Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Bis[bis(1,10-phenanthroline-κ^2N,N')-copper(I)] μ_6-oxido-dodecakis-μ_2-oxido-hexaoxidohexatungsten(VI)

Zhen-Fang Li, Bi-Song Zhang* and Chang-Sheng Wu

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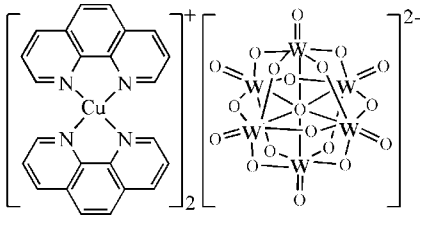
Received 2 May 2009; accepted 27 May 2009

Key indicators: single-crystal X-ray study; T = 290 K; mean σ(C–C) = 0.023 Å; R factor = 0.059; wR factor = 0.157; data-to-parameter ratio = 13.1.

The title compound, $[Cu(C_{12}H_8N_2)_2]_2[W_6O_{19}]$, consists of two $[Cu(phen)_2]^+$ cations (phen = 1,10-phenanthroline) and one typical $[W_6O_{19}]^{2-}$ isopolyanion. The Cu^I atom is coordinated by four N atoms from two bidentate chelating phen ligands in a distorted tetrahedral geometry. The hexatungstate anion, lying on an inversion center and possessing the well known Lindqvist structure, is formed by six edge-sharing WO_6 octahedra, thus exhibiting an approximate O_h symmetry. Three kinds of O atoms exist in the hexatungstate, *viz.* terminal O_a, bridging O_b and central O_c atoms. Besides the electrostatic effects between the anions and cations, weak C—H···O hydrogen bonds exist between the phen ligands and O_a or O_b atoms. The mean interplanar distances of 3.485 (1) and 3.344 (1) Å indicate π–π stacking interactions between neighboring phen ligands. These weak hydrogen bonds and π–π stacking interactions lead to a two-dimensional network.

Related literature

For general background to hexatungstate compounds, see: Khan *et al.* (1998); Meng *et al.* (2006); Zhang *et al.* (2004). For related structures, see: Li & Zhang (2008); Zhang (2008).



Experimental

Crystal data

$[Cu(C_{12}H_8N_2)_2]_2[W_6O_{19}]$
M_r = 2255.00
Triclinic, $P\overline{1}$
a = 10.364 (2) Å
b = 11.772 (2) Å
c = 11.899 (2) Å
α = 108.603 (3)°
β = 102.151 (3)°
γ = 100.694 (3)°
V = 1294.0 (4) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 14.17 mm^{-1}
T = 290 K
0.19 × 0.16 × 0.07 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.09, T_{max} = 0.39
7111 measured reflections
4932 independent reflections
3737 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.157
S = 1.00
4932 reflections
376 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 2.72 e Å^{-3}
$\Delta\rho_{min}$ = −4.78 e Å^{-3}

Table 1
Selected bond lengths (Å).

Cu1—N1	2.027 (14)	W2—O3	1.904 (11)
Cu1—N2	2.013 (11)	W2—O6	1.915 (9)
Cu1—N3	2.050 (12)	W2—O1	1.923 (8)
Cu1—N4	2.007 (11)	W2—O5^{i}	1.941 (9)
W1—O4	1.678 (10)	W2—O10	2.3314 (6)
W1—O3^{i}	1.904 (10)	W3—O7	1.691 (11)
W1—O1	1.926 (8)	W3—O5	1.899 (10)
W1—O9	1.929 (9)	W3—O9	1.907 (9)
W1—O8^{i}	1.931 (8)	W3—O6	1.912 (9)
W1—O10	2.3139 (6)	W3—O8	1.921 (9)
W2—O2	1.672 (9)	W3—O10	2.3392 (6)

Symmetry code: (i) $-x+2, -y+1, -z+1$.

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1···O3^{ii}	0.93	2.53	3.36 (2)	149
C17—H17···O4^{iii}	0.93	2.52	3.45 (2)	178
C15—H15···O9^{iii}	0.93	2.49	3.43 (1)	178

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

Data collection: *SMART* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); 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*.

The authors gratefully acknowledge financial support from the Jinhun Municipal Science and Technology (grant No. 2003-01-179).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HY2197).

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supporting information

Acta Cryst. (2009). E**65**, m741–m742 [doi:10.1107/S1600536809020170]

Bis[bis(1,10-phenanthroline-κ^2N,N')copper(I)] μ_6-oxido-dodecakis-μ_2-oxido-hexaoxidohexatungsten(VI)

Zhen-Fang Li, Bi-Song Zhang and Chang-Sheng Wu

S1. Comment

Organic–inorganic hybrid compounds comprise hexatungstate and organic components (Khan *et al.*, 1998; Meng *et al.*, 2006; Zhang *et al.*, 2004). In this context, we have studied and reported the crystal structures of dodecahydroxy-dodecatungsten henicosahydrate (Li & Zhang, 2008) and hexakis(3-hydroxo)tetra(2-hydroxo)octadeca(2-oxo)tetradecaoxodisodium(I) dodecatungsten dodecahydrate (Zhang, 2008). In this paper, we report the synthesis and structure of the title complex, $[Cu(phen)_2]_2[W_6O_{19}]$.

The analysis of crystal structure shows that the title organic–inorganic hybrid compound consists of one hexatungstate cluster anion $(W_6O_{19})^{2-}$ and two monovalent coordination cations $[Cu(phen)_2]^+$ (Fig. 1). In the $[Cu(phen)_2]^+$ cation, the Cu^I atom is coordinated by four N atoms from two bidentate chelating phen ligands in a distorted tetrahedral geometry (Table 1). The dihedral angle of the two phen ligands is 104.9 (2)°, and the bond distances of Cu—N are in the range of 2.007 (11)—2.050 (12) Å. The hexatungstate $(W_6O_{19})^{2-}$ anion, lying on an inversion center and possessing the well-known lindqvist structure, is formed by six edge-sharing WO_6 octahedra, thus exhibiting an approximate O_h symmetry. Three kinds of O atoms exist in the hexatungstate, the ending O_a (O2, O4, O7), the bridging O_b (O1, O3, O5, O6, O8, O9) and the central O_c (O10) atoms. The bond lengths of W—O are obviously different, d(W—O_a) = 1.672 (9)—1.691 (11)Å, d(W—O_b) = 1.904 (10)—1.941 (9)Å, and d(W—O_c) = 2.3139 (6)—2.3392 (6)Å. As we can see, the lengths of W—O_c are the longest and the W—O_a shortest. Besides the electrostatic effects between the anions and cations, the weak C—H···O hydrogen bonds exist between the phen ligands and O_a or O_b atoms (Fig.1, Fig.2, Fig.3 and Table 2). The mean interplanar distances of 3.485 (1) and 3.344 (1)Å indicate π–π stacking interactions between the neighboring phen ligands. These weak hydrogen bonds and π–π stacking interactions lead to a two-dimensional network.

S2. Experimental

A mixture of $CuCO_3$ (0.124 g, 1.00 mmol), phen.H_2O (0.050 g, 0.50 mmol), 2-chlorobenzoic acid (0.043 g, 0.25 mmol) and freshly prepared $(NH_4)_2(WO_2S_2)$ (0.086 g, 0.27 mmol) in a ratio of 4:2:1:1 was added to CH_3OH/H_2O (1:2, v/v) mixed solution. After stirring for 2 h, the brown suspension obtained was sealed in a 50 ml Teflon-lined stainless steel vessel (degree of filling: 40%), heated to 393 K for 7 d and then naturally cooled to room temperature. The red crystals were collected, then washed with distilled water and dried in air.

S3. Refinement

H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 Å and with U_{iso}(H) = 1.2U_{eq}(C). The largest peak in the final difference Fourier map is 0.96 Å from atom W3 and the deepest hole is 0.91 Å from atom W1.

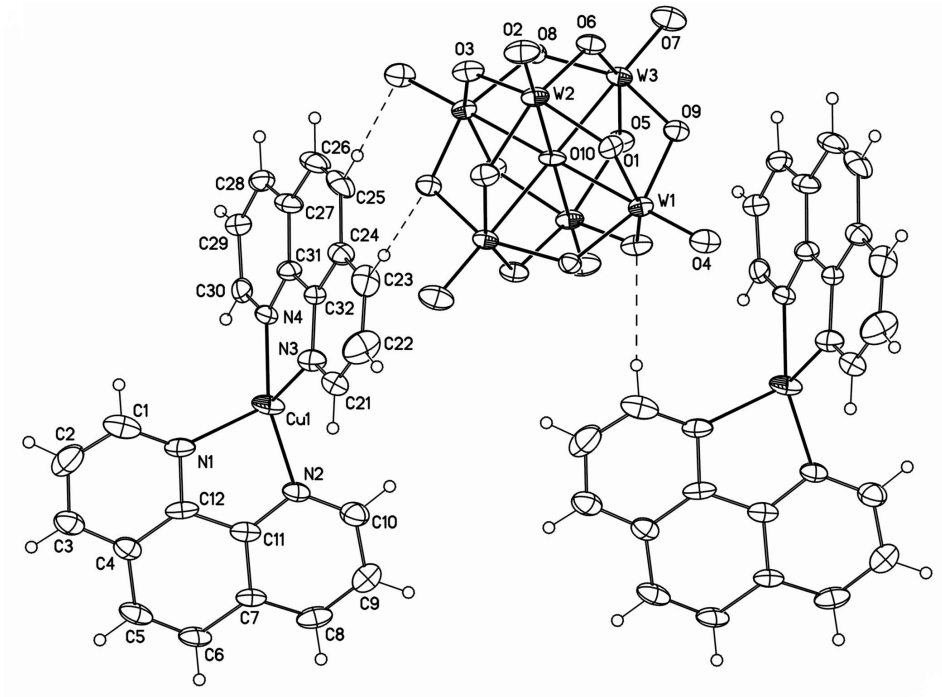

Figure 1

Molecular structure of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

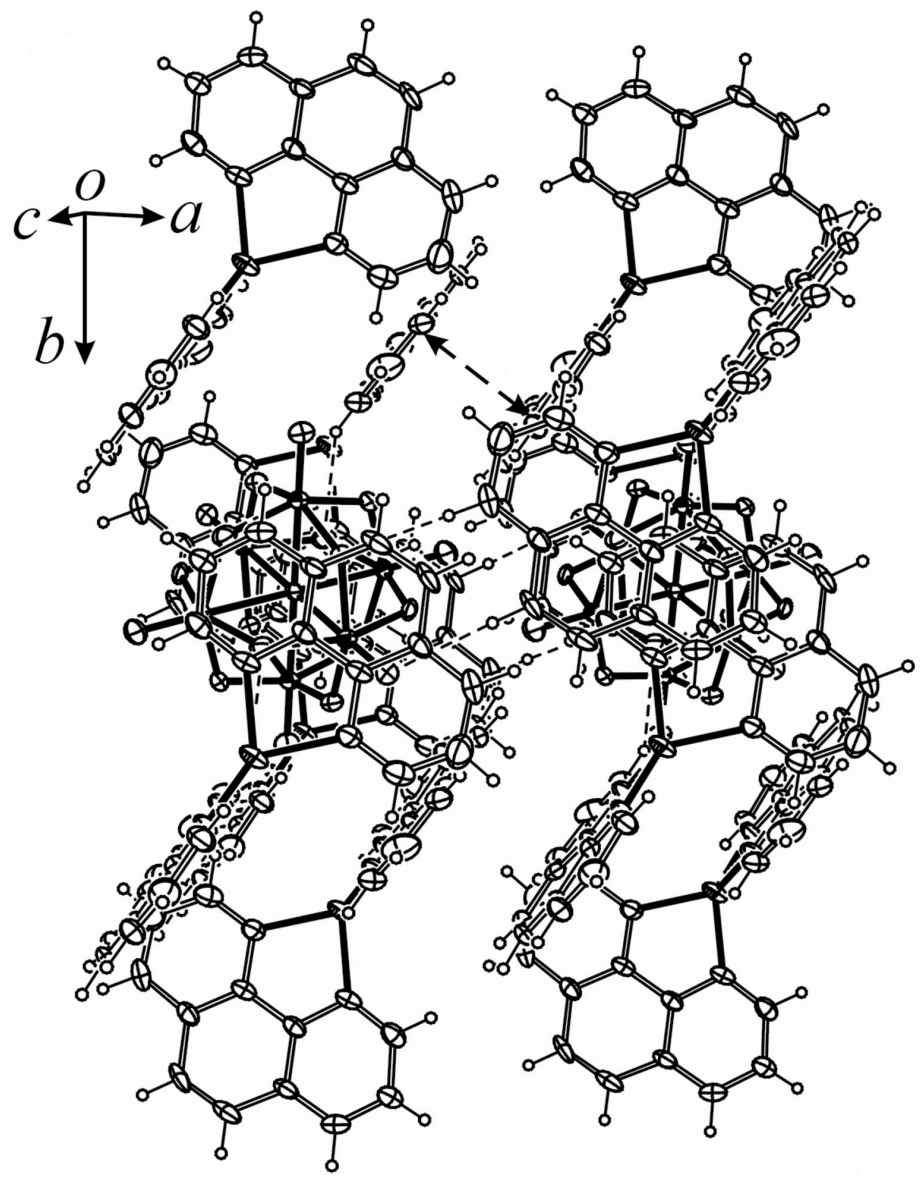

Figure 2

The π–π stacking interactions (dashed double arrows), with the mean interplanar distance of 3.485 (1) Å, and C—H···O hydrogen bonds (dashed lines) in the title compound.

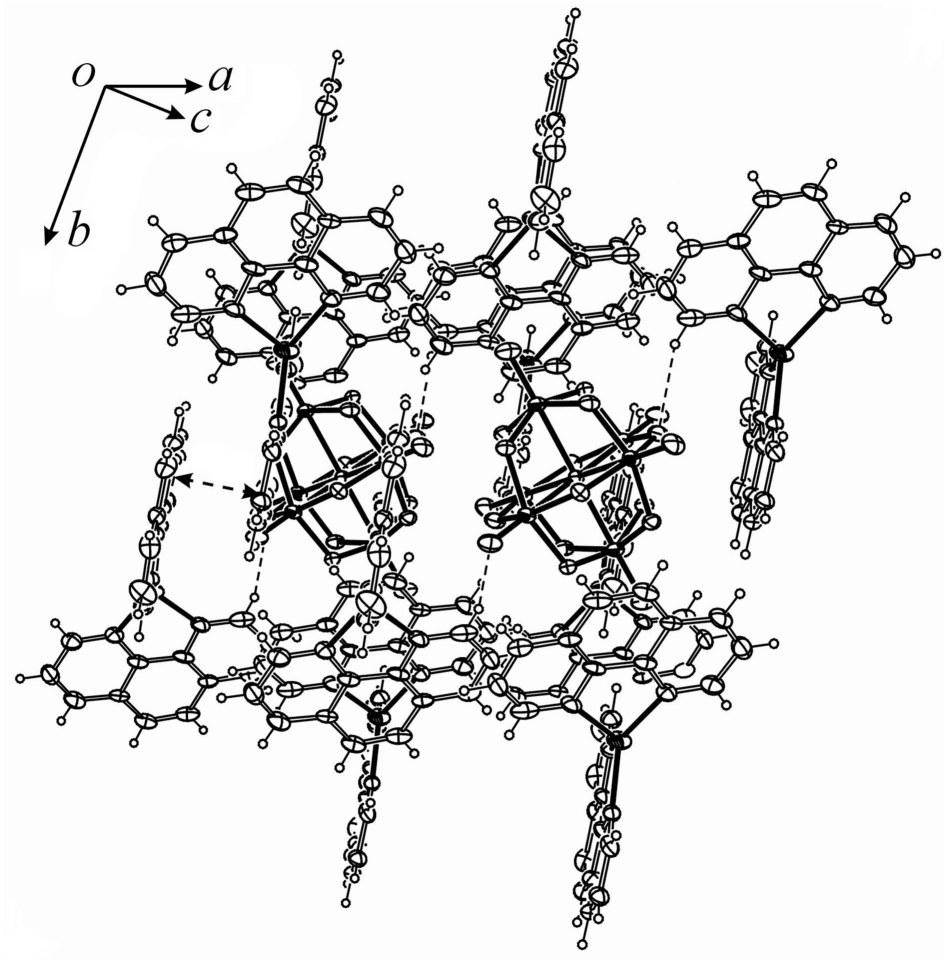

Figure 3

The π–π stacking interactions (dashed double arrows), with the mean interplanar distance of 3.344 (1) Å, and C—H···O hydrogen bonds (dashed lines) in the title compound.

Bis[bis(1,10-phenanthroline-κ^2N,N')copper(I)] μ_6-oxido-dodecakis-μ_2-oxido-hexaoxidohexatungsten(VI)

Crystal data

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Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 10.364 (2) Å
b = 11.772 (2) Å
c = 11.899 (2) Å
α = 108.603 (3)°
β = 102.151 (3)°
γ = 100.694 (3)°
V = 1294.0 (4) Å^3
Z = 1
$F(000)$ = 1030
D_x = 2.894 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 226 reflections
θ = 1.9–26.0°
μ = 14.17 mm^{-1}
T = 290 K
Block, red
0.19 × 0.16 × 0.07 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.09, T_{max} = 0.39
7111 measured reflections
4932 independent reflections
3737 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
θ_{max} = 26.0°, θ_{min} = 1.9°
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -7 \rightarrow 14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.157
S = 1.00
4932 reflections
376 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
$w = 1/[\sigma^2(F_o^2) + (0.1032P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 2.72 e Å^{-3}
$\Delta\rho_{min}$ = −4.78 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.3440 (2)	0.17655 (17)	0.7772 (2)	0.0595 (5)
W1	0.99864 (5)	0.40295 (4)	0.64114 (5)	0.03513 (18)
W2	0.79637 (5)	0.54681 (4)	0.52487 (5)	0.03706 (19)
W3	1.12578 (5)	0.68912 (4)	0.66080 (5)	0.03581 (18)
O1	0.8370 (8)	0.4620 (8)	0.6363 (8)	0.0341 (19)
O2	0.6510 (10)	0.5825 (9)	0.5417 (12)	0.059 (3)
O3	0.8394 (10)	0.6130 (8)	0.4065 (11)	0.050 (3)
O4	0.9960 (11)	0.3340 (9)	0.7445 (10)	0.051 (3)
O5	1.2619 (9)	0.6145 (8)	0.6099 (10)	0.045 (2)
O6	0.9382 (9)	0.6879 (8)	0.6456 (9)	0.041 (2)
O7	1.2177 (11)	0.8247 (9)	0.7782 (11)	0.061 (3)
O8	1.1010 (8)	0.7305 (7)	0.5155 (8)	0.035 (2)
O9	1.0969 (9)	0.5744 (8)	0.7415 (9)	0.039 (2)
O10	1.0000	0.5000	0.5000	0.031 (3)
N1	0.2642 (13)	0.0765 (10)	0.5929 (13)	0.048 (3)
N2	0.4498 (12)	0.0484 (10)	0.7689 (11)	0.044 (3)
N3	0.2306 (12)	0.2179 (10)	0.8990 (12)	0.047 (3)
N4	0.3947 (12)	0.3613 (10)	0.8196 (10)	0.042 (3)
C1	0.178 (2)	0.0906 (14)	0.504 (2)	0.068 (5)
H1	0.1385	0.1560	0.5268	0.082*
C2	0.142 (2)	0.0199 (17)	0.385 (2)	0.080 (6)
H2	0.0773	0.0344	0.3278	0.096*
C3	0.2024 (16)	−0.0766 (14)	0.3453 (16)	0.056 (4)
H3	0.1787	−0.1268	0.2618	0.068*
C4	0.2968 (15)	−0.0962 (12)	0.4310 (14)	0.044 (3)

C5	0.3614 (17)	−0.1966 (13)	0.4029 (16)	0.054 (4)
H5	0.3440	−0.2488	0.3208	0.065*
C6	0.4458 (16)	−0.2159 (13)	0.4929 (15)	0.050 (4)
H6	0.4824	−0.2835	0.4724	0.060*
C7	0.4805 (13)	−0.1353 (11)	0.6187 (14)	0.039 (3)
C8	0.5707 (16)	−0.1458 (14)	0.7184 (18)	0.058 (4)
H8	0.6135	−0.2095	0.7022	0.069*
C9	0.5981 (17)	−0.0672 (16)	0.8371 (18)	0.062 (4)
H9	0.6565	−0.0772	0.9021	0.075*
C10	0.5340 (17)	0.0312 (14)	0.8582 (16)	0.055 (4)
H10	0.5523	0.0865	0.9391	0.066*
C11	0.4206 (14)	−0.0325 (12)	0.6521 (14)	0.043 (3)
C12	0.3243 (13)	−0.0200 (11)	0.5541 (15)	0.044 (4)
C13	0.1527 (18)	0.1470 (15)	0.9380 (15)	0.057 (4)
H13	0.1458	0.0622	0.9088	0.069*
C14	0.082 (2)	0.189 (2)	1.017 (2)	0.081 (6)
H14	0.0293	0.1342	1.0418	0.097*
C15	0.0890 (16)	0.3146 (17)	1.0626 (15)	0.059 (4)
H15	0.0407	0.3452	1.1178	0.071*
C16	0.1710 (13)	0.3947 (13)	1.0228 (14)	0.044 (3)
C17	0.1811 (16)	0.5272 (16)	1.0604 (14)	0.058 (4)
H17	0.1343	0.5636	1.1145	0.069*
C18	0.2586 (16)	0.5961 (14)	1.0160 (15)	0.058 (4)
H18	0.2639	0.6805	1.0404	0.069*
C19	0.3338 (14)	0.5465 (12)	0.9329 (15)	0.046 (4)
C20	0.4137 (14)	0.6171 (12)	0.8855 (14)	0.048 (4)
H20	0.4201	0.7015	0.9061	0.058*
C21	0.4822 (15)	0.5605 (13)	0.8086 (14)	0.048 (3)
H21	0.5372	0.6056	0.7762	0.057*
C22	0.4684 (16)	0.4334 (14)	0.7791 (13)	0.047 (3)
H22	0.5159	0.3967	0.7259	0.056*
C23	0.3262 (14)	0.4188 (12)	0.8966 (14)	0.040 (3)
C24	0.2409 (14)	0.3435 (12)	0.9414 (13)	0.040 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0742 (13)	0.0385 (9)	0.0669 (13)	0.0301 (9)	0.0312 (11)	0.0058 (10)
W1	0.0357 (3)	0.0281 (3)	0.0464 (4)	0.0106 (2)	0.0163 (2)	0.0163 (3)
W2	0.0287 (3)	0.0320 (3)	0.0566 (4)	0.0150 (2)	0.0205 (3)	0.0157 (3)
W3	0.0350 (3)	0.0243 (3)	0.0448 (3)	0.0056 (2)	0.0146 (2)	0.0081 (2)
O1	0.035 (4)	0.039 (5)	0.043 (5)	0.012 (4)	0.024 (4)	0.025 (4)
O2	0.042 (6)	0.050 (6)	0.094 (9)	0.026 (5)	0.032 (6)	0.023 (6)
O3	0.045 (5)	0.032 (5)	0.076 (7)	0.013 (4)	0.019 (5)	0.020 (5)
O4	0.057 (6)	0.039 (5)	0.063 (7)	0.013 (4)	0.033 (5)	0.018 (5)
O5	0.032 (5)	0.033 (4)	0.064 (7)	0.004 (4)	0.009 (4)	0.015 (5)
O6	0.038 (5)	0.031 (4)	0.055 (6)	0.013 (4)	0.026 (4)	0.009 (4)
O7	0.061 (6)	0.037 (5)	0.077 (8)	0.003 (5)	0.030 (6)	0.009 (6)

O8	0.036 (5)	0.027 (4)	0.039 (5)	0.004 (3)	0.008 (4)	0.010 (4)
O9	0.042 (5)	0.030 (4)	0.045 (5)	0.007 (4)	0.018 (4)	0.013 (4)
O10	0.016 (5)	0.024 (5)	0.052 (8)	0.010 (4)	0.011 (5)	0.010 (6)
N1	0.050 (7)	0.034 (6)	0.067 (9)	0.025 (5)	0.022 (7)	0.014 (6)
N2	0.051 (7)	0.037 (6)	0.046 (7)	0.023 (5)	0.022 (6)	0.006 (6)
N3	0.048 (7)	0.037 (6)	0.058 (8)	0.017 (5)	0.019 (6)	0.013 (6)
N4	0.051 (7)	0.032 (5)	0.035 (6)	0.019 (5)	0.005 (5)	0.003 (5)
C1	0.073 (12)	0.034 (8)	0.090 (15)	0.007 (8)	0.036 (11)	0.008 (10)
C2	0.066 (11)	0.065 (12)	0.110 (18)	0.018 (9)	−0.004 (11)	0.051 (14)
C3	0.066 (10)	0.037 (8)	0.059 (10)	0.003 (7)	0.022 (9)	0.012 (8)
C4	0.053 (8)	0.027 (6)	0.050 (9)	0.000 (6)	0.025 (7)	0.014 (7)
C5	0.074 (11)	0.034 (7)	0.062 (10)	0.010 (7)	0.048 (9)	0.010 (8)
C6	0.063 (9)	0.037 (7)	0.068 (11)	0.028 (7)	0.046 (9)	0.017 (8)
C7	0.039 (7)	0.022 (6)	0.063 (9)	0.009 (5)	0.030 (7)	0.013 (6)
C8	0.052 (9)	0.048 (8)	0.090 (14)	0.031 (7)	0.035 (9)	0.027 (10)
C9	0.062 (10)	0.064 (10)	0.072 (12)	0.024 (8)	0.017 (9)	0.037 (10)
C10	0.071 (11)	0.045 (8)	0.053 (10)	0.023 (7)	0.026 (9)	0.011 (8)
C11	0.047 (8)	0.029 (6)	0.062 (9)	0.012 (5)	0.033 (7)	0.018 (7)
C12	0.039 (7)	0.025 (6)	0.080 (11)	0.015 (5)	0.036 (7)	0.019 (7)
C13	0.075 (11)	0.043 (8)	0.047 (9)	0.018 (8)	0.012 (8)	0.010 (8)
C14	0.085 (14)	0.088 (14)	0.109 (17)	0.035 (11)	0.059 (13)	0.061 (14)
C15	0.055 (9)	0.088 (12)	0.050 (10)	0.035 (9)	0.032 (8)	0.025 (10)
C16	0.035 (7)	0.046 (8)	0.046 (8)	0.021 (6)	0.011 (6)	0.007 (7)
C17	0.055 (9)	0.068 (10)	0.043 (9)	0.031 (8)	0.024 (8)	−0.005 (8)
C18	0.058 (9)	0.041 (8)	0.059 (10)	0.027 (7)	0.012 (8)	−0.004 (8)
C19	0.042 (7)	0.031 (7)	0.057 (10)	0.018 (6)	0.012 (7)	0.002 (7)
C20	0.052 (8)	0.029 (7)	0.053 (9)	0.008 (6)	0.001 (7)	0.012 (7)
C21	0.058 (9)	0.040 (7)	0.047 (9)	0.022 (7)	0.016 (7)	0.013 (7)
C22	0.064 (9)	0.053 (9)	0.031 (8)	0.031 (7)	0.016 (7)	0.016 (7)
C23	0.041 (7)	0.038 (7)	0.046 (8)	0.023 (6)	0.014 (6)	0.013 (7)
C24	0.050 (8)	0.034 (6)	0.035 (7)	0.022 (6)	0.008 (6)	0.008 (6)

Geometric parameters (Å, º)

Cu1—N1	2.027 (14)	C3—H3	0.9300
Cu1—N2	2.013 (11)	C4—C12	1.39 (2)
Cu1—N3	2.050 (12)	C4—C5	1.45 (2)
Cu1—N4	2.007 (11)	C5—C6	1.34 (2)
W1—O4	1.678 (10)	C5—H5	0.9300
W1—O3^{i}	1.904 (10)	C6—C7	1.42 (2)
W1—O1	1.926 (8)	C6—H6	0.9300
W1—O9	1.929 (9)	C7—C8	1.40 (2)
W1—O8^{i}	1.931 (8)	C7—C11	1.444 (18)
W1—O10	2.3139 (6)	C8—C9	1.35 (2)
W2—O2	1.672 (9)	C8—H8	0.9300
W2—O3	1.904 (11)	C9—C10	1.42 (2)
W2—O6	1.915 (9)	C9—H9	0.9300
W2—O1	1.923 (8)	C10—H10	0.9300

W2—O5^{i}	1.941 (9)	C11—C12	1.43 (2)
W2—O10	2.3314 (6)	C13—C14	1.34 (2)
W3—O7	1.691 (11)	C13—H13	0.9300
W3—O5	1.899 (10)	C14—C15	1.38 (3)
W3—O9	1.907 (9)	C14—H14	0.9300
W3—O6	1.912 (9)	C15—C16	1.41 (2)
W3—O8	1.921 (9)	C15—H15	0.9300
W3—O10	2.3392 (6)	C16—C24	1.383 (19)
N1—C1	1.31 (2)	C16—C17	1.46 (2)
N1—C12	1.393 (15)	C17—C18	1.34 (2)
N2—C10	1.321 (19)	C17—H17	0.9300
N2—C11	1.342 (18)	C18—C19	1.43 (2)
N3—C13	1.310 (19)	C18—H18	0.9300
N3—C24	1.377 (17)	C19—C20	1.39 (2)
N4—C22	1.308 (18)	C19—C23	1.407 (18)
N4—C23	1.363 (17)	C20—C21	1.36 (2)
C1—C2	1.33 (3)	C20—H20	0.9300
C1—H1	0.9300	C21—C22	1.39 (2)
C2—C3	1.40 (3)	C21—H21	0.9300
C2—H2	0.9300	C22—H22	0.9300
C3—C4	1.37 (2)	C23—C24	1.436 (19)

N4—Cu1—N2	134.8 (5)	C13—N3—C24	118.4 (13)
N4—Cu1—N1	113.4 (5)	C13—N3—Cu1	131.6 (10)
N2—Cu1—N1	83.1 (5)	C24—N3—Cu1	110.1 (10)
N4—Cu1—N3	83.3 (5)	C22—N4—C23	115.1 (11)
N2—Cu1—N3	122.9 (5)	C22—N4—Cu1	132.8 (10)
N1—Cu1—N3	124.7 (5)	C23—N4—Cu1	111.7 (9)
O4—W1—O3^{i}	105.4 (5)	N1—C1—C2	125.8 (17)
O4—W1—O1	102.4 (4)	N1—C1—H1	117.1
O3^{i}—W1—O1	152.1 (4)	C2—C1—H1	117.1
O4—W1—O9	103.8 (5)	C1—C2—C3	119.4 (18)
O3^{i}—W1—O9	87.0 (4)	C1—C2—H2	120.3
O1—W1—O9	84.9 (4)	C3—C2—H2	120.3
O4—W1—O8^{i}	103.6 (4)	C4—C3—C2	119.1 (16)
O3^{i}—W1—O8^{i}	86.7 (4)	C4—C3—H3	120.5
O1—W1—O8^{i}	88.4 (4)	C2—C3—H3	120.5
O9—W1—O8^{i}	152.6 (4)	C3—C4—C12	117.3 (14)
O4—W1—O10	179.0 (4)	C3—C4—C5	124.4 (14)
O3^{i}—W1—O10	75.4 (3)	C12—C4—C5	118.2 (14)
O1—W1—O10	76.7 (2)	C6—C5—C4	121.2 (14)
O9—W1—O10	75.8 (3)	C6—C5—H5	119.4
O8^{i}—W1—O10	76.8 (2)	C4—C5—H5	119.4
O2—W2—O3	104.0 (5)	C5—C6—C7	121.4 (13)
O2—W2—O6	104.2 (5)	C5—C6—H6	119.3
O3—W2—O6	85.8 (4)	C7—C6—H6	119.3
O2—W2—O1	104.6 (5)	C8—C7—C6	125.5 (13)
O3—W2—O1	151.4 (4)	C8—C7—C11	114.8 (13)

O6—W2—O1	86.5 (4)	C6—C7—C11	119.8 (14)
O2—W2—O5^{i}	105.0 (5)	C9—C8—C7	122.9 (14)
O3—W2—O5^{i}	85.8 (4)	C9—C8—H8	118.6
O6—W2—O5^{i}	150.8 (4)	C7—C8—H8	118.6
O1—W2—O5^{i}	87.6 (4)	C8—C9—C10	117.1 (16)
O2—W2—O10	178.9 (4)	C8—C9—H9	121.4
O3—W2—O10	75.0 (3)	C10—C9—H9	121.4
O6—W2—O10	75.4 (3)	N2—C10—C9	123.5 (15)
O1—W2—O10	76.4 (2)	N2—C10—H10	118.3
O5^{i}—W2—O10	75.4 (3)	C9—C10—H10	118.3
O7—W3—O5	103.7 (5)	N2—C11—C12	119.9 (12)
O7—W3—O9	103.7 (5)	N2—C11—C7	123.1 (14)
O5—W3—O9	87.3 (4)	C12—C11—C7	117.0 (13)
O7—W3—O6	105.1 (5)	C4—C12—N1	123.4 (15)
O5—W3—O6	151.2 (4)	C4—C12—C11	122.2 (12)
O9—W3—O6	86.1 (4)	N1—C12—C11	114.4 (13)
O7—W3—O8	104.4 (5)	N3—C13—C14	124.0 (16)
O5—W3—O8	87.2 (4)	N3—C13—H13	118.0
O9—W3—O8	151.9 (4)	C14—C13—H13	118.0
O6—W3—O8	85.6 (4)	C13—C14—C15	120.0 (17)
O7—W3—O10	179.2 (4)	C13—C14—H14	120.0
O5—W3—O10	75.9 (3)	C15—C14—H14	120.0
O9—W3—O10	75.6 (3)	C14—C15—C16	118.1 (15)
O6—W3—O10	75.3 (3)	C14—C15—H15	120.9
O8—W3—O10	76.3 (2)	C16—C15—H15	120.9
W2—O1—W1	117.0 (4)	C24—C16—C15	118.1 (13)
W2—O3—W1^{i}	119.4 (5)	C24—C16—C17	119.0 (14)
W3—O5—W2^{i}	118.7 (4)	C15—C16—C17	122.9 (14)
W3—O6—W2	119.3 (4)	C18—C17—C16	119.1 (13)
W3—O8—W1^{i}	117.0 (4)	C18—C17—H17	120.5
W3—O9—W1	118.4 (5)	C16—C17—H17	120.5
W1—O10—W1^{i}	180.000 (1)	C17—C18—C19	123.5 (13)
W1—O10—W2	89.885 (19)	C17—C18—H18	118.3
W1^{i}—O10—W2	90.115 (19)	C19—C18—H18	118.3
W1—O10—W2^{i}	90.115 (19)	C20—C19—C23	118.0 (14)
W1^{i}—O10—W2^{i}	89.885 (19)	C20—C19—C18	123.8 (13)
W2—O10—W2^{i}	180.00 (3)	C23—C19—C18	118.2 (14)
W1—O10—W3	90.18 (2)	C21—C20—C19	118.8 (12)
W1^{i}—O10—W3	89.82 (2)	C21—C20—H20	120.6
W2—O10—W3	89.97 (2)	C19—C20—H20	120.6
W2^{i}—O10—W3	90.03 (2)	C20—C21—C22	118.7 (14)
W1—O10—W3^{i}	89.82 (2)	C20—C21—H21	120.7
W1^{i}—O10—W3^{i}	90.18 (2)	C22—C21—H21	120.7
W2—O10—W3^{i}	90.03 (2)	N4—C22—C21	125.8 (14)
W2^{i}—O10—W3^{i}	89.97 (2)	N4—C22—H22	117.1
W3—O10—W3^{i}	180.00 (2)	C21—C22—H22	117.1
C1—N1—C12	115.1 (14)	N4—C23—C19	123.7 (13)
C1—N1—Cu1	133.2 (10)	N4—C23—C24	117.5 (11)

C12—N1—Cu1	111.5 (10)	C19—C23—C24	118.8 (13)
C10—N2—C11	118.6 (12)	N3—C24—C16	121.4 (13)
C10—N2—Cu1	130.3 (10)	N3—C24—C23	117.2 (12)
C11—N2—Cu1	111.0 (10)	C16—C24—C23	121.4 (12)
O6—W2—O1—W1	−77.3 (5)	O3—W2—O6—W3	−76.6 (6)
O5^{i}—W2—O1—W1	74.1 (5)	O1—W2—O6—W3	75.8 (5)
O3^{i}—W1—O1—W2	4.5 (11)	O5^{i}—W2—O6—W3	−3.0 (12)
O9—W1—O1—W2	78.0 (5)	O10—W2—O6—W3	−1.0 (4)
O8^{i}—W1—O1—W2	−75.4 (5)	O7—W3—O8—W1^{i}	179.1 (5)
O6—W2—O3—W1^{i}	75.4 (6)	O5—W3—O8—W1^{i}	75.6 (5)
O5^{i}—W2—O3—W1^{i}	−76.6 (6)	O9—W3—O8—W1^{i}	−3.3 (11)
O9—W3—O5—W2^{i}	76.2 (6)	O6—W3—O8—W1^{i}	−76.5 (5)
O6—W3—O5—W2^{i}	−0.6 (12)	O7—W3—O9—W1	−178.3 (5)
O8—W3—O5—W2^{i}	−76.3 (6)	O5—W3—O9—W1	−74.9 (5)
O7—W3—O6—W2	−178.3 (6)	O6—W3—O9—W1	77.1 (5)
O9—W3—O6—W2	−75.1 (6)	O4—W1—O9—W3	179.6 (5)
O8—W3—O6—W2	78.1 (5)	O3^{i}—W1—O9—W3	74.5 (6)
O2—W2—O6—W3	180.0 (6)	O1—W1—O9—W3	−78.9 (5)

Symmetry code: (i) −*x*+2, −*y*+1, −*z*+1.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O3^{ii}	0.93	2.53	3.36 (2)	149
C17—H17···O4^{iii}	0.93	2.52	3.45 (2)	178
C15—H15···O9^{iii}	0.93	2.49	3.43 (1)	178

Symmetry codes: (ii) −*x*+1, −*y*+1, −*z*+1; (iii) −*x*+1, −*y*+1, −*z*+2.