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A new potential NLO compound with a supramolecular layered structure: aqua(hexamethylenetetramine-κN)(iminodiacetato-$\kappa^3 O,N,O'$)copper(II)

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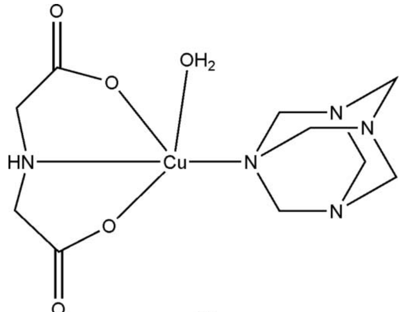
In the noncentrosymmetric title compound, $[Cu(C_4H_5NO_4)(C_6H_{12}N_4)(H_2O)]$ or [Cu(IDA)(HMTA)(H_2O)], where IDA is iminodiacetate and HMTA is hexamethylenetetramine, the asymmetric unit consists of a whole mononuclear neutral molecule, where the Cu^{II} cation is coordinated by two carboxylate O atoms and one N atom from the IDA ligand, by one N atom from the HMTA ligand and by the O atom of the coordinated water molecule, giving rise to a CuN_2O_3 distorted square-pyramidal coordination geometry. The IDA and HTMA ligands adopt terminal tri- and monocoordinated modes, respectively. All adjacent molecules within the *ac* plane are connected to each other *via* two pairs of O—H⋯O and one N—H⋯O hydrogen bond, forming a (4,4) supramolecular two-dimensional network. In the unit cell, these layers stack alternately in an ...*ABABAB*... sequence along the *b* axis. The optical absorption properties of this compound have been studied on powder samples, which had previously been examined by powder X-ray diffraction.

Comment

Second-order nonlinear optical (NLO) compounds are usually materials with advanced functionality, which must crystallize in a noncentrosymmetric space group (Chai *et al.*, 2010*a*; Bella, 2001; Kanis *et al.*, 1994). Due to the rapid development of laser techniques in recent decades, these materials have attracted more and more attention for their applications in second-harmonic generation (SHG), wave-mixing effects, optical parametric oscillator (OPO) processes, and so on. There are currently two types of inorganic second-order NLO crystal materials which have been developed into commercial products (Shen, 2002; Boyd, 2008). The first corresponds to oxide-type crystals, for instance potassium dihydrogen phosphate (KDP), ammonium dihydrogen phosphate (ADP), barium metaborate (β-BBO), lithium triborate (LBO) *etc*. These types of crystal are suitable for working in the visible and near-IR regions. The second type of inorganic second-order NLO materials corresponds to semiconductor crystals, for example tellurium, reddish silver (Ag_3AsS_3) *etc*. This type of material is suitable for working in the far-IR region.

However, these inorganic second-order NLO crystals can still not meet the various needs of optical signal processing. Thus, new second-order NLO materials of coordinated compounds have attracted widespread attention and great developments have been made in the last 20 years (Nalwa & Miyata, 1997). For this type of second-order NLO material, intramolecular charge transfer, *i.e.* metal-to-ligand charge transfer (MLCT), ligand-to-metal charge transfer (LMCT) or intra-ligand charge transfer (ILCT), is a key factor (Frazier *et al.*, 1986; Qin *et al.*, 1994), while the noncentrosymmetric character of the space group in which the coordinated compound crystallizes is an inescapable prerequisite for the possible existence of its second-order NLO properties. The controlled synthesis of noncentrosymmetric crystals is still a significant challenge, although many noncentrosymmetric coordinated compounds of this sort have been obtained so far (Bella, 2001; Kanis *et al.*, 1994). According to reports in the available literature, the cage-like hexamethylenetetramine ligand (HMTA) may easily form noncentrosymmetric coordinated crystal structures with metal cations (Chen *et al.*, 2005; Banerjee *et al.*, 2010; Guo *et al.*, 2010; Sun *et al.*, 2011). In addition, the iminodiacetate anion (IDA) is a good tridentate chelating ligand for coordinating to copper(II) to form a $[Cu(IDA)(H_2O)_2]_n$ polymeric structure (Roman-Alpiste *et al.*, 1999), which would allow interruption by N-heterocyclic donors (the auxiliary ligand) to form an asymmetric mononuclear molecule. In this work, we utilized HMTA and IDA to assemble with a copper(II) salt, and successfully obtained the title mixed-ligand coordinated compound, (I), which crystallizes in the noncentrosymmetric space group $Pca2_1$.



(I)

Compound (I) consists of a mononuclear neutral molecule (Fig. 1), made up of one *N*-coordinated HMTA ligand, one *O*,*N*,*O*′-coordinated IDA ligand, one *O*-coordinated water molecule and one Cu^{II} cation, which exhibits a distorted square-pyramidal coordination geometry with the water O atom in the apical position. Within this CuO_3N_2 square pyramid, the bond lengths (Table 1) are similar to those in

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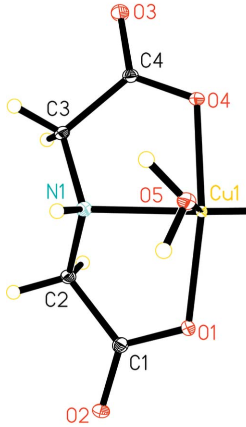

Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

analogous structures (Roman-Alpiste *et al.*, 1999; Kundu *et al.*, 2005; Chen *et al.*, 1990; Zhang *et al.*, 2008; Yang *et al.*, 2011). The IDA ligand adopts a three-coordinated terminal binding mode, and the fact that it does not exhibit the bridging mode observed in some previously reported polymeric structures containing IDA (Roman-Alpiste *et al.*, 1999; Podder *et al.*, 1979) could be attributed to the steric blocking effect of the large HTMA terminal ligand.

The mononuclear molecules of (I) are connected to each other to form a two-dimensional supramolecular layered structure, mainly by virtue of two pairs of O—H···O hydrogen bonds and one N—H···O hydrogen bond (Table 2). As shown in Fig. 2, adjacent molecules are connected (entries 1–3 in Table 2) to form supramolecular layers. From a topological point of view, the molecular centres can be regarded as supramolecular 4-connected nodes and the hydrogen-bonding interactions as linkages, thus defining a (4,4) supramolecular network structure. These layers stack with their *c*-glide-related neighbours in an alternating ...*ABABA*... fashion along the *b* axis (Fig. 3).

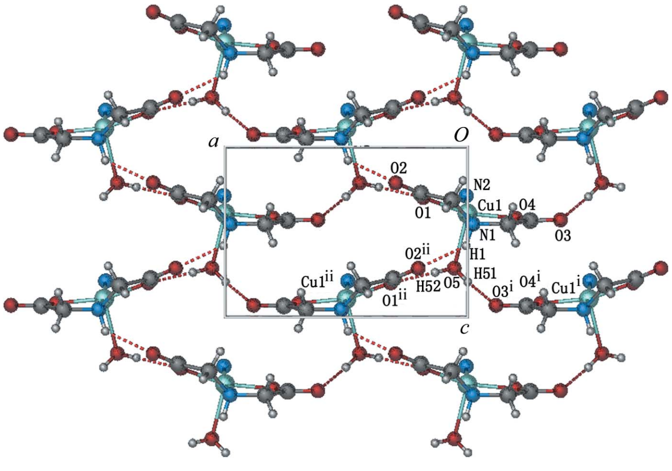

Figure 2
The supramocular layer network structure of (I), viewed along the *b*-axis direction. The structure is constructed by hydrogen-bonding interactions, shown as dashed lines (red in the electronic version of the journal), and the HMTA ligands are shown as small balls (blue). [Symmetry codes: (i) $-x - \frac{1}{2}, y, z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y, z + \frac{1}{2}$.]

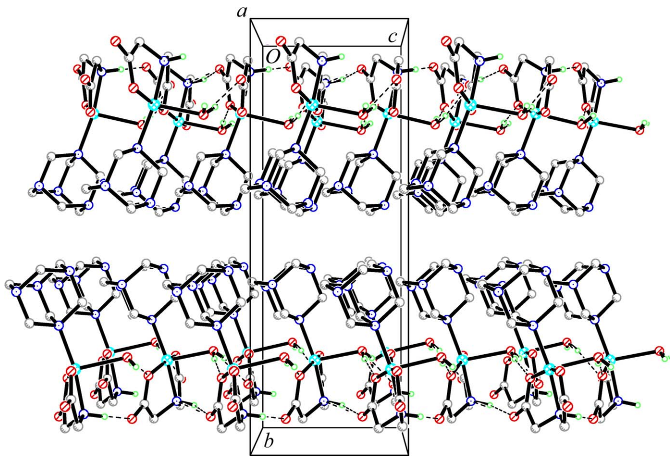

Figure 3
A layered packing diagram for (I), viewed along the *a*-axis direction. H atoms have been omitted for clarity.

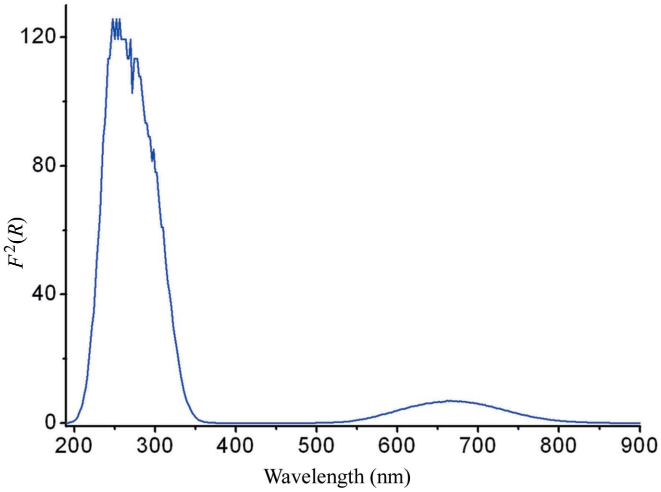

Figure 4
A plot of $F^2(R)$ *versus* wavelength for (I), showing the lack of absorption in the visible region.

The UV–vis diffuse-reflectance spectrum of (I) was measured on a powder sample previously examined by powder X-ray diffraction, and is plotted in Fig. 4 as $F^2(R)$ *versus* wavelength, according to the Kubelka–Munk function (Chai *et al.*, 2007*a*,*b*). As can be seen, there are two obvious absorption bands in the spectrum. One strong band, located in the region of about 200–350 nm, is due to the transition of ligands between different energy levels. The other, very weak, band at about 550–800 nm is due either to a *d*–*d* transition of the copper(II) centre or to an LMCT mechanism. That is to say, (I) absorbs very few photons in the visible region, so this region is a suitable window for SHG. Thus, (I) may be investigated as a potential second-order NLO material.

Experimental

The title compound, (I), was synthesized by the solution reaction of $Cu_2(OH)_2(CO_3)$ (23 mg, 0.1 mmol), H_2IDA (27 mg, 0.2 mmol) and

HTMA (29 mg, 0.2 mmol) in water (15 ml) at room temperature. The subsequent solution was filtered and left to evaporate. After several days, blue crystals of (I) were obtained in a yield of 93% (65.6 mg). Samples suitable for single-crystal X-ray diffraction were selected directly from the obtained crop.

Crystal data

$[Cu(C_4H_5NO_4)(C_6H_{12}N_4)(H_2O)]$
$M_r = 352.84$
Orthorhombic, $Pca2_1$
$a = 9.800$ (2) Å
$b = 19.039$ (4) Å
$c = 6.8975$ (15) Å
$V = 1286.9$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.73$ mm^{-1}
$T = 130$ K
0.32 × 0.16 × 0.07 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{\min} = 0.607$, $T_{\max} = 0.889$
9636 measured reflections
2760 independent reflections
2546 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.061$
$S = 1.01$
2760 reflections
198 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}
Absolute structure: Flack (1983), with 1156 Friedel pairs
Flack parameter: 0.004 (15)

Table 1
Selected bond lengths (Å).

Cu1—O4	1.9508 (15)	Cu1—N2	2.030 (2)
Cu1—O1	1.9824 (16)	Cu1—O5	2.318 (2)
Cu1—N1	1.987 (2)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O5—H51$\cdots$O3$^{\rm i}$	0.81 (2)	2.03 (2)	2.821 (3)	167 (3)
O5—H52$\cdots$O1$^{\rm ii}$	0.77 (2)	2.06 (2)	2.832 (2)	173 (3)
N1—H1$\cdots$O2$^{\rm ii}$	0.93	2.11	2.876 (3)	139

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

All H atoms bonded to C and N atoms were added at calculated positions, with C—H = 0.99 Å and C—N = 0.93 Å, and refined using a riding model, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C,N). Water H atoms were located from difference Fourier peaks and refined isotropically, with a restrained O—H distance of 0.82 (2) Å.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); 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*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG3151). Services for accessing these data are described at the back of the journal.

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supplementary materials

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A new potential NLO compound with a supramolecular layered structure: aqua(hexamethylenetetramine-*κN*)(iminodiacetato-*κ*^{3}*O*,*N*,*O′*)copper(II)

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aqua(hexamethylenetetramine-*κN*)(iminodiacetato- *κ*^{3}*O*,*N*,*O′*)copper(II)

Crystal data

$[Cu(C_4H_5NO_4)(C_6H_{12}N_4)(H_2O)]$
$M_r = 352.84$
Orthorhombic, *Pca*2$_1$
Hall symbol: P 2c -2ac
$a = 9.800$ (2) Å
$b = 19.039$ (4) Å
$c = 6.8975$ (15) Å
$V = 1286.9$ (5) Å^3
$Z = 4$
$F(000) = 732$
$D_x = 1.821$ Mg m^{-3}
Mo *Kα* radiation, $\lambda = 0.71075$ Å
Cell parameters from 3918 reflections
$\theta = 2.1–27.5°$
$\mu = 1.73$ mm^{-1}
$T = 130$ K
Plate, blue
0.32 × 0.16 × 0.07 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 14.6306 pixels mm^{-1}
CCD profile fitting scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.607$, $T_{max} = 0.889$
9636 measured reflections
2760 independent reflections
2546 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.5°$, $\theta_{min} = 2.3°$
$h = -12\rightarrow12$
$k = -24\rightarrow24$
$l = -8\rightarrow7$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.026$
$wR(F^2) = 0.061$
$S = 1.01$
2760 reflections
198 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0332P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.27$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Absolute structure: Flack (1983), with 1156 Friedel pairs
Flack parameter: 0.004 (15)

Special details

Experimental. Analysis, calculated for $C_{10}H_{19}CuN_5O_5$ (%): C 34.04, H 5.43, N 19.85, O 22.67; found: C 34.87, H 5.01, N 19.12, O 23.11. IR (KBr, *v*, cm^{-1}): 3234 *s*, 2958 *m*, 2543 *w*, 1616 *s*, 1384 *s*, 1256 *s*, 1227 *s*, 1062 *s*, 997 *s*, 911 *s*, 824 *ms*, 786 *ms*, 664 *ms*, 585 *m*, 502 *m*.

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*	$U_{iso}*/U_{eq}$
Cu1	0.00027 (2)	0.197212 (12)	0.39193 (10)	0.00979 (8)
N1	−0.02127 (17)	0.09581 (10)	0.4529 (3)	0.0112 (4)
H1	0.0133	0.0879	0.5765	0.013*
N2	0.00598 (16)	0.29694 (10)	0.2881 (3)	0.0085 (4)
N3	−0.1040 (2)	0.37629 (10)	0.0535 (3)	0.0158 (4)
N4	−0.02168 (18)	0.42196 (10)	0.3641 (4)	0.0140 (5)
N5	0.1408 (2)	0.38550 (10)	0.1147 (3)	0.0140 (4)
C1	0.1937 (2)	0.10073 (12)	0.2734 (4)	0.0137 (5)
C2	0.0652 (2)	0.05800 (11)	0.3128 (4)	0.0128 (5)
H2A	0.0144	0.0507	0.1904	0.015*
H2B	0.0903	0.0114	0.3657	0.015*
C3	−0.1665 (2)	0.07701 (11)	0.4530 (4)	0.0121 (5)
H3A	−0.1888	0.0524	0.5754	0.014*
H3B	−0.1849	0.0443	0.3444	0.014*
C4	−0.2576 (2)	0.14163 (11)	0.4328 (3)	0.0119 (5)
C5	−0.1031 (2)	0.30530 (11)	0.1353 (4)	0.0148 (5)
H5A	−0.0872	0.2709	0.0301	0.018*
H5B	−0.1934	0.2952	0.1933	0.018*
C6	−0.0202 (2)	0.35078 (13)	0.4425 (4)	0.0137 (5)
H6A	−0.1091	0.3409	0.5049	0.016*
H6B	0.0516	0.3473	0.5430	0.016*
C7	0.1404 (2)	0.31484 (11)	0.1963 (4)	0.0127 (5)
H7A	0.2135	0.3111	0.2949	0.015*
H7B	0.1603	0.2805	0.0923	0.015*
C8	0.1109 (2)	0.43607 (12)	0.2700 (4)	0.0156 (5)
H8A	0.1101	0.4841	0.2151	0.019*
H8B	0.1842	0.4339	0.3686	0.019*
C9	−0.1278 (2)	0.42641 (12)	0.2116 (4)	0.0161 (5)
H9A	−0.2182	0.4170	0.2701	0.019*
H9B	−0.1292	0.4746	0.1580	0.019*
C10	0.0303 (2)	0.39039 (13)	−0.0297 (4)	0.0170 (5)
H10A	0.0305	0.4381	−0.0871	0.020*
H10B	0.0481	0.3564	−0.1353	0.020*
O1	0.18308 (15)	0.16815 (8)	0.2986 (3)	0.0134 (3)

O2	0.29669 (15)	0.07122 (8)	0.2125 (3)	0.0181 (4)
O3	−0.38293 (15)	0.13328 (8)	0.4293 (3)	0.0202 (4)
O4	−0.19778 (15)	0.20125 (7)	0.4182 (3)	0.0143 (4)
O5	0.05476 (18)	0.22227 (9)	0.7116 (3)	0.0147 (3)
H52	0.126 (2)	0.2055 (14)	0.727 (5)	0.031 (10)*
H51	−0.001 (2)	0.2024 (14)	0.778 (5)	0.021 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.00771 (12)	0.00726 (12)	0.01439 (14)	0.00032 (9)	0.00182 (11)	0.00077 (16)
N1	0.0117 (9)	0.0115 (10)	0.0104 (11)	−0.0005 (7)	−0.0004 (7)	−0.0005 (8)
N2	0.0083 (9)	0.0083 (10)	0.0090 (11)	0.0004 (6)	0.0010 (8)	−0.0010 (8)
N3	0.0171 (10)	0.0134 (10)	0.0170 (11)	−0.0001 (8)	−0.0040 (9)	0.0023 (9)
N4	0.0176 (10)	0.0102 (9)	0.0141 (15)	−0.0013 (7)	0.0033 (10)	−0.0035 (9)
N5	0.0132 (10)	0.0131 (10)	0.0156 (11)	0.0014 (8)	0.0031 (9)	0.0032 (9)
C1	0.0133 (11)	0.0158 (11)	0.0119 (12)	0.0010 (9)	0.0028 (10)	0.0030 (10)
C2	0.0111 (11)	0.0097 (10)	0.0175 (12)	0.0004 (8)	0.0040 (10)	−0.0028 (9)
C3	0.0091 (10)	0.0118 (11)	0.0153 (13)	−0.0008 (8)	0.0025 (9)	0.0013 (9)
C4	0.0103 (9)	0.0138 (10)	0.0115 (13)	0.0015 (8)	0.0009 (10)	0.0015 (9)
C5	0.0153 (12)	0.0110 (11)	0.0183 (14)	−0.0004 (9)	−0.0089 (11)	0.0021 (10)
C6	0.0179 (11)	0.0130 (11)	0.0103 (14)	0.0001 (8)	0.0028 (9)	−0.0010 (9)
C7	0.0107 (11)	0.0132 (11)	0.0144 (13)	0.0010 (8)	0.0033 (10)	0.0019 (10)
C8	0.0137 (11)	0.0106 (11)	0.0223 (15)	−0.0028 (9)	−0.0015 (11)	0.0025 (10)
C9	0.0153 (11)	0.0108 (11)	0.0222 (14)	0.0038 (9)	0.0021 (11)	0.0063 (11)
C10	0.0211 (12)	0.0176 (13)	0.0123 (12)	0.0031 (10)	0.0004 (10)	0.0062 (10)
O1	0.0113 (8)	0.0102 (8)	0.0188 (9)	0.0011 (6)	0.0016 (7)	0.0021 (7)
O2	0.0123 (8)	0.0151 (8)	0.0269 (10)	0.0035 (6)	0.0067 (8)	0.0023 (8)
O3	0.0093 (7)	0.0177 (8)	0.0336 (12)	−0.0006 (6)	−0.0010 (8)	0.0045 (8)
O4	0.0092 (7)	0.0120 (7)	0.0218 (10)	0.0009 (5)	0.0039 (8)	0.0012 (7)
O5	0.0110 (8)	0.0157 (8)	0.0174 (9)	0.0015 (7)	0.0007 (8)	0.0018 (8)

Geometric parameters (Å, º)

Cu1—O4	1.9508 (15)	C1—C2	1.523 (3)
Cu1—O1	1.9824 (16)	C2—H2A	0.9900
Cu1—N1	1.987 (2)	C2—H2B	0.9900
Cu1—N2	2.030 (2)	C3—C4	1.527 (3)
Cu1—O5	2.318 (2)	C3—H3A	0.9900
N1—C2	1.473 (3)	C3—H3B	0.9900
N1—C3	1.467 (3)	C4—O3	1.238 (3)
N1—H1	0.9300	C4—O4	1.282 (2)
N2—C7	1.501 (3)	C5—H5A	0.9900
N2—C6	1.500 (3)	C5—H5B	0.9900
N2—C5	1.510 (3)	C6—H6A	0.9900
N3—C10	1.461 (3)	C6—H6B	0.9900
N3—C5	1.464 (3)	C7—H7A	0.9900
N3—C9	1.468 (3)	C7—H7B	0.9900
N4—C6	1.459 (3)	C8—H8A	0.9900
N4—C8	1.477 (3)	C8—H8B	0.9900

N4—C9	1.482 (3)	C9—H9A	0.9900
N5—C7	1.458 (3)	C9—H9B	0.9900
N5—C8	1.470 (3)	C10—H10A	0.9900
N5—C10	1.474 (3)	C10—H10B	0.9900
C1—O2	1.229 (3)	O5—H52	0.773 (17)
C1—O1	1.299 (3)	O5—H51	0.805 (17)

O4—Cu1—O1	160.08 (8)	H3A—C3—H3B	107.9
O4—Cu1—N1	85.01 (7)	O3—C4—O4	124.47 (19)
O1—Cu1—N1	83.89 (7)	O3—C4—C3	118.60 (19)
O4—Cu1—N2	91.33 (6)	O4—C4—C3	116.93 (18)
O1—Cu1—N2	96.98 (7)	N3—C5—N2	111.75 (19)
N1—Cu1—N2	170.50 (9)	N3—C5—H5A	109.3
O4—Cu1—O5	97.63 (8)	N2—C5—H5A	109.3
O1—Cu1—O5	99.11 (7)	N3—C5—H5B	109.3
N1—Cu1—O5	91.33 (8)	N2—C5—H5B	109.3
N2—Cu1—O5	97.86 (8)	H5A—C5—H5B	107.9
C2—N1—C3	116.04 (19)	N4—C6—N2	111.9 (2)
C2—N1—Cu1	105.96 (14)	N4—C6—H6A	109.2
C3—N1—Cu1	109.89 (14)	N2—C6—H6A	109.2
C2—N1—H1	108.2	N4—C6—H6B	109.2
C3—N1—H1	108.2	N2—C6—H6B	109.2
Cu1—N1—H1	108.2	H6A—C6—H6B	107.9
C7—N2—C6	107.13 (17)	N5—C7—N2	112.00 (18)
C7—N2—C5	107.6 (2)	N5—C7—H7A	109.2
C6—N2—C5	107.60 (17)	N2—C7—H7A	109.2
C7—N2—Cu1	112.67 (13)	N5—C7—H7B	109.2
C6—N2—Cu1	112.59 (16)	N2—C7—H7B	109.2
C5—N2—Cu1	109.00 (13)	H7A—C7—H7B	107.9
C10—N3—C5	108.40 (19)	N5—C8—N4	112.11 (19)
C10—N3—C9	108.41 (19)	N5—C8—H8A	109.2
C5—N3—C9	108.3 (2)	N4—C8—H8A	109.2
C6—N4—C8	108.84 (17)	N5—C8—H8B	109.2
C6—N4—C9	108.84 (17)	N4—C8—H8B	109.2
C8—N4—C9	107.1 (2)	H8A—C8—H8B	107.9
C7—N5—C8	108.81 (19)	N3—C9—N4	112.26 (19)
C7—N5—C10	108.51 (19)	N3—C9—H9A	109.2
C8—N5—C10	107.76 (19)	N4—C9—H9A	109.2
O2—C1—O1	124.2 (2)	N3—C9—H9B	109.2
O2—C1—C2	119.7 (2)	N4—C9—H9B	109.2
O1—C1—C2	115.96 (18)	H9A—C9—H9B	107.9
N1—C2—C1	109.35 (18)	N3—C10—N5	112.6 (2)
N1—C2—H2A	109.8	N3—C10—H10A	109.1
C1—C2—H2A	109.8	N5—C10—H10A	109.1
N1—C2—H2B	109.8	N3—C10—H10B	109.1
C1—C2—H2B	109.8	N5—C10—H10B	109.1
H2A—C2—H2B	108.3	H10A—C10—H10B	107.8
N1—C3—C4	111.77 (18)	C1—O1—Cu1	113.03 (13)
N1—C3—H3A	109.3	C4—O4—Cu1	115.32 (13)

C4—C3—H3A	109.3	Cu1—O5—H52	105 (3)
N1—C3—H3B	109.3	Cu1—O5—H51	107 (2)
C4—C3—H3B	109.3	H52—O5—H51	109 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H51···O3^{i}	0.81 (2)	2.03 (2)	2.821 (3)	167 (3)
O5—H52···O1^{ii}	0.77 (2)	2.06 (2)	2.832 (2)	173 (3)
N1—H1···O2^{ii}	0.93	2.11	2.876 (3)	139
C3—H3*B*···O2^{iii}	0.99	2.39	3.293 (3)	152
C8—H8*B*···N5^{ii}	0.99	2.58	3.536 (3)	162

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