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Poly[tetrakis(2,2′-bipyridine)undeca-μ-oxido-hexaoxidodicopper(II)hexavanadium(V)]

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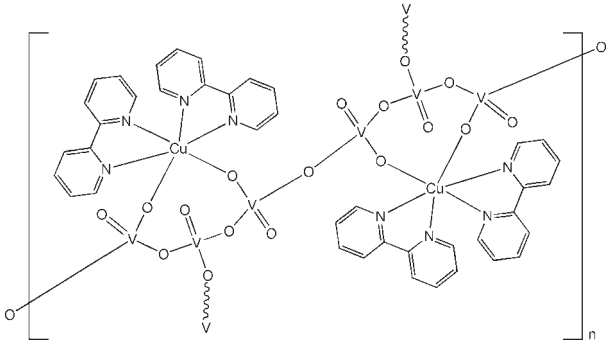
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.031; wR factor = 0.087; data-to-parameter ratio = 12.0.

In the title organic–inorganic hybrid vanadate complex, $[Cu_2V_6O_{17}(C_{10}H_8N_2)_4]_n$, the Cu^{II} atom is six-coordinated by two chelating 2,2′-bipyridine (bipy) ligands and two vanadate O atoms in a distorted octahedral geometry. Two $[Cu(bipy)_2V_3O_8]$ units are linked by a bridging O atom, which lies on an inversion center, forming a dimeric unit. The dimeric units are further connected by bridging vanadate O atoms into a two-dimensional layer parallel to (100). The layers are connected by weak C—H···O hydrogen bonds.

Related literature

For the introduction of some transition metal complexes into inorganic framework structures, see: Cao *et al.* (2003); Liu *et al.* (2001); Zhang *et al.* (2000).



Experimental

Crystal data

$[Cu_2V_6O_{17}(C_{10}H_8N_2)_4]$
M_r = 1329.46
Monoclinic, $P2_1/c$
a = 15.512 (3) Å
b = 14.761 (3) Å
c = 10.470 (2) Å
β = 92.00 (3)°
V = 2395.9 (8) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.07 mm^{-1}
T = 293 K
0.57 × 0.40 × 0.30 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.385, T_{max} = 0.577
20154 measured reflections
4742 independent reflections
4010 reflections with $I > 2\sigma(I)$
R_{int} = 0.027

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.031
$wR(F^2)$ = 0.087
S = 1.05
4742 reflections
395 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.67 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C11—H8···O1	0.87 (3)	2.52 (3)	3.093 (4)	124 (2)
C14—H5···O5^{i}	0.89 (4)	2.51 (3)	3.159 (5)	131 (3)
C18—H3···O5^{ii}	0.90 (4)	2.46 (4)	3.315 (5)	157 (3)
C19—H2···O9^{iii}	0.98 (4)	2.32 (4)	3.156 (5)	144 (3)

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); 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: HY2298).

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Poly[tetrakis(2,2′-bipyridine)undeca-μ-oxido-hexaoxidodicopper(II)hexavanadium(V)]

Ji-Wen Cui, Xiao-Bing Cui, Hai-Hui Yu, Ji-Qing Xu and Shu-Hong Wang

S1. Comment

An important advance for the design of organic-inorganic hybrid materials is to introduce some transition metal complexes (TMCs) into the backbone of inorganic oxides (Liu *et al.*, 2001; Zhang *et al.*, 2000). We are interested in introducing transition metal complexes into inorganic frameworks and understanding the role of metal complexes on the modification of inorganic framework structures (Cao *et al.*, 2003). In an effort to further explore the structural diversity of the M/V/O/L system (M = transition metal, L = organic ligand), we have prepared the title compound.

The asymmetric unit of the title compound contains a $[Cu(bipy)_2(V_3O_{8.5})]$ (bipy = 2,2′-bipyridine) unit, as shown in Fig.1. The V^V centers exhibit VO_4 tetrahedral coordination environments with V—O_t (terminal O atom) distances ranging from 1.580 (3) to 1.610 (2) Å and V—O_b (bridging O atom) distances ranging from 1.630 (2) to 1.821 (2) Å. The Cu^{II} atom is six-coordinated by two bipy ligands and two vanadate O atoms (O1 and O4) in a distorted octahedral geometry, with Cu—N = 2.055 (2)–2.125 (2) Å and Cu—O = 2.025 (2) and 2.082 (2) Å. Two $[Cu(bipy)_2V_3O_8]$ units are linked by a bridging O2 atom, which lies on an inversion center, with a V—O distance of 1.7813 (6) Å, generating a dimeric $[Cu_2(bipy)_4V_6O_{17}]$ unit. As illustrated in Fig. 2, each dimeric unit is joined to four adjacent ones through O6 and its symmetry equivalents, generating a two-dimensional network grafted with $[Cu(bipy)_2]^{2+}$ complex. In addition, the adjacent two-dimension layers further stack into a three-dimensional structure via weak C—H···O hydrogen-bonding interactions (Table 1).

S2. Experimental

A mixture of $Na_2WO_4.2H_2O$ (1.20 g, 3.6 mmol), V_2O_5 (0.33 g, 1.8 mmol), $Cu(CH_3CO_2)_2.4H_2O$ (0.3 g, 1.2 mmol), bipy (0.18 g, 1.2 mmol) and distilled water (20 ml, 1111 mmol) in a molar ratio of 6:3:2:2:1850 was stirred for 120 min. The pH value of the mixture was necessarily adjusted to 4 with dilute H_3PO_4 solution. The resultant mixture was sealed in a 25 ml Teflon-lined autoclave and heated at 553 K for 72 h. The autoclave was then cooled to room temperature. The crystalline product was filtered, washed with distilled water and dried at ambient temperature to give 0.335 g solids of the title compound.

S3. Refinement

All H atoms were located from difference Fourier maps and refined isotropically.

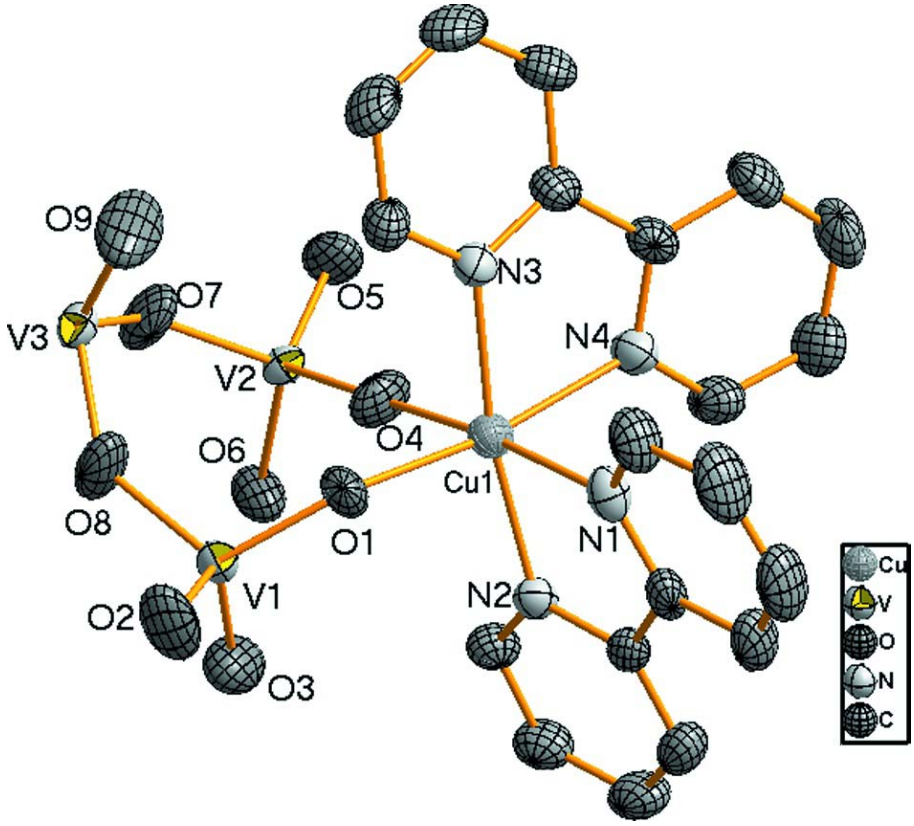

Figure 1

The asymmetric unit of the title compound, with displacement ellipsoids at the 50% probability level.

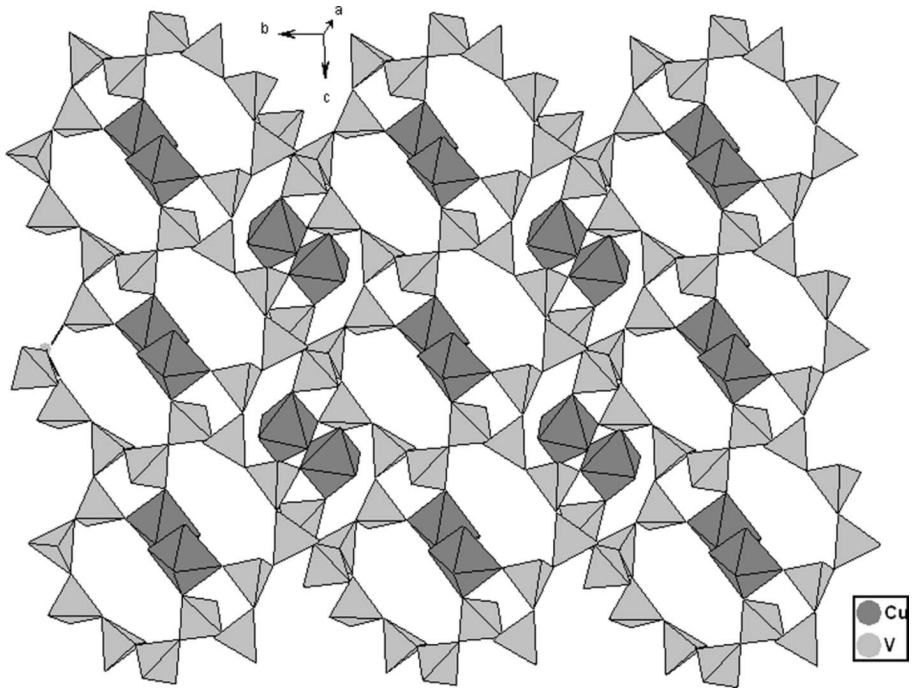

Figure 2

A polyhedral representation of the two-dimensional layer-like structure in the title compound. H and C atoms of bipy molecules are omitted for clarity.

Poly[tetrakis(2,2′-bipyridine)undeca-μ-oxido- hexaoxidodicopper(II)hexavanadium(V)]

Crystal data

$[Cu_2V_6O_{17}(C_{10}H_8N_2)_4]$
M_r = 1329.46
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
a = 15.512 (3) Å
b = 14.761 (3) Å
c = 10.470 (2) Å
β = 92.00 (3)°
V = 2395.9 (8) Å^3
Z = 2
$F(000)$ = 1320
D_x = 1.843 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 7302 reflections
θ = 2.4–26.0°
μ = 2.07 mm^{-1}
T = 293 K
Block, red
0.57 × 0.40 × 0.30 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
T_{min} = 0.385, T_{max} = 0.577
20154 measured reflections
4742 independent reflections
4010 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 26.1°, θ_{min} = 2.4°
h = −19→19
k = −18→18
l = −12→12

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.087$
$S = 1.05$
4742 reflections
395 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
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2 + 1.8261P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.67$ e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.23318 (2)	0.97904 (2)	0.20082 (3)	0.02820 (11)
V1	0.08531 (3)	1.05781 (3)	0.42475 (4)	0.02542 (12)
V2	0.31303 (3)	1.19857 (3)	0.31446 (4)	0.02286 (12)
V3	0.25041 (3)	1.14320 (3)	0.60425 (4)	0.02692 (12)
O1	0.14691 (13)	0.98560 (13)	0.3484 (2)	0.0341 (5)
O2	0.0000	1.0000	0.5000	0.0553 (10)
O3	0.04662 (16)	1.13047 (15)	0.3236 (2)	0.0510 (6)
O4	0.27773 (15)	1.10202 (14)	0.2580 (2)	0.0427 (5)
O5	0.41332 (14)	1.21072 (16)	0.2836 (2)	0.0436 (5)
O6	0.25003 (15)	1.28957 (15)	0.2414 (2)	0.0430 (5)
O7	0.30503 (16)	1.20006 (18)	0.4860 (2)	0.0510 (6)
O8	0.14570 (16)	1.12151 (18)	0.5470 (2)	0.0551 (7)
O9	0.2978 (2)	1.05097 (19)	0.6372 (3)	0.0846 (11)
N1	0.17768 (16)	0.86159 (15)	0.1249 (2)	0.0318 (5)
N2	0.15122 (14)	1.03192 (15)	0.0616 (2)	0.0268 (5)
N3	0.32645 (15)	0.91624 (15)	0.3159 (2)	0.0294 (5)
N4	0.33465 (15)	0.96215 (17)	0.0718 (2)	0.0318 (5)
C1	0.1889 (2)	0.7771 (2)	0.1683 (3)	0.0430 (8)
C2	0.1533 (3)	0.7026 (2)	0.1050 (4)	0.0546 (11)
C3	0.1052 (3)	0.7157 (2)	−0.0051 (4)	0.0527 (10)
C4	0.0924 (2)	0.8026 (2)	−0.0504 (4)	0.0437 (8)
C5	0.12893 (18)	0.87492 (19)	0.0171 (3)	0.0313 (6)
C6	0.11711 (17)	0.97065 (19)	−0.0214 (3)	0.0292 (6)
C7	0.0741 (2)	0.9974 (3)	−0.1329 (3)	0.0428 (8)
C8	0.0654 (2)	1.0887 (3)	−0.1598 (3)	0.0453 (8)
C9	0.0985 (2)	1.1508 (2)	−0.0744 (3)	0.0393 (7)
C10	0.14073 (19)	1.1201 (2)	0.0355 (3)	0.0333 (6)
C11	0.3215 (2)	0.9033 (2)	0.4409 (3)	0.0407 (7)
C12	0.3903 (3)	0.8710 (3)	0.5148 (4)	0.0550 (10)
C13	0.4660 (3)	0.8537 (3)	0.4584 (4)	0.0615 (12)
C14	0.4726 (2)	0.8668 (3)	0.3293 (4)	0.0498 (9)
C15	0.40065 (19)	0.8971 (2)	0.2594 (3)	0.0340 (7)
C16	0.40090 (19)	0.9128 (2)	0.1201 (3)	0.0343 (6)
C17	0.4643 (2)	0.8791 (3)	0.0428 (4)	0.0478 (9)

C18	0.4617 (3)	0.8992 (3)	−0.0851 (4)	0.0562 (10)
C19	0.3964 (2)	0.9526 (3)	−0.1333 (3)	0.0509 (9)
C20	0.3348 (2)	0.9822 (3)	−0.0522 (3)	0.0409 (8)
H1	0.299 (2)	1.013 (2)	−0.078 (3)	0.032 (9)*
H2	0.387 (2)	0.969 (3)	−0.223 (4)	0.057 (11)*
H3	0.508 (3)	0.880 (2)	−0.129 (4)	0.053 (11)*
H4	0.498 (2)	0.846 (3)	0.078 (4)	0.050 (11)*
H5	0.522 (3)	0.856 (2)	0.292 (3)	0.052 (11)*
H6	0.510 (3)	0.835 (3)	0.498 (4)	0.065 (12)*
H7	0.384 (3)	0.867 (3)	0.598 (4)	0.072 (13)*
H8	0.272 (2)	0.916 (2)	0.474 (3)	0.030 (8)*
H9	0.1628 (19)	1.159 (2)	0.094 (3)	0.026 (8)*
H10	0.091 (2)	1.207 (3)	−0.088 (3)	0.052 (11)*
H11	0.034 (3)	1.110 (3)	−0.245 (4)	0.070 (12)*
H12	0.056 (2)	0.956 (3)	−0.177 (4)	0.050 (11)*
H13	0.065 (3)	0.813 (3)	−0.128 (4)	0.072 (14)*
H14	0.077 (3)	0.658 (3)	−0.049 (4)	0.077 (13)*
H15	0.164 (3)	0.651 (3)	0.129 (4)	0.060 (12)*
H16	0.223 (2)	0.772 (2)	0.247 (3)	0.040 (9)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.02821 (19)	0.02505 (19)	0.0313 (2)	0.00175 (13)	−0.00022 (14)	−0.00123 (13)
V1	0.0201 (2)	0.0241 (2)	0.0322 (3)	−0.00464 (17)	0.00256 (18)	−0.00629 (18)
V2	0.0239 (2)	0.0238 (2)	0.0208 (2)	−0.00305 (17)	−0.00113 (17)	0.00312 (17)
V3	0.0344 (3)	0.0247 (2)	0.0215 (2)	0.00049 (19)	−0.00231 (19)	−0.00010 (18)
O1	0.0324 (11)	0.0333 (11)	0.0370 (11)	0.0057 (9)	0.0089 (9)	−0.0015 (9)
O2	0.0417 (19)	0.0462 (19)	0.080 (3)	−0.0205 (16)	0.0305 (18)	−0.0156 (18)
O3	0.0606 (16)	0.0355 (12)	0.0561 (15)	0.0119 (11)	−0.0094 (12)	−0.0029 (11)
O4	0.0535 (14)	0.0283 (11)	0.0450 (13)	−0.0079 (10)	−0.0142 (11)	−0.0008 (9)
O5	0.0289 (11)	0.0584 (15)	0.0438 (13)	−0.0057 (10)	0.0052 (9)	0.0031 (11)
O6	0.0523 (14)	0.0443 (13)	0.0329 (11)	0.0190 (11)	0.0073 (10)	0.0107 (10)
O7	0.0553 (15)	0.0756 (17)	0.0221 (11)	−0.0188 (13)	0.0007 (10)	0.0027 (11)
O8	0.0452 (14)	0.0773 (18)	0.0430 (14)	−0.0242 (13)	0.0016 (11)	−0.0233 (12)
O9	0.140 (3)	0.0501 (16)	0.0618 (18)	0.0471 (18)	−0.0262 (19)	−0.0005 (14)
N1	0.0354 (14)	0.0246 (12)	0.0361 (14)	−0.0028 (10)	0.0089 (11)	−0.0038 (10)
N2	0.0231 (12)	0.0260 (12)	0.0312 (12)	0.0005 (9)	−0.0015 (9)	−0.0020 (9)
N3	0.0325 (13)	0.0271 (12)	0.0286 (12)	0.0054 (10)	−0.0012 (10)	−0.0004 (9)
N4	0.0277 (13)	0.0359 (13)	0.0317 (13)	0.0023 (10)	0.0020 (10)	0.0009 (10)
C1	0.053 (2)	0.0291 (16)	0.047 (2)	−0.0013 (14)	0.0123 (17)	−0.0002 (14)
C2	0.074 (3)	0.0237 (17)	0.068 (3)	−0.0073 (17)	0.027 (2)	−0.0034 (16)
C3	0.060 (2)	0.0374 (19)	0.061 (2)	−0.0164 (17)	0.0191 (19)	−0.0196 (17)
C4	0.0414 (19)	0.0415 (19)	0.048 (2)	−0.0090 (15)	0.0062 (16)	−0.0190 (15)
C5	0.0275 (15)	0.0319 (15)	0.0350 (16)	−0.0018 (12)	0.0076 (12)	−0.0102 (12)
C6	0.0220 (13)	0.0353 (15)	0.0303 (15)	−0.0013 (11)	0.0019 (11)	−0.0073 (12)
C7	0.0378 (18)	0.055 (2)	0.0354 (18)	−0.0037 (16)	−0.0039 (14)	−0.0108 (16)
C8	0.0395 (19)	0.059 (2)	0.0368 (18)	0.0058 (16)	−0.0055 (14)	0.0090 (16)

C9	0.0369 (18)	0.0387 (18)	0.0423 (18)	0.0035 (14)	0.0011 (14)	0.0102 (14)
C10	0.0311 (16)	0.0285 (15)	0.0399 (17)	0.0003 (12)	−0.0034 (13)	0.0004 (13)
C11	0.047 (2)	0.0427 (18)	0.0322 (17)	0.0091 (15)	−0.0002 (15)	−0.0034 (14)
C12	0.076 (3)	0.056 (2)	0.0317 (19)	0.014 (2)	−0.0137 (18)	0.0014 (16)
C13	0.060 (3)	0.067 (3)	0.055 (2)	0.025 (2)	−0.026 (2)	−0.0006 (19)
C14	0.039 (2)	0.056 (2)	0.054 (2)	0.0190 (17)	−0.0066 (17)	−0.0005 (17)
C15	0.0329 (16)	0.0292 (15)	0.0397 (17)	0.0067 (12)	−0.0023 (13)	−0.0009 (12)
C16	0.0293 (15)	0.0335 (15)	0.0401 (17)	0.0057 (12)	0.0023 (13)	0.0003 (13)
C17	0.042 (2)	0.050 (2)	0.052 (2)	0.0176 (17)	0.0068 (17)	−0.0025 (17)
C18	0.057 (2)	0.063 (2)	0.050 (2)	0.0111 (19)	0.0220 (19)	−0.0076 (18)
C19	0.054 (2)	0.065 (2)	0.0344 (19)	0.0032 (18)	0.0077 (16)	0.0014 (17)
C20	0.0333 (18)	0.053 (2)	0.0360 (18)	0.0042 (16)	−0.0004 (14)	0.0054 (15)

Geometric parameters (Å, º)

Cu1—O4	2.025 (2)	C2—H15	0.82 (4)
Cu1—N2	2.055 (2)	C3—C4	1.380 (5)
Cu1—N3	2.069 (2)	C3—H14	1.06 (4)
Cu1—N1	2.081 (2)	C4—C5	1.390 (4)
Cu1—O1	2.082 (2)	C4—H13	0.91 (4)
Cu1—N4	2.125 (2)	C5—C6	1.479 (4)
V1—O3	1.609 (2)	C6—C7	1.382 (5)
V1—O1	1.656 (2)	C7—C8	1.382 (5)
V1—O2	1.7813 (6)	C7—H12	0.82 (4)
V1—O8	1.821 (2)	C8—C9	1.367 (5)
V2—O5	1.610 (2)	C8—H11	1.05 (4)
V2—O4	1.630 (2)	C9—C10	1.380 (4)
V2—O7	1.805 (2)	C9—H10	0.85 (4)
V2—O6	1.814 (2)	C10—H9	0.90 (3)
V3—O9	1.580 (3)	C11—C12	1.381 (5)
V3—O7	1.740 (2)	C11—H8	0.87 (3)
V3—O8	1.741 (2)	C12—C13	1.358 (6)
V3—O6^{i}	1.746 (2)	C12—H7	0.88 (4)
O2—V1^{ii}	1.7813 (6)	C13—C14	1.373 (6)
O6—V3^{iii}	1.746 (2)	C13—H6	0.83 (4)
N1—C1	1.336 (4)	C14—C15	1.388 (4)
N1—C5	1.351 (4)	C14—H5	0.89 (4)
N2—C10	1.338 (4)	C15—C16	1.477 (4)
N2—C6	1.349 (3)	C16—C17	1.387 (4)
N3—C11	1.328 (4)	C17—C18	1.370 (5)
N3—C15	1.342 (4)	C17—H4	0.79 (4)
N4—C20	1.332 (4)	C18—C19	1.366 (5)
N4—C16	1.344 (4)	C18—H3	0.90 (4)
C1—C2	1.389 (5)	C19—C20	1.372 (5)
C1—H16	0.97 (3)	C19—H2	0.98 (4)
C2—C3	1.365 (6)	C20—H1	0.77 (3)
O4—Cu1—N2	93.75 (9)	C1—C2—H15	121 (3)

O4—Cu1—N3	90.30 (9)	C2—C3—C4	119.3 (3)
N2—Cu1—N3	170.39 (9)	C2—C3—H14	117 (2)
O4—Cu1—N1	172.68 (9)	C4—C3—H14	123 (2)
N2—Cu1—N1	78.93 (10)	C3—C4—C5	119.2 (4)
N3—Cu1—N1	96.93 (10)	C3—C4—H13	121 (3)
O4—Cu1—O1	87.74 (9)	C5—C4—H13	120 (3)
N2—Cu1—O1	96.38 (9)	N1—C5—C4	121.3 (3)
N3—Cu1—O1	92.48 (9)	N1—C5—C6	115.3 (2)
N1—Cu1—O1	93.10 (9)	C4—C5—C6	123.4 (3)
O4—Cu1—N4	92.31 (10)	N2—C6—C7	121.3 (3)
N2—Cu1—N4	92.71 (9)	N2—C6—C5	115.0 (2)
N3—Cu1—N4	78.41 (9)	C7—C6—C5	123.7 (3)
N1—Cu1—N4	88.01 (9)	C6—C7—C8	119.5 (3)
O1—Cu1—N4	170.89 (9)	C6—C7—H12	114 (3)
O3—V1—O1	108.66 (12)	C8—C7—H12	126 (3)
O3—V1—O2	110.17 (10)	C9—C8—C7	119.2 (3)
O1—V1—O2	110.81 (8)	C9—C8—H11	120 (2)
O3—V1—O8	106.82 (13)	C7—C8—H11	121 (2)
O1—V1—O8	112.34 (12)	C8—C9—C10	118.8 (3)
O2—V1—O8	107.96 (8)	C8—C9—H10	120 (3)
O5—V2—O4	109.82 (12)	C10—C9—H10	121 (3)
O5—V2—O7	107.40 (12)	N2—C10—C9	122.7 (3)
O4—V2—O7	109.75 (11)	N2—C10—H9	116.5 (19)
O5—V2—O6	110.05 (11)	C9—C10—H9	120.8 (19)
O4—V2—O6	108.97 (11)	N3—C11—C12	122.1 (3)
O7—V2—O6	110.83 (11)	N3—C11—H8	116 (2)
O9—V3—O7	109.65 (17)	C12—C11—H8	122 (2)
O9—V3—O8	109.78 (17)	C13—C12—C11	119.0 (4)
O7—V3—O8	108.38 (12)	C13—C12—H7	123 (3)
O9—V3—O6^{i}	108.97 (14)	C11—C12—H7	118 (3)
O7—V3—O6^{i}	109.07 (11)	C12—C13—C14	119.9 (3)
O8—V3—O6^{i}	110.97 (12)	C12—C13—H6	124 (3)
V1—O1—Cu1	141.73 (12)	C14—C13—H6	116 (3)
V1^{ii}—O2—V1	180.00 (3)	C13—C14—C15	118.6 (4)
V2—O4—Cu1	175.90 (14)	C13—C14—H5	120 (2)
V3^{iii}—O6—V2	138.61 (13)	C15—C14—H5	121 (2)
V3—O7—V2	138.95 (15)	N3—C15—C14	121.5 (3)
V3—O8—V1	141.98 (16)	N3—C15—C16	115.7 (3)
C1—N1—C5	118.9 (3)	C14—C15—C16	122.8 (3)
C1—N1—Cu1	126.9 (2)	N4—C16—C17	121.5 (3)
C5—N1—Cu1	114.19 (18)	N4—C16—C15	115.3 (3)
C10—N2—C6	118.6 (3)	C17—C16—C15	123.1 (3)
C10—N2—Cu1	125.6 (2)	C18—C17—C16	119.7 (3)
C6—N2—Cu1	114.90 (18)	C18—C17—H4	125 (3)
C11—N3—C15	119.0 (3)	C16—C17—H4	115 (3)
C11—N3—Cu1	125.1 (2)	C19—C18—C17	118.8 (3)
C15—N3—Cu1	115.52 (19)	C19—C18—H3	125 (2)
C20—N4—C16	117.4 (3)	C17—C18—H3	115 (2)

C20—N4—Cu1	128.3 (2)	C18—C19—C20	118.6 (3)
C16—N4—Cu1	113.47 (19)	C18—C19—H2	126 (2)
N1—C1—C2	122.1 (4)	C20—C19—H2	115 (2)
N1—C1—H16	116 (2)	N4—C20—C19	123.9 (3)
C2—C1—H16	122 (2)	N4—C20—H1	117 (3)
C3—C2—C1	119.2 (4)	C19—C20—H1	119 (3)
C3—C2—H15	119 (3)		

O3—V1—O1—Cu1	36.1 (2)	N1—Cu1—N4—C16	−90.4 (2)
O2—V1—O1—Cu1	157.26 (16)	C5—N1—C1—C2	1.1 (5)
O8—V1—O1—Cu1	−81.9 (2)	Cu1—N1—C1—C2	−175.5 (3)
O4—Cu1—O1—V1	37.4 (2)	N1—C1—C2—C3	0.0 (6)
N2—Cu1—O1—V1	−56.2 (2)	C1—C2—C3—C4	−0.6 (6)
N3—Cu1—O1—V1	127.6 (2)	C2—C3—C4—C5	0.1 (5)
N1—Cu1—O1—V1	−135.4 (2)	C1—N1—C5—C4	−1.6 (4)
O5—V2—O6—V3^{iii}	33.7 (3)	Cu1—N1—C5—C4	175.4 (2)
O4—V2—O6—V3^{iii}	−86.8 (2)	C1—N1—C5—C6	177.8 (3)
O7—V2—O6—V3^{iii}	152.3 (2)	Cu1—N1—C5—C6	−5.3 (3)
O9—V3—O7—V2	81.2 (3)	C3—C4—C5—N1	1.0 (5)
O8—V3—O7—V2	−38.6 (3)	C3—C4—C5—C6	−178.3 (3)
O6^{i}—V3—O7—V2	−159.5 (2)	C10—N2—C6—C7	1.7 (4)
O5—V2—O7—V3	−138.5 (2)	Cu1—N2—C6—C7	−167.8 (2)
O4—V2—O7—V3	−19.1 (3)	C10—N2—C6—C5	−177.9 (2)
O6—V2—O7—V3	101.3 (3)	Cu1—N2—C6—C5	12.6 (3)
O9—V3—O8—V1	−54.8 (3)	N1—C5—C6—N2	−4.8 (4)
O7—V3—O8—V1	64.9 (3)	C4—C5—C6—N2	174.6 (3)
O6^{i}—V3—O8—V1	−175.4 (2)	N1—C5—C6—C7	175.7 (3)
O3—V1—O8—V3	−109.6 (3)	C4—C5—C6—C7	−5.0 (5)
O1—V1—O8—V3	9.4 (3)	N2—C6—C7—C8	−0.4 (5)
O2—V1—O8—V3	131.9 (2)	C5—C6—C7—C8	179.1 (3)
N2—Cu1—N1—C1	−174.2 (3)	C6—C7—C8—C9	−0.9 (5)
N3—Cu1—N1—C1	14.6 (3)	C7—C8—C9—C10	0.8 (5)
O1—Cu1—N1—C1	−78.3 (3)	C6—N2—C10—C9	−1.8 (4)
N4—Cu1—N1—C1	92.6 (3)	Cu1—N2—C10—C9	166.5 (2)
N2—Cu1—N1—C5	9.10 (19)	C8—C9—C10—N2	0.6 (5)
N3—Cu1—N1—C5	−162.12 (19)	C15—N3—C11—C12	0.1 (5)
O1—Cu1—N1—C5	105.0 (2)	Cu1—N3—C11—C12	−171.9 (3)
N4—Cu1—N1—C5	−84.0 (2)	N3—C11—C12—C13	1.4 (6)
O4—Cu1—N2—C10	−0.6 (2)	C11—C12—C13—C14	−1.2 (6)
N1—Cu1—N2—C10	179.4 (3)	C12—C13—C14—C15	−0.4 (6)
O1—Cu1—N2—C10	87.5 (2)	C11—N3—C15—C14	−1.9 (5)
N4—Cu1—N2—C10	−93.1 (2)	Cu1—N3—C15—C14	170.9 (3)
O4—Cu1—N2—C6	168.1 (2)	C11—N3—C15—C16	179.7 (3)
N1—Cu1—N2—C6	−11.84 (19)	Cu1—N3—C15—C16	−7.5 (3)
O1—Cu1—N2—C6	−103.8 (2)	C13—C14—C15—N3	2.0 (5)
N4—Cu1—N2—C6	75.6 (2)	C13—C14—C15—C16	−179.6 (3)
O4—Cu1—N3—C11	80.5 (3)	C20—N4—C16—C17	−3.9 (5)
N1—Cu1—N3—C11	−100.6 (3)	Cu1—N4—C16—C17	166.7 (3)

O1—Cu1—N3—C11	−7.2 (3)	C20—N4—C16—C15	176.4 (3)
N4—Cu1—N3—C11	172.8 (3)	Cu1—N4—C16—C15	−13.0 (3)
O4—Cu1—N3—C15	−91.7 (2)	N3—C15—C16—N4	13.9 (4)
N1—Cu1—N3—C15	87.1 (2)	C14—C15—C16—N4	−164.5 (3)
O1—Cu1—N3—C15	−179.5 (2)	N3—C15—C16—C17	−165.8 (3)
N4—Cu1—N3—C15	0.6 (2)	C14—C15—C16—C17	15.8 (5)
O4—Cu1—N4—C20	−93.8 (3)	N4—C16—C17—C18	2.6 (5)
N2—Cu1—N4—C20	0.1 (3)	C15—C16—C17—C18	−177.8 (3)
N3—Cu1—N4—C20	176.4 (3)	C16—C17—C18—C19	0.2 (6)
N1—Cu1—N4—C20	78.9 (3)	C17—C18—C19—C20	−1.5 (6)
O4—Cu1—N4—C16	96.9 (2)	C16—N4—C20—C19	2.6 (5)
N2—Cu1—N4—C16	−169.2 (2)	Cu1—N4—C20—C19	−166.4 (3)
N3—Cu1—N4—C16	7.1 (2)	C18—C19—C20—N4	0.1 (6)

Symmetry codes: (i) x, $-y+5/2$, $z+1/2$; (ii) $-x$, $-y+2$, $-z+1$; (iii) x, $-y+5/2$, $z-1/2$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H8···O1	0.87 (3)	2.52 (3)	3.093 (4)	124 (2)
C14—H5···O5^{iv}	0.89 (4)	2.51 (3)	3.159 (5)	131 (3)
C18—H3···O5^{v}	0.90 (4)	2.46 (4)	3.315 (5)	157 (3)
C19—H2···O9^{vi}	0.98 (4)	2.32 (4)	3.156 (5)	144 (3)

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