0.0304 (6)
H23	0.5134	0.8866	0.5641	0.037*
C24	0.60281 (14)	0.9153 (2)	0.65759 (16)	0.0332 (6)
H24	0.6209	0.9726	0.6379	0.040*
C25	0.63942 (14)	0.8809 (2)	0.72990 (16)	0.0326 (6)
H25	0.6837	0.9133	0.7603	0.039*
C26	0.61112 (13)	0.7992 (2)	0.75755 (15)	0.0274 (6)
H26	0.6363	0.7771	0.8078	0.033*
N31	0.55029 (10)	0.51615 (16)	0.72530 (10)	0.0192 (4)
C32	0.52812 (12)	0.4162 (2)	0.73492 (12)	0.0198 (5)
C33	0.55661 (13)	0.3240 (2)	0.71713 (14)	0.0256 (6)
H33	0.5398	0.2552	0.7241	0.031*
C34	0.60933 (14)	0.3325 (2)	0.68938 (15)	0.0306 (6)
H34	0.6288	0.2703	0.6762	0.037*
C35	0.63307 (13)	0.4337 (2)	0.68120 (14)	0.0292 (6)
H35	0.6701	0.4419	0.6633	0.035*
C36	0.60264 (13)	0.5230 (2)	0.69927 (14)	0.0246 (6)
H36	0.6194	0.5921	0.6931	0.030*
C41	0.29850 (14)	0.7499 (2)	0.11874 (14)	0.0279 (6)
C42	0.35522 (13)	0.7675 (2)	0.09577 (14)	0.0277 (6)
C43	0.38757 (14)	0.8649 (2)	0.09320 (14)	0.0306 (6)
C411	0.26362 (14)	0.6494 (2)	0.10597 (15)	0.0319 (6)
N411	0.23421 (14)	0.5681 (2)	0.09626 (15)	0.0423 (6)
C412	0.27632 (14)	0.8256 (2)	0.15939 (16)	0.0336 (7)
N412	0.25669 (15)	0.8829 (2)	0.19377 (16)	0.0490 (7)
O421	0.38154 (10)	0.67546 (15)	0.07861 (11)	0.0320 (4)
C421	0.38097 (15)	0.6646 (2)	0.00419 (15)	0.0328 (7)
H42A	0.3818	0.7364	-0.0173	0.039*
H42B	0.3370	0.6267	-0.0287	0.039*
C422	0.44608 (15)	0.6018 (3)	0.01022 (16)	0.0372 (7)

H42C	0.4463	0.5326	0.0344	0.056*
H42D	0.4893	0.6423	0.0400	0.056*
H42E	0.4452	0.5893	-0.0398	0.056*
C431	0.45341 (16)	0.8685 (2)	0.08320 (15)	0.0325 (6)
N431	0.50640 (14)	0.8706 (2)	0.07531 (14)	0.0407 (6)
C432	0.35529 (15)	0.9663 (2)	0.09688 (15)	0.0336 (7)
N432	0.32946 (14)	1.0475 (2)	0.09803 (14)	0.0444 (7)
O1W	0.27576 (16)	0.8453 (2)	0.34988 (16)	0.0719 (8)
H1A	0.2652	0.8601	0.2946	0.108*
H1B	0.2792	0.9216	0.3686	0.108*

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Fe1	0.0155 (2)	0.0166 (2)	0.0175 (2)	0.000	0.00660 (17)	0.000
N11	0.0195 (10)	0.0186 (11)	0.0227 (9)	0.0007 (8)	0.0098 (8)	-0.0005 (8)
C12	0.0232 (12)	0.0187 (13)	0.0224 (11)	0.0009 (9)	0.0106 (9)	-0.0008 (10)
C13	0.0317 (14)	0.0304 (15)	0.0233 (12)	0.0002 (11)	0.0125 (10)	0.0044 (11)
C14	0.0263 (13)	0.0384 (16)	0.0188 (12)	0.0045 (11)	0.0039 (10)	0.0011 (11)
C15	0.0212 (13)	0.0354 (16)	0.0273 (13)	-0.0058 (10)	0.0037 (10)	-0.0023 (11)
C16	0.0220 (12)	0.0292 (14)	0.0242 (12)	-0.0048 (10)	0.0063 (10)	0.0006 (11)
N21	0.0191 (10)	0.0204 (11)	0.0237 (10)	-0.0035 (8)	0.0111 (8)	-0.0029 (8)
C22	0.0218 (12)	0.0222 (13)	0.0235 (12)	0.0000 (9)	0.0129 (10)	-0.0019 (10)
C23	0.0327 (14)	0.0308 (15)	0.0309 (13)	-0.0023 (12)	0.0158 (11)	0.0046 (12)
C24	0.0359 (15)	0.0270 (16)	0.0456 (17)	-0.0067 (12)	0.0256 (13)	0.0027 (13)
C25	0.0296 (14)	0.0319 (17)	0.0390 (15)	-0.0118 (11)	0.0166 (12)	-0.0091 (13)
C26	0.0236 (13)	0.0308 (15)	0.0283 (13)	-0.0046 (10)	0.0108 (10)	-0.0034 (11)
N31	0.0165 (9)	0.0233 (11)	0.0164 (9)	-0.0001 (8)	0.0049 (7)	-0.0015 (8)
C32	0.0192 (11)	0.0206 (13)	0.0153 (10)	0.0011 (9)	0.0020 (9)	0.0006 (9)
C33	0.0274 (13)	0.0224 (13)	0.0240 (12)	0.0022 (10)	0.0069 (10)	-0.0022 (10)
C34	0.0323 (14)	0.0284 (15)	0.0283 (13)	0.0112 (11)	0.0089 (11)	-0.0065 (11)
C35	0.0221 (13)	0.0385 (16)	0.0289 (13)	0.0050 (11)	0.0120 (10)	-0.0062 (12)
C36	0.0208 (12)	0.0286 (15)	0.0252 (12)	-0.0012 (10)	0.0097 (10)	-0.0029 (11)
C41	0.0266 (13)	0.0309 (15)	0.0255 (13)	0.0098 (11)	0.0094 (10)	-0.0001 (11)
C42	0.0280 (14)	0.0316 (16)	0.0212 (12)	0.0136 (11)	0.0073 (10)	0.0041 (11)
C43	0.0367 (15)	0.0294 (15)	0.0243 (12)	0.0098 (12)	0.0103 (11)	0.0033 (12)
C411	0.0309 (14)	0.0361 (18)	0.0337 (14)	0.0121 (12)	0.0181 (11)	0.0016 (13)
N411	0.0415 (15)	0.0421 (17)	0.0533 (16)	0.0046 (12)	0.0293 (12)	-0.0022 (13)
C412	0.0285 (14)	0.0407 (17)	0.0313 (14)	0.0078 (12)	0.0115 (11)	-0.0004 (13)
N412	0.0537 (17)	0.0511 (19)	0.0526 (17)	0.0065 (13)	0.0320 (14)	-0.0113 (14)
O421	0.0390 (11)	0.0284 (10)	0.0362 (10)	0.0148 (8)	0.0229 (9)	0.0049 (9)
C421	0.0348 (15)	0.0347 (17)	0.0249 (13)	0.0064 (11)	0.0073 (11)	-0.0050 (12)
C422	0.0374 (16)	0.0439 (19)	0.0344 (15)	0.0101 (13)	0.0185 (12)	-0.0034 (13)
C431	0.0419 (16)	0.0264 (15)	0.0259 (13)	0.0037 (12)	0.0097 (11)	0.0032 (12)
N431	0.0456 (15)	0.0380 (15)	0.0426 (14)	-0.0037 (12)	0.0218 (12)	-0.0023 (12)
C432	0.0392 (16)	0.0348 (17)	0.0223 (13)	0.0068 (13)	0.0074 (11)	0.0021 (12)
N432	0.0554 (16)	0.0350 (16)	0.0346 (13)	0.0173 (12)	0.0090 (12)	-0.0008 (12)
O1W	0.095 (2)	0.0594 (19)	0.0708 (18)	0.0148 (15)	0.0428 (16)	0.0088 (14)



Geometric parameters (Å, °)

Fe1—N11	1.9744 (19)	C32—C32 <sup>i</sup>	1.473 (5)
Fe1—N11 <sup>i</sup>	1.9744 (19)	C32—C33	1.389 (3)
Fe1—N21 <sup>i</sup>	1.979 (2)	C33—H33	0.9500
Fe1—N21	1.979 (2)	C33—C34	1.378 (4)
Fe1—N31	1.971 (2)	C34—H34	0.9500
Fe1—N31 <sup>i</sup>	1.971 (2)	C34—C35	1.379 (4)
N11—C12	1.356 (3)	C35—H35	0.9500
N11—C16	1.345 (3)	C35—C36	1.382 (4)
C12—C13	1.395 (3)	C36—H36	0.9500
C12—C22	1.470 (3)	C41—C42	1.405 (4)
C13—H13	0.9500	C41—C411	1.411 (4)
C13—C14	1.377 (4)	C41—C412	1.413 (4)
C14—H14	0.9500	C42—C43	1.388 (4)
C14—C15	1.380 (4)	C42—O421	1.360 (3)
C15—H15	0.9500	C43—C431	1.423 (4)
C15—C16	1.384 (3)	C43—C432	1.436 (4)
C16—H16	0.9500	C411—N411	1.151 (4)
N21—C22	1.359 (3)	C412—N412	1.151 (4)
N21—C26	1.347 (3)	O421—C421	1.452 (3)
C22—C23	1.387 (4)	C421—H42A	0.9900
C23—H23	0.9500	C421—H42B	0.9900
C23—C24	1.383 (4)	C421—C422	1.499 (4)
C24—H24	0.9500	C422—H42C	0.9800
C24—C25	1.378 (4)	C422—H42D	0.9800
C25—H25	0.9500	C422—H42E	0.9800
C25—C26	1.377 (4)	C431—N431	1.144 (4)
C26—H26	0.9500	C432—N432	1.142 (4)
N31—C32	1.360 (3)	O1W—H1A	1.0292
N31—C36	1.347 (3)	O1W—H1B	1.0099
N11—Fe1—N11 <sup>i</sup>	172.46 (12)	N21—C26—C25	122.8 (2)
N11 <sup>i</sup> —Fe1—N21	93.27 (8)	N21—C26—H26	118.6
N11—Fe1—N21 <sup>i</sup>	93.26 (8)	C25—C26—H26	118.6
N11 <sup>i</sup> —Fe1—N21 <sup>i</sup>	81.35 (8)	C32—N31—Fe1	115.38 (16)
N11—Fe1—N21	81.35 (8)	C36—N31—Fe1	127.14 (17)
N21—Fe1—N21 <sup>i</sup>	89.33 (12)	C36—N31—C32	117.5 (2)
N31—Fe1—N11	90.87 (8)	N31—C32—C32 <sup>i</sup>	113.83 (14)
N31 <sup>i</sup> —Fe1—N11 <sup>i</sup>	90.87 (8)	N31—C32—C33	122.0 (2)
N31 <sup>i</sup> —Fe1—N11	94.84 (8)	C33—C32—C32 <sup>i</sup>	124.21 (16)
N31—Fe1—N11 <sup>i</sup>	94.84 (8)	C32—C33—H33	120.1
N31—Fe1—N21	94.70 (8)	C34—C33—C32	119.8 (3)
N31—Fe1—N21 <sup>i</sup>	174.62 (8)	C34—C33—H33	120.1
N31 <sup>i</sup> —Fe1—N21	174.62 (8)	C33—C34—H34	120.8
N31 <sup>i</sup> —Fe1—N21 <sup>i</sup>	94.70 (8)	C33—C34—C35	118.4 (2)
N31—Fe1—N31 <sup>i</sup>	81.50 (12)	C35—C34—H34	120.8
C12—N11—Fe1	115.46 (15)	C34—C35—H35	120.2
C16—N11—Fe1	126.50 (17)	C34—C35—C36	119.6 (3)
C16—N11—C12	117.9 (2)	C36—C35—H35	120.2

N11—C12—C13	122.0 (2)	N31—C36—C35	122.8 (3)
N11—C12—C22	113.9 (2)	N31—C36—H36	118.6
C13—C12—C22	124.2 (2)	C35—C36—H36	118.6
C12—C13—H13	120.4	C42—C41—C411	119.9 (2)
C14—C13—C12	119.2 (2)	C42—C41—C412	123.7 (3)
C14—C13—H13	120.4	C411—C41—C412	116.3 (3)
C13—C14—H14	120.5	C43—C42—C41	127.2 (2)
C13—C14—C15	119.0 (2)	O421—C42—C41	113.3 (2)
C15—C14—H14	120.5	O421—C42—C43	119.4 (2)
C14—C15—H15	120.4	C42—C43—C431	121.0 (3)
C14—C15—C16	119.3 (2)	C42—C43—C432	122.3 (3)
C16—C15—H15	120.4	C431—C43—C432	116.7 (3)
N11—C16—C15	122.6 (2)	N411—C411—C41	178.5 (3)
N11—C16—H16	118.7	N412—C412—C41	176.4 (4)
C15—C16—H16	118.7	C42—O421—C421	118.3 (2)
C22—N21—Fe1	114.96 (15)	O421—C421—H42A	110.1
C26—N21—Fe1	127.25 (17)	O421—C421—H42B	110.1
C26—N21—C22	117.7 (2)	O421—C421—C422	108.0 (2)
N21—C22—C12	114.2 (2)	H42A—C421—H42B	108.4
N21—C22—C23	122.0 (2)	C422—C421—H42A	110.1
C23—C22—C12	123.8 (2)	C422—C421—H42B	110.1
C22—C23—H23	120.4	C421—C422—H42C	109.5
C24—C23—C22	119.2 (2)	C421—C422—H42D	109.5
C24—C23—H23	120.4	C421—C422—H42E	109.5
C23—C24—H24	120.5	H42C—C422—H42D	109.5
C25—C24—C23	118.9 (3)	H42C—C422—H42E	109.5
C25—C24—H24	120.5	H42D—C422—H42E	109.5
C24—C25—H25	120.4	N431—C431—C43	179.5 (3)
C26—C25—C24	119.3 (2)	N432—C432—C43	178.3 (3)
C26—C25—H25	120.4	H1A—O1W—H1B	99.5
Fe1—N11—C12—C13	-176.4 (2)	N21—Fe1—N31—C36	3.60 (19)
Fe1—N11—C12—C22	2.3 (3)	N21—C22—C23—C24	0.3 (4)
Fe1—N11—C16—C15	175.1 (2)	C22—C12—C13—C14	-177.4 (2)
Fe1—N21—C22—C12	-3.3 (3)	C22—N21—C26—C25	-0.2 (4)
Fe1—N21—C22—C23	176.4 (2)	C22—C23—C24—C25	0.7 (4)
Fe1—N21—C26—C25	-176.8 (2)	C23—C24—C25—C26	-1.4 (4)
Fe1—N31—C32—C32 <sup>i</sup>	-2.2 (3)	C24—C25—C26—N21	1.2 (4)
Fe1—N31—C32—C33	177.50 (17)	C26—N21—C22—C12	179.7 (2)
Fe1—N31—C36—C35	-177.79 (18)	C26—N21—C22—C23	-0.6 (4)
N11—Fe1—N21—C22	3.54 (17)	N31—Fe1—N11—C12	-97.82 (18)
N11 <sup>i</sup> —Fe1—N21—C22	-171.15 (17)	N31 <sup>i</sup> —Fe1—N11—C12	-179.37 (17)
N11—Fe1—N21—C26	-179.8 (2)	N31 <sup>i</sup> —Fe1—N11—C16	4.6 (2)
N11 <sup>i</sup> —Fe1—N21—C26	5.5 (2)	N31—Fe1—N11—C16	86.2 (2)
N11 <sup>i</sup> —Fe1—N31—C32	91.00 (16)	N31—Fe1—N21—C22	93.71 (17)
N11—Fe1—N31—C32	-93.92 (16)	N31—Fe1—N21—C26	-89.7 (2)
N11—Fe1—N31—C36	84.99 (19)	N31 <sup>i</sup> —Fe1—N31—C32	0.84 (11)
N11 <sup>i</sup> —Fe1—N31—C36	-90.1 (2)	N31 <sup>i</sup> —Fe1—N31—C36	179.8 (2)
N11—C12—C13—C14	1.1 (4)	N31—C32—C33—C34	0.5 (3)

N11—C12—C22—N21	0.6 (3)	C32—N31—C36—C35	1.1 (3)
N11—C12—C22—C23	-179.1 (2)	C32 <sup>i</sup> —C32—C33—C34	-179.8 (3)
C12—N11—C16—C15	-0.9 (4)	C32—C33—C34—C35	1.0 (4)
C12—C13—C14—C15	-1.3 (4)	C33—C34—C35—C36	-1.4 (4)
C12—C22—C23—C24	180.0 (2)	C34—C35—C36—N31	0.4 (4)
C13—C12—C22—N21	179.3 (2)	C36—N31—C32—C32 <sup>i</sup>	178.7 (2)
C13—C12—C22—C23	-0.4 (4)	C36—N31—C32—C33	-1.5 (3)
C13—C14—C15—C16	0.5 (4)	C41—C42—C43—C431	167.2 (2)
C14—C15—C16—N11	0.6 (4)	C41—C42—C43—C432	-15.7 (4)
C16—N11—C12—C13	0.0 (4)	C41—C42—O421—C421	122.0 (2)
C16—N11—C12—C22	178.7 (2)	C42—O421—C421—C422	145.8 (2)
N21 <sup>i</sup> —Fe1—N11—C12	85.63 (18)	C43—C42—C41—C411	169.1 (2)
N21—Fe1—N11—C12	-3.20 (17)	C43—C42—C41—C412	-15.5 (4)
N21—Fe1—N11—C16	-179.2 (2)	C43—C42—O421—C421	-61.3 (3)
N21 <sup>i</sup> —Fe1—N11—C16	-90.4 (2)	C411—C41—C42—O421	-14.6 (3)
N21 <sup>i</sup> —Fe1—N21—C22	-89.86 (17)	C412—C41—C42—O421	160.8 (2)
N21 <sup>i</sup> —Fe1—N21—C26	86.8 (2)	O421—C42—C43—C431	-8.9 (4)
N21—Fe1—N31—C32	-175.31 (16)	O421—C42—C43—C432	168.2 (2)

Symmetry code: (i)  $-x+1, y, -z+3/2$ .

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

Cg1 represents the centroid of the N11/C12–C16 ring.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C14—H14 $\cdots$ O1W	0.95	2.52	3.316 (4)	141
C15—H15 $\cdots$ N432 <sup>ii</sup>	0.95	2.50	3.296 (4)	142
C23—H23 $\cdots$ N431 <sup>iii</sup>	0.95	2.59	3.439 (4)	148
C26—H26 $\cdots$ Cg1 <sup>i</sup>	0.95	2.91	3.697 (3)	141
O1W—H1A $\cdots$ N412	1.03	1.93	2.950 (4)	173
O1W—H1B $\cdots$ N411 <sup>iv</sup>	1.01	2.00	3.000 (4)	169

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