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Poly[[aqua-μ-cyanido-tetrakis(ethylenediamine)dicopper(II)] [nona-μ-cyanido-dizincate(II)dicuprate(I)]]

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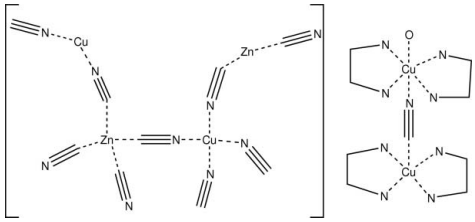
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.013 Å; R factor = 0.037; wR factor = 0.101; data-to-parameter ratio = 15.9.

The title compound, $\{[Cu_2(CN)(C_2H_8N_2)_4(H_2O)][Cu_2Zn_2(CN)_9]\}_n$, is a host–guest structure in which the host is constituted by the Zn^{II} and Cu^{I} atoms bridged by cyanide ions, and the guest consists of Cu^{II}, ethylenediamine, a cyanide and a water molecule. The guest and host species are linked through five N—H···N hydrogen bonds. Zn^{II} and Cu^{I} in the host (or cation), have tetrahedral coordination. Cu^{II} in the guest (or anion) are penta- and hexacoordinated, leading to distorted square-pyramidal and square-bipyramidal structures, respectively

Related literature

For related literature, see: Akyuz *et al.* (1974); Iwamoto & Shriver (1972); Macrae *et al.* (2006).



Experimental

Crystal data

$\{[Cu_2(CN)(C_2H_8N_2)_4(H_2O)][Cu_2Zn_2(CN)_9]\}$
M_r = 901.52
Monoclinic, $P2_1/c$
a = 18.1816 (9) Å
b = 12.4844 (7) Å
c = 16.1923 (8) Å
β = 109.246 (11)°
V = 3470.0 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 3.81 mm^{-1}
T = 293 (2) K
0.26 × 0.19 × 0.16 mm

Data collection

Enraf-Nonius MACH3 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.929, T_{max} = 0.983
(expected range = 0.514–0.544)
6961 measured reflections
6089 independent reflections
3637 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.101
S = 1.04
6089 reflections
382 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.75 e Å^{-3}
$\Delta\rho_{min}$ = −0.56 e Å^{-3}

Table 1
Selected torsion angles (°).

Zn1—C7—N8—Cu2	−178 (5)

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

D—H···A	D—H	H···A	D···A	D—H···A
N41—H41A···N9^{i}	0.90	2.48	3.352 (7)	165
N41—H41B···N16^{ii}	0.90	2.42	3.242 (9)	153
N44—H44B···N11	0.90	2.60	3.234 (7)	128
N45—H45A···N16^{ii}	0.90	2.13	3.020 (8)	170
N35—H35A···N11^{i}	0.90	2.58	3.280 (7)	136

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2425).

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Poly[[aqua-μ-cyanido-tetrakis(ethylenediamine)dicopper(II)] [nona-μ-cyanido-dizincate(II)dicuprate(I)]]

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S1. Comment

Cyanide–metal complexes which form host frameworks, is one of the archetypal host–guest materials and its discovery has spawned a very rich structural chemistry. Hofmann type clathrates of the general formula $MLNi(CN)_4.g$ (*M*=bivalent metal ion, *L*-Ligand, g-guest) have been studied extensively (Akyuz *et al.*, 1974). However, studies on clathrates with $Men_2Ni(CN)_4$ and $MenM'(CN)_4$ (*M*′=Cd, Zn, Hg, Ni; en=ethylenediamine) as hosts are limited in literature (Iwamoto & Shriver, 1972). During the process of synthesizing $Men_2M'(CN)_4$ (*M*′=Cd, Zn, Hg), the single crystals of the title compound were obtained.

The asymmetric unit contains two Zn^{II} and two Cu^{I} atoms linked through nine cyanido ions and two Cu^{II}-en_2 bridged through a CN group and a lattice water molecule as guest (Fig. 1). All the metal atoms in the host, Zn^{II} and Cu^{I}, are observed to be tetra-coordinated whereas Cu^{II} atoms are penta- and hexa coordinated in the guest. The en molecules in guest are in the *gauche* conformation. The angle between the planes N35—Cu3—N38 and N31—Cu3—N34 is 16.6 (1)° while this value is 53.3 (2)° for planes N45—Cu4—N48 and N41—Cu4—N44. These values replicate the angle of orientation between the en_2 molecules.

There are five intermolecular N—H···N hydrogen bonds in the structure through which guest and host molecules are linked (Table 2; Fig. 2).

S2. Experimental

5 mmol of ethylenediamine was added to 2.5 mmol of $CuCl_2$ in 10 ml of water. This solution was mixed up with the 10 ml of water containing 2.5 mmol of $K_2Zn(CN)_4$. Tiny needle-shaped crystals were found within a week, at room temperature by slow evaporation.

S3. Refinement

All the H atoms were positioned geometrically and refined using a riding model, with C—H = 0.9 Å and N—H= 0.97 Å with $U_{iso}(H) = 1.2U_{eq}$ (C or N). Attempts to locate the H atoms of the water oxygen present in the lattice were not successfull, due to the presence of heavy atoms in the structure.

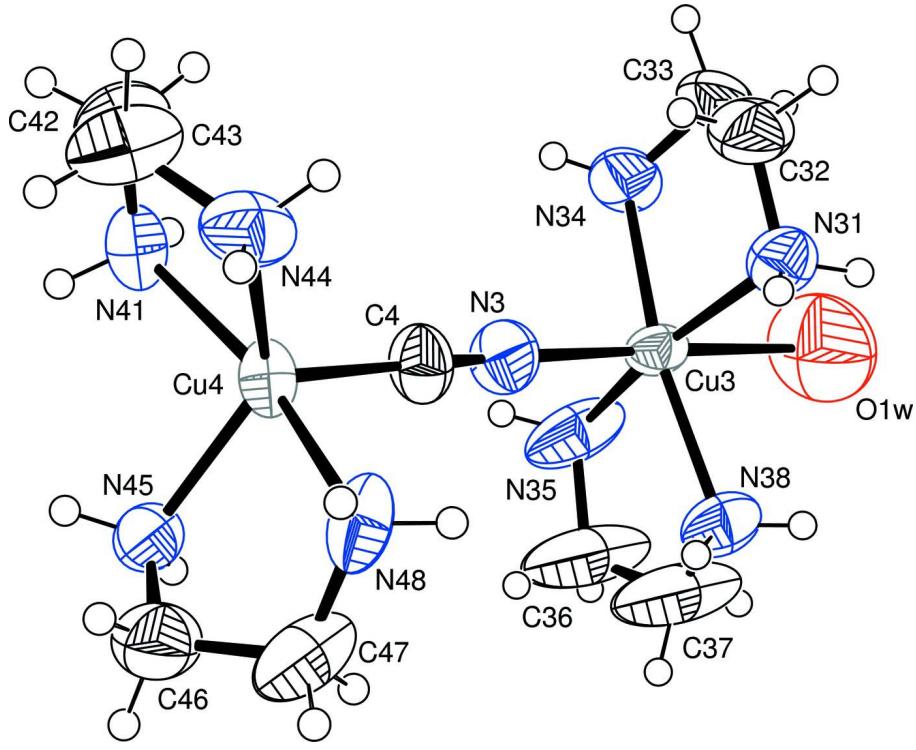

Figure 1

The asymmetric unit of the title compound, with the atom-numbering scheme and 50% probability displacement ellipsoids.

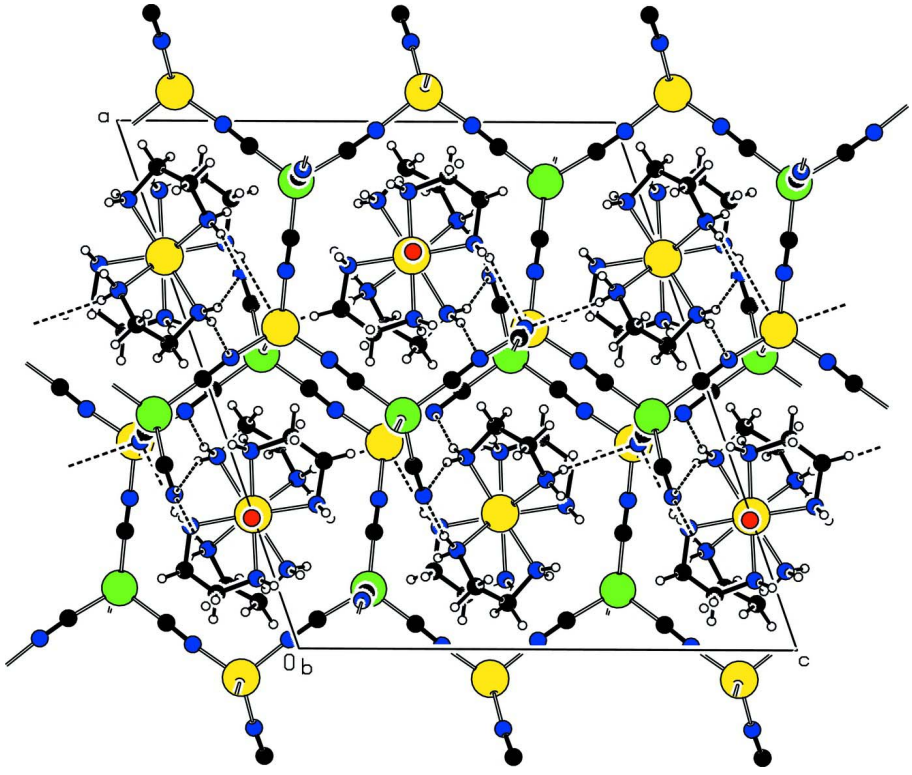

Figure 2

Packing diagram of the molecules viewed down the b-axis. H-bonds are shown as dashed lines.

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Crystal data

$\{[Cu_2(CN)(C_2H_8N_2)_4(H_2O)][Cu_2Zn_2(CN)_9]\}$
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$b = 12.4844\ (7)$ Å
$c = 16.1923\ (8)$ Å
$\beta = 109.246\ (11)°$
$V = 3470.0\ (3)$ Å^3
$Z = 4$
$F(000) = 1800$
$D_x = 1.726$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10.3–13.6°$
$\mu = 3.81$ mm^{-1}
$T = 293$ K
Needle, blue
0.26 × 0.19 × 0.16 mm

Data collection

Enraf-Nonius MACH3 sealed tube diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.929$, $T_{max} = 0.983$
6961 measured reflections
6089 independent reflections
3637 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.0°$
$h = -21\rightarrow20$
$k = -1\rightarrow14$
$l = 0\rightarrow19$
3 standard reflections every 60 min
intensity decay: none

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.101$
$S = 1.04$
6089 reflections
382 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
$w = 1/[\sigma^2(F_o^2) + (0.0329P)^2 + 8.1818P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.75$ e Å^{-3}
$\Delta\rho_{min} = -0.56$ 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}
Zn1	0.11314 (4)	0.68154 (6)	0.68142 (4)	0.03848 (18)
Zn2	0.55735 (4)	0.79273 (5)	1.12894 (4)	0.03891 (18)
Cu1	−0.05596 (4)	0.78446 (5)	0.86348 (4)	0.03212 (17)
Cu2	0.39149 (3)	0.81159 (5)	0.81452 (4)	0.02642 (15)
C1	0.0475 (3)	0.7268 (5)	0.7513 (3)	0.0402 (14)
N2	0.0068 (3)	0.7495 (4)	0.7895 (3)	0.0476 (13)
C3	0.1056 (3)	0.5226 (5)	0.6729 (4)	0.0353 (13)
N4	0.0915 (3)	0.4338 (4)	0.6600 (3)	0.0468 (13)
C5	0.0553 (3)	0.7155 (5)	0.5575 (4)	0.0409 (14)
N6	0.0167 (3)	0.7182 (4)	0.4860 (3)	0.0515 (14)
C7	0.2213 (3)	0.7327 (5)	0.7319 (4)	0.0396 (14)
N8	0.2837 (3)	0.7603 (4)	0.7642 (3)	0.0443 (12)
N9	0.4488 (3)	0.7682 (4)	0.9355 (3)	0.0455 (12)
C10	0.4898 (3)	0.7781 (5)	1.0063 (4)	0.0408 (14)
N11	0.3914 (3)	0.9700 (4)	0.8244 (3)	0.0404 (12)
C12	0.4097 (3)	1.0570 (5)	0.8421 (4)	0.0339 (13)
N13	0.4524 (3)	0.7726 (4)	0.7388 (3)	0.0445 (12)
C14	0.4932 (3)	0.7508 (5)	0.7007 (3)	0.0377 (13)
C15	0.6530 (4)	0.7099 (5)	1.1432 (4)	0.0510 (16)
N16	0.7093 (4)	0.6706 (6)	1.1437 (5)	0.108 (3)
N17	−0.1511 (5)	0.6910 (7)	0.8548 (5)	0.108 (3)
C18	−0.2042 (5)	0.6461 (9)	0.8560 (7)	0.137 (5)
Cu4	0.25758 (5)	0.92268 (6)	0.49821 (6)	0.0483 (2)
N41	0.3639 (3)	0.9584 (5)	0.4690 (4)	0.0615 (16)
H41A	0.3808	0.8993	0.4491	0.074*

H41B	0.3544	1.0093	0.4274	0.074*
C42	0.4230 (4)	0.9960 (7)	0.5493 (5)	0.082 (2)
H42A	0.4503	0.9350	0.5827	0.098*
H42B	0.4608	1.0402	0.5345	0.098*
C43	0.3869 (5)	1.0576 (8)	0.6019 (6)	0.094 (3)
H43A	0.3675	1.1249	0.5729	0.112*
H43B	0.4252	1.0736	0.6584	0.112*
N44	0.3220 (3)	0.9955 (5)	0.6141 (3)	0.0709 (18)
H44A	0.2911	1.0394	0.6321	0.085*
H44B	0.3412	0.9453	0.6555	0.085*
N45	0.1873 (3)	0.9957 (5)	0.3858 (3)	0.0560 (15)
H45A	0.2144	1.0475	0.3699	0.067*
H45B	0.1726	0.9472	0.3423	0.067*
C46	0.1189 (4)	1.0420 (7)	0.3983 (5)	0.080 (2)
H46A	0.0794	1.0549	0.3420	0.096*
H46B	0.1321	1.1100	0.4285	0.096*
C47	0.0879 (5)	0.9660 (8)	0.4513 (5)	0.090 (3)
H47A	0.0453	0.9994	0.4652	0.108*
H47B	0.0683	0.9017	0.4176	0.108*
N48	0.1501 (4)	0.9382 (5)	0.5316 (4)	0.0691 (17)
H48A	0.1391	0.8760	0.5532	0.083*
H48B	0.1555	0.9897	0.5721	0.083*
Cu3	0.25415 (4)	0.49772 (6)	0.50091 (5)	0.04579 (18)
N31	0.2732 (3)	0.4842 (5)	0.6358 (3)	0.0608 (15)
H31A	0.2465	0.5351	0.6531	0.073*
H31B	0.2574	0.4196	0.6480	0.073*
N38	0.1321 (3)	0.4859 (5)	0.4631 (4)	0.0679 (17)
H38A	0.1187	0.4332	0.4932	0.082*
H38B	0.1119	0.5478	0.4743	0.082*
N34	0.3741 (3)	0.4748 (5)	0.5404 (4)	0.0677 (17)
H34A	0.3858	0.4238	0.5074	0.081*
H34B	0.3979	0.5360	0.5339	0.081*
N35	0.2314 (3)	0.4734 (7)	0.3669 (4)	0.096 (3)
H35A	0.2573	0.5219	0.3458	0.116*
H35B	0.2467	0.4074	0.3572	0.116*
C33	0.4008 (4)	0.4424 (8)	0.6318 (5)	0.083 (3)
H33A	0.4556	0.4596	0.6581	0.100*
H33B	0.3949	0.3655	0.6357	0.100*
C32	0.3559 (4)	0.4971 (8)	0.6801 (5)	0.084 (3)
H32A	0.3696	0.4677	0.7386	0.101*
H32B	0.3688	0.5727	0.6850	0.101*
C37	0.1033 (5)	0.4634 (13)	0.3725 (6)	0.153 (4)
H37A	0.0909	0.3876	0.3658	0.184*
H37B	0.0547	0.5021	0.3480	0.184*
N3	0.2591 (4)	0.6693 (4)	0.4970 (5)	0.0652 (15)
C36	0.1473 (5)	0.4855 (13)	0.3244 (6)	0.153 (4)
H36A	0.1370	0.5588	0.3040	0.184*
H36B	0.1314	0.4395	0.2732	0.184*

C4	0.2595 (4)	0.7598 (5)	0.4957 (5)	0.0597 (17)
O1W	0.2468 (5)	0.2864 (6)	0.4956 (6)	0.161 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zn1	0.0349 (3)	0.0439 (4)	0.0356 (4)	−0.0074 (3)	0.0101 (3)	−0.0064 (3)
Zn2	0.0438 (4)	0.0372 (4)	0.0365 (4)	−0.0040 (3)	0.0143 (3)	−0.0010 (3)
Cu1	0.0380 (4)	0.0311 (4)	0.0274 (3)	0.0056 (3)	0.0109 (3)	0.0005 (3)
Cu2	0.0245 (3)	0.0282 (3)	0.0249 (3)	−0.0051 (3)	0.0059 (3)	−0.0044 (3)
C1	0.044 (3)	0.043 (4)	0.030 (3)	−0.004 (3)	0.007 (3)	−0.006 (3)
N2	0.056 (3)	0.053 (3)	0.038 (3)	0.011 (3)	0.021 (3)	−0.006 (2)
C3	0.031 (3)	0.041 (4)	0.038 (3)	−0.007 (3)	0.017 (3)	−0.004 (3)
N4	0.050 (3)	0.042 (3)	0.048 (3)	−0.009 (3)	0.017 (3)	−0.003 (3)
C5	0.042 (3)	0.040 (3)	0.040 (3)	−0.006 (3)	0.012 (3)	0.003 (3)
N6	0.059 (3)	0.055 (4)	0.033 (3)	−0.015 (3)	0.006 (2)	0.000 (3)
C7	0.040 (3)	0.040 (3)	0.039 (3)	−0.011 (3)	0.014 (3)	−0.010 (3)
N8	0.033 (3)	0.054 (3)	0.043 (3)	−0.013 (2)	0.009 (2)	−0.014 (3)
N9	0.049 (3)	0.050 (3)	0.034 (3)	−0.004 (3)	0.010 (2)	0.002 (2)
C10	0.044 (3)	0.041 (4)	0.036 (3)	−0.004 (3)	0.011 (3)	0.003 (3)
N11	0.040 (3)	0.033 (3)	0.047 (3)	−0.002 (2)	0.012 (2)	−0.008 (2)
C12	0.034 (3)	0.035 (4)	0.031 (3)	−0.002 (3)	0.009 (2)	−0.003 (3)
N13	0.045 (3)	0.048 (3)	0.045 (3)	−0.002 (3)	0.020 (2)	−0.011 (3)
C14	0.041 (3)	0.039 (3)	0.032 (3)	−0.003 (3)	0.010 (3)	−0.005 (3)
C15	0.052 (4)	0.045 (4)	0.056 (4)	0.004 (3)	0.017 (3)	−0.014 (3)
N16	0.063 (4)	0.111 (6)	0.140 (7)	0.027 (4)	0.019 (4)	−0.059 (5)
N17	0.117 (6)	0.096 (6)	0.088 (5)	0.006 (5)	0.005 (5)	0.038 (5)
C18	0.071 (6)	0.148 (10)	0.158 (10)	−0.068 (6)	−0.010 (6)	0.104 (8)
Cu4	0.0679 (5)	0.0376 (4)	0.0450 (4)	−0.0025 (4)	0.0263 (4)	0.0003 (4)
N41	0.080 (4)	0.047 (3)	0.068 (4)	0.004 (3)	0.039 (3)	0.008 (3)
C42	0.066 (5)	0.097 (7)	0.091 (6)	0.000 (5)	0.037 (5)	−0.016 (5)
C43	0.062 (5)	0.123 (8)	0.088 (6)	−0.011 (5)	0.015 (5)	−0.031 (6)
N44	0.064 (4)	0.105 (5)	0.041 (3)	0.004 (4)	0.014 (3)	−0.004 (4)
N45	0.053 (3)	0.071 (4)	0.042 (3)	−0.010 (3)	0.014 (3)	0.003 (3)
C46	0.063 (5)	0.106 (7)	0.067 (5)	−0.001 (5)	0.015 (4)	0.013 (5)
C47	0.065 (5)	0.137 (8)	0.074 (6)	−0.038 (5)	0.029 (5)	−0.024 (6)
N48	0.090 (4)	0.063 (4)	0.070 (4)	−0.023 (3)	0.046 (4)	−0.003 (3)
Cu3	0.0310 (3)	0.0597 (4)	0.0480 (4)	0.0039 (4)	0.0149 (3)	−0.0018 (5)
N31	0.052 (3)	0.073 (4)	0.063 (4)	0.002 (3)	0.026 (3)	0.001 (3)
N38	0.045 (3)	0.088 (5)	0.078 (4)	0.001 (3)	0.030 (3)	−0.010 (4)
N34	0.046 (3)	0.088 (5)	0.076 (4)	0.024 (3)	0.029 (3)	0.016 (4)
N35	0.053 (4)	0.159 (7)	0.088 (5)	−0.027 (4)	0.037 (4)	−0.049 (5)
C33	0.040 (4)	0.125 (8)	0.079 (6)	0.021 (4)	0.012 (4)	0.039 (5)
C32	0.065 (5)	0.129 (8)	0.049 (4)	−0.017 (5)	0.005 (4)	−0.002 (5)
C37	0.047 (4)	0.319 (13)	0.088 (5)	−0.012 (6)	0.014 (3)	−0.032 (7)
N3	0.066 (4)	0.040 (3)	0.088 (4)	0.003 (3)	0.023 (3)	0.000 (4)
C36	0.047 (4)	0.319 (13)	0.088 (5)	−0.012 (6)	0.014 (3)	−0.032 (7)
C4	0.072 (5)	0.042 (4)	0.072 (4)	0.006 (4)	0.033 (4)	0.004 (4)

O1W	0.178 (8)	0.106 (6)	0.189 (9)	0.019 (6)	0.048 (7)	−0.001 (7)

Geometric parameters (Å, º)

Zn1—C7	1.971 (6)	C43—H43B	0.9700
Zn1—C1	1.979 (6)	N44—H44A	0.9000
Zn1—C5	1.980 (6)	N44—H44B	0.9000
Zn1—C3	1.991 (6)	N45—C46	1.445 (9)
Zn2—C10	1.969 (6)	N45—H45A	0.9000
Zn2—C15	1.970 (6)	N45—H45B	0.9000
Zn2—C14^{i}	1.974 (6)	C46—C47	1.508 (11)
Zn2—C12^{ii}	1.978 (6)	C46—H46A	0.9700
Cu1—N2	1.957 (5)	C46—H46B	0.9700
Cu1—N4^{iii}	1.968 (5)	C47—N48	1.456 (9)
Cu1—N6^{i}	1.989 (5)	C47—H47A	0.9700
Cu1—N17	2.053 (9)	C47—H47B	0.9700
Cu2—N13	1.966 (5)	N48—H48A	0.9000
Cu2—N8	1.966 (5)	N48—H48B	0.9000
Cu2—N9	1.968 (5)	Cu3—N34	2.081 (5)
Cu2—N11	1.984 (5)	Cu3—N35	2.092 (6)
C1—N2	1.144 (7)	Cu3—N31	2.102 (5)
C3—N4	1.142 (7)	Cu3—N38	2.103 (5)
N4—Cu1^{iv}	1.968 (5)	Cu3—N3	2.145 (5)
C5—N6	1.139 (7)	N31—C32	1.445 (8)
N6—Cu1^{v}	1.989 (5)	N31—H31A	0.9000
C7—N8	1.134 (6)	N31—H31B	0.9000
N9—C10	1.149 (7)	N38—C37	1.413 (10)
N11—C12	1.145 (7)	N38—H38A	0.9000
C12—Zn2^{ii}	1.978 (6)	N38—H38B	0.9000
N13—C14	1.142 (6)	N34—C33	1.455 (9)
C14—Zn2^{v}	1.974 (5)	N34—H34A	0.9000
C15—N16	1.132 (8)	N34—H34B	0.9000
N17—C18	1.122 (9)	N35—C36	1.464 (10)
Cu4—C4	2.034 (7)	N35—H35A	0.9000
Cu4—N45	2.060 (5)	N35—H35B	0.9000
Cu4—N44	2.066 (5)	C33—C32	1.471 (10)
Cu4—N41	2.182 (5)	C33—H33A	0.9700
Cu4—N48	2.202 (6)	C33—H33B	0.9700
N41—C42	1.465 (9)	C32—H32A	0.9700
N41—H41A	0.9000	C32—H32B	0.9700
N41—H41B	0.9000	C37—C36	1.317 (12)
C42—C43	1.455 (10)	C37—H37A	0.9700
C42—H42A	0.9700	C37—H37B	0.9700
C42—H42B	0.9700	N3—C4	1.131 (8)
C43—N44	1.479 (10)	C36—H36A	0.9700
C43—H43A	0.9700	C36—H36B	0.9700
C7—Zn1—C1	112.2 (2)	H45A—N45—H45B	108.0

C7—Zn1—C5	118.4 (2)	N45—C46—C47	109.1 (7)
C1—Zn1—C5	107.4 (2)	N45—C46—H46A	109.9
C7—Zn1—C3	112.9 (2)	C47—C46—H46A	109.9
C1—Zn1—C3	106.5 (2)	N45—C46—H46B	109.9
C5—Zn1—C3	98.1 (2)	C47—C46—H46B	109.9
C10—Zn2—C15	107.6 (2)	H46A—C46—H46B	108.3
C10—Zn2—C14^{i}	105.9 (2)	N48—C47—C46	109.5 (6)
C15—Zn2—C14^{i}	117.2 (3)	N48—C47—H47A	109.8
C10—Zn2—C12^{ii}	111.5 (2)	C46—C47—H47A	109.8
C15—Zn2—C12^{ii}	106.5 (2)	N48—C47—H47B	109.8
C14^{i}—Zn2—C12^{ii}	108.2 (2)	C46—C47—H47B	109.8
N2—Cu1—N4^{iii}	108.3 (2)	H47A—C47—H47B	108.2
N2—Cu1—N6^{i}	106.1 (2)	C47—N48—Cu4	107.0 (4)
N4^{iii}—Cu1—N6^{i}	106.0 (2)	C47—N48—H48A	110.3
N2—Cu1—N17	118.7 (3)	Cu4—N48—H48A	110.3
N4^{iii}—Cu1—N17	108.0 (3)	C47—N48—H48B	110.3
N6^{i}—Cu1—N17	109.1 (3)	Cu4—N48—H48B	110.3
N13—Cu2—N8	110.53 (19)	H48A—N48—H48B	108.6
N13—Cu2—N9	109.3 (2)	N34—Cu3—N35	97.3 (2)
N8—Cu2—N9	116.8 (2)	N34—Cu3—N31	82.7 (2)
N13—Cu2—N11	108.2 (2)	N35—Cu3—N31	166.9 (3)
N8—Cu2—N11	109.3 (2)	N34—Cu3—N38	168.0 (2)
N9—Cu2—N11	102.0 (2)	N35—Cu3—N38	81.9 (2)
N2—C1—Zn1	176.6 (5)	N31—Cu3—N38	95.4 (2)
C1—N2—Cu1	175.3 (5)	N34—Cu3—N3	95.5 (2)
N4—C3—Zn1	170.7 (5)	N35—Cu3—N3	96.3 (3)
C3—N4—Cu1^{iv}	174.0 (5)	N31—Cu3—N3	96.7 (3)
N6—C5—Zn1	168.4 (5)	N38—Cu3—N3	96.4 (2)
C5—N6—Cu1^{v}	175.8 (5)	C32—N31—Cu3	107.2 (4)
N8—C7—Zn1	177.2 (5)	C32—N31—H31A	110.3
C7—N8—Cu2	177.1 (5)	Cu3—N31—H31A	110.3
C10—N9—Cu2	156.9 (5)	C32—N31—H31B	110.3
N9—C10—Zn2	178.1 (5)	Cu3—N31—H31B	110.3
C12—N11—Cu2	163.4 (5)	H31A—N31—H31B	108.5
N11—C12—Zn2^{ii}	178.8 (5)	C37—N38—Cu3	108.2 (5)
C14—N13—Cu2	174.4 (5)	C37—N38—H38A	110.1
N13—C14—Zn2^{v}	175.9 (5)	Cu3—N38—H38A	110.1
N16—C15—Zn2	171.4 (8)	C37—N38—H38B	110.1
C18—N17—Cu1	173.3 (11)	Cu3—N38—H38B	110.1
C4—Cu4—N45	115.8 (3)	H38A—N38—H38B	108.4
C4—Cu4—N44	116.7 (3)	C33—N34—Cu3	108.3 (4)
N45—Cu4—N44	127.5 (2)	C33—N34—H34A	110.0
C4—Cu4—N41	100.2 (2)	Cu3—N34—H34A	110.0
N45—Cu4—N41	93.1 (2)	C33—N34—H34B	110.0
N44—Cu4—N41	80.2 (2)	Cu3—N34—H34B	110.0
C4—Cu4—N48	96.6 (2)	H34A—N34—H34B	108.4
N45—Cu4—N48	80.5 (2)	C36—N35—Cu3	107.0 (5)
N44—Cu4—N48	91.3 (2)	C36—N35—H35A	110.3

N41—Cu4—N48	163.1 (2)	Cu3—N35—H35A	110.3
C42—N41—Cu4	108.5 (4)	C36—N35—H35B	110.3
C42—N41—H41A	110.0	Cu3—N35—H35B	110.3
Cu4—N41—H41A	110.0	H35A—N35—H35B	108.6
C42—N41—H41B	110.0	N34—C33—C32	110.8 (6)
Cu4—N41—H41B	110.0	N34—C33—H33A	109.5
H41A—N41—H41B	108.4	C32—C33—H33A	109.5
C43—C42—N41	110.4 (6)	N34—C33—H33B	109.5
C43—C42—H42A	109.6	C32—C33—H33B	109.5
N41—C42—H42A	109.6	H33A—C33—H33B	108.1
C43—C42—H42B	109.6	N31—C32—C33	110.7 (6)
N41—C42—H42B	109.6	N31—C32—H32A	109.5
H42A—C42—H42B	108.1	C33—C32—H32A	109.5
C42—C43—N44	109.5 (8)	N31—C32—H32B	109.5
C42—C43—H43A	109.8	C33—C32—H32B	109.5
N44—C43—H43A	109.8	H32A—C32—H32B	108.1
C42—C43—H43B	109.8	C36—C37—N38	118.8 (9)
N44—C43—H43B	109.8	C36—C37—H37A	107.6
H43A—C43—H43B	108.2	N38—C37—H37A	107.6
C43—N44—Cu4	110.4 (5)	C36—C37—H37B	107.6
C43—N44—H44A	109.6	N38—C37—H37B	107.6
Cu4—N44—H44A	109.6	H37A—C37—H37B	107.0
C43—N44—H44B	109.6	C4—N3—Cu3	177.7 (6)
Cu4—N44—H44B	109.6	C37—C36—N35	116.4 (9)
H44A—N44—H44B	108.1	C37—C36—H36A	108.2
C46—N45—Cu4	111.4 (4)	N35—C36—H36A	108.2
C46—N45—H45A	109.3	C37—C36—H36B	108.2
Cu4—N45—H45A	109.3	N35—C36—H36B	108.2
C46—N45—H45B	109.3	H36A—C36—H36B	107.3
Cu4—N45—H45B	109.3	N3—C4—Cu4	177.0 (7)

C7—Zn1—C1—N2	−167 (9)	N41—C42—C43—N44	51.5 (10)
C5—Zn1—C1—N2	61 (9)	C42—C43—N44—Cu4	−42.6 (8)
C3—Zn1—C1—N2	−43 (9)	C4—Cu4—N44—C43	114.3 (6)
Zn1—C1—N2—Cu1	120 (8)	N45—Cu4—N44—C43	−68.5 (6)
N4^{iii}—Cu1—N2—C1	127 (7)	N41—Cu4—N44—C43	17.8 (5)
N6^{i}—Cu1—N2—C1	13 (7)	N48—Cu4—N44—C43	−147.6 (5)
N17—Cu1—N2—C1	−110 (7)	C4—Cu4—N45—C46	108.5 (5)
C7—Zn1—C3—N4	−161 (3)	N44—Cu4—N45—C46	−68.7 (6)
C1—Zn1—C3—N4	75 (3)	N41—Cu4—N45—C46	−148.6 (5)
C5—Zn1—C3—N4	−36 (3)	N48—Cu4—N45—C46	15.6 (5)
Zn1—C3—N4—Cu1^{iv}	−35 (8)	Cu4—N45—C46—C47	−41.1 (7)
C7—Zn1—C5—N6	144 (3)	N45—C46—C47—N48	53.5 (9)
C1—Zn1—C5—N6	−88 (3)	C46—C47—N48—Cu4	−38.1 (8)
C3—Zn1—C5—N6	22 (3)	C4—Cu4—N48—C47	−102.2 (6)
Zn1—C5—N6—Cu1^{v}	28 (10)	N45—Cu4—N48—C47	12.9 (5)
C1—Zn1—C7—N8	53 (11)	N44—Cu4—N48—C47	140.8 (5)
C5—Zn1—C7—N8	179 (100)	N41—Cu4—N48—C47	81.7 (10)

C3—Zn1—C7—N8	−67 (11)	N34—Cu3—N31—C32	15.6 (5)
Zn1—C7—N8—Cu2	−178 (5)	N35—Cu3—N31—C32	106.4 (11)
N13—Cu2—N8—C7	−52 (10)	N38—Cu3—N31—C32	−176.3 (5)
N9—Cu2—N8—C7	−178 (100)	N3—Cu3—N31—C32	−79.2 (5)
N11—Cu2—N8—C7	67 (10)	N34—Cu3—N38—C37	−84.1 (14)
N13—Cu2—N9—C10	94.8 (12)	N35—Cu3—N38—C37	2.9 (8)
N8—Cu2—N9—C10	−138.7 (12)	N31—Cu3—N38—C37	−164.2 (8)
N11—Cu2—N9—C10	−19.6 (12)	N3—Cu3—N38—C37	98.4 (8)
Cu2—N9—C10—Zn2	134 (17)	N35—Cu3—N34—C33	−156.0 (6)
C15—Zn2—C10—N9	117 (18)	N31—Cu3—N34—C33	10.8 (6)
C14^{i}—Zn2—C10—N9	−9 (18)	N38—Cu3—N34—C33	−70.6 (13)
C12^{ii}—Zn2—C10—N9	−127 (18)	N3—Cu3—N34—C33	106.9 (6)
N13—Cu2—N11—C12	−71.8 (17)	N34—Cu3—N35—C36	179.7 (8)
N8—Cu2—N11—C12	167.8 (16)	N31—Cu3—N35—C36	90.5 (13)
N9—Cu2—N11—C12	43.4 (17)	N38—Cu3—N35—C36	11.8 (8)
Cu2—N11—C12—Zn2^{ii}	73 (30)	N3—Cu3—N35—C36	−83.9 (8)
N8—Cu2—N13—C14	−157 (5)	Cu3—N34—C33—C32	−35.7 (8)
N9—Cu2—N13—C14	−28 (5)	Cu3—N31—C32—C33	−39.7 (8)
N11—Cu2—N13—C14	83 (5)	N34—C33—C32—N31	51.8 (10)
Cu2—N13—C14—Zn2^{v}	154 (4)	Cu3—N38—C37—C36	−20.3 (16)
C10—Zn2—C15—N16	60 (4)	N34—Cu3—N3—C4	−150 (20)
C14^{i}—Zn2—C15—N16	179 (100)	N35—Cu3—N3—C4	112 (20)
C12^{ii}—Zn2—C15—N16	−59 (4)	N31—Cu3—N3—C4	−66 (20)
N2—Cu1—N17—C18	180 (100)	N38—Cu3—N3—C4	30 (20)
N4^{iii}—Cu1—N17—C18	−57 (6)	N38—C37—C36—N35	33 (2)
N6^{i}—Cu1—N17—C18	58 (6)	Cu3—N35—C36—C37	−27.3 (15)
C4—Cu4—N41—C42	−106.7 (5)	Cu3—N3—C4—Cu4	31 (34)
N45—Cu4—N41—C42	136.4 (5)	N45—Cu4—C4—N3	−114 (16)
N44—Cu4—N41—C42	8.9 (5)	N44—Cu4—C4—N3	63 (16)
N48—Cu4—N41—C42	69.3 (10)	N41—Cu4—C4—N3	147 (16)
Cu4—N41—C42—C43	−34.7 (9)	N48—Cu4—C4—N3	−31 (16)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N41—H41*A*···N9^{v}	0.90	2.48	3.352 (7)	165
N41—H41*B*···N16^{vi}	0.90	2.42	3.242 (9)	153
N44—H44*B*···N11	0.90	2.60	3.234 (7)	128
N45—H45*A*···N16^{vi}	0.90	2.13	3.020 (8)	170
N35—H35*A*···N11^{v}	0.90	2.58	3.280 (7)	136

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