



Crystal structure of poly[(2,2'-bipyridine- κ^2N,N')-tetrakis(μ -cyanido- $\kappa^2N:C$)dinickel(II)]

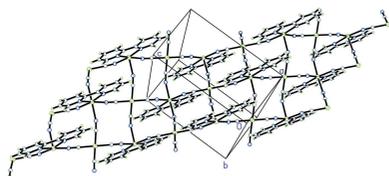
Minghui Zuo, Haiyu Wang, Jie Xu, Lingling Zhu and Shuxin Cui*

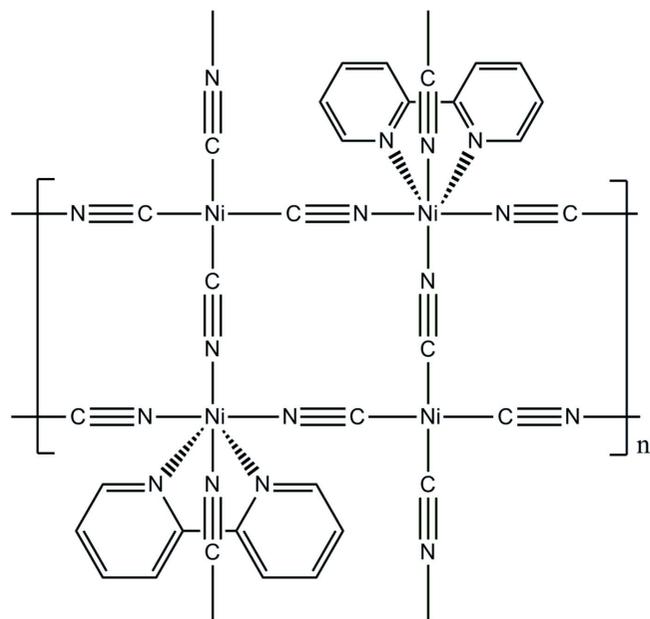
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The polymeric title complex, $[\text{Ni}_2(\text{CN})_4(\text{C}_{10}\text{H}_8\text{N}_2)]_n$, was obtained serendipitously under hydrothermal conditions. The asymmetric unit consists of one half of an $[\text{Ni}(\text{CN})_4]^{2-}$ anion with the Ni^{2+} cation situated on an inversion centre, and one half of an $[\text{Ni}(2,2'\text{-bpy})]^{2+}$ cation (2,2'-bpy is 2,2'-bipyridine), with the second Ni^{2+} cation situated on a twofold rotation axis. The two Ni^{2+} cations exhibit different coordination spheres. Whereas the coordination of the metal in the anion is that of a slightly distorted square defined by four C-bound cyanide ligands, the coordination in the cation is that of a distorted octahedron defined by four N-bound cyanide ligands and two N atoms from the chelating 2,2'-bpy ligand. The two different Ni^{2+} cations are alternately bridged by the cyanide ligands, resulting in a two-dimensional structure extending parallel to (010). Within the sheets, π - π interactions between pyridine rings of neighbouring 2,2'-bpy ligands, with a centroid-to-centroid distance of 3.687 (3) Å, are present. The crystal packing is dominated by van der Waals forces. A weak C—H \cdots N interaction between adjacent sheets is also observed.

1. Chemical context

Coordination metal complexes have been the subject of intensive investigation not only due to their potential application to material science as catalytic, conductive, luminescent, magnetic, porous, chiral or non-linear optical materials (Janiak *et al.*, 2003), but also because of their intriguing structural diversity (Kong *et al.*, 2008). The assembly of functional molecular building blocks into crystalline polymeric materials through coordination bonds or other weak interactions has many advantages over traditional stepwise syntheses and was demonstrated to be an effective approach to fabricating new materials (Kopotkov *et al.*, 2014). Using this approach, numerous materials with interesting structures and properties have been prepared through the reactions of cyanidometallate building blocks (Cui *et al.*, 2011; Zhang & Lachgar, 2015). These compounds show novel functionalities due to strong interactions mediated by the linear cyanide bridges. The probably oldest and most interesting example is the Prussian blue framework, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot 14\text{H}_2\text{O}$, and its analogues derived from the assembly of hexacyanidometallate anions $[\text{M}(\text{CN})_6]_n$ and transition-metal ions (Li *et al.*, 2008). For instance, cyanide-bridged bimetallic assemblies were obtained from $\text{K}_3[\text{Fe}(\text{CN})_6]$ as a source of cyanidometallate anions, metal cations, and aromatic nitrogen-containing ligands. These compounds show interesting magnetic and other properties that can be affected through the careful choice of the building-block components (Shen *et al.*, 2014).





Our own efforts are focused to assemble metallic complexes and the achievement of tuning their properties by crystal engineering of the terminal/bridging ligands. However, the hydrothermal reaction of Ni(acetate)₂, 2,2'-bipyridine and K₃[Fe(CN)₆] did not yield the expected bimetallic system analogous to coordinated iron ions which were reported in literature (Colacio *et al.*, 2003), but to the serendipitous formation of the polymeric complex (I), [Ni₂(CN)₄(C₁₀H₈N₂)_n], the crystal structure of which is reported here.

2. Structural commentary

The asymmetric unit of the structure of (I) contains formally one half of an [Ni(CN)₄]²⁻ (Ni1) anion, and one half of an

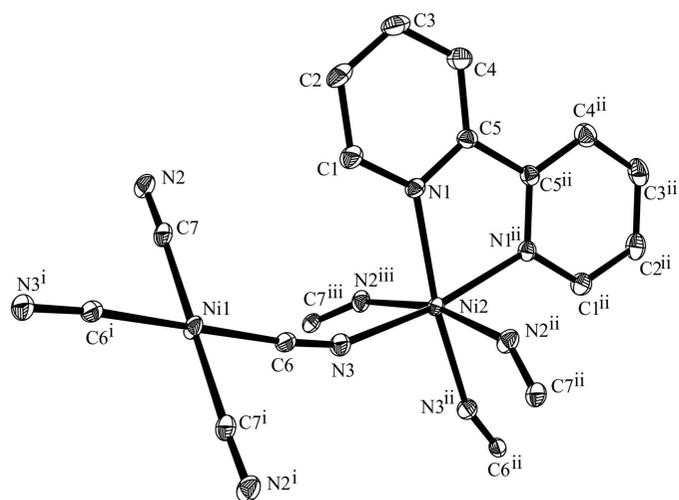


Figure 1
The principal building units of complex (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. For symmetry codes, see text.

Table 1
Selected bond lengths (Å).

Ni1—C6	1.863 (3)	Ni2—N1	2.102 (2)
Ni1—C7	1.871 (3)	Ni2—N2 ⁱ	2.116 (2)
Ni2—N3	2.071 (2)		

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

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>
C1—H1...N3	0.96 (3)	2.54 (3)	3.129 (3)	120 (2)

[Ni(2,2'-bpy)]²⁺ (Ni2) cation (2,2'-bpy is 2,2'-bipyridine). The anion is completed by inversion symmetry, whereas the cation is completed by a twofold rotation axis (Fig. 1). The Ni1 atom shows a slightly distorted square-planar geometry through coordination by four C atoms (C6 and C6ⁱ, C7 and C7ⁱ) [symmetry code: (i) $x + 2, -y, -z + 1$] from four cyanide groups, bridging Ni1 to four adjacent Ni2 atoms. The latter exhibits an overall distorted octahedral environment, being defined by four N atoms (N3, N3ⁱⁱ, N2ⁱⁱ, N2ⁱⁱⁱ) [symmetry codes: (ii) $-x + 1, y, -z + \frac{3}{2}$; (iii) $x - 1, y, z$] from four [Ni(CN)₄]²⁻ groups, and two N atoms (N1 and N1ⁱⁱ) of one 2,2'-bpy ligand. The corresponding N1—Ni2—N1 bite angle is 77.32 (13)°. Relevant bond lengths involving the two metal cations are compiled in Table 1. As depicted in Fig. 2, the cyanide groups bridge nickel cations, forming undulating sheets of composition [Ni₂(CN)₄(2,2'-bpy)₂] parallel to (010), constituted by alternation of Ni1 and Ni2 ions.

3. Supramolecular features

Within a sheet, π - π interactions between pyridine rings with a centroid-to-centroid distance of 3.687 (3) Å are present. The adhesion of the sheets in the crystal packing is dominated by van der Waals forces. However, a weak non-classical C—H...N interaction (Table 2) between neighbouring sheets may participate in the stabilization of the crystal packing.

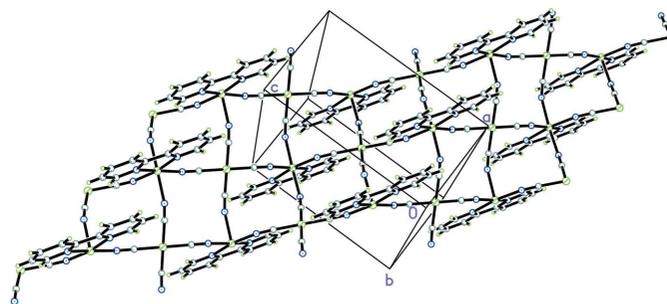


Figure 2
A view of the polymeric sheet of complex (I). Ni atoms are represented by hatched green spheres, C atoms are grey, N atoms blue and H atoms green.

Table 3
Experimental details.

Crystal data	
Chemical formula	[Ni ₂ (CN) ₄ (C ₁₀ H ₈ N ₂)]
<i>M_r</i>	377.68
Crystal system, space group	Monoclinic, <i>C2/c</i>
Temperature (K)	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.519 (5), 16.698 (5), 12.019 (5)
β (°)	90.852 (5)
<i>V</i> (Å ³)	1308.2 (12)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	2.88
Crystal size (mm)	0.40 × 0.10 × 0.06
Data collection	
Diffractometer	Siemens SMART CCD
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	3858, 1156, 1039
<i>R</i> _{int}	0.032
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.594
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.028, 0.074, 1.10
No. of reflections	1156
No. of parameters	118
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.71, -0.40

Computer programs: *SMART* and *SAINT* (Bruker, 2007), *SHELXS97*, *SHELXL97* and *XP* in *SHELXTL* (Sheldrick, 2008).

4. Synthesis and crystallization

Ni(acetate)₂ (0.159 g, 0.64 mmol), 2,2'-bipyridine (0.047 g, 0.3 mmol) and K₃[Fe(CN)₆] (0.21 g, 0.64 mmol) dissolved in aqueous solution of 1M NaCl (8 ml) were added to a 15 ml Teflon-lined autoclave and heated at 433 K for 3 d. The

autoclave was then cooled to room temperature. Green block-shaped crystals of (I) deposited on the wall of the container and were collected and air-dried.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. Hydrogen atoms bound to carbon were found in a difference map and were refined with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Acknowledgements

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supporting information

Acta Cryst. (2015). E71, 709-711 [doi:10.1107/S2056989015009706]

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Computing details

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINTE* (Bruker, 2007); data reduction: *SAINTE* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

Poly[(2,2'-bipyridine- κ^2N,N')tetrakis(μ -cyanido- $\kappa^2N:C$)dinickel(II)]

Crystal data

$[\text{Ni}_2(\text{CN})_4(\text{C}_{10}\text{H}_8\text{N}_2)]$

$M_r = 377.68$

Monoclinic, *C2/c*

Hall symbol: -C 2yc

$a = 6.519$ (5) Å

$b = 16.698$ (5) Å

$c = 12.019$ (5) Å

$\beta = 90.852$ (5)°

$V = 1308.2$ (12) Å³

$Z = 4$

$F(000) = 760$

$D_x = 1.918$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71069$ Å

Cell parameters from 3858 reflections

$\theta = 1.0\text{--}25.0^\circ$

$\mu = 2.88$ mm⁻¹

$T = 293$ K

Block, green

$0.40 \times 0.10 \times 0.06$ mm

Data collection

Siemens SMART CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 9 pixels mm⁻¹

ω scans

3858 measured reflections

1156 independent reflections

1039 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 3.4^\circ$

$h = -7 \rightarrow 7$

$k = -19 \rightarrow 16$

$l = -14 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.028$

$wR(F^2) = 0.074$

$S = 1.10$

1156 reflections

118 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 atoms treated by a mixture of independent
and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0374P)^2 + 0.9543P]$

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

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

$\Delta\rho_{\text{max}} = 0.71$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.40$ e Å⁻³

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	1.0000	0.0000	0.5000	0.01983 (19)
Ni2	0.5000	0.12867 (3)	0.7500	0.01682 (18)
C6	0.8027 (4)	0.02639 (16)	0.6043 (2)	0.0207 (6)
C1	0.8426 (4)	0.22353 (19)	0.6347 (3)	0.0275 (7)
N3	0.6828 (3)	0.04836 (14)	0.6654 (2)	0.0242 (5)
N1	0.6675 (3)	0.22697 (13)	0.6906 (2)	0.0198 (5)
C5	0.5950 (4)	0.29952 (16)	0.7170 (2)	0.0207 (6)
C7	1.1817 (4)	0.07283 (17)	0.5669 (2)	0.0220 (6)
C4	0.6937 (5)	0.36889 (18)	0.6855 (3)	0.0305 (7)
N2	1.2931 (3)	0.11329 (14)	0.6143 (2)	0.0240 (5)
C3	0.8723 (5)	0.3640 (2)	0.6262 (3)	0.0343 (8)
C2	0.9471 (5)	0.29004 (19)	0.6008 (3)	0.0317 (7)
H2	1.062 (5)	0.284 (2)	0.562 (3)	0.043 (10)*
H4	0.636 (4)	0.4223 (19)	0.711 (3)	0.031 (8)*
H1	0.892 (5)	0.171 (2)	0.616 (3)	0.033 (9)*
H3	0.940 (5)	0.409 (2)	0.608 (3)	0.038 (9)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ni1	0.0146 (3)	0.0249 (3)	0.0202 (3)	-0.00164 (17)	0.0062 (2)	-0.0069 (2)
Ni2	0.0146 (3)	0.0183 (3)	0.0177 (3)	0.000	0.0058 (2)	0.000
C6	0.0184 (13)	0.0189 (14)	0.0248 (16)	-0.0028 (11)	0.0033 (12)	-0.0031 (12)
C1	0.0244 (15)	0.0288 (17)	0.0297 (18)	-0.0016 (12)	0.0091 (13)	-0.0005 (13)
N3	0.0212 (12)	0.0240 (13)	0.0275 (15)	0.0002 (9)	0.0066 (11)	-0.0042 (11)
N1	0.0186 (11)	0.0217 (12)	0.0192 (13)	-0.0020 (9)	0.0026 (9)	0.0021 (10)
C5	0.0217 (14)	0.0197 (15)	0.0208 (16)	-0.0016 (10)	-0.0013 (12)	0.0022 (11)
C7	0.0176 (13)	0.0254 (15)	0.0233 (16)	0.0018 (11)	0.0084 (12)	-0.0024 (12)
C4	0.0314 (17)	0.0264 (17)	0.034 (2)	-0.0035 (12)	0.0005 (14)	0.0030 (13)
N2	0.0187 (12)	0.0289 (13)	0.0245 (15)	-0.0021 (10)	0.0054 (10)	-0.0033 (11)
C3	0.0331 (18)	0.0323 (19)	0.037 (2)	-0.0125 (14)	0.0004 (15)	0.0098 (15)
C2	0.0241 (16)	0.0390 (19)	0.0323 (19)	-0.0083 (13)	0.0084 (14)	0.0054 (15)

Geometric parameters (Å, °)

Ni1—C6 ⁱ	1.863 (3)	C1—C2	1.368 (4)
Ni1—C6	1.863 (3)	C1—H1	0.95 (3)
Ni1—C7 ⁱ	1.871 (3)	N1—C5	1.340 (3)
Ni1—C7	1.871 (3)	C5—C4	1.381 (4)
Ni2—N3 ⁱⁱ	2.071 (2)	C5—C5 ⁱⁱ	1.480 (5)
Ni2—N3	2.071 (2)	C7—N2	1.139 (4)
Ni2—N1	2.102 (2)	C4—C3	1.377 (5)
Ni2—N1 ⁱⁱ	2.102 (2)	C4—H4	1.02 (3)
Ni2—N2 ⁱⁱⁱ	2.116 (2)	N2—Ni2 ^v	2.116 (2)
Ni2—N2 ^{iv}	2.116 (2)	C3—C2	1.364 (5)
C6—N3	1.140 (4)	C3—H3	0.90 (4)
C1—N1	1.335 (4)	C2—H2	0.89 (4)
C6 ⁱ —Ni1—C6	180.0	N1—C1—C2	123.3 (3)
C6 ⁱ —Ni1—C7 ⁱ	89.76 (12)	N1—C1—H1	117 (2)
C6—Ni1—C7 ⁱ	90.24 (12)	C2—C1—H1	120 (2)
C6 ⁱ —Ni1—C7	90.24 (12)	C6—N3—Ni2	158.3 (2)
C6—Ni1—C7	89.76 (12)	C1—N1—C5	117.7 (2)
C7 ⁱ —Ni1—C7	180.00 (13)	C1—N1—Ni2	126.15 (19)
N3 ⁱⁱ —Ni2—N3	99.29 (14)	C5—N1—Ni2	116.02 (18)
N3 ⁱⁱ —Ni2—N1	167.94 (10)	N1—C5—C4	121.7 (3)
N3—Ni2—N1	91.91 (10)	N1—C5—C5 ⁱⁱ	115.32 (15)
N3 ⁱⁱ —Ni2—N1 ⁱⁱ	91.91 (10)	C4—C5—C5 ⁱⁱ	122.95 (18)
N3—Ni2—N1 ⁱⁱ	167.94 (10)	N2—C7—Ni1	174.8 (3)
N1—Ni2—N1 ⁱⁱ	77.32 (13)	C3—C4—C5	119.6 (3)
N3 ⁱⁱ —Ni2—N2 ⁱⁱⁱ	86.28 (10)	C3—C4—H4	122.1 (18)
N3—Ni2—N2 ⁱⁱⁱ	84.71 (10)	C5—C4—H4	118.2 (18)
N1—Ni2—N2 ⁱⁱⁱ	99.29 (9)	C7—N2—Ni2 ^v	148.4 (2)
N1 ⁱⁱ —Ni2—N2 ⁱⁱⁱ	91.61 (9)	C2—C3—C4	118.5 (3)
N3 ⁱⁱ —Ni2—N2 ^{iv}	84.71 (10)	C2—C3—H3	122 (2)
N3—Ni2—N2 ^{iv}	86.28 (10)	C4—C3—H3	120 (2)
N1—Ni2—N2 ^{iv}	91.61 (9)	C3—C2—C1	119.1 (3)
N1 ⁱⁱ —Ni2—N2 ^{iv}	99.29 (9)	C3—C2—H2	122 (2)
N2 ⁱⁱⁱ —Ni2—N2 ^{iv}	166.06 (13)	C1—C2—H2	119 (2)
N3—C6—Ni1	174.8 (2)		
N3 ⁱⁱ —Ni2—N3—C6	173.2 (7)	N3—Ni2—N1—C5	174.8 (2)
N1—Ni2—N3—C6	-11.3 (6)	N1 ⁱⁱ —Ni2—N1—C5	0.33 (14)
N1 ⁱⁱ —Ni2—N3—C6	15.2 (9)	N2 ⁱⁱⁱ —Ni2—N1—C5	89.9 (2)
N2 ⁱⁱⁱ —Ni2—N3—C6	87.8 (6)	N2 ^{iv} —Ni2—N1—C5	-98.8 (2)
N2 ^{iv} —Ni2—N3—C6	-102.8 (6)	C1—N1—C5—C4	1.7 (4)
C2—C1—N1—C5	-1.9 (5)	Ni2—N1—C5—C4	178.3 (2)
C2—C1—N1—Ni2	-178.2 (2)	C1—N1—C5—C5 ⁱⁱ	-177.6 (3)
N3 ⁱⁱ —Ni2—N1—C1	149.5 (4)	Ni2—N1—C5—C5 ⁱⁱ	-0.9 (4)
N3—Ni2—N1—C1	-8.8 (2)	N1—C5—C4—C3	-0.6 (5)
N1 ⁱⁱ —Ni2—N1—C1	176.7 (3)	C5 ⁱⁱ —C5—C4—C3	178.6 (3)

N2 ⁱⁱⁱ —Ni2—N1—C1	−93.7 (2)	C5—C4—C3—C2	−0.3 (5)
N2 ^{iv} —Ni2—N1—C1	77.5 (2)	C4—C3—C2—C1	0.1 (5)
N3 ⁱⁱ —Ni2—N1—C5	−26.9 (5)	N1—C1—C2—C3	1.0 (5)

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

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
C1—H1 \cdots N3	0.96 (3)	2.54 (3)	3.129 (3)	120 (2)