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Crystal structure of *trans*-diaqua(3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane)copper(II) pamoate

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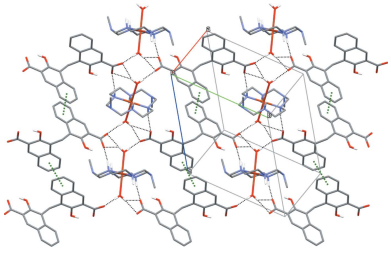
The asymmetric unit of the title compound, *trans*-diaqua(3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane-$\kappa^4N^1,N^5,N^8,N^{12}$)copper(II) 4,4′-methylenebis(3-hydroxynaphthalene-2-carboxylate), $[Cu(C_{10}H_{26}N_6)(H_2O)_2]\cdot(C_{23}H_{14}O_6)$ {$[Cu(L)(H_2O)_2](pam)$, where L = 3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane and pam = dianion of pamoic acid} consists of two independent halves of the $[Cu(L)(H_2O)_2]^{2+}$ cation and one dicarboxylate anion. The Cu^{II} atoms, lying on inversion centres, are coordinated by the four secondary N atoms of the macrocyclic ligands and the mutually *trans* O atoms of the water molecules in a tetragonally elongated octahedral geometry. The average equatorial Cu—N bond length is significantly shorter than the average axial Cu—O bond length [2.007 (10) and 2.486 (18) Å, respectively]. The macrocyclic ligand in the complex cations adopts the most energetically stable *trans*-III conformation. The complex cations and anions are connected *via* hydrogen-bonding interactions between the N—H groups of the macrocycles and the O—H groups of coordinated water molecules as the proton donors and the O atoms of the carboxylate as the proton acceptors into layers lying parallel to the $(1\bar{1}1)$ plane.

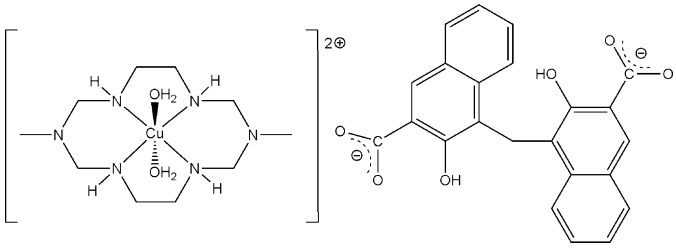
1. Chemical context

Coordination compounds of cyclam-like tetradentate azamacrocyclic ligands (cyclam = 1,4,8,11-tetraazacyclotetradecane) have attracted considerable attention because of their high thermodynamic stability, kinetic inertness, unusual redox properties and spectroscopic features (Melson, 1979; Yatsimirskii & Lampeka, 1985). Transition-metal complexes of this type of equatorial ligand possess two *trans* vacant sites in the axial positions and are suitable building blocks for the construction of metal–organic frameworks (MOFs) with potential applications in many areas including sorption, separation, gas storage, heterogeneous catalysis *etc* (Lampeka & Tsymbal, 2004; Suh & Moon, 2007; Suh *et al.*, 2012; Stackhouse & Ma, 2018; Lee & Moon, 2018). The Cu^{II} complexes of N^3,N^{10}-dialkyl-substituted diazacyclam (diazacyclam = 1,3,5,8,10,12-hexaazacyclotetradecane), readily obtainable *via* template-directed Mannich condensation of bis(ethylenediamine) complexes with formaldehyde and primary amines (Costisor & Linert, 2000), represent widespread systems in this kind of investigation.

Pamoic acid [4,4′-methylene-bis(3-hydroxynaphthalene-2-carboxylic acid), H_2pam] is widely used as a counter-ion in



pharmaceutical formulations (Du *et al.*, 2007 and references cited therein). This dicarboxylic acid is built from two naphthalene fragments, each bearing carboxylic and hydroxyl substituents and linked by a methylene bridge. The combination of this potentially bridging ligand with a biometal complex (*e.g.* Cu^{II}) could be a promising candidate for the construction of the Bio–MOFs attracting currently considerable attention (Cai *et al.*, 2019).



Here, we report the synthesis and the crystal structure of the title diaqua–Cu^{II} complex with a diazacyclam ligand and pamoate dianion, namely *trans*-diaqua(3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane-$\kappa^4N^1,N^5,N^8,N^{12}$)-copper(II) pamoate, [Cu*L*$(H_2O)_2$](pam), (I).

2. Structural commentary

The title compound (I) contains two crystallographically independent centrosymmetric complex cations. Each Cu^{II} ion lies on an inversion centre and is coordinated in the equatorial plane by four secondary amine N atoms of the azamacrocyclic ligand in a square-planar fashion, and by two O atoms from the water molecules in the axial positions, resulting in a tetragonally distorted octahedral geometry (Table 1, Fig. 1).

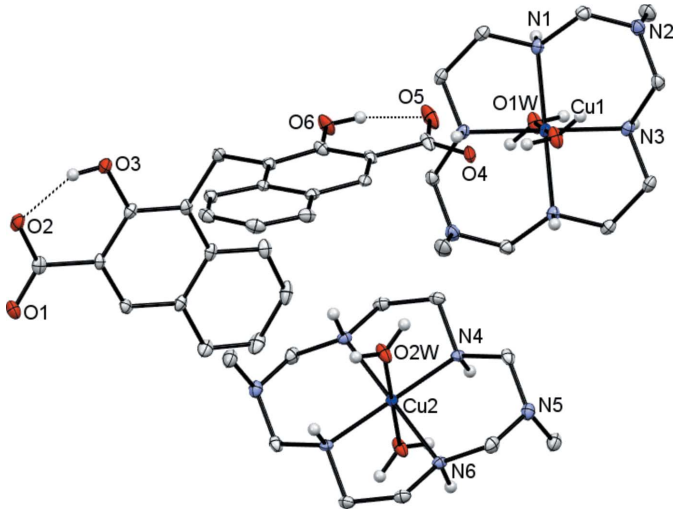


Figure 1
View of the molecular structure of (I), showing the partial atom-labelling scheme, with thermal displacement ellipsoids drawn at the 30% probability level. H atoms at carbon atoms have been omitted for clarity. Intra-anion hydrogen-bonding interactions are shown as dashed lines.

Table 1
Selected bond lengths (Å).

Cu1—N3	2.000 (2)	Cu2—N4	1.9987 (19)
Cu1—N1	2.017 (2)	Cu2—N6	2.0113 (19)
Cu1—O1w	2.5033 (19)	Cu2—O2w	2.4681 (18)

The CuN_4 fragments in (I) are strictly planar; at the same time they display some rhombic distortion. In particular, the Cu1—N3 and Cu2—N4 distances [av. 2.000 (1) Å] are shorter than those for Cu1—N1 and Cu2—N6 bonds [av. 2.014 (3) Å]. The axial bonds Cu—O*W* [av. 2.486 (17) Å] are longer than the equatorial bonds, which can be attributed to a large Jahn–Teller distortion. The coordinated macrocyclic ligand in both cations adopts the most energetically favourable *trans*-III (*R*,*R*,*S*,*S*) conformation (Bosnich *et al.*, 1965) with the five- and six-membered chelate rings in *gauche* and *chair* conformations, respectively. The bite angles in the five- and six-membered chelate rings equal 86.53 (8) and 93.47 (8)°, respectively. The methyl substituents at the distal nitrogen atoms in the six-membered chelate rings are axially oriented. Therewith, the C—N—C angles at non-coordinated nitrogen atoms (*ca* 115°) are larger than the canonical value for an sp^3-hybridized nitrogen atom (109°), thus indicating their partial sp^2 character.

The V-shaped pamoate dianion is fully deprotonated to counterbalance the charge of the complex unit and possesses a twisted conformation with the joint angle between the naphthalene rings being 115.6 (2)° and the angle between the mean planes of naphthalene fragments being 88.6 (2)°. The carboxylic groups adopt a transoid configuration to minimize unfavorable steric hindrance (Du *et al.*, 2007). The C—O bond lengths in each carboxylic group are somewhat different [1.248 (3) *versus* 1.271 (3) and 1.245 (3) *versus* 1.279 (4) Å for the O1—C11—O2 and O4—C22—O5 fragments, respectively], thus indicating their incomplete delocalization. As expected, each hydroxylic group exhibits a strong intra-anion O—H···O bond with the adjacent carboxyl oxygen (*D*···*A* distances *ca* 2.5 Å; Table 2).

3. Supramolecular features

Each carboxylate group of the pamoate anion acts as a proton acceptor by the formation of N—H···O hydrogen bonds with adjacent secondary amine groups of the azamacrocyclic ligand and bifurcated O*W*—H···(O,O) hydrogen bonds with a coordinated water molecule of the same cation (Fig. 2 and Table 2). Additionally, the benzene fragments of the naphthalene rings are involved in two kinds of intermolecular π–π interactions [interplanar separation of 3.470 and 3.717 Å; centroid-to-centroid distances of 3.8996 (15) and 4.2107 (15) Å, respectively] (Fig. 2). These supramolecular interactions (Steed & Atwood, 2009) generate sheets of interacting ions parallel to $(1\bar{1}1)$, and additional N1—H1···O3 contacts and C—H···O interactions link these sheets into a three-dimensional network.

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O3^{i}	1.00	2.50	3.272 (3)	134
N3—H3···O5	1.00	1.89	2.836 (3)	156
N4—H4···O2^{i}	1.00	1.90	2.822 (3)	152
O3—H3*C*···O2	0.84	1.75	2.502 (2)	148
O6—H6*C*···O5	0.84	1.75	2.514 (3)	150
O1*W*—H1*WA*···O1^{ii}	0.86	1.88	2.746 (2)	178
O1*W*—H1*WB*···O4	0.86	2.31	3.136 (3)	162
O1*W*—H1*WB*···O5	0.86	2.41	3.087 (3)	136
O2*W*—H2*WA*···O1^{i}	0.86	2.05	2.901 (2)	169
O2*W*—H2*WA*···O2^{i}	0.86	2.61	3.280 (2)	136
O2*W*—H2*WB*···O4^{iii}	0.86	1.88	2.743 (3)	176
C2—H2*B*···O1^{iv}	0.99	2.48	3.435 (3)	162
C5—H5*B*···O2^{i}	0.98	2.45	3.316 (3)	147

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

4. Database survey

A search of the Cambridge Structural Database (CSD, version 5.39, last update August 2018; Groom *et al.*, 2016) indicated that 65 Cu^{II} complexes of N^3,N^{10}-disubstituted diazacyclams with various alkyl pendant groups have been reported and the majority of them were investigated as building blocks for supramolecular chemistry. Among them, eight hits deal with a diaqua azamacrocyclic Cu^{II} cation. Surprisingly, only one structure with the dimethyl-substituted macrocycle *L* has been reported, *i.e.* $[Cu(L)](ClO_4)_2$ (LAWXIR; Zhang *et al.*, 2005) and the title compound (I) is the first example of a $[Cu(L)(H_2O)_2]^{2+}$ cation described so far.

A search for pamoic acid gave 97 hits, only four of which concern compounds consisting of uncoordinated pamoate dianion and metal complex cations, *i.e.*, $[M(H_2O)_2(phen)_2]$-(pam)·H_2O [*M* = Zn^{II} (MEBGOQ), Mn^{II} (SIQDOM), Cd^{II} (YOLDEJ), phen = phenanthroline] and $[Mn(H_2O)_4(DMF)_2]$(pam) (SIQCOL) (Ma *et al.*, 2006; Du *et al.*, 2007; Shi *et al.*, 2008). Except for nine hits concerning the non-deprotonated pamoic acid, all other 84 structures are coordination polymers, thus demonstrating the availability of the pamoic acid anion for the design of MOFs.

5. Synthesis and crystallization

All chemicals and solvents used in this work were purchased from Sigma–Aldrich and used without further purification. The starting complex, $[Cu(L)](ClO_4)_2$, was prepared by a method reported in the literature (Suh & Kang, 1988). The title compound (I) was prepared as follows. To a water/DMF solution (1/3 by volume, 5 ml) of $[Cu(L)](ClO_4)_2$ (123 mg, 0.25 mmol) was added a DMF solution (10 ml) containing pamoic acid (97 mg, 0.25 mmol) and 0.2 ml of triethylamine. A pink precipitate was formed in three days. This was filtered off, washed with a small amount of DMF and diethyl ether, and dried in air. Yield: 82 mg (46%). Analysis calculated for $C_{33}H_{44}N_6CuO_8$: C 55.33, H 6.19, N 11.73%. Found: C 55.42, H 6.24, N 11.62%. Single crystals suitable for X-ray diffraction analysis were selected from the sample resulting from the synthesis.

Safety note: Perchlorate salts of metal complexes are potentially explosive and should be handled with care.

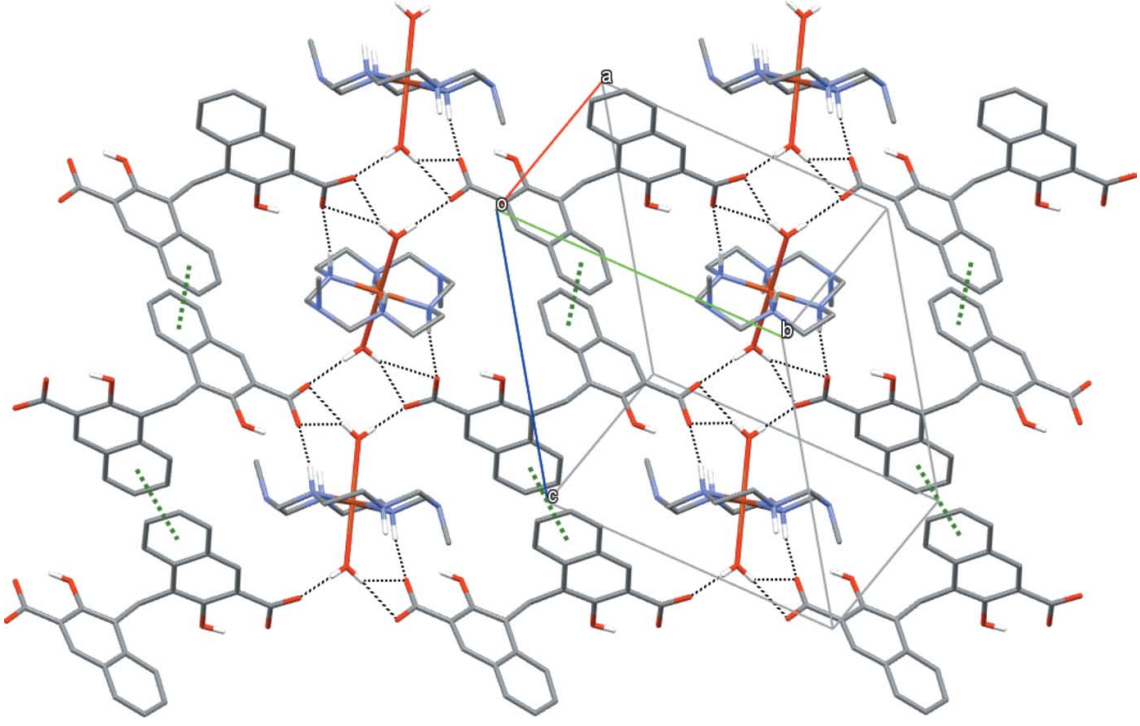


Figure 2
Sheets of complex molecules parallel to the $(1\bar{1}1)$ plane. Supramolecular interactions are shown as dashed lines (black for hydrogen bonding and green for π–π interactions). H atoms at carbon atoms and intra-anion hydrogen bonds are not shown.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 3. All H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms, with C—H distances of 0.95 (ring H atoms) or 0.98–0.99 Å (open-chain H atoms), N—H distance of 1.0 Å, hydroxyl O—H distance of 0.84 Å and aqua O—H distance of 0.86 Å with U_{iso}(H) values of 1.2 or 1.5U_{eq} times that of the parent atoms.

Table 3
Experimental details.

Crystal data	
Chemical formula	$[Cu(C_{10}H_{26}N_6)(H_2O)_2]C_{23}H_{14}O_6$
M_r	716.28
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	100
a, b, c (Å)	9.8877 (6), 12.1406 (7), 14.5760 (9)
α, β, γ (°)	71.594 (3), 81.128 (3), 88.249 (3)
V (Å^3)	1640.06 (17)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.73
Crystal size (mm)	0.20 × 0.18 × 0.12
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2007)
T_{min}, T_{max}	0.868, 0.918
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	52866, 6401, 4540
R_{int}	0.080
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.617
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.090, 1.03
No. of reflections	6401
No. of parameters	438
No. of restraints	6
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.34, −0.39

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXS2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

References

Bosnich, B., Poon, C. K. & Tobe, M. C. (1965). *Inorg. Chem.* **4**, 1102–1108.
Bruker (2007). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Cai, H., Huang, Y.-L. & Li, D. (2019). *Coord. Chem. Rev.* **378**, 207–221.
Costisor, O. & Linert, W. (2000). *Rev. Inorg. Chem.* **1**, 63–126.
Du, M., Li, C.-P., Zhao, X.-J. & Yu, Q. (2007). *CrystEngComm*, **9**, 1011–1028.
Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* B**72**, 171–179.
Lampeka, Ya. D. & Tsymbal, L. V. (2004). *Theor. Exp. Chem.* **40**, 345–371.
Lee, J. H. & Moon, H. R. (2018). *J. Incl. Phenom. Macrocycl. Chem.* **92**, 237–249.
Ma, A.-Q., Jia, Z.-B. & Wang, G.-P. (2006). *Acta Cryst.* E**62**, m21–m23.
Macrae, C. F., Bruno, I. J., Chisholm, J. A., Edgington, P. R., McCabe, P., Pidcock, E., Rodriguez-Monge, L., Taylor, R., van de Streek, J. & Wood, P. A. (2008). *J. Appl. Cryst.* **41**, 466–470.
Melson, G. A. (1979). Editor. *Coordination Chemistry of Macrocyclic Compounds*, New York: Plenum Press.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Shi, Q., Sun, Y., Sheng, L., Ma, K., Hu, M., Hu, X. & Huang, S. (2008). *Cryst. Growth Des.* **8**, 3401–3407.
Stackhouse, C. A. & Ma, S. (2018). *Polyhedron*, **145**, 154–165.
Steed, J. W. & Atwood, J. L. (2009). *Supramolecular Chemistry*, 2nd ed. Chichester: John Wiley & Sons.
Suh, M. P. & Kang, S.-G. (1988). *Inorg. Chem.* **27**, 2544–2546.
Suh, M. P. & Moon, H. R. (2007). *Advances in Inorganic Chemistry*, Vol. 59, edited by R. van Eldik & K. Bowman-James, pp. 39–79. San Diego: Academic Press.
Suh, M. P., Park, H. J., Prasad, T. K. & Lim, D.-W. (2012). *Chem. Rev.* **112**, 782–835.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Yatsimirskii, K. B. & Lampeka, Ya. D. (1985). *Physicochemistry of Metals Complexes with Macrocyclic Ligands*. Kiev: Naukova Dumka. [In Russian.]
Zhang, B., Kou, H.-Z., Cui, A.-L. & Wang, R.-J. (2005). *Jiegou Huaxue (Chin. J. Struct. Chem.)*, **24**, 1259–1263.

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Crystal structure of *trans*-diaqua(3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane)copper(II) pamoate

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Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS2014* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *publCIF* (Westrip, 2010).

trans-Diaqua(3,10-dimethyl-1,3,5,8,10,12-hexaazacyclotetradecane-$\kappa^4N^1,N^5,N^8,N^{12}$)copper(II) 4,4′-methylenebis(3-hydroxynaphthalene-2-carboxylate)

Crystal data

$[Cu(C_{10}H_{26}N_6)(H_2O)_2]C_{23}H_{14}O_6$
M_r = 716.28
Triclinic, $P\overline{1}$
a = 9.8877 (6) Å
b = 12.1406 (7) Å
c = 14.5760 (9) Å
α = 71.594 (3)°
β = 81.128 (3)°
γ = 88.249 (3)°
V = 1640.06 (17) Å^3
Z = 2
$F(000)$ = 754
D_x = 1.450 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 8230 reflections
θ = 2.4–25.6°
μ = 0.73 mm^{-1}
T = 100 K
Block, pink
0.20 × 0.18 × 0.12 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2007)
T_{min} = 0.868, T_{max} = 0.918
52866 measured reflections
6401 independent reflections
4540 reflections with $I > 2\sigma(I)$
R_{int} = 0.080
θ_{max} = 26.0°, θ_{min} = 1.9°
h = −12→12
k = −14→14
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.090
S = 1.03
6401 reflections
438 parameters
6 restraints
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0378P)^2 + 0.6293P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	1.0000	0.5000	0.5000	0.01499 (12)
Cu2	0.5000	0.5000	0.0000	0.01582 (12)
N1	0.8280 (2)	0.58002 (17)	0.45737 (15)	0.0199 (5)
H1	0.8412	0.6050	0.3843	0.024*
N2	0.7064 (2)	0.40151 (18)	0.47031 (15)	0.0239 (5)
N3	0.9443 (2)	0.34915 (17)	0.48721 (14)	0.0194 (5)
H3	0.9644	0.3562	0.4162	0.023*
C4	0.8207 (3)	0.6863 (2)	0.48671 (19)	0.0223 (6)
H4A	0.7880	0.6669	0.5578	0.027*
H4B	0.7566	0.7417	0.4510	0.027*
C1	0.6994 (3)	0.5083 (2)	0.49364 (19)	0.0239 (6)
H1A	0.6785	0.4901	0.5656	0.029*
H1B	0.6232	0.5545	0.4650	0.029*
C2	0.7977 (3)	0.3164 (2)	0.52012 (19)	0.0235 (6)
H2A	0.7810	0.2416	0.5096	0.028*
H2B	0.7761	0.3046	0.5912	0.028*
C3	1.0361 (3)	0.2604 (2)	0.53813 (19)	0.0224 (6)
H3A	1.0350	0.1910	0.5164	0.027*
H3B	1.0057	0.2365	0.6097	0.027*
C5	0.7162 (3)	0.4154 (2)	0.3666 (2)	0.0332 (7)
H5A	0.7205	0.3388	0.3573	0.050*
H5B	0.6356	0.4560	0.3418	0.050*
H5C	0.7991	0.4607	0.3309	0.050*
N6	0.5743 (2)	0.35155 (17)	0.08194 (14)	0.0190 (5)
H6	0.6453	0.3239	0.0379	0.023*
N4	0.6263 (2)	0.58227 (17)	0.05243 (14)	0.0169 (5)
H4	0.5701	0.6038	0.1072	0.020*
N5	0.5995 (2)	0.77617 (18)	−0.06320 (15)	0.0234 (5)
C7	0.4716 (3)	0.2553 (2)	0.13005 (19)	0.0244 (6)
H7A	0.5187	0.1862	0.1671	0.029*
H7B	0.4038	0.2788	0.1776	0.029*
C8	0.6454 (3)	0.3839 (2)	0.15230 (18)	0.0229 (6)
H8A	0.7082	0.3217	0.1807	0.028*
H8B	0.5780	0.3952	0.2061	0.028*
C9	0.7253 (3)	0.4959 (2)	0.09671 (19)	0.0222 (6)
H9A	0.7709	0.5232	0.1418	0.027*
H9B	0.7963	0.4836	0.0452	0.027*
C6	0.6926 (3)	0.6918 (2)	−0.01746 (19)	0.0223 (6)
H6A	0.7471	0.7270	0.0181	0.027*

H6B	0.7568	0.6723	−0.0690	0.027*
C10	0.5140 (3)	0.8320 (2)	−0.0004 (2)	0.0290 (7)
H10A	0.4544	0.8878	−0.0391	0.043*
H10B	0.4577	0.7730	0.0525	0.043*
H10C	0.5724	0.8727	0.0276	0.043*
C11	0.4511 (3)	−0.3050 (2)	0.24922 (17)	0.0210 (6)
C12	0.4904 (3)	−0.1995 (2)	0.27246 (17)	0.0169 (6)
C13	0.6302 (3)	−0.1758 (2)	0.27572 (17)	0.0188 (6)
C14	0.6685 (3)	−0.0783 (2)	0.29585 (17)	0.0181 (6)
C15	0.5639 (3)	−0.0083 (2)	0.32585 (17)	0.0191 (6)
C16	0.5905 (3)	0.0822 (2)	0.36370 (18)	0.0250 (6)
H16	0.6820	0.0984	0.3687	0.030*
C17	0.4868 (3)	0.1461 (2)	0.3929 (2)	0.0327 (7)
H17	0.5068	0.2043	0.4199	0.039*
C18	0.3508 (3)	0.1271 (2)	0.3835 (2)	0.0346 (7)
H18	0.2799	0.1739	0.4022	0.041*
C19	0.3211 (3)	0.0418 (2)	0.34780 (19)	0.0275 (7)
H19	0.2292	0.0299	0.3409	0.033*
C20	0.4247 (3)	−0.0295 (2)	0.32067 (17)	0.0200 (6)
C21	0.3934 (3)	−0.1235 (2)	0.29063 (17)	0.0187 (6)
H21	0.3018	−0.1346	0.2827	0.022*
C22	1.0315 (3)	0.3478 (3)	0.2154 (2)	0.0297 (7)
C23	0.9735 (2)	0.2584 (2)	0.17946 (19)	0.0199 (6)
C24	0.9275 (3)	0.1467 (2)	0.24487 (18)	0.0216 (6)
C25	0.8696 (2)	0.0657 (2)	0.21366 (17)	0.0178 (6)
C26	0.8648 (2)	0.0906 (2)	0.11176 (18)	0.0168 (5)
C27	0.8225 (2)	0.0078 (2)	0.07126 (18)	0.0203 (6)
H27	0.7934	−0.0675	0.1132	0.024*
C28	0.8227 (3)	0.0346 (2)	−0.02714 (19)	0.0250 (6)
H28	0.7950	−0.0227	−0.0526	0.030*
C29	0.8634 (3)	0.1459 (2)	−0.09125 (19)	0.0285 (7)
H29	0.8607	0.1640	−0.1593	0.034*
C30	0.9069 (3)	0.2277 (2)	−0.05578 (19)	0.0253 (6)
H30	0.9349	0.3025	−0.0995	0.030*
C31	0.9107 (2)	0.2024 (2)	0.04560 (18)	0.0189 (6)
C32	0.9621 (2)	0.2839 (2)	0.08278 (19)	0.0203 (6)
H32	0.9897	0.3589	0.0393	0.024*
C33	0.8189 (3)	−0.0505 (2)	0.28762 (18)	0.0208 (6)
H33A	0.8729	−0.1128	0.2698	0.025*
H33B	0.8376	−0.0519	0.3528	0.025*
O1	0.32781 (19)	−0.32344 (15)	0.24857 (13)	0.0262 (4)
O2	0.54697 (19)	−0.37048 (15)	0.23045 (13)	0.0253 (4)
O3	0.72922 (18)	−0.25007 (14)	0.25674 (13)	0.0242 (4)
H3C	0.6944	−0.3007	0.2389	0.036*
O4	1.06005 (19)	0.44690 (16)	0.15717 (16)	0.0377 (5)
O5	1.0477 (2)	0.31618 (19)	0.30534 (15)	0.0416 (6)
O6	0.9387 (2)	0.11959 (17)	0.34181 (13)	0.0319 (5)
H6C	0.9751	0.1758	0.3514	0.048*

O1W	1.07942 (19)	0.56232 (16)	0.31930 (13)	0.0303 (5)
H1WA	1.1574	0.5988	0.2985	0.045*
H1WB	1.0603	0.5205	0.2849	0.045*
O2W	0.32694 (18)	0.51823 (16)	0.13556 (13)	0.0289 (5)
H2WA	0.3381	0.5611	0.1708	0.043*
H2WB	0.2426	0.4986	0.1394	0.043*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0177 (2)	0.0117 (2)	0.0152 (2)	−0.00018 (18)	−0.00184 (18)	−0.00397 (17)
Cu2	0.0159 (2)	0.0148 (2)	0.0163 (2)	−0.00108 (18)	−0.00325 (18)	−0.00389 (18)
N1	0.0235 (12)	0.0179 (11)	0.0181 (11)	−0.0009 (9)	−0.0016 (9)	−0.0062 (9)
N2	0.0277 (13)	0.0216 (12)	0.0224 (12)	−0.0033 (10)	−0.0082 (10)	−0.0044 (10)
N3	0.0248 (12)	0.0166 (11)	0.0157 (10)	0.0005 (9)	−0.0033 (9)	−0.0036 (9)
C4	0.0272 (15)	0.0188 (14)	0.0218 (14)	0.0048 (11)	−0.0041 (12)	−0.0075 (11)
C1	0.0198 (15)	0.0239 (15)	0.0252 (14)	0.0004 (11)	−0.0018 (11)	−0.0043 (12)
C2	0.0266 (16)	0.0189 (14)	0.0235 (14)	−0.0052 (12)	−0.0056 (12)	−0.0030 (12)
C3	0.0297 (16)	0.0142 (13)	0.0221 (14)	0.0029 (11)	−0.0045 (12)	−0.0040 (11)
C5	0.0401 (18)	0.0313 (16)	0.0332 (16)	−0.0010 (14)	−0.0185 (14)	−0.0109 (13)
N6	0.0192 (12)	0.0179 (11)	0.0183 (11)	0.0017 (9)	−0.0026 (9)	−0.0038 (9)
N4	0.0126 (11)	0.0189 (11)	0.0190 (11)	0.0020 (9)	−0.0014 (9)	−0.0065 (9)
N5	0.0256 (13)	0.0190 (12)	0.0239 (12)	−0.0029 (10)	0.0006 (10)	−0.0061 (10)
C7	0.0265 (16)	0.0194 (14)	0.0215 (14)	−0.0014 (12)	0.0010 (12)	−0.0003 (11)
C8	0.0223 (15)	0.0265 (15)	0.0206 (13)	0.0054 (12)	−0.0069 (11)	−0.0068 (12)
C9	0.0177 (14)	0.0282 (15)	0.0240 (14)	0.0044 (12)	−0.0077 (11)	−0.0111 (12)
C6	0.0169 (15)	0.0235 (15)	0.0260 (14)	−0.0055 (12)	0.0035 (12)	−0.0100 (12)
C10	0.0319 (17)	0.0210 (15)	0.0339 (16)	0.0007 (12)	−0.0008 (13)	−0.0106 (13)
C11	0.0306 (17)	0.0190 (14)	0.0108 (12)	−0.0038 (13)	−0.0002 (11)	−0.0021 (11)
C12	0.0226 (15)	0.0136 (13)	0.0131 (12)	−0.0037 (11)	0.0000 (10)	−0.0030 (10)
C13	0.0231 (15)	0.0154 (13)	0.0154 (13)	0.0013 (11)	0.0009 (11)	−0.0035 (11)
C14	0.0234 (15)	0.0148 (13)	0.0126 (12)	−0.0040 (11)	−0.0018 (11)	0.0004 (10)
C15	0.0287 (16)	0.0134 (13)	0.0112 (12)	−0.0029 (11)	0.0016 (11)	−0.0002 (10)
C16	0.0308 (16)	0.0223 (14)	0.0195 (14)	−0.0076 (12)	0.0022 (12)	−0.0050 (12)
C17	0.050 (2)	0.0204 (15)	0.0275 (15)	−0.0080 (14)	0.0092 (14)	−0.0135 (13)
C18	0.0360 (19)	0.0261 (16)	0.0377 (17)	0.0003 (14)	0.0134 (14)	−0.0137 (14)
C19	0.0242 (16)	0.0229 (15)	0.0311 (15)	−0.0015 (12)	0.0072 (12)	−0.0076 (13)
C20	0.0250 (15)	0.0139 (13)	0.0169 (13)	−0.0004 (11)	0.0029 (11)	−0.0016 (11)
C21	0.0182 (14)	0.0167 (13)	0.0175 (13)	−0.0047 (11)	−0.0009 (11)	−0.0007 (11)
C22	0.0136 (15)	0.0359 (18)	0.048 (2)	−0.0057 (13)	0.0084 (13)	−0.0299 (16)
C23	0.0114 (13)	0.0225 (14)	0.0286 (15)	−0.0029 (11)	0.0009 (11)	−0.0135 (12)
C24	0.0182 (14)	0.0287 (15)	0.0205 (13)	−0.0029 (12)	−0.0017 (11)	−0.0118 (12)
C25	0.0153 (14)	0.0188 (13)	0.0193 (13)	−0.0010 (11)	−0.0021 (11)	−0.0061 (11)
C26	0.0112 (13)	0.0169 (13)	0.0228 (13)	0.0003 (10)	−0.0025 (10)	−0.0072 (11)
C27	0.0176 (14)	0.0205 (14)	0.0233 (14)	−0.0017 (11)	−0.0018 (11)	−0.0080 (11)
C28	0.0206 (15)	0.0325 (16)	0.0267 (15)	−0.0009 (12)	−0.0049 (12)	−0.0151 (13)
C29	0.0248 (16)	0.0410 (18)	0.0190 (14)	0.0022 (13)	−0.0064 (12)	−0.0073 (13)
C30	0.0190 (15)	0.0272 (15)	0.0234 (14)	0.0004 (12)	−0.0025 (12)	0.0003 (12)

C31	0.0135 (13)	0.0205 (14)	0.0211 (13)	0.0040 (11)	−0.0024 (11)	−0.0047 (11)
C32	0.0110 (13)	0.0167 (13)	0.0317 (15)	0.0002 (10)	0.0000 (11)	−0.0070 (12)
C33	0.0237 (15)	0.0168 (13)	0.0206 (13)	−0.0015 (11)	−0.0072 (11)	−0.0020 (11)
O1	0.0259 (11)	0.0282 (10)	0.0274 (10)	−0.0085 (8)	−0.0012 (8)	−0.0133 (8)
O2	0.0339 (11)	0.0203 (10)	0.0270 (10)	0.0040 (9)	−0.0069 (9)	−0.0139 (8)
O3	0.0240 (10)	0.0182 (10)	0.0325 (11)	0.0020 (8)	−0.0035 (8)	−0.0116 (8)
O4	0.0215 (11)	0.0226 (11)	0.0751 (15)	−0.0041 (9)	−0.0059 (10)	−0.0245 (11)
O5	0.0363 (13)	0.0581 (15)	0.0435 (13)	−0.0177 (11)	0.0053 (10)	−0.0381 (12)
O6	0.0359 (12)	0.0423 (12)	0.0222 (10)	−0.0133 (10)	−0.0075 (9)	−0.0143 (9)
O1W	0.0328 (11)	0.0330 (11)	0.0267 (10)	−0.0130 (9)	0.0071 (9)	−0.0159 (9)
O2W	0.0228 (10)	0.0384 (11)	0.0321 (11)	−0.0106 (9)	0.0054 (8)	−0.0237 (9)

Geometric parameters (Å, º)

Cu1—N3	2.000 (2)	C10—H10A	0.9800
Cu1—N3^{i}	2.000 (2)	C10—H10B	0.9800
Cu1—N1	2.017 (2)	C10—H10C	0.9800
Cu1—N1^{i}	2.017 (2)	C11—O1	1.248 (3)
Cu1—O1w	2.5033 (19)	C11—O2	1.271 (3)
Cu1—O1w^{i}	2.5033 (18)	C11—C12	1.501 (3)
Cu2—N4	1.9987 (19)	C12—C21	1.364 (3)
Cu2—N4^{ii}	1.9987 (19)	C12—C13	1.431 (4)
Cu2—N6	2.0113 (19)	C13—O3	1.367 (3)
Cu2—N6^{ii}	2.0114 (19)	C13—C14	1.383 (3)
Cu2—O2w	2.4681 (18)	C14—C15	1.424 (4)
Cu2—O2w^{ii}	2.4681 (18)	C14—C33	1.514 (3)
N1—C4	1.479 (3)	C15—C16	1.423 (3)
N1—C1	1.491 (3)	C15—C20	1.426 (4)
N1—H1	1.0000	C16—C17	1.363 (4)
N2—C1	1.438 (3)	C16—H16	0.9500
N2—C2	1.442 (3)	C17—C18	1.406 (4)
N2—C5	1.455 (3)	C17—H17	0.9500
N3—C3	1.476 (3)	C18—C19	1.355 (4)
N3—C2	1.480 (3)	C18—H18	0.9500
N3—H3	1.0000	C19—C20	1.411 (4)
C4—C3^{i}	1.518 (4)	C19—H19	0.9500
C4—H4A	0.9900	C20—C21	1.403 (3)
C4—H4B	0.9900	C21—H21	0.9500
C1—H1A	0.9900	C22—O4	1.245 (3)
C1—H1B	0.9900	C22—O5	1.279 (4)
C2—H2A	0.9900	C22—C23	1.507 (4)
C2—H2B	0.9900	C23—C32	1.366 (4)
C3—C4^{i}	1.518 (4)	C23—C24	1.429 (4)
C3—H3A	0.9900	C24—O6	1.367 (3)
C3—H3B	0.9900	C24—C25	1.378 (3)
C5—H5A	0.9800	C25—C26	1.427 (3)
C5—H5B	0.9800	C25—C33	1.523 (3)
C5—H5C	0.9800	C26—C27	1.417 (3)

N6—C8	1.481 (3)	C26—C31	1.434 (3)
N6—C7	1.492 (3)	C27—C28	1.366 (4)
N6—H6	1.0000	C27—H27	0.9500
N4—C9	1.476 (3)	C28—C29	1.407 (4)
N4—C6	1.493 (3)	C28—H28	0.9500
N4—H4	1.0000	C29—C30	1.362 (4)
N5—C6	1.429 (3)	C29—H29	0.9500
N5—C7^{ii}	1.432 (3)	C30—C31	1.418 (3)
N5—C10	1.460 (3)	C30—H30	0.9500
C7—N5^{ii}	1.432 (3)	C31—C32	1.409 (3)
C7—H7A	0.9900	C32—H32	0.9500
C7—H7B	0.9900	C33—H33A	0.9900
C8—C9	1.518 (4)	C33—H33B	0.9900
C8—H8A	0.9900	O3—H3C	0.8400
C8—H8B	0.9900	O6—H6C	0.8400
C9—H9A	0.9900	O1W—H1WA	0.8641
C9—H9B	0.9900	O1W—H1WB	0.8606
C6—H6A	0.9900	O2W—H2WA	0.8578
C6—H6B	0.9900	O2W—H2WB	0.8629

N3—Cu1—N3^{i}	180.00	H9A—C9—H9B	108.6
N3—Cu1—N1	93.47 (8)	N5—C6—N4	114.6 (2)
N3^{i}—Cu1—N1	86.53 (8)	N5—C6—H6A	108.6
N3—Cu1—N1^{i}	86.53 (8)	N4—C6—H6A	108.6
N3^{i}—Cu1—N1^{i}	93.47 (8)	N5—C6—H6B	108.6
N1—Cu1—N1^{i}	180.0	N4—C6—H6B	108.6
N4—Cu2—N4^{ii}	180.00	H6A—C6—H6B	107.6
N4—Cu2—N6	86.53 (8)	N5—C10—H10A	109.5
N4^{ii}—Cu2—N6	93.47 (8)	N5—C10—H10B	109.5
N4—Cu2—N6^{ii}	93.47 (8)	H10A—C10—H10B	109.5
N4^{ii}—Cu2—N6^{ii}	86.53 (8)	N5—C10—H10C	109.5
N6—Cu2—N6^{ii}	180.0	H10A—C10—H10C	109.5
C4—N1—C1	112.6 (2)	H10B—C10—H10C	109.5
C4—N1—Cu1	105.83 (15)	O1—C11—O2	123.7 (2)
C1—N1—Cu1	115.85 (15)	O1—C11—C12	118.9 (2)
C4—N1—H1	107.4	O2—C11—C12	117.4 (2)
C1—N1—H1	107.4	C21—C12—C13	118.5 (2)
Cu1—N1—H1	107.4	C21—C12—C11	120.6 (2)
C1—N2—C2	115.5 (2)	C13—C12—C11	120.9 (2)
C1—N2—C5	114.8 (2)	O3—C13—C14	118.8 (2)
C2—N2—C5	113.9 (2)	O3—C13—C12	119.5 (2)
C3—N3—C2	112.89 (18)	C14—C13—C12	121.7 (2)
C3—N3—Cu1	106.69 (15)	C13—C14—C15	118.4 (2)
C2—N3—Cu1	115.45 (16)	C13—C14—C33	119.6 (2)
C3—N3—H3	107.1	C15—C14—C33	122.0 (2)
C2—N3—H3	107.1	C16—C15—C14	123.1 (2)
Cu1—N3—H3	107.1	C16—C15—C20	117.2 (2)
N1—C4—C3^{i}	107.4 (2)	C14—C15—C20	119.7 (2)

N1—C4—H4A	110.2	C17—C16—C15	121.1 (3)
C3^{i}—C4—H4A	110.2	C17—C16—H16	119.5
N1—C4—H4B	110.2	C15—C16—H16	119.5
C3^{i}—C4—H4B	110.2	C16—C17—C18	120.9 (3)
H4A—C4—H4B	108.5	C16—C17—H17	119.5
N2—C1—N1	113.6 (2)	C18—C17—H17	119.5
N2—C1—H1A	108.8	C19—C18—C17	119.8 (3)
N1—C1—H1A	108.8	C19—C18—H18	120.1
N2—C1—H1B	108.8	C17—C18—H18	120.1
N1—C1—H1B	108.8	C18—C19—C20	121.0 (3)
H1A—C1—H1B	107.7	C18—C19—H19	119.5
N2—C2—N3	113.67 (19)	C20—C19—H19	119.5
N2—C2—H2A	108.8	C21—C20—C19	121.3 (2)
N3—C2—H2A	108.8	C21—C20—C15	118.8 (2)
N2—C2—H2B	108.8	C19—C20—C15	119.9 (2)
N3—C2—H2B	108.8	C12—C21—C20	122.1 (2)
H2A—C2—H2B	107.7	C12—C21—H21	118.9
N3—C3—C4^{i}	107.57 (19)	C20—C21—H21	118.9
N3—C3—H3A	110.2	O4—C22—O5	124.0 (3)
C4^{i}—C3—H3A	110.2	O4—C22—C23	119.0 (3)
N3—C3—H3B	110.2	O5—C22—C23	117.0 (3)
C4^{i}—C3—H3B	110.2	C32—C23—C24	118.5 (2)
H3A—C3—H3B	108.5	C32—C23—C22	120.0 (2)
N2—C5—H5A	109.5	C24—C23—C22	121.4 (2)
N2—C5—H5B	109.5	O6—C24—C25	118.7 (2)
H5A—C5—H5B	109.5	O6—C24—C23	119.3 (2)
N2—C5—H5C	109.5	C25—C24—C23	122.0 (2)
H5A—C5—H5C	109.5	C24—C25—C26	119.0 (2)
H5B—C5—H5C	109.5	C24—C25—C33	119.4 (2)
C8—N6—C7	113.11 (19)	C26—C25—C33	121.5 (2)
C8—N6—Cu2	105.86 (15)	C27—C26—C25	123.1 (2)
C7—N6—Cu2	115.23 (15)	C27—C26—C31	117.6 (2)
C8—N6—H6	107.4	C25—C26—C31	119.2 (2)
C7—N6—H6	107.4	C28—C27—C26	121.1 (2)
Cu2—N6—H6	107.4	C28—C27—H27	119.4
C9—N4—C6	113.30 (18)	C26—C27—H27	119.4
C9—N4—Cu2	106.73 (14)	C27—C28—C29	120.9 (2)
C6—N4—Cu2	116.27 (15)	C27—C28—H28	119.6
C9—N4—H4	106.6	C29—C28—H28	119.6
C6—N4—H4	106.6	C30—C29—C28	120.0 (2)
Cu2—N4—H4	106.6	C30—C29—H29	120.0
C6—N5—C7^{ii}	115.2 (2)	C28—C29—H29	120.0
C6—N5—C10	116.4 (2)	C29—C30—C31	120.7 (2)
C7^{ii}—N5—C10	114.1 (2)	C29—C30—H30	119.6
N5^{ii}—C7—N6	113.9 (2)	C31—C30—H30	119.6
N5^{ii}—C7—H7A	108.8	C32—C31—C30	121.4 (2)
N6—C7—H7A	108.8	C32—C31—C26	119.0 (2)
N5^{ii}—C7—H7B	108.8	C30—C31—C26	119.5 (2)

N6—C7—H7B	108.8	C23—C32—C31	122.0 (2)
H7A—C7—H7B	107.7	C23—C32—H32	119.0
N6—C8—C9	107.5 (2)	C31—C32—H32	119.0
N6—C8—H8A	110.2	C14—C33—C25	115.6 (2)
C9—C8—H8A	110.2	C14—C33—H33A	108.4
N6—C8—H8B	110.2	C25—C33—H33A	108.4
C9—C8—H8B	110.2	C14—C33—H33B	108.4
H8A—C8—H8B	108.5	C25—C33—H33B	108.4
N4—C9—C8	107.08 (19)	H33A—C33—H33B	107.4
N4—C9—H9A	110.3	C13—O3—H3C	109.5
C8—C9—H9A	110.3	C24—O6—H6C	109.5
N4—C9—H9B	110.3	H1WA—O1W—H1WB	114.2
C8—C9—H9B	110.3	H2WA—O2W—H2WB	113.5

C1—N1—C4—C3^{i}	169.94 (19)	C18—C19—C20—C15	−3.3 (4)
Cu1—N1—C4—C3^{i}	42.4 (2)	C16—C15—C20—C21	−175.3 (2)
C2—N2—C1—N1	68.3 (3)	C14—C15—C20—C21	3.3 (3)
C5—N2—C1—N1	−67.3 (3)	C16—C15—C20—C19	3.2 (3)
C4—N1—C1—N2	−177.0 (2)	C14—C15—C20—C19	−178.3 (2)
Cu1—N1—C1—N2	−55.0 (2)	C13—C12—C21—C20	−5.8 (3)
C1—N2—C2—N3	−69.9 (3)	C11—C12—C21—C20	174.5 (2)
C5—N2—C2—N3	66.1 (3)	C19—C20—C21—C12	−174.1 (2)
C3—N3—C2—N2	−179.3 (2)	C15—C20—C21—C12	4.4 (3)
Cu1—N3—C2—N2	57.6 (2)	O4—C22—C23—C32	4.7 (4)
C2—N3—C3—C4^{i}	−169.0 (2)	O5—C22—C23—C32	−175.6 (2)
Cu1—N3—C3—C4^{i}	−41.1 (2)	O4—C22—C23—C24	−174.3 (2)
C8—N6—C7—N5^{ii}	179.2 (2)	O5—C22—C23—C24	5.4 (4)
Cu2—N6—C7—N5^{ii}	57.3 (3)	C32—C23—C24—O6	179.7 (2)
C7—N6—C8—C9	−169.3 (2)	C22—C23—C24—O6	−1.2 (4)
Cu2—N6—C8—C9	−42.3 (2)	C32—C23—C24—C25	−1.5 (4)
C6—N4—C9—C8	−171.1 (2)	C22—C23—C24—C25	177.6 (2)
Cu2—N4—C9—C8	−41.8 (2)	O6—C24—C25—C26	−176.4 (2)
N6—C8—C9—N4	57.0 (3)	C23—C24—C25—C26	4.8 (4)
C7^{ii}—N5—C6—N4	−67.8 (3)	O6—C24—C25—C33	0.5 (4)
C10—N5—C6—N4	69.6 (3)	C23—C24—C25—C33	−178.3 (2)
C9—N4—C6—N5	178.7 (2)	C24—C25—C26—C27	172.3 (2)
Cu2—N4—C6—N5	54.5 (3)	C33—C25—C26—C27	−4.5 (4)
O1—C11—C12—C21	−1.3 (3)	C24—C25—C26—C31	−4.7 (4)
O2—C11—C12—C21	178.1 (2)	C33—C25—C26—C31	178.5 (2)
O1—C11—C12—C13	178.9 (2)	C25—C26—C27—C28	−178.4 (2)
O2—C11—C12—C13	−1.6 (3)	C31—C26—C27—C28	−1.3 (4)
C21—C12—C13—O3	−179.3 (2)	C26—C27—C28—C29	−0.8 (4)
C11—C12—C13—O3	0.5 (3)	C27—C28—C29—C30	1.8 (4)
C21—C12—C13—C14	−0.5 (3)	C28—C29—C30—C31	−0.5 (4)
C11—C12—C13—C14	179.2 (2)	C29—C30—C31—C32	176.6 (2)
O3—C13—C14—C15	−173.3 (2)	C29—C30—C31—C26	−1.7 (4)
C12—C13—C14—C15	7.9 (3)	C27—C26—C31—C32	−175.8 (2)
O3—C13—C14—C33	5.4 (3)	C25—C26—C31—C32	1.4 (3)

C12—C13—C14—C33	−173.4 (2)	C27—C26—C31—C30	2.6 (3)
C13—C14—C15—C16	169.3 (2)	C25—C26—C31—C30	179.7 (2)
C33—C14—C15—C16	−9.4 (3)	C24—C23—C32—C31	−2.1 (4)
C13—C14—C15—C20	−9.2 (3)	C22—C23—C32—C31	178.9 (2)
C33—C14—C15—C20	172.1 (2)	C30—C31—C32—C23	−176.3 (2)
C14—C15—C16—C17	−179.0 (2)	C26—C31—C32—C23	2.1 (4)
C20—C15—C16—C17	−0.5 (3)	C13—C14—C33—C25	119.6 (3)
C15—C16—C17—C18	−2.1 (4)	C15—C14—C33—C25	−61.7 (3)
C16—C17—C18—C19	2.0 (4)	C24—C25—C33—C14	120.9 (3)
C17—C18—C19—C20	0.7 (4)	C26—C25—C33—C14	−62.3 (3)
C18—C19—C20—C21	175.1 (2)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O3^{iii}	1.00	2.50	3.272 (3)	134
N3—H3···O5	1.00	1.89	2.836 (3)	156
N4—H4···O2^{iii}	1.00	1.90	2.822 (3)	152
O3—H3*C*···O2	0.84	1.75	2.502 (2)	148
O6—H6*C*···O5	0.84	1.75	2.514 (3)	150
O1*W*—H1*WA*···O1^{iv}	0.86	1.88	2.746 (2)	178
O1*W*—H1*WB*···O4	0.86	2.31	3.136 (3)	162
O1*W*—H1*WB*···O5	0.86	2.41	3.087 (3)	136
O2*W*—H2*WA*···O1^{iii}	0.86	2.05	2.901 (2)	169
O2*W*—H2*WA*···O2^{iii}	0.86	2.61	3.280 (2)	136
O2*W*—H2*WB*···O4^{v}	0.86	1.88	2.743 (3)	176
C2—H2*B*···O1^{vi}	0.99	2.48	3.435 (3)	162
C5—H5*B*···O2^{iii}	0.98	2.45	3.316 (3)	147

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