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# *catena*-Poly[[[tetraaquazinc(II)]-$\mu$-4-amino-3,5-di-3-pyridyl-4*H*-1,2,4-triazole] sulfate monohydrate] and poly[[bis($\mu$-4-amino-3,5-di-4-pyridyl-4*H*-1,2,4-triazole)diaquacopper(II)] dinitrate octahydrate]

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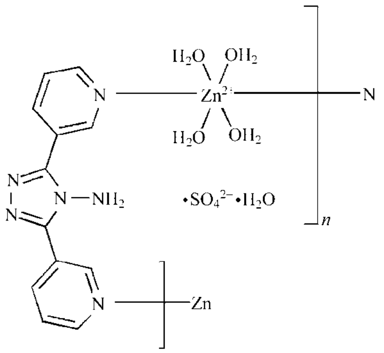
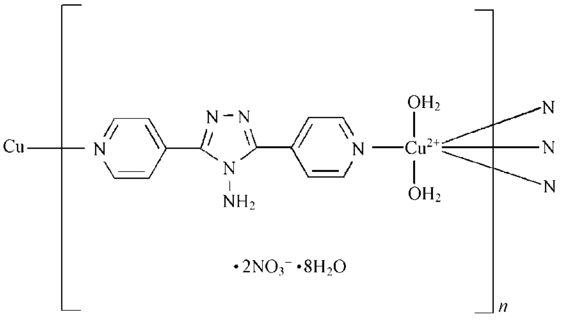
The isomeric bent triazole-containing ligands 4-amino-3,5-di-3-pyridyl-4*H*-1,2,4-triazole (*L*1) and 4-amino-3,5-di-4-pyridyl-4*H*-1,2,4-triazole (*L*2) have been used to create the two novel title complexes *catena*-poly[[[tetraaquazinc(II)]-$\mu$-4-amino-3,5-di-3-pyridyl-4*H*-1,2,4-triazole] sulfate monohydrate], $\{[Zn(C_{12}H_{10}N_6)(H_2O)_4]SO_4\cdot H_2O\}_n$, (I), and poly[[diaquabis($\mu$-4-amino-3,5-di-4-pyridyl-4*H*-1,2,4-triazole)copper(II)] dinitrate octahydrate], $\{[Cu(C_{12}H_{10}N_6)_2(H_2O)_2](NO_3)_2\cdot 8H_2O\}_n$, (II). The $Zn^{II}$ and $Cu^{II}$ atoms are all six-coordinated in approximately octahedral environments. Compound (I) presents a sinusoidal chain generated by $ZnO_4$ cores which are bridged by *L*1 ligands in a *cisoid* conformation. These sinusoidal chains are bound to each other by O—H$\cdots$O hydrogen bonds between coordinated water molecules of neighboring chains into a two-dimensional network. These layers stack in an ...*ABAB*... sequence and are further linked into a three-dimensional framework through O—H$\cdots$N hydrogen bonds between coordinated water molecules and the N atoms of the triazole rings. In (II), the $Cu^{II}$ centers are bridged by the *L*2 ligands to form a two-dimensional network with square grids. All of the two-dimensional nets also stack alternately along the crystallographic *a* axis. Neighboring layers are further linked into a three-dimensional framework *via* interlayer N—H$\cdots$N hydrogen bonds between –$NH_2$ groups of the triazole rings and the N atoms in the triazole rings.

## Comment

Intelligent ligand design and the proper choice of a metal center are the main keys to the design of intriguing and functional coordination polymers (Gardner *et al.*, 1995; Natarajan *et al.*, 2005). It is well known that the relative orientations of the nitrogen donors and variation of the bridging space may result in unusual building blocks, which can lead to the construction of supramolecular motifs that have not been achieved using normal rigid linear organic ligands. As part of our continuing study of coordination polymers with bridging nitrogen-donor ligands (Dong *et al.*, 2003), we report here two novel coordination polymers, namely, *catena*-poly[[[tetraaquazinc(II)]-$\mu$-4-amino-3,5-di-3-pyridyl-4*H*-1,2,4-triazole] sulfate monohydrate], (I), and poly[[diaquabis($\mu$-4-amino-3,5-di-4-pyridyl-4*H*-1,2,4-triazole)copper(II)] dinitrate octahydrate], (II), generated from the isomeric bent ligands 4-amino-3,5-di-3-pyridyl-1,2,4-triazole (*L*1) and 4-amino-3,5-di-4-pyridyl-1,2,4-triazole (*L*2), respectively.



(I)



(II)

Compound (I) crystallizes with only one type of crystallographic $Zn^{II}$ center, six-coordinated in an approximately octahedral environment with two *trans*-positioned pyridyl nitrogen donors of two *L*1 ligands and four O atoms of coordinated water molecules (Fig. 1). The corresponding Zn—N distances are 2.162 (3) Å for $N6^{ii}$ [symmetry code: (ii) $x-1, -y+\frac{1}{2}, z-\frac{1}{2}$] and 2.172 (3) Å for N1, which are slightly longer than the Zn—N bond (2.078 Å) in $[Zn(H_2O)_4(L3)Zn(L4)_2]\cdot H_2O$ [*L*3 is *N*-(3-pyridyl)isonicotinamide and *L*4 is isonicotinic acid; Kumar *et al.*, 2006]. The Zn—O bond lengths range from 2.038 (3) to 2.162 (2) Å, being very close to the Zn—O bond lengths found in $[Zn_3(4,4'\text{-bipy})_4(OAc)_4](ClO_4)_2\cdot 2H_2O$ (OAc is acetate and 4,4′-bipy is 4,4′-bipyridine; Woodward *et al.*, 2006).

The asymmetric unit in (I) contains one $Zn^{II}$ ion, one *L*1 ligand, one sulfate anion, four coordinated water molecules and one water molecule of crystallization. Each *L*1 ligand is

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bound to two $Zn^{II}$ centers and is bent with a *cisoid* conformation; the two terminal pyridyl groups and the bridging triazole heterocyclic ring do not lie in the same plane. The torsion angles for the two pyridyl rings are −29.8 (6) (C9—C8—C7—N2) and 5.5 (6)° (N3—C6—C4—C3). The corresponding dihedral angles between the planes of the three rings are 30.7 (2) (between N1/C8–C12 and N2–N4/C6/C7), 7.7 (2) (N2–N4/C6/C7 and N6/C1–C5) and 25.3 (2)° (N1/C8–C12 and N6/C1–C5). The coordinating N1 and N6 atoms are on the same side of the molecule and the N—Zn—N angle [171.54 (11)°] is close to 180°, so that the $ZnO_4$ units are bridged by the *L*1 ligands through the pyridyl N atoms into a one-dimensional sinusoidal chain along the crystallographic *a* axis, with a Zn···Zn separation of *ca* 9.64 Å. These sinusoidal chains are bound to each other by interpolymer O—H···O hydrogen bonds between coordinated water molecules to generate a two-dimensional network parallel to the *ac* plane (Table 1 and Fig. 2). These layers stack in an ...*ABAB*... sequence along the *b* axis to form a three-dimensional framework linked through O—H···N hydrogen bonds between coordinated water molecules and the N atoms on the triazole rings (Fig. 3). When viewed down the crystallographic *c* axis, honeycomb-like channels are evident, in which the uncoordinated sulfate counter-ions and water molecule are located. All the amine groups on the triazole rings project into these channels and interact with the framework through hydrogen bonds.

The asymmetric unit in (II) contains one $Cu^{II}$ ion, two *L*2 ligands, two nitrate anions, two coordinated water molecules and eight water molecules of crystallization. Each *L*2 ligand is bound to two $Cu^{II}$ atoms. The $Cu^{II}$ atoms in (II) are six-coordinated in a significantly stretched octahedral environment, which is built up by four N atoms [N1, N7, $N6^{viii}$ and $N12^{ix}$; symmetry codes: (viii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (ix) $x, -y+\frac{5}{2}, z+\frac{1}{2}$] from four *L*2 ligands in the equatorial plane and two O atoms of water molecules in the axial sites (Fig. 4). Unlike the reasonably regular octahedral geometry in (I), the Cu—O bonds in (II) are severely asymmetric and much longer [2.3569 (16) and 2.6034 (18) Å] than the Cu—N bonds [mean = 2.022 (2) Å]. This phenomenon is presumably due to

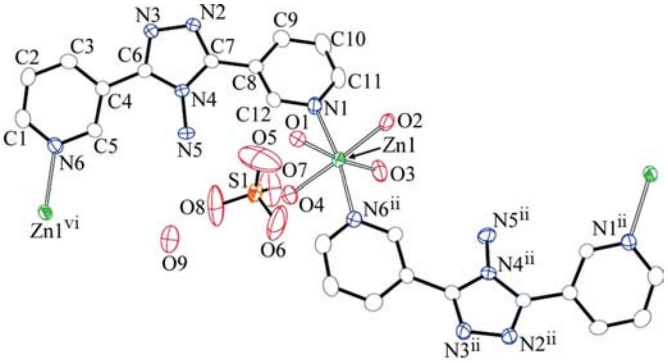

**Figure 1**
A view of (I), showing the coordination around Zn. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. [Symmetry codes: (ii) $x-1, -y+\frac{1}{2}, z-\frac{1}{2}$; (vi) $x+1, -y+\frac{1}{2}, z+\frac{1}{2}$.]

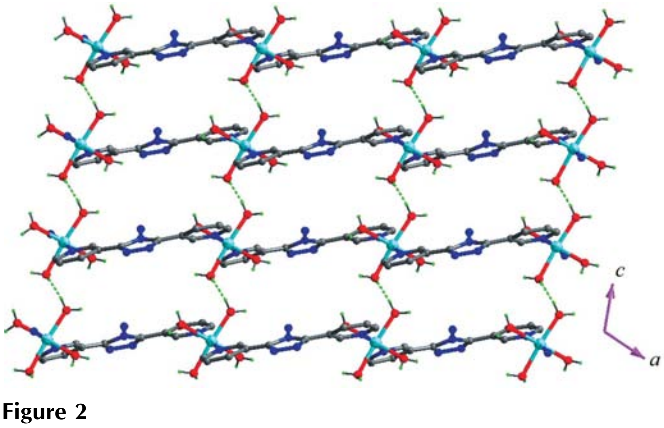

**Figure 2**
A perspective view of the hydrogen-bonded two-dimensional network in (I). Hydrogen bonds are indicated by dashed lines.

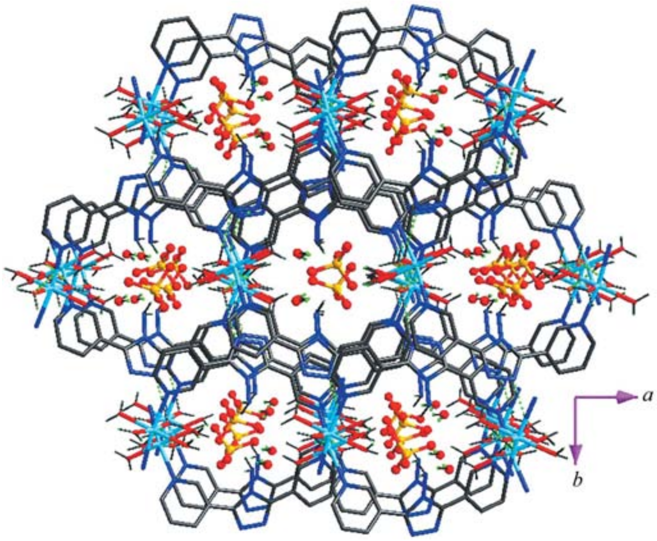

**Figure 3**
A perspective view of the three-dimensional network of (I) along the crystallographic *c* axis. S, O and H atoms in sulfate anions and water molecules of crystallization in the channels are shown as spheres.

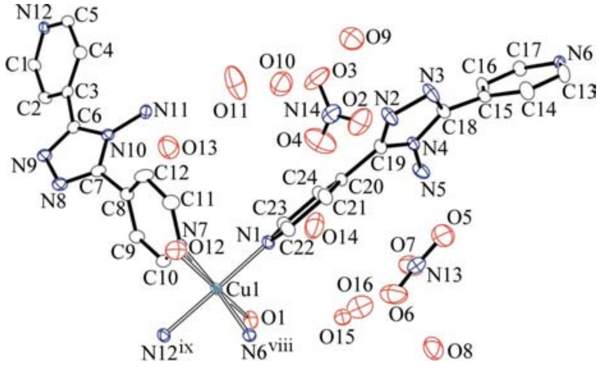

**Figure 4**
A view of (II), showing the coordination around Cu. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity. [Symmetry codes: (viii) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (ix) $x, -y+\frac{5}{2}, z+\frac{1}{2}$.]

copper(II) Jahn–Teller distortion and consequently weak axial Cu—OH$_2$ bonds. The Cu$^{II}$ centers are bridged by *L*2 ligands to form a two-dimensional network parallel to the *bc* plane and consisting of an essentially square grid (Fig. 5). The dimensions of the squares are *ca* 14 × 14 Å, which is significantly larger than the corresponding dimensions (*ca* 8 × 8 Å) in [Cu(4,4′-bipy)$_2$(H$_2$O)$_2$]·SiF$_6$ (Noro *et al.*, 2002). When viewed down the crystallographic *a* axis, the nitrate anions and eight crystallization water molecules are seen to be located in the voids in the grid. The shortest intralayer Cu···Cu distance is 14.369 (1) Å, *ca* 5 Å longer than the shortest interlayer Cu···Cu distance [9.250 (1) Å]. These two-dimensional layers are arranged alternately along the *a* axis and are further linked into a three-dimensional framework through interlayer N—H···N hydrogen bonds. The hydrogen-bonding system involves uncoordinated N atoms of the triazole ring and H atoms of the –NH$_2$ group of the triazole ring of a neighboring layer (Table 2 and Fig. 6). The nitrate anions and crystallization water molecules are located between the layers and interact with the framework *via* O—H···O and N—H···O hydrogen bonds (Table 2).

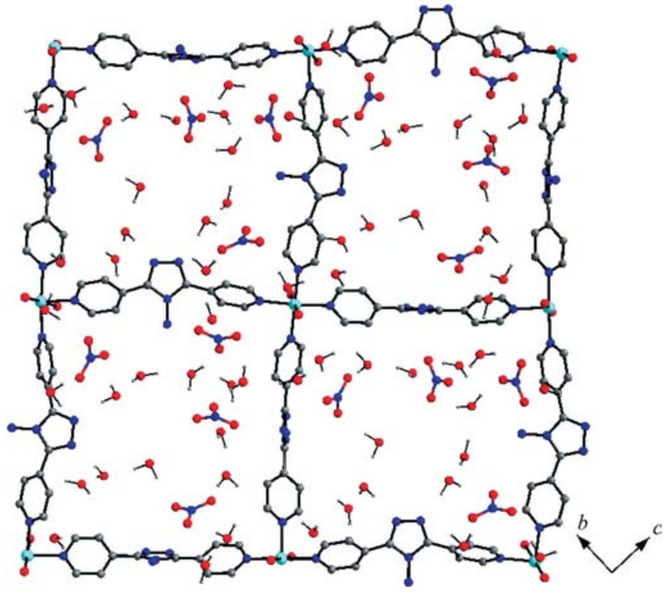

**Figure 5**
A perspective view of the two-dimensional network in (II) along the *a* axis.

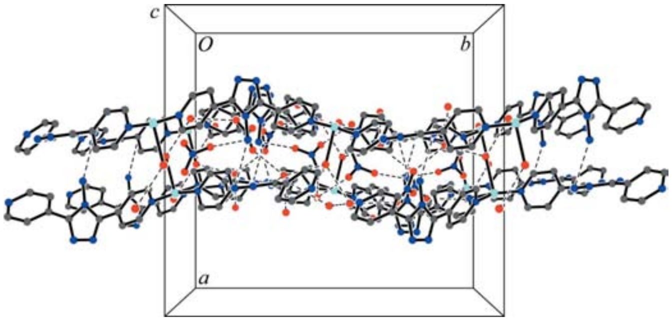

**Figure 6**
A view of the stacking of the sheets in (II) along the *a* axis. H atoms have been omitted for clarity. Hydrogen bonds are indicated by dashed lines.

The ligands in (I) and (II) are both bent triazole-bridged ligands, and the essential difference between *L*1 and *L*2 is the relative orientation of the donor N atoms on the pyridyl rings; *L*1 is a 3,3′-bipyridyl-type ligand, while *L*2 is a 4,4′-bipyridyl-type ligand. Both ligands act as bidentate bridging ligands; however, in (I), each Zn$^{II}$ center is linked to two other Zn atoms *via* two axially bound ligands, while in (II), each Cu$^{II}$ center is linked to four others *via* four equatorially bound ligands. Thus, the polymer in (I) exhibits a sinusoidal chain and the polymer in (II) presents a two-dimensional network in the form of a square grid. This study clearly demonstrates that the relative orientations of the nitrogen donors on the pyridyl rings cause the ligands to act as distinct building blocks, leading to different frameworks. We expect ligands of this type to be viable agents for the creation of more new complexes with interesting topology and physical properties.

## Experimental

All the solvents and reagents were commercially available and used as received. *L*1 and *L*2 were prepared according to the method described by Traisnel *et al.* (1999). *L*1 (12 mg, 0.05 mmol) and ZnSO$_4$·7H$_2$O (14 mg, 0.05 mmol) were dissolved in water (2 ml). Upon slow evaporation, colourless block-shaped crystals were obtained in 61% yield (based on *L*1). *L*2 (12 mg, 0.05 mmol) and Cu(NO$_3$)$_2$·3H$_2$O (12 mg, 0.05 mmol) were mixed in water (2 ml). After *ca* one week, blue block-shaped crystals were obtained in 63% yield based on *L*2. Crystals of (I) and (II) suitable for single-crystal X-ray diffraction were selected directly from the sample as prepared.

### Compound (I)

*Crystal data*

[Zn(C$_{12}$H$_{10}$N$_6$)(H$_2$O)$_4$]SO$_4$·H$_2$O
$M_r$ = 489.77
Monoclinic, $P2_1/c$
$a$ = 10.3593 (19) Å
$b$ = 17.437 (3) Å
$c$ = 11.532 (2) Å
$\beta$ = 114.121 (3)°
$V$ = 1901.2 (6) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.46 mm$^{-1}$
$T$ = 298 K
0.27 × 0.12 × 0.11 mm

*Data collection*

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.694, $T_{\max}$ = 0.856
9776 measured reflections
3346 independent reflections
2790 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.037

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N5—H2N5···O5 | 0.89 | 2.20 | 3.056 (6) | 160 |
| O4—H1O4···O7$^{i}$ | 0.86 | 1.91 | 2.755 (5) | 170 |
| O3—H2O3···O9$^{ii}$ | 0.85 | 1.80 | 2.652 (4) | 175 |
| O1—H1O1···N2$^{iii}$ | 0.85 | 1.94 | 2.792 (4) | 177 |
| O9—H1O9···O8 | 0.84 | 1.99 | 2.793 (5) | 157 |
| O9—H2O9···O7$^{i}$ | 0.85 | 2.05 | 2.876 (5) | 165 |
| O2—H2O2···O8$^{iv}$ | 0.85 | 1.79 | 2.625 (4) | 166 |
| O1—H2O1···O6$^{i}$ | 0.85 | 1.75 | 2.581 (5) | 167 |
| O4—H2O4···O5 | 0.84 | 2.28 | 3.074 (8) | 157 |
| O3—H1O3···O1$^{v}$ | 0.85 | 1.89 | 2.740 (4) | 173 |

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

### *Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.117$
$S = 1.07$
3346 reflections
262 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.93$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.67$ e Å$^{-3}$

## Compound (II)

### *Crystal data*

$[Cu(C_{12}H_{10}N_6)_2(H_2O)_2]$-$(NO_3)_2 \cdot 8H_2O$
$M_r = 844.24$
Orthorhombic, *Pbca*
$a = 18.2543$ (17) Å
$b = 19.8942$ (18) Å
$c = 20.7455$ (19) Å
$V = 7533.8$ (12) Å$^3$
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.67$ mm$^{-1}$
$T = 173$ K
0.48 × 0.47 × 0.16 mm

### *Data collection*

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.740$, $T_{\max} = 0.901$
37726 measured reflections
6994 independent reflections
5639 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.046$

### *Refinement*

$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.096$
$S = 1.02$
6994 reflections
496 parameters
H-atom parameters constrained
$\Delta\rho_{\max} = 0.44$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.24$ e Å$^{-3}$

H atoms attached to carbon were placed in geometrically idealized positions [arene C—H = 0.93 Å for (I) and 0.95 Å for (II)] and refined using a riding model, with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(C). The $NH_2$ and aqua H atoms were located by difference Fourier synthesis and refined as riding atoms, with N—H distances of 0.86–0.92 Å and O—H distances of 0.84–0.86 Å, and with $U_{\rm iso}$(H) values of $1.2U_{\rm eq}$(N) and $1.5U_{\rm eq}$(O).

For both compounds, data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT* (Bruker, 1997); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O12—H12*B*···O9$^{i}$ | 0.85 | 2.03 | 2.872 (3) | 171 |
| O13—H13*B*···O5$^{ii}$ | 0.85 | 2.04 | 2.881 (3) | 169 |
| O13—H13*A*···O11 | 0.85 | 1.85 | 2.688 (2) | 169 |
| O12—H12*A*···O13 | 0.85 | 2.02 | 2.861 (2) | 170 |
| O14—H14*B*···O3$^{iii}$ | 0.85 | 2.00 | 2.808 (3) | 157 |
| O8—H8*B*···O16 | 0.85 | 1.94 | 2.774 (3) | 170 |
| O8—H8*A*···O6$^{iv}$ | 0.84 | 2.04 | 2.871 (3) | 166 |
| O10—H10*A*···O14$^{iii}$ | 0.85 | 2.11 | 2.948 (3) | 170 |
| O9—H9*A*···O8$^{v}$ | 0.85 | 1.89 | 2.724 (3) | 166 |
| O10—H10*B*···O9 | 0.85 | 2.02 | 2.824 (3) | 158 |
| O11—H11*D*···N9$^{vi}$ | 0.86 | 2.05 | 2.906 (2) | 174 |
| O11—H11*C*···O10 | 0.86 | 1.95 | 2.787 (3) | 164 |
| N5—H5*A*···O7 | 0.90 | 2.14 | 3.010 (2) | 163 |
| O16—H16*A*···O15 | 0.85 | 1.96 | 2.806 (2) | 171 |
| O1—H1*B*···O13$^{iv}$ | 0.84 | 2.03 | 2.869 (2) | 173 |
| N5—H5*B*···O2 | 0.91 | 2.13 | 2.958 (3) | 151 |
| O15—H15*B*···O7 | 0.85 | 2.00 | 2.849 (2) | 176 |
| N11—H11*B*···N3$^{ii}$ | 0.92 | 2.08 | 2.900 (3) | 148 |
| O1—H1*A*···O15 | 0.84 | 1.97 | 2.804 (2) | 172 |
| O16—H16*B*···O14 | 0.85 | 2.26 | 3.102 (3) | 169 |
| O15—H15*A*···N8$^{vii}$ | 0.85 | 1.98 | 2.823 (2) | 171 |
| O14—H14*A*···O4 | 0.85 | 1.96 | 2.802 (3) | 169 |

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3191). Services for accessing these data are described at the back of the journal.

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