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Poly[[diaquadeca-μ_2-cyanido-$\kappa^{20}C$:N-hexacyanido-κ^6C-bis(μ_2-5-methylpyrimidine-κ^2N:N')bis(5-methylpyrimidine-κN)tricopper(II)-ditungstate(V)] dihydrate]

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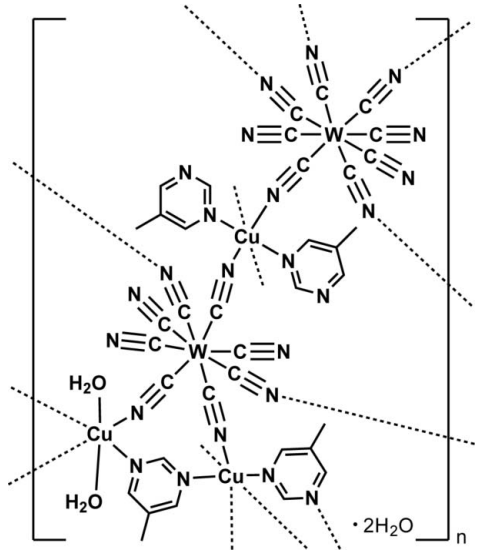
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.007 Å; R factor = 0.029; wR factor = 0.079; data-to-parameter ratio = 17.0.

In the title complex, $\{[Cu_3[W(CN)_8]_2(C_5H_6N_2)_4(H_2O)_2]\cdot 2H_2O\}_n$, the coordination polyhedron of the eight-coordinated W^V atom is a bicapped trigonal prism, in which five CN groups are bridged to Cu^{II} ions, and the other three CN groups are terminally bound. Two of the Cu^{II} ions lie on a centre of inversion and each of the three independent Cu^{II} cations is pseudo-octahedrally coordinated. In the crystal structure, cyanido-bridged-Cu—W—Cu layers are linked by pillars involving the third independent Cu^{II} ion, generating a three-dimensional network with non-coordinating water molecules and 5-methylpyrimidine molecules. O—H···O and O—H···N hydrogen bonds involve the coordinating and non-coordinating water molecules, the CN groups and the 5-methylpyrimidine molecules.

Related literature

For background to functional three-dimensional networks, see: Catala *et al.* (2005); Garde *et al.* (1999); Herrera *et al.* (2004, 2008); Imoto *et al.* (2012); Leipoldt *et al.* (1994); Ohkoshi & Tokoro (2012); Ohkoshi *et al.* (2011); Sieklucka *et al.* (2009); Zhong *et al.* (2000). For related structures, see: Ohkoshi *et al.* (2007, 2012); Podgajny *et al.* (2002).



Experimental

Crystal data

$[Cu_3W_2(CN)_{16}(C_5H_6N_2)_4(H_2O)_2]\cdot 2H_2O$
M_r = 1423.19
Triclinic, $P\overline{1}$
a = 7.5953 (4) Å
b = 11.8232 (7) Å
c = 14.7017 (8) Å
α = 79.614 (1)°
β = 84.824 (2)°
γ = 73.090 (1)°
V = 1241.45 (12) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 5.94 mm^{-1}
T = 296 K
0.16 × 0.10 × 0.05 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.452, T_{max} = 0.772
12240 measured reflections
5666 independent reflections
5465 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.079
S = 1.24
5666 reflections
333 parameters
6 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 3.02 e Å^{-3}
$\Delta\rho_{min}$ = −0.86 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N6^{i}	0.92 (2)	1.86 (2)	2.771 (5)	167 (5)
O1—H2···O2	0.93 (2)	1.79 (2)	2.700 (4)	165 (4)
O2—H3···N12^{ii}	0.95 (2)	2.00 (3)	2.914 (5)	161 (4)
O2—H4···N2^{iii}	0.93 (2)	2.02 (2)	2.944 (5)	169 (6)

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PyMOLWin* (DeLano, 2007); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supporting information for this paper is available from the IUCr electronic archives (Reference: TK5281).

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supporting information

Acta Cryst. (2014). E**70**, m47–m48 [doi:10.1107/S1600536814000166]

Poly[[diaquadeca-μ_2-cyanido-$\kappa^{20}C$:N-hexacyanido-κ^6C-bis(μ_2-5-methylpyrimidine-κ^2N:N')bis(5-methylpyrimidine-κN)tricopper(II)ditungstate(V)] dihydrate]

Yoshihide Tsunobuchi, Souhei Kaneko, Koji Nakabayashi and Shin-ichi Ohkoshi

S1. Experimental

S1.1. Synthesis and crystallization

The title compound was prepared by reacting an aqueous solution of $Cs_3[W(CN)_8]\cdot 2H_2O$ (1.2×10^{-2} mol dm^{-3}) with a mixed aqueous solution of $CuCl_2\cdot 2H_2O$ (1.8×10^{-2} mol dm^{-3}), 5-methylpyrimidine (2.4×10^{-2} mol dm^{-3}) at room temperature. The prepared compound was a green plate-type crystal. Elemental analyses: calcd for $Cu_3[W(CN)_8]_2$(5-methylpyrimidine)$_4\cdot 4H_2O$, Calculated: Cu, 13.40; W, 25.83; C, 30.38; H, 2.27; N, 23.63%. Found: Cu, 13.12; W, 25.96; C, 30.05; H, 2.35; N, 23.64%. In the Infrared (IR) spectra, cyano stretching peaks were observed at 2204, 2194, 2169, 2161, 2148, and 2142 cm^{-1}.

S1.2. Refinement

The H atoms of the 5-methylpyrimidine molecules were placed in calculated positions with C—H = 0.95 Å, and refined using a riding model with U_{iso}(H) = 1.2 U_{eq}(C). The H atoms of water molecules were placed by using restraints of 0.96 (2) Å for O—H distances and DANG of 1.5 (4) Å for H—H distances. The maximum and minimum residual electron density peaks were located 0.74 and 1.60 Å, respectively, from the W1 and C3 atoms.

S2. Results and discussion

Synthesis of various kinds of three-dimensional network complexes exhibiting long-range magnetic ordering is an important issue. From this perspective, octacyanometalate $[M(CN)_8]$ (M = Mo, W, Nb)-based magnets have been studied because they show high T_C (Garde *et al.*, 1999; Zhong *et al.*, 2000; Herrera *et al.*, 2008; Sieklucka *et al.*, 2009; Imoto *et al.*, 2012) and functionalities such as photomagnetism (Herrera *et al.*, 2004; Catala *et al.*, 2005; Ohkoshi *et al.*, 2011, 2012) and chemically sensitive magnetism (Ohkoshi *et al.*, 2007). In addition, octacyanometalates have an advantage to construct various crystal structures due to the versatility that they can adopt different spatial configurations depending on their chemical environment, *e.g.*, square antiprism (D_{4d}), dodecahedron (D_{2d}), and bicapped trigonal prism (C_{2v}) (Leipoldt *et al.*, 1994). Several octacyanometalate-based magnets of Cu—W systems such as $\{[Cu_3[W(CN)_8]_2]\cdot 3.4H_2O\}_n$ (Garde *et al.*, 1999), $\{[Cu_3[W(CN)_8]_2(pyrimidine)_2]\cdot 8H_2O\}_n$ (Ohkoshi *et al.*, 2007), $\{[Cu_3[W(CN)_8]_2(pyrimidine)_4]\cdot 4H_2O\}_n$ (Ohkoshi *et al.*, 2012), $\{[(tetrenH_5)_{0.8}Cu_4[W(CN)_8]_4]\cdot 7.2H_2O\}_n$ (Podgajny *et al.*, 2002), have been reported. Here, we present a new candidate for copper-octacyanotungstate-based magnets, $\{[Cu_3[W(CN)_8]_2(5\text{-methylpyrimidine})_4(H_2O)_2]\cdot 2H_2O\}_n$.

The asymmetric unit of the present compound consists of a $[W(CN)_8]^{3-}$ anion, a one-half of [Cu1(5-methylpyrimidine)$_2$]$^{2+}$ cation, a one-half of [Cu2(5-methylpyrimidine)$_2$]$^{2+}$ cation, a one-half of $[Cu3(H_2O)_2]^{2+}$ cation, and a water molecule (Fig. 1). The coordination geometry of W is an eight-coordinated bicapped trigonal prism, where five CN

groups of $[W(CN)_8]$ are bridged to Cu^{2+} ions (two Cu1, two Cu2 and one Cu3), and the other three CN groups are free. The coordination geometries of the three types of Cu^{2+} ions (Cu1, Cu2 and Cu3) are six-coordinated pseudo-octahedron. Cu1 is coordinated to four nitrogen atoms of CN ligands, two nitrogen atoms of 5-methylpyrimidine molecules. Cu2 is coordinated to four nitrogen atoms of CN ligands, two nitrogen atoms of 5-methylpyrimidine molecules. Cu3 is coordinated to two nitrogen atoms of CN ligands, two nitrogen atoms of 5-methylpyrimidine molecules, and two oxygen atoms of H_2O molecules. The cyano-bridged-Cu1—W—Cu2 layers are linked by Cu3 pillar unit (Figs. 2 and 3) and then, involving non-coordinated water molecules, the 3-D structure is constructed. In the crystal structure, the coordinated water make hydrogen bonds with the non-coordinated water (O1—H2···O2, 2.700 (4)) and the CN groups (O1—H1···N6, 2.771 (5)). Besides, hydrogen bonds between the non-coordinated water and the CN groups (O2—H4···N2, 2.944 (5)) or the 5-methylpyrimidine molecules (O2—H3···N12, 2.914 (5)).

The magnetization *versus*. temperature curve at 10 Oe showed a spontaneous magnetization with a Curie temperature (T_C) of 10 K, the coercive field (H_c) of 150 Oe at 2 K, and, the saturation magnetization (M_s) value of 3.1 μ_B. This M_s value agrees with the expected value of 3.0 μ_B, indicating that this compound is a ferrimagnet in which W^V (S = 1/2) and Cu^{II} (S = 1/2, Cu1 and Cu2) in the layer are ferromagnetically coupled and W^V and the bridged Cu^{II} (S = 1/2, Cu3) are antiferromagnetically coupled.

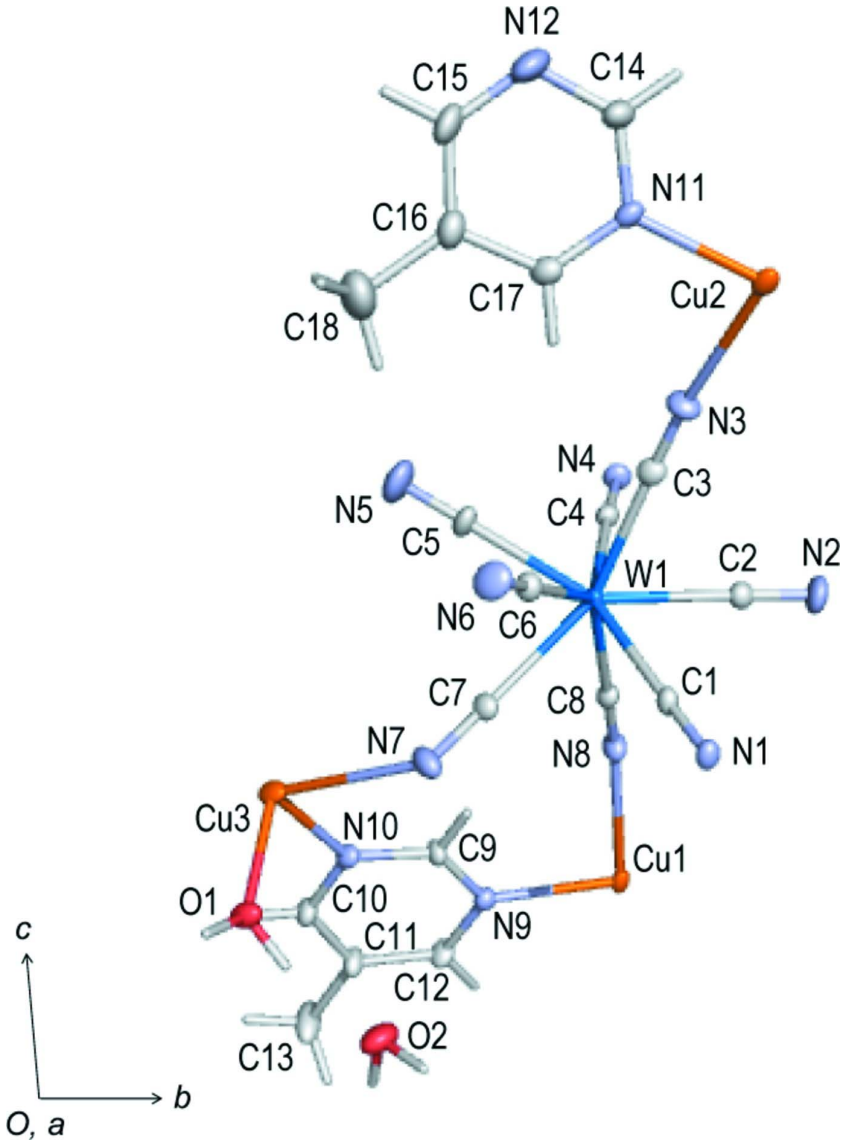

Figure 1

Displacement ellipsoid plot (30% probability level) of the atoms comprising the asymmetric unit of $\{[Cu_3[W(CN)_8]_2(C_5H_6N_2)_4(H_2O)_2]\cdot 2H_2O\}_n$. Symmetry codes: (i) $+x,+y,+z$ and (ii) $-x,-y,-z$.

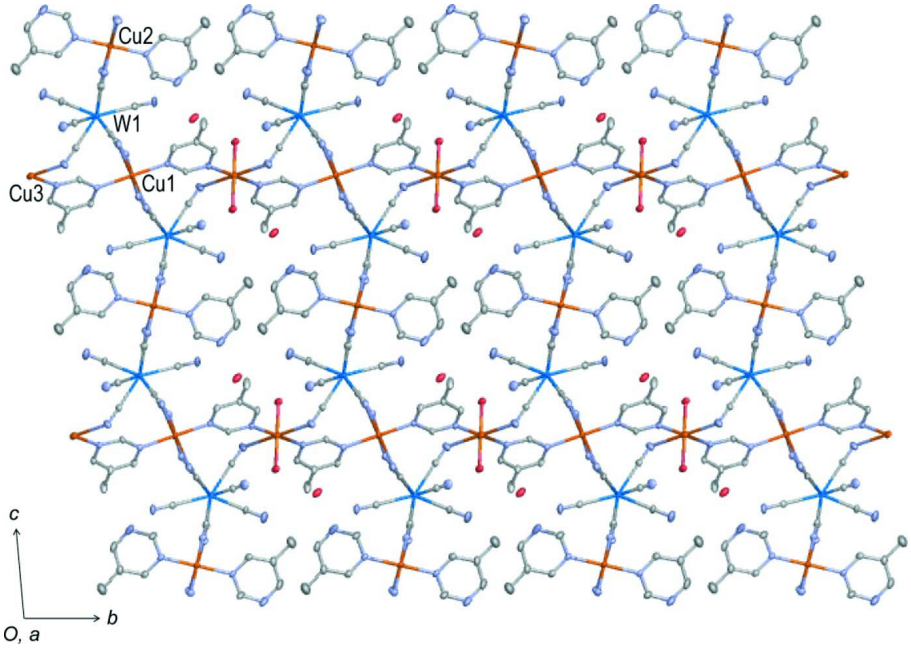

Figure 2

Crystal structure of $\{[Cu_3[W(CN)_8]_2(C_5H_6N_2)_4(H_2O)_2]\cdot 2H_2O\}_n$ along the *a* axis. Blue, orange, gray, light blue, and red represent W, Cu, C, N, and O atoms, respectively. Hydrogen atoms are omitted for clarity.

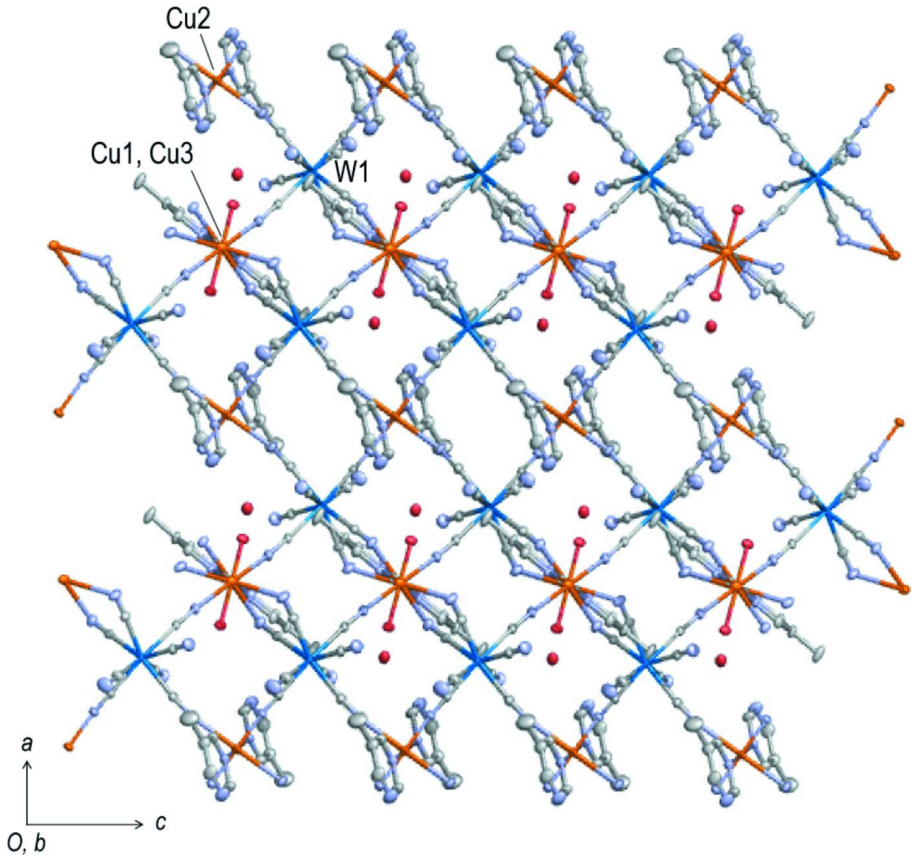

Figure 3

Crystal structure of $\{[Cu_3[W(CN)_8]_2(C_5H_6N_2)_4(H_2O)_2]\cdot 2H_2O\}_n$ along the *b* axis. Blue, orange, gray, light blue, and red represent W, Cu, C, N, and O atoms, respectively. Hydrogen atoms are omitted for clarity.

Poly[[diaquadeca-μ_2-cyanido-$\kappa^{20}C$:*N*-hexacyanido-κ^6C-bis(μ_2-5-methylpyrimidine-κ^2N:*N*′)bis(5-methylpyrimidine-κN)tricopper(II)ditungstate(V)] dihydrate]

Crystal data

$[Cu_3W_2(CN)_{16}(C_5H_6N_2)_4(H_2O)_2]\cdot 2H_2O$
M_r = 1423.19
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 7.5953 (4) Å
b = 11.8232 (7) Å
c = 14.7017 (8) Å
α = 79.614 (1)°
β = 84.824 (2)°
γ = 73.090 (1)°
V = 1241.45 (12) Å^3
Z = 1
F(000) = 683
D_x = 1.904 Mg m^{-3}
Mo *K*α radiation, λ = 0.71075 Å
Cell parameters from 10947 reflections
θ = 3.0–27.5°
μ = 5.94 mm^{-1}
T = 296 K
Platelet, green
0.16 × 0.10 × 0.05 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.00 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.452, T_{max} = 0.772
12240 measured reflections

5666 independent reflections
5465 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.0°$
$h = -9 \rightarrow 9$
$k = -15 \rightarrow 14$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.029$
$wR(F^2) = 0.079$
$S = 1.24$
5666 reflections
333 parameters
6 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
$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2 + 0.3667P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 3.02$ e Å^{-3}
$\Delta\rho_{min} = -0.86$ 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 (Å²)

	x	y	z	U_{iso}*/U_{eq}
W1	0.548569 (15)	0.875339 (10)	0.768726 (8)	0.01497 (6)
Cu1	1.0000	1.0000	1.0000	0.01979 (14)
Cu2	0.0000	1.0000	0.5000	0.02293 (14)
Cu3	1.0000	0.5000	1.0000	0.02754 (15)
O1	0.9257 (4)	0.4659 (3)	1.12961 (19)	0.0325 (6)
O2	0.8939 (5)	0.6502 (3)	1.2207 (3)	0.0446 (8)
N1	0.2221 (4)	0.9864 (3)	0.9186 (2)	0.0253 (6)
N2	0.4282 (6)	1.1699 (3)	0.7155 (3)	0.0439 (10)
N3	0.2648 (5)	0.9438 (3)	0.5964 (3)	0.0352 (8)
N4	0.8430 (4)	0.9479 (3)	0.6057 (2)	0.0274 (7)
N5	0.7737 (7)	0.6301 (4)	0.6849 (4)	0.0615 (13)
N6	0.2689 (5)	0.7008 (4)	0.8104 (3)	0.0437 (9)
N7	0.6975 (5)	0.6771 (3)	0.9555 (3)	0.0376 (9)
N8	0.8384 (5)	0.9585 (3)	0.8789 (2)	0.0309 (7)
N9	1.1037 (4)	0.8172 (3)	1.0463 (2)	0.0222 (6)
N10	1.1143 (4)	0.6182 (3)	1.0366 (2)	0.0240 (6)
N11	0.0743 (4)	0.8306 (3)	0.4682 (2)	0.0271 (7)
N12	0.0945 (6)	0.6994 (4)	0.3619 (3)	0.0550 (12)
C1	0.3400 (5)	0.9497 (3)	0.8680 (2)	0.0219 (7)
C2	0.4714 (5)	1.0702 (4)	0.7326 (3)	0.0262 (8)

C3	0.3692 (5)	0.9207 (4)	0.6532 (3)	0.0272 (8)
C4	0.7413 (5)	0.9202 (3)	0.6609 (2)	0.0219 (7)
C5	0.6973 (6)	0.7146 (3)	0.7133 (3)	0.0323 (9)
C6	0.3645 (5)	0.7610 (3)	0.7957 (3)	0.0269 (8)
C7	0.6405 (5)	0.7462 (3)	0.8920 (3)	0.0260 (8)
C8	0.7391 (5)	0.9303 (3)	0.8395 (3)	0.0231 (7)
C9	1.0448 (5)	0.7368 (3)	1.0154 (3)	0.0227 (7)
H9	0.9472	0.7651	0.9758	0.027*
C10	1.2529 (5)	0.5779 (3)	1.0949 (3)	0.0281 (8)
H10	1.3036	0.4958	1.1111	0.034*
C11	1.3227 (5)	0.6550 (3)	1.1315 (3)	0.0286 (8)
C12	1.2427 (5)	0.7751 (4)	1.1046 (3)	0.0292 (8)
H12	1.2865	0.8296	1.1276	0.035*
C13	1.4754 (7)	0.6078 (4)	1.1980 (4)	0.0532 (14)
H13A	1.5110	0.5219	1.2077	0.064*
H13B	1.4340	0.6354	1.2558	0.064*
H13C	1.5790	0.6360	1.1730	0.064*
C14	0.0516 (6)	0.8084 (4)	0.3854 (3)	0.0413 (10)
H14	0.0022	0.8735	0.3403	0.050*
C15	0.1642 (7)	0.6077 (4)	0.4271 (4)	0.0501 (12)
H15	0.1950	0.5309	0.4125	0.060*
C16	0.1936 (7)	0.6203 (4)	0.5156 (4)	0.0423 (11)
C17	0.1426 (6)	0.7371 (4)	0.5327 (3)	0.0332 (9)
H17	0.1568	0.7507	0.5916	0.040*
C18	0.2772 (12)	0.5161 (6)	0.5890 (5)	0.083 (2)
H18A	0.2844	0.5452	0.6451	0.099*
H18B	0.3987	0.4749	0.5684	0.099*
H18C	0.2019	0.4620	0.6003	0.099*
H1	0.868 (7)	0.410 (3)	1.159 (3)	0.052 (15)*
H2	0.913 (6)	0.520 (3)	1.170 (3)	0.047 (14)*
H3	0.981 (5)	0.653 (5)	1.262 (3)	0.044 (14)*
H4	0.785 (4)	0.699 (5)	1.244 (4)	0.08 (2)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
W1	0.01514 (9)	0.01469 (9)	0.01571 (9)	−0.00529 (6)	0.00316 (6)	−0.00411 (6)
Cu1	0.0179 (3)	0.0139 (3)	0.0246 (3)	−0.0026 (2)	0.0084 (2)	−0.0033 (2)
Cu2	0.0273 (3)	0.0226 (3)	0.0205 (3)	−0.0112 (3)	0.0107 (3)	−0.0063 (3)
Cu3	0.0403 (4)	0.0269 (3)	0.0249 (3)	−0.0228 (3)	0.0015 (3)	−0.0074 (3)
O1	0.0436 (16)	0.0348 (16)	0.0273 (14)	−0.0244 (14)	0.0064 (12)	−0.0076 (12)
O2	0.0377 (17)	0.056 (2)	0.0461 (19)	−0.0118 (16)	0.0010 (15)	−0.0275 (17)
N1	0.0222 (14)	0.0207 (15)	0.0297 (16)	−0.0032 (12)	0.0065 (13)	−0.0039 (13)
N2	0.052 (2)	0.0182 (18)	0.057 (3)	−0.0024 (17)	−0.003 (2)	−0.0084 (17)
N3	0.0321 (18)	0.042 (2)	0.0337 (19)	−0.0125 (16)	−0.0125 (15)	−0.0027 (16)
N4	0.0259 (15)	0.0313 (17)	0.0242 (15)	−0.0099 (14)	0.0073 (13)	−0.0038 (13)
N5	0.076 (3)	0.035 (2)	0.068 (3)	−0.006 (2)	0.019 (3)	−0.024 (2)
N6	0.048 (2)	0.043 (2)	0.052 (2)	−0.0315 (19)	0.0051 (18)	−0.0095 (18)

N7	0.050 (2)	0.0295 (19)	0.0361 (19)	−0.0172 (17)	−0.0145 (17)	0.0056 (16)
N8	0.0343 (17)	0.0225 (16)	0.0375 (18)	−0.0093 (14)	−0.0094 (15)	−0.0026 (14)
N9	0.0204 (14)	0.0214 (15)	0.0237 (15)	−0.0041 (12)	0.0020 (12)	−0.0058 (13)
N10	0.0310 (16)	0.0206 (15)	0.0244 (15)	−0.0138 (13)	0.0000 (13)	−0.0033 (12)
N11	0.0303 (16)	0.0279 (16)	0.0260 (16)	−0.0092 (14)	0.0038 (13)	−0.0122 (14)
N12	0.064 (3)	0.051 (3)	0.053 (3)	−0.003 (2)	−0.012 (2)	−0.031 (2)
C1	0.0194 (16)	0.0170 (16)	0.0269 (17)	−0.0041 (13)	0.0024 (14)	−0.0012 (14)
C2	0.0224 (18)	0.026 (2)	0.0273 (19)	−0.0029 (15)	0.0001 (15)	−0.0046 (16)
C3	0.0276 (18)	0.0292 (19)	0.0279 (18)	−0.0138 (16)	0.0020 (16)	−0.0045 (16)
C4	0.0210 (16)	0.0225 (17)	0.0212 (17)	−0.0045 (14)	0.0014 (14)	−0.0051 (14)
C5	0.040 (2)	0.0203 (18)	0.034 (2)	−0.0060 (17)	0.0104 (18)	−0.0099 (16)
C6	0.0270 (18)	0.0239 (18)	0.0299 (19)	−0.0087 (15)	0.0015 (15)	−0.0032 (15)
C7	0.0311 (19)	0.0220 (18)	0.0274 (19)	−0.0125 (16)	−0.0013 (16)	−0.0020 (16)
C8	0.0279 (17)	0.0190 (16)	0.0233 (17)	−0.0085 (14)	0.0001 (15)	−0.0030 (14)
C9	0.0266 (18)	0.0149 (16)	0.0270 (18)	−0.0075 (14)	−0.0051 (15)	0.0008 (14)
C10	0.0301 (18)	0.0183 (17)	0.037 (2)	−0.0066 (15)	−0.0039 (16)	−0.0065 (15)
C11	0.0229 (17)	0.0195 (17)	0.042 (2)	−0.0009 (15)	−0.0094 (16)	−0.0066 (16)
C12	0.0270 (18)	0.0244 (19)	0.041 (2)	−0.0109 (15)	−0.0042 (17)	−0.0110 (17)
C13	0.047 (3)	0.030 (2)	0.085 (4)	−0.001 (2)	−0.038 (3)	−0.014 (3)
C14	0.049 (3)	0.040 (2)	0.032 (2)	0.000 (2)	−0.008 (2)	−0.0137 (19)
C15	0.054 (3)	0.030 (2)	0.065 (3)	0.002 (2)	−0.006 (3)	−0.023 (2)
C16	0.047 (3)	0.027 (2)	0.050 (3)	−0.004 (2)	−0.001 (2)	−0.009 (2)
C17	0.042 (2)	0.033 (2)	0.028 (2)	−0.0157 (19)	0.0000 (18)	−0.0070 (18)
C18	0.120 (6)	0.043 (3)	0.070 (4)	−0.007 (4)	−0.010 (4)	0.006 (3)

Geometric parameters (Å, º)

W1—C1	2.156 (3)	N4—C4	1.141 (5)
W1—C8	2.160 (4)	N4—Cu2^{ii}	1.991 (3)
W1—C4	2.160 (4)	N5—C5	1.131 (5)
W1—C5	2.167 (4)	N6—C6	1.139 (5)
W1—C3	2.167 (4)	N7—C7	1.148 (5)
W1—C7	2.171 (4)	N8—C8	1.144 (5)
W1—C6	2.178 (4)	N9—C9	1.323 (5)
W1—C2	2.182 (4)	N9—C12	1.341 (5)
Cu1—N1^{i}	1.962 (3)	N10—C9	1.335 (5)
Cu1—N1^{ii}	1.962 (3)	N10—C10	1.338 (5)
Cu1—N9	2.081 (3)	N11—C14	1.328 (5)
Cu1—N9^{iii}	2.081 (3)	N11—C17	1.329 (6)
Cu1—N8^{iii}	2.444 (3)	N12—C15	1.326 (7)
Cu1—N8	2.444 (3)	N12—C14	1.334 (6)
Cu2—N4^{iv}	1.991 (3)	C9—H9	0.9300
Cu2—N4^{v}	1.991 (3)	C10—C11	1.383 (5)
Cu2—N11^{vi}	2.044 (3)	C10—H10	0.9300
Cu2—N11	2.044 (3)	C11—C12	1.372 (5)
Cu2—N3	2.427 (3)	C11—C13	1.497 (6)
Cu2—N3^{vi}	2.427 (3)	C12—H12	0.9300
Cu3—O1	1.943 (3)	C13—H13A	0.9600

Cu3—O1^{vii}	1.943 (3)	C13—H13B	0.9600
Cu3—N10^{vii}	2.015 (3)	C13—H13C	0.9600
Cu3—N10	2.015 (3)	C14—H14	0.9300
O1—H1	0.924 (19)	C15—C16	1.380 (7)
O1—H2	0.931 (19)	C15—H15	0.9300
O2—H3	0.950 (19)	C16—C17	1.385 (6)
O2—H4	0.933 (19)	C16—C18	1.508 (8)
N1—C1	1.146 (5)	C17—H17	0.9300
N1—Cu1^{v}	1.962 (3)	C18—H18A	0.9600
N2—C2	1.115 (6)	C18—H18B	0.9600
N3—C3	1.145 (5)	C18—H18C	0.9600

C1—W1—C8	86.95 (13)	N10^{vii}—Cu3—N10	179.999 (1)
C1—W1—C4	143.19 (14)	Cu3—O1—H1	129 (3)
C8—W1—C4	75.63 (14)	Cu3—O1—H2	122 (3)
C1—W1—C5	145.49 (14)	H1—O1—H2	106 (3)
C8—W1—C5	108.53 (15)	H3—O2—H4	102 (3)
C4—W1—C5	71.32 (15)	C1—N1—Cu1^{v}	160.6 (3)
C1—W1—C3	96.29 (14)	C3—N3—Cu2	169.1 (3)
C8—W1—C3	145.84 (14)	C4—N4—Cu2^{ii}	174.1 (3)
C4—W1—C3	81.95 (14)	C8—N8—Cu1	164.1 (3)
C5—W1—C3	87.73 (16)	C9—N9—C12	116.7 (3)
C1—W1—C7	80.17 (14)	C9—N9—Cu1	121.9 (3)
C8—W1—C7	69.75 (14)	C12—N9—Cu1	121.2 (3)
C4—W1—C7	121.55 (14)	C9—N10—C10	117.1 (3)
C5—W1—C7	76.96 (15)	C9—N10—Cu3	123.4 (2)
C3—W1—C7	144.35 (14)	C10—N10—Cu3	118.9 (2)
C1—W1—C6	73.46 (14)	C14—N11—C17	117.4 (4)
C8—W1—C6	140.10 (14)	C14—N11—Cu2	122.6 (3)
C4—W1—C6	138.18 (14)	C17—N11—Cu2	120.0 (3)
C5—W1—C6	75.27 (15)	C15—N12—C14	116.6 (4)
C3—W1—C6	72.22 (14)	N1—C1—W1	175.9 (3)
C7—W1—C6	72.80 (14)	N2—C2—W1	178.3 (5)
C1—W1—C2	71.57 (14)	N3—C3—W1	175.3 (3)
C8—W1—C2	75.22 (14)	N4—C4—W1	177.1 (4)
C4—W1—C2	72.72 (14)	N5—C5—W1	179.3 (4)
C5—W1—C2	141.37 (15)	N6—C6—W1	179.6 (4)
C3—W1—C2	73.68 (15)	N7—C7—W1	176.8 (4)
C7—W1—C2	135.68 (15)	N8—C8—W1	178.4 (3)
C6—W1—C2	127.18 (14)	N9—C9—N10	125.2 (3)
N1^{i}—Cu1—N1^{ii}	179.999 (1)	N9—C9—H9	117.4
N1^{i}—Cu1—N9	93.24 (12)	N10—C9—H9	117.4
N1^{ii}—Cu1—N9	86.76 (12)	N10—C10—C11	121.9 (3)
N1^{i}—Cu1—N9^{iii}	86.76 (12)	N10—C10—H10	119.1
N1^{ii}—Cu1—N9^{iii}	93.24 (12)	C11—C10—H10	119.1
N9—Cu1—N9^{iii}	179.998 (1)	C12—C11—C10	116.3 (3)
N1^{i}—Cu1—N8^{iii}	90.31 (13)	C12—C11—C13	122.8 (4)
N1^{ii}—Cu1—N8^{iii}	89.69 (13)	C10—C11—C13	120.9 (4)

N9—Cu1—N8^{iii}	89.69 (12)	N9—C12—C11	122.7 (3)
N9^{iii}—Cu1—N8^{iii}	90.31 (12)	N9—C12—H12	118.6
N1^{i}—Cu1—N8	89.69 (13)	C11—C12—H12	118.6
N1^{ii}—Cu1—N8	90.31 (13)	C11—C13—H13A	109.5
N9—Cu1—N8	90.31 (12)	C11—C13—H13B	109.5
N9^{iii}—Cu1—N8	89.69 (12)	H13A—C13—H13B	109.5
N8^{iii}—Cu1—N8	180.000 (1)	C11—C13—H13C	109.5
N4^{iv}—Cu2—N4^{v}	179.998 (1)	H13A—C13—H13C	109.5
N4^{iv}—Cu2—N11^{vi}	89.30 (13)	H13B—C13—H13C	109.5
N4^{v}—Cu2—N11^{vi}	90.70 (13)	N11—C14—N12	124.8 (5)
N4^{iv}—Cu2—N11	90.70 (13)	N11—C14—H14	117.6
N4^{v}—Cu2—N11	89.30 (13)	N12—C14—H14	117.6
N11^{vi}—Cu2—N11	179.999 (1)	N12—C15—C16	123.5 (4)
N4^{iv}—Cu2—N3	88.44 (13)	N12—C15—H15	118.3
N4^{v}—Cu2—N3	91.56 (13)	C16—C15—H15	118.3
N11^{vi}—Cu2—N3	90.62 (13)	C15—C16—C17	115.1 (4)
N11—Cu2—N3	89.38 (13)	C15—C16—C18	123.5 (5)
N4^{iv}—Cu2—N3^{vi}	91.56 (13)	C17—C16—C18	121.5 (5)
N4^{v}—Cu2—N3^{vi}	88.44 (13)	N11—C17—C16	122.6 (4)
N11^{vi}—Cu2—N3^{vi}	89.38 (13)	N11—C17—H17	118.7
N11—Cu2—N3^{vi}	90.62 (13)	C16—C17—H17	118.7
N3—Cu2—N3^{vi}	180.0	C16—C18—H18A	109.5
O1—Cu3—O1^{vii}	180.00 (17)	C16—C18—H18B	109.5
O1—Cu3—N10^{vii}	92.98 (12)	H18A—C18—H18B	109.5
O1^{vii}—Cu3—N10^{vii}	87.01 (12)	C16—C18—H18C	109.5
O1—Cu3—N10	87.02 (12)	H18A—C18—H18C	109.5
O1^{vii}—Cu3—N10	92.98 (12)	H18B—C18—H18C	109.5

N4^{iv}—Cu2—N3—C3	153.2 (18)	Cu2^{ii}—N4—C4—W1	−113 (6)
N4^{v}—Cu2—N3—C3	−26.8 (18)	C1—W1—C4—N4	24 (7)
N11^{vi}—Cu2—N3—C3	63.9 (18)	C8—W1—C4—N4	−40 (7)
N11—Cu2—N3—C3	−116.1 (18)	C5—W1—C4—N4	−156 (7)
N3^{vi}—Cu2—N3—C3	−35 (58)	C3—W1—C4—N4	114 (7)
N1^{i}—Cu1—N8—C8	−24.6 (11)	C7—W1—C4—N4	−95 (7)
N1^{ii}—Cu1—N8—C8	155.4 (11)	C6—W1—C4—N4	165 (7)
N9—Cu1—N8—C8	68.6 (11)	C2—W1—C4—N4	38 (7)
N9^{iii}—Cu1—N8—C8	−111.4 (11)	C1—W1—C5—N5	13 (39)
N8^{iii}—Cu1—N8—C8	−67 (100)	C8—W1—C5—N5	126 (39)
N1^{i}—Cu1—N9—C9	79.9 (3)	C4—W1—C5—N5	−167 (100)
N1^{ii}—Cu1—N9—C9	−100.1 (3)	C3—W1—C5—N5	−84 (39)
N9^{iii}—Cu1—N9—C9	178 (28)	C7—W1—C5—N5	63 (39)
N8^{iii}—Cu1—N9—C9	170.2 (3)	C6—W1—C5—N5	−12 (39)
N8—Cu1—N9—C9	−9.8 (3)	C2—W1—C5—N5	−144 (39)
N1^{i}—Cu1—N9—C12	−104.5 (3)	C1—W1—C6—N6	−81 (62)
N1^{ii}—Cu1—N9—C12	75.5 (3)	C8—W1—C6—N6	−17 (62)
N9^{iii}—Cu1—N9—C12	−7 (28)	C4—W1—C6—N6	122 (62)
N8^{iii}—Cu1—N9—C12	−14.2 (3)	C5—W1—C6—N6	85 (62)
N8—Cu1—N9—C12	165.8 (3)	C3—W1—C6—N6	177 (100)

O1—Cu3—N10—C9	−108.2 (3)	C7—W1—C6—N6	4 (62)
O1^{vii}—Cu3—N10—C9	71.8 (3)	C2—W1—C6—N6	−131 (62)
N10^{vii}—Cu3—N10—C9	56 (80)	C1—W1—C7—N7	−151 (6)
O1—Cu3—N10—C10	63.1 (3)	C8—W1—C7—N7	−60 (6)
O1^{vii}—Cu3—N10—C10	−116.9 (3)	C4—W1—C7—N7	−3 (6)
N10^{vii}—Cu3—N10—C10	−133 (80)	C5—W1—C7—N7	55 (6)
N4^{iv}—Cu2—N11—C14	−55.8 (4)	C3—W1—C7—N7	122 (6)
N4^{v}—Cu2—N11—C14	124.2 (4)	C6—W1—C7—N7	134 (6)
N11^{vi}—Cu2—N11—C14	−19 (27)	C2—W1—C7—N7	−100 (6)
N3—Cu2—N11—C14	−144.2 (4)	Cu1—N8—C8—W1	−6 (14)
N3^{vi}—Cu2—N11—C14	35.8 (4)	C1—W1—C8—N8	44 (13)
N4^{iv}—Cu2—N11—C17	126.5 (3)	C4—W1—C8—N8	−168 (13)
N4^{v}—Cu2—N11—C17	−53.5 (3)	C5—W1—C8—N8	−104 (13)
N11^{vi}—Cu2—N11—C17	164 (27)	C3—W1—C8—N8	141 (12)
N3—Cu2—N11—C17	38.1 (3)	C7—W1—C8—N8	−36 (13)
N3^{vi}—Cu2—N11—C17	−141.9 (3)	C6—W1—C8—N8	−15 (13)
Cu1^{v}—N1—C1—W1	31 (5)	C2—W1—C8—N8	116 (13)
C8—W1—C1—N1	−173 (4)	C12—N9—C9—N10	−1.0 (6)
C4—W1—C1—N1	126 (4)	Cu1—N9—C9—N10	174.7 (3)
C5—W1—C1—N1	−54 (4)	C10—N10—C9—N9	1.0 (6)
C3—W1—C1—N1	41 (4)	Cu3—N10—C9—N9	172.4 (3)
C7—W1—C1—N1	−103 (4)	C9—N10—C10—C11	−0.3 (6)
C6—W1—C1—N1	−28 (4)	Cu3—N10—C10—C11	−172.1 (3)
C2—W1—C1—N1	112 (4)	N10—C10—C11—C12	−0.3 (6)
C1—W1—C2—N2	−17 (16)	N10—C10—C11—C13	178.8 (4)
C8—W1—C2—N2	−109 (16)	C9—N9—C12—C11	0.3 (6)
C4—W1—C2—N2	172 (16)	Cu1—N9—C12—C11	−175.4 (3)
C5—W1—C2—N2	150 (16)	C10—C11—C12—N9	0.3 (6)
C3—W1—C2—N2	85 (16)	C13—C11—C12—N9	−178.8 (4)
C7—W1—C2—N2	−70 (16)	C17—N11—C14—N12	−0.9 (7)
C6—W1—C2—N2	34 (16)	Cu2—N11—C14—N12	−178.6 (4)
Cu2—N3—C3—W1	17 (6)	C15—N12—C14—N11	0.2 (8)
C1—W1—C3—N3	−30 (4)	C14—N12—C15—C16	−0.1 (8)
C8—W1—C3—N3	−124 (4)	N12—C15—C16—C17	0.7 (8)
C4—W1—C3—N3	−173 (4)	N12—C15—C16—C18	−178.4 (6)
C5—W1—C3—N3	116 (4)	C14—N11—C17—C16	1.5 (7)
C7—W1—C3—N3	52 (5)	Cu2—N11—C17—C16	179.3 (4)
C6—W1—C3—N3	40 (4)	C15—C16—C17—N11	−1.4 (7)
C2—W1—C3—N3	−99 (4)	C18—C16—C17—N11	177.7 (5)

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+2; (ii) *x*+1, *y*, *z*; (iii) −*x*+2, −*y*+2, −*z*+2; (iv) −*x*+1, −*y*+2, −*z*+1; (v) *x*−1, *y*, *z*; (vi) −*x*, −*y*+2, −*z*+1; (vii) −*x*+2, −*y*+1, −*z*+2.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N6^{viii}	0.92 (2)	1.86 (2)	2.771 (5)	167 (5)
O1—H2···O2	0.93 (2)	1.79 (2)	2.700 (4)	165 (4)

O2—H3···N12^{ix}	0.95 (2)	2.00 (3)	2.914 (5)	161 (4)
O2—H4···N2^{i}	0.93 (2)	2.02 (2)	2.944 (5)	169 (6)

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+2; (viii) −*x*+1, −*y*+1, −*z*+2; (ix) *x*+1, *y*, *z*+1.