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Poly[[di-μ_4-4,4′-oxydiphthalato-tetrakis-[μ_2-1,1′-(*p*-phenylenedimethylene)di-1*H*-imidazole]tetracopper(II)] monohydrate]

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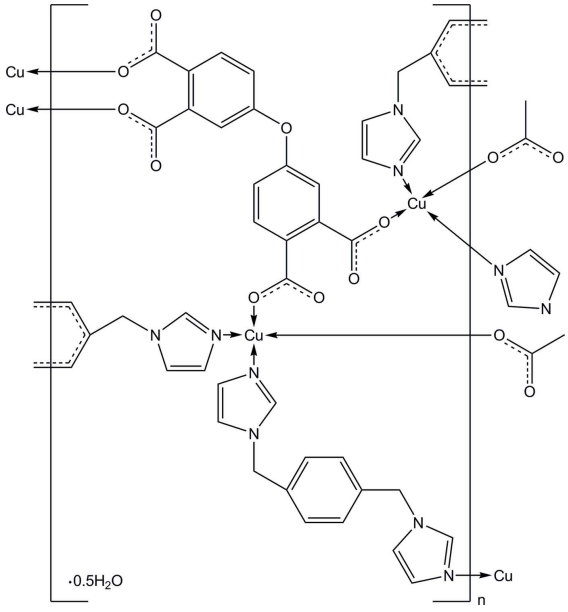
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.009 Å; disorder in solvent or counterion; R factor = 0.064; wR factor = 0.169; data-to-parameter ratio = 12.6.

In the title compound, $\{[Cu_4(C_{16}H_6O_9)_2(C_{14}H_{14}N_4)_4]\cdot H_2O\}_n$, the water molecule is disordered over two positions; site-occupancy factors were fixed at 0.25. The Cu^{II} atom exhibits a square-planar coordination geometry with two O atoms of the two 4,4′-oxydiphthalate ligands and two N atoms of the two 1,4-bis(imidazol-1-ylmethyl)benzene groups. A three-dimensional honeycomb framework structure is formed. Aromatic π–π stacking interactions are observed, with a centroid–centroid distance of 3.373 (5) Å.

Related literature

For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$[Cu_4(C_{16}H_6O_9)_2(C_{14}H_{14}N_4)_4]\cdot H_2O$
M_r = 1909.76
Monoclinic, $P2_1/n$
a = 18.750 (3) Å
b = 10.3283 (17) Å
c = 22.386 (4) Å
β = 97.388 (3)°
V = 4299.1 (13) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.06 mm^{-1}
T = 294 (2) K
0.22 × 0.18 × 0.16 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: none
18013 measured reflections
7404 independent reflections
4497 reflections with $I > 2\sigma(I)$
R_{int} = 0.068

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.169
S = 1.02
7404 reflections
586 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.75 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2005); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2401).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, S1–19.
Bruker (2005). *SHELXTL*, *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

supporting information

Acta Cryst. (2008). E**64**, m169 [https://doi.org/10.1107/S1600536807065713]

Poly[[di-μ_4-4,4′-oxydiphthalato-tetrakis[μ_2-1,1′-(*p*-phenylenedimethylene)di-1*H*-imidazole]tetracopper(II)] monohydrate]

Wu Zhang, Li Yao and Ruojie Tao

S1. Comment

As part of our ongoing studies, we synthesized the title compound, (I), and report herein its crystal structure.

In the molecule of (I), (Fig. 1) the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). When the crystal structure was solved, the water molecule was found to be disordered.

The Cu^{II} atom exhibits a square-planar coordination geometry with two O atoms of the two 4,4′-oxydiphthalic acid (H_4ODPA) and two N atoms of the two 1,4-bis(imidazol-1-yl-methyl)benzene (BIX) groups, respectively. Four carboxylic O atoms of H_4ODPA coordinate four different Cu ion and a three-dimensional honeycomb framework built from Cu ion and H_4ODPA (Figs. 2 and 3) joined by BIX groups (Fig. 4).

The π-π stacking interactions between aromatic rings of *Cg*1 and *Cg*2 [*Cg*1 and *Cg*2 are (N7,N8,C16—C18) and ($N3^{i}$,$N4^{i}$,$C31^{i}$—$C33^{i}$) ring centroids, respectively, symmetry code: (i) 2 - *x*, 1 - *y*, 1 - *z*] are observed, with a centroid-centroid distance of 3.373 (5) Å.

S2. Experimental

The compound, (I), was synthesized hydrothermally in a Teflon-lined autoclave (23 ml) by heating a mixture of H_4ODPA (0.1 mmol), BIX (0.1 mmol), $Cu(NO_3)_2.4H_2O$ (0.2 mmol) and one drop of Et_3N (pH ~ 8–9) in water (10 ml) at 393 K for 3 d. Blue single crystals were collected in 55% yield based on $Cu(NO_3)_2.4H_2O$.

S3. Refinement

When the crystal structure was solved, the water molecule was found to be disordered. During refinement, the occupancies of disordered O and H atoms were kept fixed as 0.25. H atoms were positioned geometrically, with O—H = 0.85 Å (for H_2O) and C—H = 0.93 and 0.97 Å for aromatic and methylene H, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C,*O*).

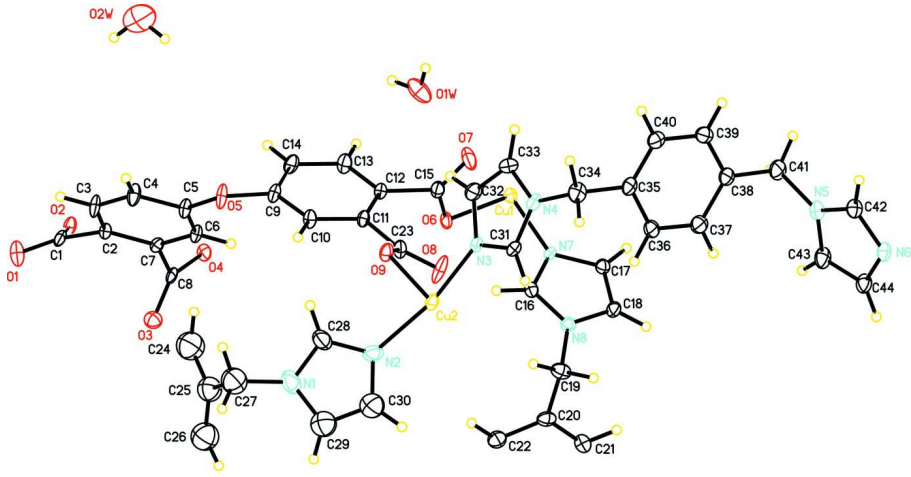

Figure 1

The molecular structure of the title molecule with the atom-numbering scheme. Displacement ellipsoids are drawn at the 20% probability level.

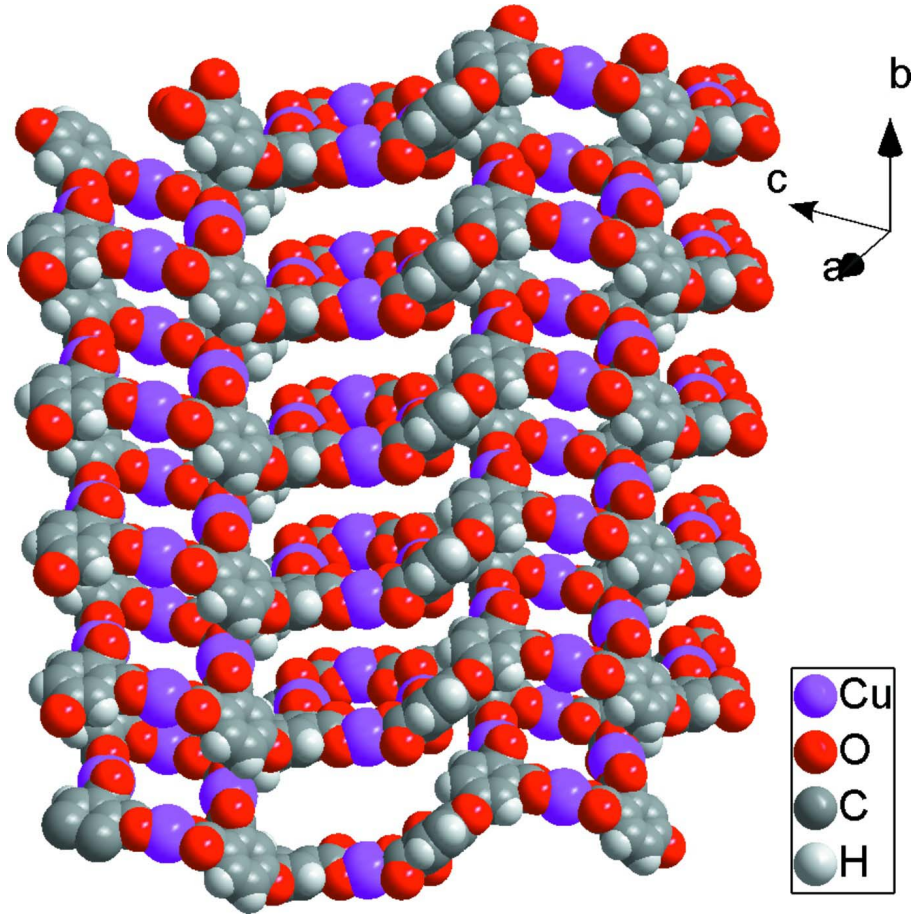

Figure 2

The three-dimensional framework built from Cu ion and H_4ODPA.

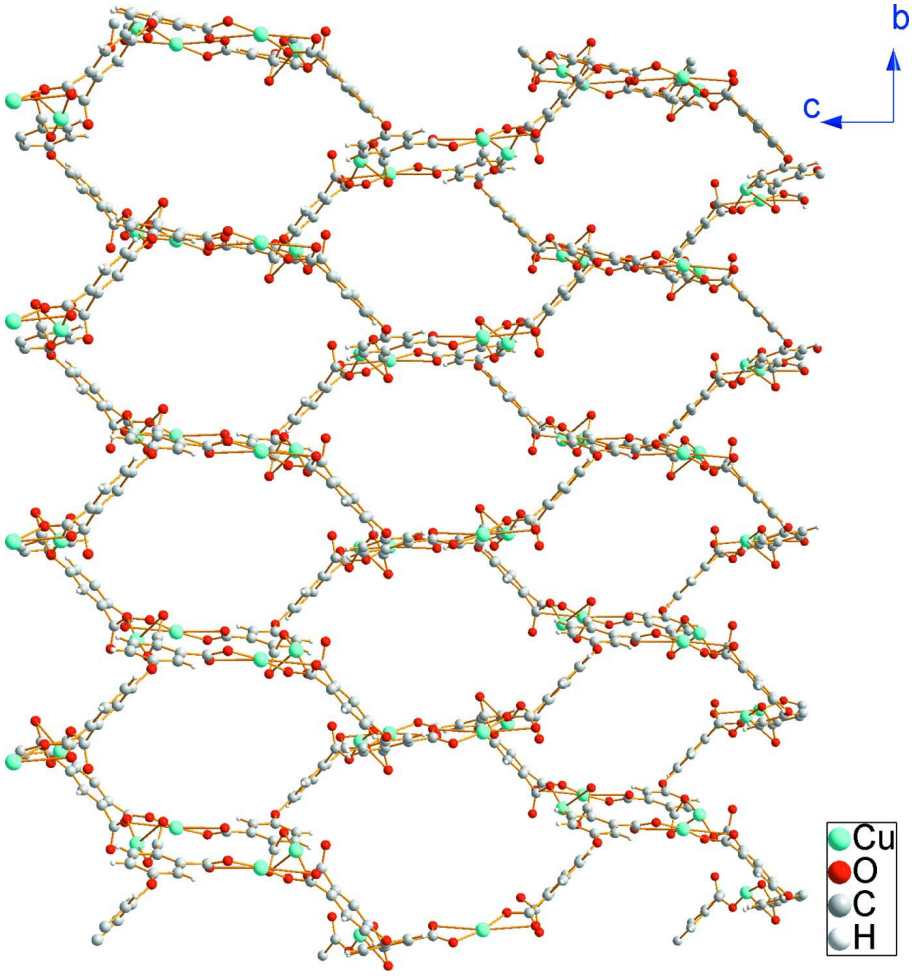

Figure 3

The three-dimensional framework built from Cu ion and H_4ODPA, viewed along the *a* axis.

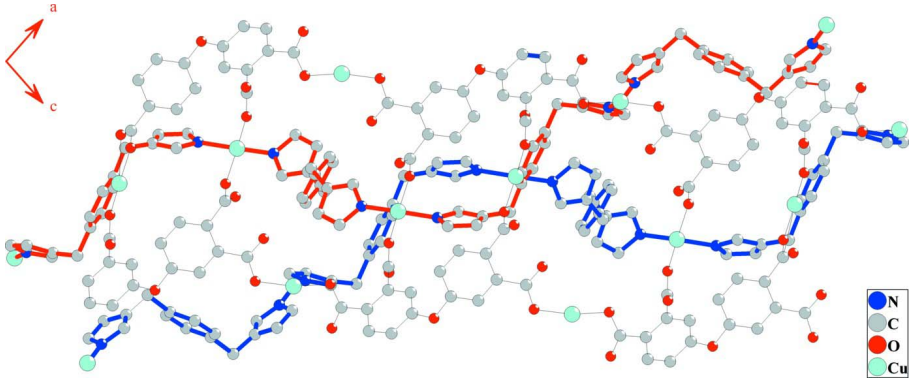

Figure 4

The crystal structure of (I), viewed along the *b* axis.

poly[[di-μ_4-4,4′-oxydiphthalato-tetrakis[μ_2-1,1′-(*p*- phenylenedimethylene)di-1*H*-imidazole]tetracopper(II)] monohydrate]

Crystal data

$[Cu_4(C_{16}H_6O_9)_2(C_{14}H_{14}N_4)_4]\cdot H_2O$
$M_r = 1909.76$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 18.750$ (3) Å
$b = 10.3283$ (17) Å
$c = 22.386$ (4) Å
$\beta = 97.388$ (3)°
$V = 4299.1$ (13) Å^3
$Z = 2$
$F(000) = 1956$
$D_x = 1.475$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2326 reflections
$\theta = 4.8$–40.6°
$\mu = 1.06$ mm^{-1}
$T = 294$ K
Block, blue
0.22 × 0.18 × 0.16 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
18013 measured reflections
7404 independent reflections
4497 reflections with $I > 2\sigma(I)$
$R_{int} = 0.068$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.2°$
$h = -21\rightarrow22$
$k = -12\rightarrow11$
$l = -26\rightarrow21$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.064$
$wR(F^2) = 0.169$
$S = 1.02$
7404 reflections
586 parameters
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
$w = 1/[\sigma^2(F_o^2) + (0.070P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.75$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Cu1	0.89629 (4)	0.53392 (7)	0.32168 (3)	0.0318 (2)	
Cu2	0.76895 (4)	0.45820 (7)	0.61410 (3)	0.0365 (2)	
O1	0.2712 (2)	0.0667 (5)	0.2379 (2)	0.0592 (14)	
O2	0.3459 (2)	0.1096 (4)	0.17161 (17)	0.0389 (10)	

O3	0.4802 (2)	−0.0241 (4)	0.25179 (18)	0.0470 (11)
O4	0.53069 (19)	0.1398 (3)	0.20835 (17)	0.0356 (10)
O5	0.4896 (2)	0.4422 (4)	0.39105 (18)	0.0486 (12)
O6	0.81238 (19)	0.4642 (4)	0.35422 (17)	0.0369 (10)
O7	0.8091 (2)	0.6633 (4)	0.3895 (2)	0.0621 (14)
O8	0.7925 (2)	0.4500 (5)	0.49595 (19)	0.0681 (16)
O9	0.7022 (2)	0.5057 (4)	0.54384 (17)	0.0391 (10)
N1	0.6103 (4)	0.1859 (7)	0.6206 (3)	0.087 (2)
N2	0.7097 (4)	0.2996 (6)	0.6185 (3)	0.0688 (19)
N3	0.8023 (2)	0.6380 (4)	0.6258 (2)	0.0314 (11)
N4	0.8525 (3)	0.8122 (5)	0.6697 (2)	0.0401 (13)
N5	1.2382 (3)	0.9385 (5)	0.6755 (2)	0.0461 (14)
N6	1.3302 (3)	0.9248 (5)	0.7477 (2)	0.0404 (13)
N7	0.9593 (2)	0.4597 (4)	0.3892 (2)	0.0292 (11)
N8	0.9949 (3)	0.3544 (4)	0.4721 (2)	0.0340 (12)
C1	0.3260 (3)	0.1165 (6)	0.2242 (3)	0.0349 (14)
C2	0.3741 (3)	0.1944 (5)	0.2689 (2)	0.0293 (13)
C3	0.3417 (3)	0.2817 (6)	0.3037 (3)	0.0464 (17)
H3	0.2917	0.2853	0.2997	0.056*
C4	0.3806 (3)	0.3634 (6)	0.3439 (3)	0.0465 (18)
H4	0.3575	0.4209	0.3670	0.056*
C5	0.4546 (3)	0.3585 (6)	0.3493 (3)	0.0358 (15)
C6	0.4879 (3)	0.2719 (6)	0.3161 (2)	0.0326 (14)
H6	0.5378	0.2679	0.3207	0.039*
C7	0.4484 (3)	0.1900 (5)	0.2756 (2)	0.0280 (13)
C8	0.4889 (3)	0.0921 (6)	0.2425 (2)	0.0308 (14)
C9	0.5605 (3)	0.4739 (6)	0.3875 (3)	0.0356 (14)
C10	0.6079 (3)	0.4676 (6)	0.4391 (2)	0.0344 (14)
H10	0.5913	0.4442	0.4750	0.041*
C11	0.6802 (3)	0.4953 (5)	0.4390 (2)	0.0305 (14)
C12	0.7040 (3)	0.5312 (5)	0.3850 (2)	0.0310 (13)
C13	0.6548 (3)	0.5428 (6)	0.3346 (3)	0.0430 (16)
H13	0.6704	0.5707	0.2990	0.052*
C14	0.5830 (3)	0.5145 (6)	0.3348 (3)	0.0435 (16)
H14	0.5505	0.5229	0.2999	0.052*
C15	0.7821 (3)	0.5590 (6)	0.3789 (3)	0.0369 (15)
C16	0.9387 (3)	0.3942 (5)	0.4348 (2)	0.0312 (14)
H16	0.8911	0.3784	0.4400	0.037*
C17	1.0338 (3)	0.4608 (5)	0.3990 (3)	0.0347 (14)
H17	1.0637	0.5001	0.3743	0.042*
C18	1.0554 (3)	0.3968 (6)	0.4493 (3)	0.0407 (15)
H18	1.1028	0.3830	0.4661	0.049*
C19	0.9927 (4)	0.2740 (6)	0.5262 (3)	0.0477 (17)
H19A	0.9486	0.2917	0.5431	0.057*
H19B	1.0328	0.2970	0.5562	0.057*
C20	0.9965 (4)	0.1321 (6)	0.5124 (3)	0.0426 (16)
C21	1.0591 (4)	0.0760 (7)	0.4987 (3)	0.0533 (19)
H21	1.0997	0.1270	0.4973	0.064*

C22	0.9378 (4)	0.0547 (6)	0.5130 (3)	0.0498 (18)	
H22	0.8948	0.0907	0.5215	0.060*	
C23	0.7299 (3)	0.4818 (6)	0.4961 (3)	0.0380 (15)	
C24	0.4858 (6)	0.1297 (12)	0.5001 (5)	0.124 (4)	
H24	0.4766	0.2182	0.4992	0.149*	
C25	0.5183 (5)	0.0706 (10)	0.5526 (4)	0.094 (3)	
C26	0.5323 (6)	−0.0552 (11)	0.5505 (5)	0.121 (4)	
H26	0.5556	−0.0948	0.5849	0.145*	
C27	0.5349 (5)	0.1519 (10)	0.6110 (4)	0.107 (3)	
H27A	0.5060	0.2301	0.6077	0.128*	
H27B	0.5227	0.1025	0.6451	0.128*	
C28	0.6384 (5)	0.2971 (8)	0.6047 (3)	0.069 (2)	
H28	0.6115	0.3649	0.5861	0.082*	
C29	0.6657 (6)	0.1172 (11)	0.6487 (5)	0.104 (3)	
H29	0.6632	0.0361	0.6664	0.125*	
C30	0.7242 (6)	0.1869 (9)	0.6463 (4)	0.096 (3)	
H30	0.7702	0.1605	0.6621	0.115*	
C31	0.8442 (3)	0.6847 (6)	0.6730 (3)	0.0341 (14)	
H31	0.8654	0.6342	0.7048	0.041*	
C32	0.7838 (3)	0.7438 (6)	0.5905 (3)	0.0455 (17)	
H32	0.7541	0.7423	0.5538	0.055*	
C33	0.8146 (4)	0.8496 (7)	0.6164 (3)	0.0502 (18)	
H33	0.8109	0.9334	0.6011	0.060*	
C34	0.8975 (3)	0.8937 (7)	0.7129 (3)	0.0510 (18)	
H34A	0.9039	0.8510	0.7518	0.061*	
H34B	0.8729	0.9751	0.7174	0.061*	
C35	0.9698 (3)	0.9209 (6)	0.6940 (3)	0.0388 (15)	
C36	1.0180 (3)	0.8213 (6)	0.6928 (3)	0.0466 (17)	
H36	1.0055	0.7385	0.7041	0.056*	
C37	1.0846 (4)	0.8426 (6)	0.6749 (3)	0.0508 (18)	
H37	1.1161	0.7737	0.6729	0.061*	
C38	1.1049 (3)	0.9674 (7)	0.6599 (3)	0.0428 (16)	
C39	1.0563 (4)	1.0655 (6)	0.6628 (3)	0.0463 (17)	
H39	1.0688	1.1496	0.6533	0.056*	
C40	0.9896 (4)	1.0418 (6)	0.6793 (3)	0.0443 (16)	
H40	0.9574	1.1099	0.6805	0.053*	
C41	1.1763 (4)	0.9926 (7)	0.6379 (3)	0.0539 (19)	
H41A	1.1748	0.9571	0.5976	0.065*	
H41B	1.1830	1.0854	0.6351	0.065*	
C42	1.2778 (3)	0.9996 (6)	0.7212 (3)	0.0423 (17)	
H42	1.2695	1.0841	0.7329	0.051*	
C43	1.2665 (4)	0.8178 (7)	0.6734 (3)	0.056 (2)	
H43	1.2500	0.7527	0.6464	0.067*	
C44	1.3231 (3)	0.8088 (7)	0.7177 (3)	0.0507 (18)	
H44	1.3521	0.7363	0.7263	0.061*	
O1W	0.7029 (11)	0.8502 (19)	0.4349 (8)	0.078 (6)	0.25
H1WA	0.6679	0.8401	0.4072	0.094*	0.25
H1WB	0.6981	0.9239	0.4508	0.094*	0.25

O2W	0.2753 (15)	0.958 (3)	0.5136 (11)	0.132 (10)	0.25
H2WA	0.2509	0.8898	0.5057	0.158*	0.25
H2WB	0.3130	0.9378	0.5370	0.158*	0.25

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0238 (4)	0.0364 (4)	0.0365 (4)	−0.0029 (3)	0.0080 (3)	0.0031 (3)
Cu2	0.0295 (4)	0.0462 (5)	0.0309 (4)	0.0004 (4)	−0.0069 (3)	0.0008 (4)
O1	0.036 (3)	0.081 (4)	0.061 (3)	−0.020 (3)	0.012 (2)	−0.026 (3)
O2	0.027 (2)	0.057 (3)	0.030 (2)	−0.004 (2)	−0.0077 (19)	−0.006 (2)
O3	0.050 (3)	0.043 (3)	0.049 (3)	0.002 (2)	0.010 (2)	−0.002 (2)
O4	0.026 (2)	0.037 (2)	0.048 (3)	0.0025 (18)	0.020 (2)	−0.0085 (19)
O5	0.018 (2)	0.084 (3)	0.043 (3)	−0.006 (2)	0.001 (2)	−0.032 (2)
O6	0.022 (2)	0.045 (3)	0.045 (2)	−0.008 (2)	0.0082 (19)	0.005 (2)
O7	0.042 (3)	0.051 (3)	0.096 (4)	−0.021 (2)	0.017 (3)	−0.021 (3)
O8	0.021 (3)	0.142 (5)	0.038 (3)	0.015 (3)	−0.005 (2)	−0.008 (3)
O9	0.030 (2)	0.061 (3)	0.025 (2)	−0.004 (2)	−0.0029 (19)	0.0044 (19)
N1	0.086 (6)	0.090 (5)	0.077 (5)	−0.041 (5)	−0.023 (4)	0.017 (4)
N2	0.079 (5)	0.043 (4)	0.072 (4)	−0.005 (3)	−0.035 (4)	0.012 (3)
N3	0.020 (3)	0.040 (3)	0.034 (3)	0.001 (2)	0.001 (2)	0.000 (2)
N4	0.030 (3)	0.046 (4)	0.042 (3)	0.007 (2)	−0.002 (3)	−0.004 (3)
N5	0.038 (3)	0.053 (4)	0.047 (3)	−0.011 (3)	0.003 (3)	−0.007 (3)
N6	0.028 (3)	0.052 (4)	0.042 (3)	−0.002 (3)	0.007 (3)	−0.010 (3)
N7	0.023 (3)	0.029 (3)	0.035 (3)	0.003 (2)	0.002 (2)	0.005 (2)
N8	0.039 (3)	0.028 (3)	0.034 (3)	0.000 (2)	0.002 (3)	−0.001 (2)
C1	0.019 (3)	0.041 (4)	0.042 (4)	0.007 (3)	−0.006 (3)	−0.005 (3)
C2	0.023 (3)	0.038 (3)	0.027 (3)	−0.002 (3)	0.001 (3)	−0.004 (3)
C3	0.015 (3)	0.070 (5)	0.054 (4)	−0.003 (3)	0.002 (3)	−0.021 (4)
C4	0.024 (4)	0.064 (5)	0.051 (4)	0.002 (3)	0.005 (3)	−0.029 (4)
C5	0.022 (3)	0.055 (4)	0.030 (3)	−0.002 (3)	0.001 (3)	−0.012 (3)
C6	0.018 (3)	0.050 (4)	0.030 (3)	0.001 (3)	0.003 (3)	−0.005 (3)
C7	0.024 (3)	0.037 (3)	0.024 (3)	0.005 (3)	0.006 (3)	0.000 (3)
C8	0.020 (3)	0.039 (4)	0.030 (3)	0.001 (3)	−0.010 (3)	−0.007 (3)
C9	0.021 (3)	0.049 (4)	0.035 (4)	0.003 (3)	−0.001 (3)	−0.015 (3)
C10	0.026 (3)	0.054 (4)	0.024 (3)	−0.005 (3)	0.007 (3)	−0.007 (3)
C11	0.024 (3)	0.040 (4)	0.026 (3)	−0.002 (3)	−0.002 (3)	−0.007 (3)
C12	0.023 (3)	0.038 (3)	0.032 (3)	−0.001 (3)	0.002 (3)	−0.003 (3)
C13	0.032 (4)	0.069 (5)	0.029 (3)	−0.004 (3)	0.006 (3)	0.002 (3)
C14	0.035 (4)	0.063 (5)	0.028 (3)	0.000 (3)	−0.012 (3)	−0.003 (3)
C15	0.028 (4)	0.049 (4)	0.032 (3)	−0.003 (3)	0.001 (3)	0.006 (3)
C16	0.029 (3)	0.032 (3)	0.035 (3)	−0.002 (3)	0.009 (3)	−0.007 (3)
C17	0.031 (4)	0.033 (3)	0.040 (4)	0.000 (3)	0.007 (3)	0.000 (3)
C18	0.028 (4)	0.035 (4)	0.058 (4)	0.005 (3)	0.002 (3)	−0.003 (3)
C19	0.069 (5)	0.038 (4)	0.035 (4)	−0.004 (3)	0.003 (3)	0.000 (3)
C20	0.059 (5)	0.038 (4)	0.028 (3)	0.003 (4)	−0.004 (3)	0.004 (3)
C21	0.047 (5)	0.048 (5)	0.064 (5)	−0.010 (3)	0.003 (4)	0.002 (4)
C22	0.048 (4)	0.043 (4)	0.059 (4)	0.008 (4)	0.011 (4)	−0.003 (3)

C23	0.027 (4)	0.054 (4)	0.033 (4)	−0.008 (3)	0.003 (3)	0.001 (3)
C24	0.128 (4)	0.122 (4)	0.123 (4)	−0.004 (2)	0.015 (2)	0.002 (2)
C25	0.095 (3)	0.093 (3)	0.092 (3)	−0.005 (2)	0.007 (2)	0.000 (2)
C26	0.123 (4)	0.120 (4)	0.118 (4)	−0.001 (2)	0.012 (2)	0.001 (2)
C27	0.108 (4)	0.107 (4)	0.106 (4)	−0.006 (2)	0.014 (2)	0.002 (2)
C28	0.074 (6)	0.061 (5)	0.067 (5)	−0.024 (5)	−0.009 (5)	0.011 (4)
C29	0.105 (4)	0.102 (4)	0.104 (4)	−0.002 (2)	0.009 (2)	0.004 (2)
C30	0.095 (3)	0.093 (3)	0.097 (3)	−0.001 (2)	0.008 (2)	0.002 (2)
C31	0.027 (4)	0.039 (4)	0.036 (4)	0.008 (3)	0.002 (3)	0.000 (3)
C32	0.045 (4)	0.052 (4)	0.036 (4)	−0.001 (3)	−0.007 (3)	0.000 (3)
C33	0.052 (5)	0.038 (4)	0.059 (5)	0.009 (3)	0.003 (4)	0.010 (4)
C34	0.052 (5)	0.052 (4)	0.047 (4)	−0.001 (4)	0.001 (4)	−0.022 (3)
C35	0.036 (4)	0.046 (4)	0.031 (3)	0.000 (3)	−0.007 (3)	−0.013 (3)
C36	0.043 (4)	0.038 (4)	0.057 (4)	−0.007 (3)	−0.004 (4)	−0.009 (3)
C37	0.048 (5)	0.041 (4)	0.059 (5)	0.000 (3)	−0.007 (4)	−0.011 (3)
C38	0.042 (4)	0.049 (4)	0.034 (3)	−0.007 (4)	−0.010 (3)	−0.002 (3)
C39	0.056 (5)	0.041 (4)	0.037 (4)	−0.006 (3)	−0.011 (4)	0.001 (3)
C40	0.048 (4)	0.042 (4)	0.039 (4)	0.002 (3)	−0.009 (3)	−0.009 (3)
C41	0.050 (5)	0.067 (5)	0.040 (4)	−0.011 (4)	−0.014 (4)	0.001 (3)
C42	0.040 (4)	0.048 (4)	0.039 (4)	−0.003 (3)	0.005 (3)	−0.012 (3)
C43	0.043 (4)	0.054 (5)	0.068 (5)	−0.004 (4)	−0.003 (4)	−0.027 (4)
C44	0.035 (4)	0.047 (4)	0.071 (5)	0.002 (3)	0.007 (4)	−0.014 (4)
O1W	0.103 (14)	0.074 (12)	0.067 (11)	−0.033 (11)	0.046 (11)	−0.003 (10)
O2W	0.136 (17)	0.177 (18)	0.097 (14)	0.039 (14)	0.068 (13)	0.054 (14)

Geometric parameters (Å, º)

Cu1—O4^{i}	1.939 (3)	C12—C15	1.516 (8)
Cu1—N7	1.951 (4)	C13—C14	1.379 (8)
Cu1—O6	1.954 (4)	C13—H13	0.9300
Cu1—N6^{ii}	1.983 (5)	C14—H14	0.9300
Cu2—O2^{iii}	1.937 (4)	C16—H16	0.9300
Cu2—O9	1.943 (4)	C17—C18	1.324 (8)
Cu2—N3	1.966 (5)	C17—H17	0.9300
Cu2—N2	1.989 (6)	C18—H18	0.9300
N1—C28	1.331 (9)	C19—C20	1.502 (8)
N1—C29	1.346 (11)	C19—H19A	0.9700
N1—C27	1.445 (10)	C19—H19B	0.9700
N2—C30	1.332 (10)	C20—C22	1.361 (8)
N2—C28	1.333 (9)	C20—C21	1.379 (9)
N3—C31	1.324 (7)	C21—C22^{vii}	1.377 (9)
N3—C32	1.367 (7)	C21—H21	0.9300
N4—C31	1.329 (7)	C22—C21^{vii}	1.377 (9)
N4—C33	1.362 (7)	C22—H22	0.9300
N4—C34	1.465 (7)	C24—C26^{viii}	1.375 (12)
N5—C42	1.341 (7)	C24—C25	1.393 (12)
N5—C43	1.358 (8)	C24—H24	0.9300
N5—C41	1.455 (8)	C25—C26	1.328 (12)

N6—C42	1.329 (7)	C25—C27	1.552 (12)
N6—C44	1.372 (7)	C26—C24^{viii}	1.375 (12)
N6—Cu1^{iv}	1.983 (5)	C26—H26	0.9300
N7—C16	1.324 (7)	C27—H27A	0.9700
N7—C17	1.386 (7)	C27—H27B	0.9700
N8—C16	1.323 (7)	C28—H28	0.9300
N8—C18	1.374 (7)	C29—C30	1.319 (12)
N8—C19	1.474 (7)	C29—H29	0.9300
O1—C1	1.224 (7)	C30—H30	0.9300
O2—C1	1.281 (7)	C31—H31	0.9300
O2—Cu2^{v}	1.937 (4)	C32—C33	1.334 (8)
O3—C8	1.233 (7)	C32—H32	0.9300
O4—C8	1.262 (6)	C33—H33	0.9300
O4—Cu1^{vi}	1.939 (3)	C34—C35	1.498 (8)
O5—C5	1.376 (6)	C34—H34A	0.9700
O5—C9	1.382 (6)	C34—H34B	0.9700
O6—C15	1.291 (7)	C35—C40	1.355 (8)
O7—C15	1.201 (7)	C35—C36	1.371 (8)
O8—C23	1.219 (7)	C36—C37	1.377 (8)
O9—C23	1.271 (7)	C36—H36	0.9300
C1—C2	1.494 (7)	C37—C38	1.398 (8)
C2—C7	1.382 (7)	C37—H37	0.9300
C2—C3	1.383 (7)	C38—C39	1.369 (9)
C3—C4	1.373 (8)	C38—C41	1.508 (9)
C3—H3	0.9300	C39—C40	1.372 (9)
C4—C5	1.378 (8)	C39—H39	0.9300
C4—H4	0.9300	C40—H40	0.9300
C5—C6	1.364 (7)	C41—H41A	0.9700
C6—C7	1.383 (7)	C41—H41B	0.9700
C6—H6	0.9300	C42—H42	0.9300
C7—C8	1.515 (7)	C43—C44	1.360 (8)
C9—C10	1.364 (8)	C43—H43	0.9300
C9—C14	1.369 (8)	C44—H44	0.9300
C10—C11	1.387 (7)	O1W—H1WA	0.8506
C10—H10	0.9300	O1W—H1WB	0.8499
C11—C12	1.390 (7)	O2W—H2WA	0.8504
C11—C23	1.488 (8)	O2W—H2WB	0.8500
C12—C13	1.367 (8)		

O4^{i}—Cu1—N7	96.09 (17)	N8—C18—H18	126.3
O4^{i}—Cu1—O6	167.24 (17)	N8—C19—C20	111.9 (5)
N7—Cu1—O6	90.15 (17)	N8—C19—H19A	109.2
O4^{i}—Cu1—N6^{ii}	88.99 (18)	C20—C19—H19A	109.2
N7—Cu1—N6^{ii}	169.2 (2)	N8—C19—H19B	109.2
O6—Cu1—N6^{ii}	86.79 (18)	C20—C19—H19B	109.2
O2^{iii}—Cu2—O9	167.58 (17)	H19A—C19—H19B	107.9
O2^{iii}—Cu2—N3	93.20 (18)	C22—C20—C21	117.9 (6)
O9—Cu2—N3	91.71 (18)	C22—C20—C19	120.8 (6)

O2^{iii}—Cu2—N2	92.5 (2)	C21—C20—C19	121.3 (6)
O9—Cu2—N2	86.7 (2)	C22^{vii}—C21—C20	120.8 (6)
N3—Cu2—N2	160.3 (2)	C22^{vii}—C21—H21	119.6
C28—N1—C29	105.8 (8)	C20—C21—H21	119.6
C28—N1—C27	125.6 (8)	C20—C22—C21^{vii}	121.3 (6)
C29—N1—C27	128.6 (8)	C20—C22—H22	119.4
C30—N2—C28	103.3 (7)	C21^{vii}—C22—H22	119.4
C30—N2—Cu2	131.3 (6)	O8—C23—O9	123.5 (6)
C28—N2—Cu2	123.7 (5)	O8—C23—C11	121.3 (5)
C31—N3—C32	104.5 (5)	O9—C23—C11	115.3 (5)
C31—N3—Cu2	126.6 (4)	C26^{viii}—C24—C25	119.0 (11)
C32—N3—Cu2	128.7 (4)	C26^{viii}—C24—H24	120.5
C31—N4—C33	106.2 (5)	C25—C24—H24	120.5
C31—N4—C34	126.4 (5)	C26—C25—C24	117.8 (10)
C33—N4—C34	127.3 (6)	C26—C25—C27	122.6 (10)
C42—N5—C43	106.1 (6)	C24—C25—C27	119.5 (10)
C42—N5—C41	125.6 (6)	C25—C26—C24^{viii}	123.2 (11)
C43—N5—C41	128.2 (6)	C25—C26—H26	118.4
C42—N6—C44	105.6 (5)	C24^{viii}—C26—H26	118.4
C42—N6—Cu1^{iv}	126.5 (4)	N1—C27—C25	110.1 (8)
C44—N6—Cu1^{iv}	127.4 (5)	N1—C27—H27A	109.6
C16—N7—C17	105.7 (5)	C25—C27—H27A	109.6
C16—N7—Cu1	126.2 (4)	N1—C27—H27B	109.6
C17—N7—Cu1	128.1 (4)	C25—C27—H27B	109.6
C16—N8—C18	107.2 (5)	H27A—C27—H27B	108.2
C16—N8—C19	126.1 (5)	N1—C28—N2	112.0 (8)
C18—N8—C19	126.6 (5)	N1—C28—H28	124.0
C1—O2—Cu2^{v}	110.5 (4)	N2—C28—H28	124.0
C8—O4—Cu1^{vi}	120.7 (4)	C30—C29—N1	106.8 (10)
C5—O5—C9	119.2 (4)	C30—C29—H29	126.6
C15—O6—Cu1	107.4 (4)	N1—C29—H29	126.6
C23—O9—Cu2	110.0 (4)	C29—C30—N2	112.0 (10)
O1—C1—O2	124.1 (6)	C29—C30—H30	124.0
O1—C1—C2	120.9 (5)	N2—C30—H30	124.0
O2—C1—C2	115.0 (5)	N3—C31—N4	112.2 (5)
C7—C2—C3	118.1 (5)	N3—C31—H31	123.9
C7—C2—C1	124.6 (5)	N4—C31—H31	123.9
C3—C2—C1	117.2 (5)	C33—C32—N3	109.8 (6)
C4—C3—C2	122.3 (5)	C33—C32—H32	125.1
C4—C3—H3	118.9	N3—C32—H32	125.1
C2—C3—H3	118.9	C32—C33—N4	107.3 (6)
C3—C4—C5	118.7 (5)	C32—C33—H33	126.4
C3—C4—H4	120.7	N4—C33—H33	126.4
C5—C4—H4	120.7	N4—C34—C35	112.7 (5)
C6—C5—O5	124.8 (5)	N4—C34—H34A	109.1
C6—C5—C4	120.1 (5)	C35—C34—H34A	109.1
O5—C5—C4	115.0 (5)	N4—C34—H34B	109.1
C5—C6—C7	121.0 (5)	C35—C34—H34B	109.1

C5—C6—H6	119.5	H34A—C34—H34B	107.8
C7—C6—H6	119.5	C40—C35—C36	119.0 (6)
C2—C7—C6	119.8 (5)	C40—C35—C34	121.8 (6)
C2—C7—C8	122.1 (5)	C36—C35—C34	119.2 (6)
C6—C7—C8	118.0 (5)	C35—C36—C37	120.7 (6)
O3—C8—O4	126.0 (5)	C35—C36—H36	119.7
O3—C8—C7	118.8 (5)	C37—C36—H36	119.7
O4—C8—C7	115.2 (5)	C36—C37—C38	120.2 (6)
C10—C9—C14	120.3 (5)	C36—C37—H37	119.9
C10—C9—O5	117.8 (5)	C38—C37—H37	119.9
C14—C9—O5	121.8 (5)	C39—C38—C37	117.9 (6)
C9—C10—C11	121.3 (5)	C39—C38—C41	120.8 (6)
C9—C10—H10	119.4	C37—C38—C41	121.3 (6)
C11—C10—H10	119.4	C38—C39—C40	121.0 (6)
C10—C11—C12	118.6 (5)	C38—C39—H39	119.5
C10—C11—C23	118.9 (5)	C40—C39—H39	119.5
C12—C11—C23	122.5 (5)	C35—C40—C39	121.2 (6)
C13—C12—C11	118.9 (5)	C35—C40—H40	119.4
C13—C12—C15	117.7 (5)	C39—C40—H40	119.4
C11—C12—C15	123.4 (5)	N5—C41—C38	114.9 (5)
C12—C13—C14	122.3 (5)	N5—C41—H41A	108.6
C12—C13—H13	118.8	C38—C41—H41A	108.6
C14—C13—H13	118.8	N5—C41—H41B	108.6
C9—C14—C13	118.4 (6)	C38—C41—H41B	108.6
C9—C14—H14	120.8	H41A—C41—H41B	107.5
C13—C14—H14	120.8	N6—C42—N5	111.9 (6)
O7—C15—O6	124.6 (6)	N6—C42—H42	124.1
O7—C15—C12	122.6 (6)	N5—C42—H42	124.1
O6—C15—C12	112.2 (5)	N5—C43—C44	108.0 (6)
N8—C16—N7	111.0 (5)	N5—C43—H43	126.0
N8—C16—H16	124.5	C44—C43—H43	126.0
N7—C16—H16	124.5	C43—C44—N6	108.4 (6)
C18—C17—N7	108.8 (5)	C43—C44—H44	125.8
C18—C17—H17	125.6	N6—C44—H44	125.8
N7—C17—H17	125.6	H1WA—O1W—H1WB	107.7
C17—C18—N8	107.4 (5)	H2WA—O2W—H2WB	107.7
C17—C18—H18	126.3		

O2^{iii}—Cu2—N2—C30	−6.4 (8)	C17—N7—C16—N8	−0.2 (6)
O9—Cu2—N2—C30	161.2 (8)	Cu1—N7—C16—N8	178.3 (3)
N3—Cu2—N2—C30	−113.0 (9)	C16—N7—C17—C18	0.2 (6)
O2^{iii}—Cu2—N2—C28	156.5 (6)	Cu1—N7—C17—C18	−178.3 (4)
O9—Cu2—N2—C28	−35.9 (6)	N7—C17—C18—N8	−0.1 (7)
N3—Cu2—N2—C28	49.9 (10)	C16—N8—C18—C17	0.0 (6)
O2^{iii}—Cu2—N3—C31	−21.3 (4)	C19—N8—C18—C17	177.2 (5)
O9—Cu2—N3—C31	170.1 (4)	C16—N8—C19—C20	90.6 (7)
N2—Cu2—N3—C31	85.2 (8)	C18—N8—C19—C20	−86.1 (7)
O2^{iii}—Cu2—N3—C32	164.4 (5)	N8—C19—C20—C22	−108.8 (7)

O9—Cu2—N3—C32	−4.2 (5)	N8—C19—C20—C21	71.3 (8)
N2—Cu2—N3—C32	−89.1 (8)	C22—C20—C21—C22^{vii}	−1.0 (11)
O4^{i}—Cu1—N7—C16	167.2 (4)	C19—C20—C21—C22^{vii}	178.9 (6)
O6—Cu1—N7—C16	−1.6 (5)	C21—C20—C22—C21^{vii}	1.0 (11)
N6^{ii}—Cu1—N7—C16	−75.0 (11)	C19—C20—C22—C21^{vii}	−178.9 (6)
O4^{i}—Cu1—N7—C17	−14.6 (5)	Cu2—O9—C23—O8	−8.9 (8)
O6—Cu1—N7—C17	176.5 (5)	Cu2—O9—C23—C11	171.2 (4)
N6^{ii}—Cu1—N7—C17	103.1 (10)	C10—C11—C23—O8	148.2 (6)
O4^{i}—Cu1—O6—C15	−16.0 (9)	C12—C11—C23—O8	−30.0 (9)
N7—Cu1—O6—C15	103.5 (4)	C10—C11—C23—O9	−31.9 (8)
N6^{ii}—Cu1—O6—C15	−86.9 (4)	C12—C11—C23—O9	149.9 (6)
O2^{iii}—Cu2—O9—C23	−15.4 (10)	C26^{viii}—C24—C25—C26	2.2 (18)
N3—Cu2—O9—C23	97.9 (4)	C26^{viii}—C24—C25—C27	−176.4 (9)
N2—Cu2—O9—C23	−101.8 (4)	C24—C25—C26—C24^{viii}	−2.3 (19)
Cu2^{v}—O2—C1—O1	11.7 (8)	C27—C25—C26—C24^{viii}	176.2 (10)
Cu2^{v}—O2—C1—C2	−166.8 (4)	C28—N1—C27—C25	96.3 (11)
O1—C1—C2—C7	139.2 (6)	C29—N1—C27—C25	−86.4 (12)
O2—C1—C2—C7	−42.3 (8)	C26—C25—C27—N1	80.0 (12)
O1—C1—C2—C3	−44.3 (8)	C24—C25—C27—N1	−101.5 (11)
O2—C1—C2—C3	134.2 (6)	C29—N1—C28—N2	3.2 (10)
C7—C2—C3—C4	0.4 (9)	C27—N1—C28—N2	−178.9 (8)
C1—C2—C3—C4	−176.4 (6)	C30—N2—C28—N1	−2.7 (10)
C2—C3—C4—C5	0.5 (10)	Cu2—N2—C28—N1	−169.6 (5)
C9—O5—C5—C6	21.9 (9)	C28—N1—C29—C30	−2.4 (11)
C9—O5—C5—C4	−160.5 (6)	C27—N1—C29—C30	179.8 (9)
C3—C4—C5—C6	−1.4 (10)	N1—C29—C30—N2	0.8 (12)
C3—C4—C5—O5	−179.2 (6)	C28—N2—C30—C29	1.1 (11)
O5—C5—C6—C7	179.0 (5)	Cu2—N2—C30—C29	166.6 (7)
C4—C5—C6—C7	1.6 (9)	C32—N3—C31—N4	0.5 (6)
C3—C2—C7—C6	−0.3 (8)	Cu2—N3—C31—N4	−174.9 (4)
C1—C2—C7—C6	176.2 (5)	C33—N4—C31—N3	−1.2 (6)
C3—C2—C7—C8	176.1 (5)	C34—N4—C31—N3	−177.4 (5)
C1—C2—C7—C8	−7.4 (9)	C31—N3—C32—C33	0.4 (7)
C5—C6—C7—C2	−0.7 (8)	Cu2—N3—C32—C33	175.7 (4)
C5—C6—C7—C8	−177.2 (5)	N3—C32—C33—N4	−1.1 (7)
Cu1^{vi}—O4—C8—O3	−13.5 (8)	C31—N4—C33—C32	1.3 (7)
Cu1^{vi}—O4—C8—C7	164.6 (3)	C34—N4—C33—C32	177.5 (5)
C2—C7—C8—O3	−61.2 (7)	C31—N4—C34—C35	96.8 (7)
C6—C7—C8—O3	115.3 (6)	C33—N4—C34—C35	−78.6 (8)
C2—C7—C8—O4	120.6 (6)	N4—C34—C35—C40	114.0 (6)
C6—C7—C8—O4	−63.0 (7)	N4—C34—C35—C36	−67.6 (8)
C5—O5—C9—C10	−132.2 (6)	C40—C35—C36—C37	−2.3 (9)
C5—O5—C9—C14	49.9 (8)	C34—C35—C36—C37	179.3 (6)
C14—C9—C10—C11	−3.4 (9)	C35—C36—C37—C38	2.4 (10)
O5—C9—C10—C11	178.6 (5)	C36—C37—C38—C39	−1.0 (9)
C9—C10—C11—C12	0.6 (9)	C36—C37—C38—C41	−177.5 (6)
C9—C10—C11—C23	−177.6 (5)	C37—C38—C39—C40	−0.5 (9)
C10—C11—C12—C13	2.5 (8)	C41—C38—C39—C40	176.0 (6)

C23—C11—C12—C13	−179.3 (6)	C36—C35—C40—C39	0.8 (9)
C10—C11—C12—C15	−177.7 (6)	C34—C35—C40—C39	179.2 (5)
C23—C11—C12—C15	0.5 (9)	C38—C39—C40—C35	0.6 (9)
C11—C12—C13—C14	−3.0 (9)	C42—N5—C41—C38	−91.1 (7)
C15—C12—C13—C14	177.3 (6)	C43—N5—C41—C38	86.8 (8)
C10—C9—C14—C13	3.0 (9)	C39—C38—C41—N5	132.6 (6)
O5—C9—C14—C13	−179.1 (6)	C37—C38—C41—N5	−50.9 (8)
C12—C13—C14—C9	0.2 (10)	C44—N6—C42—N5	−0.8 (7)
Cu1—O6—C15—O7	−13.0 (7)	Cu1^{iv}—N6—C42—N5	−173.7 (4)
Cu1—O6—C15—C12	158.9 (4)	C43—N5—C42—N6	0.8 (7)
C13—C12—C15—O7	94.4 (8)	C41—N5—C42—N6	179.1 (5)
C11—C12—C15—O7	−85.4 (8)	C42—N5—C43—C44	−0.5 (7)
C13—C12—C15—O6	−77.7 (7)	C41—N5—C43—C44	−178.7 (6)
C11—C12—C15—O6	102.5 (6)	N5—C43—C44—N6	0.0 (8)
C18—N8—C16—N7	0.1 (6)	C42—N6—C44—C43	0.5 (7)
C19—N8—C16—N7	−177.1 (5)	Cu1^{iv}—N6—C44—C43	173.3 (4)

Symmetry codes: (i) −*x*+3/2, *y*+1/2, −*z*+1/2; (ii) *x*−1/2, −*y*+3/2, *z*−1/2; (iii) *x*+1/2, −*y*+1/2, *z*+1/2; (iv) *x*+1/2, −*y*+3/2, *z*+1/2; (v) *x*−1/2, −*y*+1/2, *z*−1/2; (vi) −*x*+3/2, *y*−1/2, −*z*+1/2; (vii) −*x*+2, −*y*, −*z*+1; (viii) −*x*+1, −*y*, −*z*+1.