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Crystal structures of bis- and hexakis[(6,6′-dihydroxybipyridine)copper(II)] nitrate coordination complexes

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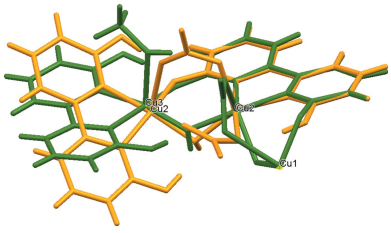
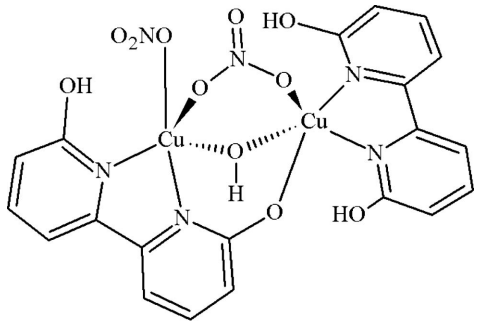
Two multinuclear complexes synthesized from $Cu(NO_3)_2$ and 6,6′-dihydroxybipyridine (dhbp) exhibit bridging nitrate and hydroxide ligands. The dinuclear complex (6,6′-dihydroxybipyridine-2κ^2N,N')[μ-6-(6-hydroxypyridin-2-yl)-pyridin-2-olato-1:2$\kappa^3N,N':O^2$](μ-hydroxido-1:2$\kappa^2O:O'$)(μ-nitrato-1:2$\kappa^2O:O'$)-(nitrato-1κO)dicopper(II), $[Cu_2(C_{10}H_7N_2O_2)(OH)(NO_3)_2(C_{10}H_8N_2O_2)]$ or [Cu(6-OH-6′-O-bpy)(NO_3)(μ-OH)(μ-NO_3)Cu(6,6′-dhbp)], (I), with a 2:1 ratio of nitrate to hydroxide anions and one partially deprotonated dhbp ligand, forms from a water–ethanol mixture at neutral pH. The hexanuclear complex bis(μ_3-bipyridine-2,2′-diolato-$\kappa^3O:N,N':O'$)tetrakis(6,6′-dihydroxybipyridine-κ^2N,N')tetrakis(μ-hydroxido-$\kappa^2O:O'$)bis(methanol-κO)tetrakis(μ-nitrato-$\kappa^2O:O'$)-hexacopper(II), $[Cu_6(C_{10}H_6N_2O_2)_2(CH_4O)_2(OH)_4(NO_3)_4(C_{10}H_8N_2O_2)_4]$ or [Cu(6,6′-dhbp)(μ-NO_3)$_2$(μ-OH)Cu(6,6′-O-bpy)(μ-OH)Cu(6,6′dhbp)(CH_3OH)]$_2$, (II), with a 1:1 NO_3–OH ratio and two fully protonated and fully deprotonated dhbp ligands, was obtained by methanol recrystallization of material obtained at pH 3. Complex (II) lies across an inversion center. Complexes (I) and (II) both display intramolecular O—H···O hydrogen bonding. Intermolecular O—H···O hydrogen bonding links symmetry-related molecules forming chains along [100] for complex (I) with π-stacking along [010] and [001]. Complex (II) forms intermolecular O—H···O hydrogen-bonded chains along [010] with π-stacking along [100] and [001].

1. Chemical context

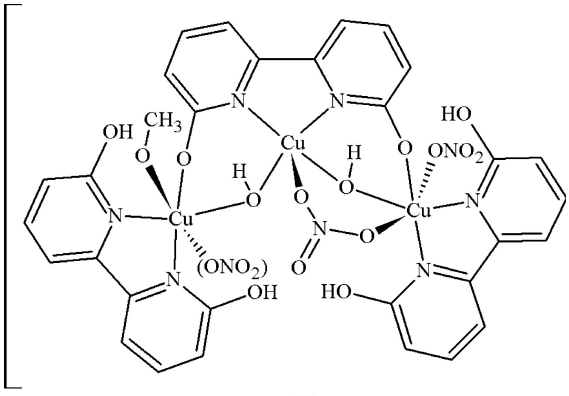
Catalytic processes in nature are often facilitated by enzymes that feature transition metals in their active sites. Many of these reactions would be of tremendous interest could they be copied using simpler and technologically feasible conditions. One such process is water oxidation as observed in photosynthesis, and the use of transition metal complexes to mimic the reactivity of photosystem II have captured the attention of an increasing number of research groups over the last few years (Kikuchi & Tanaka, 2014; Singh & Spiccia, 2013). One complex that especially caught our interest was $[Cp^*Ir(bpy)Cl]^+$ (Blakemore *et al.*, 2010) which features a bipyridine (bpy) type ligand. In our research into catalytic water oxidation, we are trying to enhance proton-coupled electron transfer (PCET) in metal-complex catalysts by incorporating hydrogen-bond donors and acceptors in near proximity to the potentially catalytic metal atoms to mimic the active center of a protein–metal complex. When applying this principal to the Blakemore-type $[Cp^*Ir(bpy)Cl]^+$ complex by swapping normal bipyridine for dihydroxybipyridine (6,6′-dhbp), we were indeed able to increase the catalytic turnover



rate and control water oxidation rates by adjusting pH levels (DePasquale *et al.*, 2013). The ligand 6,6′-dhbp has also been used in combination with ruthenium terpyridine (tpy) fragments to yield the complex [(tpy)Ru(6,6′-dhbp)(H_2O)] (Marelius *et al.*, 2014).



(I)



(II)

Our focus has most recently shifted to the investigation of copper(II) bipyridine complexes analogous to $[(bpy)Cu(OH)_2]_2^{2+}$ (Barnett *et al.*, 2012). We isolated discrete mono-copper complexes from copper(II) sulfate with a selection of modified bipyridine ligands and investigated the compounds spectroscopically, crystallographically and for their catalytic water oxidation capacity (Gerlach *et al.*, 2014). When swapping sulfate for nitrate as the counter-ion we found that the resulting complexes are no longer mononuclear. Instead, larger aggregates with two or six copper(II) atoms formed that feature coordinating nitrate as well as hydroxyl ligands. As a result of their aggregation and the varied coordination environment of their copper atoms, these complexes are not ideally suited for homogenous water oxidation catalysis. Instead they feature quite intriguing and fascinating solid structures which we would like to describe and present.

2. Structural commentary

The dinuclear copper(II) dhbp complex (I) contains nitrate as a co-ligand with both a fully protonated and a mono-deprotonated dhbp ligand (see Fig. 1). Two unique 6,6′-dhbp binding modes were observed for this copper(II) nitrate complex illustrating the structural flexibility of this ligand. The [6,6′-$(OH)_2$bpy] ligand exhibits the typically observed bipyridine (*N*,*N*) coordination mode through N3 and N4 binding to Cu2. A new coordination mode is observed for the mono-deprotonated (6-O-6′-OH-bpy) ligand in which it bridges two metals, through (*N*,*N*) coordination of N1,N2 to Cu1 and through bridging to Cu2 *via* the pyridinolate oxygen O2 [1.946 (3) Å]. The C—O bond lengths (Å) for the dhbp ligands are 1.335 (5) (C1—O1), 1.322 (5) (C11—O3), and 1.316 (4) (C20—O4) for the protonated hydroxyl groups and slightly shorter at 1.310 (4) (C10—O2) for the pyridinolate, reflecting double-bond character. Both copper atoms have a distorted square-pyramidal geometry with $\tau = 0.394$ at Cu1 and $\tau = 0.119$ at Cu2 (Addison *et al.*, 1984). This structure has a close Cu···Cu distance of 3.158 (9) Å. Complex (I) features three strong intramolecular hydrogen bonds (Jeffrey, 2003) with O···O distances (Å) as follows: 2.583 (4) for O1 to O6 (dhbp to nitrate) with bond angle O—H···O of 163 (5)°, 2.528 (4) for O4 to O2 (dhbp to deprotonated dhbp) with bond angle of 161 (5)°, and 2.510 (4) for O3 to O5 (dhbp to hydroxyl) with bond angle of 164 (5)°. One intermolecular hydrogen bond tethers one dimer of complex (I) to the next in a head-to-tail fashion *via* a 2.802 (4) Å hydrogen bond from O5 to O11 (hydroxyl to nitrate) with a bond angle of 164 (4)°. Numerical details of the hydrogen bonds are given in Table 1.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H15···O11^{i}	0.75 (4)	2.08 (4)	2.802 (4)	164 (4)
O1—H1···O6	0.83 (2)	1.78 (2)	2.583 (4)	163 (5)
O3—H3*B*···O5	0.83 (2)	1.70 (2)	2.510 (4)	164 (5)
O4—H4*B*···O2	0.83 (2)	1.73 (2)	2.528 (4)	161 (5)

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

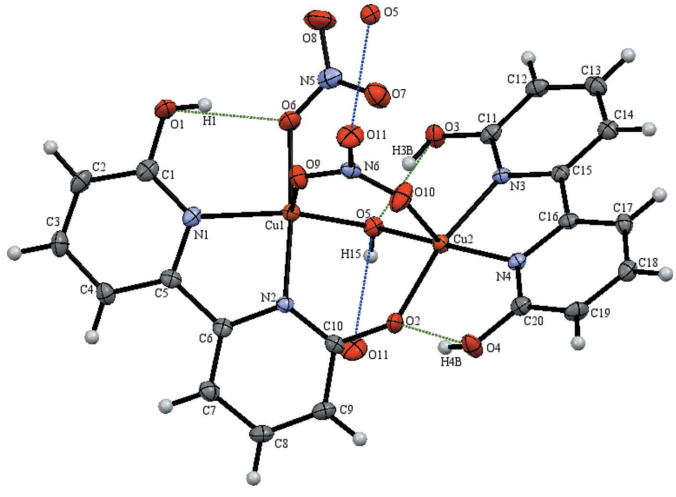


Figure 1
The numbering scheme of complex (I), with donor–acceptor distances of intramolecular hydrogen bonds colored green and of intermolecular hydrogen bonds colored blue, represented with displacement ellipsoids at the 50% probability level. Additional symmetry-related atoms O5 and O11 were generated by translation along the *a* axis.

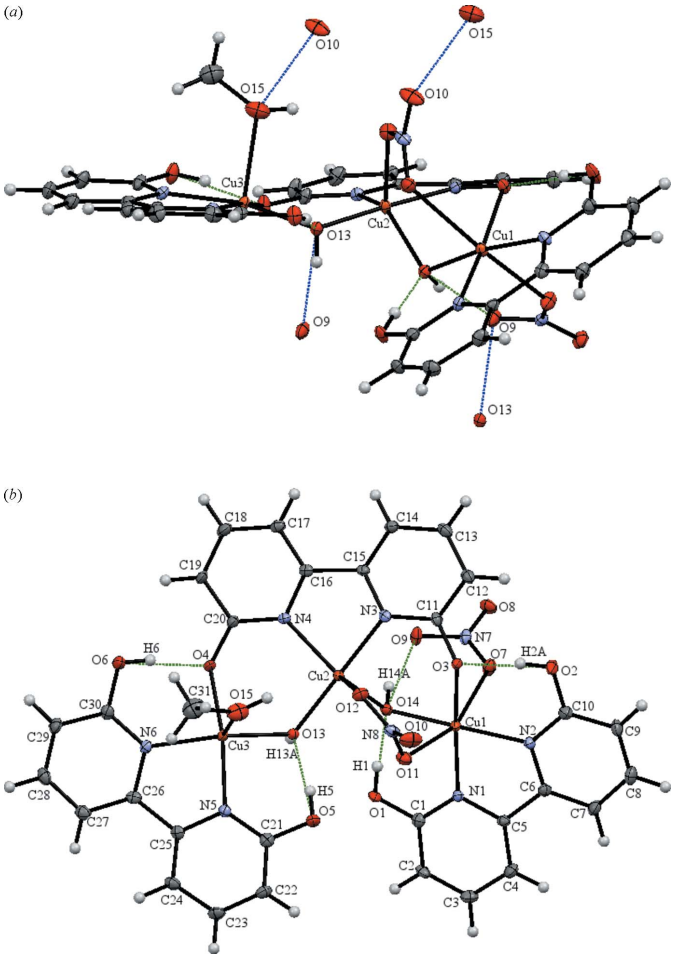


Figure 2
(*a*) The asymmetric unit of complex (II) represented with displacement ellipsoids at the 50% probability level. H atoms not involved in hydrogen bonding are omitted for clarity. The donor–acceptor distances are shown as green for intramolecular hydrogen bonds and shown as blue for intermolecular hydrogen bonds (O10–O15) and inter-asymmetric unit hydrogen bonds (O9 –O13). Additional symmetry-related atoms O10 and O15 were generated by the symmetry operator $1-x, -y, 1-z$, and O9 and O13 were generated *via* the inversion center $1-x, 1-y, 1-z$ at the center of the hexanuclear complex. (*b*) The asymmetric unit of complex (II) oriented to show donor–acceptor distances of intramolecular hydrogen bonds, in green, of the protonated dhbp ligands.

The hexanuclear copper(II) dhbp complex (II) is comprised of a dimer of the asymmetric portion of the molecule which contains three symmetry-unique copper atoms, two fully protonated and one fully deprotonated dhbp, two bridging hydroxide and two nitrate ligands (see Fig. 2). This asymmetric trinuclear unit is related through an inversion center to the full hexanuclear complex (see Fig. 3). Two copper atoms, Cu1 and Cu3, are hexa-coordinate with a distorted octahedral geometry whereas Cu2 is penta-coordinate with a distorted trigonal–pyramidal geometry with $\tau = 0.746$ (Addison *et al.*, 1984). Similar to the dinuclear complex, each copper atom is coordinated by one hydroxybipyridine ligand with one bridging hydroxyl ligand between Cu1 to Cu2 and Cu2 to Cu3. The dihydroxybipyridine ligand bound to Cu2 (dhbp2) is doubly deprotonated with each deprotonated oxygen bound to the

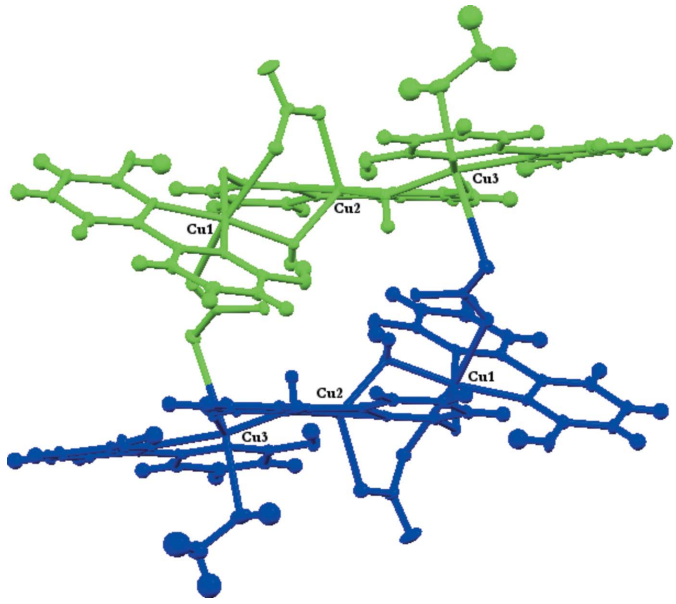


Figure 3
The full hexanuclear complex (II) represented with displacement ellipsoids at the 50% probability level and H atoms not involved in hydrogen bonding are omitted for clarity. The two symmetry-related units of the hexamer are shown in blue and green to better visualize the relation of the asymmetric unit through the inversion center.

flanking Cu1 and Cu3 metal sites, O3 and O4, respectively. The remaining coordination sphere of Cu1 entails one dhbp (*N*,*N* bound), one bridging hydroxide to Cu2 (O14), one bridging nitrate to Cu2 (O11), and one bridging nitrate (O7) which tethers the two asymmetric units. The coordination of Cu2 entails one deprotonated dhbp (*N*,*N* bound), one bridging nitrate to Cu1 (O12), and two bridging hydroxides to Cu1 and Cu3 (O14 and O13, respectively). The remaining coordination sphere of Cu3 entails one dhbp (*N*,*N* bound), one methanol (O15), one bridging hydroxide (O13), and one bridging nitrate

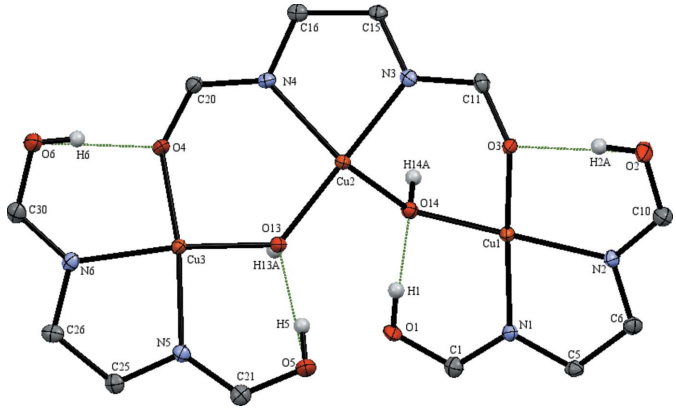


Figure 4
The three unique copper atoms of complex (II) are displayed with the coordination relevant atoms of the bound dhbp ligands and bridging hydroxides with displacement ellipsoids at the 50% probability level and the donor–acceptor distances of intramolecular hydrogen bonds of the protonated dhbps represented in green.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O14	0.84	1.61	2.448 (3)	175
O2—H2A···O3	0.84	1.66	2.499 (3)	172
O5—H5···O13	0.84	1.70	2.536 (3)	170
O6—H6···O4	0.84	1.67	2.495 (3)	168
O13—H13A···O9^{i}	0.83 (2)	1.98 (2)	2.763 (3)	158 (4)
O14—H14A···O9	0.82 (2)	1.94 (2)	2.738 (3)	163 (4)
O15—H15···O10^{ii}	0.85 (5)	2.42 (5)	2.790 (4)	107 (4)

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

(O8) which tethers the two asymmetric units. Each deprotonated oxygen of dhbp acts as an acceptor for intramolecular hydrogen bonds from the two protonated dhbp ligands, O2 to O3 at 2.499 (3) Å (O—H···O bond angle of 172°), and O6 to O4 at 2.495 (3) Å (O—H···O bond angle of 168°) shown in Fig. 4. The remaining hydroxyl groups of the protonated dhbps form strong hydrogen bonds to the bridging hydroxides where O1 donates to O14 [2.448 (3) Å, O—H···O bond angle of 175°] of the hydroxide bridging Cu1 and Cu2, and O5 donates to O13 [2.536 (3) Å, O—H···O bond angle of 170°] of the hydroxide bridging Cu2 and Cu3 (Table 2). Interestingly, both Cu—Cu bridging hydroxides form an intermediate strength intramolecular hydrogen bond to the bridging nitrate linking the two asymmetric units of the hexamer, with O···O distances (Å) of O13 and O14 to O9 being 2.763 (3) [O—H···O angle of 158 (4)°] and 2.738 (3) [O—H···O angle of 163 (4)°], respectively. C—O bond lengths of the protonated and deprotonated dhbp ligands of the hexa and dinuclear complexes are similar; C···O distances (Å) are 1.302 (4) and 1.312 (4) for the copper coordinating oxygen atoms, and 1.324 (4), 1.304 (4), 1.330 (4), and 1.321 (4) for the hydroxyl O atoms, with the longer of the four values belonging to the hydroxyl groups hydrogen-bound to the neighboring deprotonated dhbp ligand, and the shorter two being associated with those hydrogen-bound to the bridging hydroxyl groups. These reduced lengths reflect increased C—O double-bond character upon deprotonation. One intermolecular hydrogen bond of intermediate strength connects the bound methanol to the non-coordinating oxygen of the Cu1–Cu2 bridging nitrate of another molecule, O15 to O10 at 2.790 (4) Å [O—H···O bond angle of 107 (4)°].

Comparison of complex (I) to the asymmetric component of complex (II) indicates some structural similarities, Fig. 5. The overall structure of complex (I) can be reasonably well overlaid with the dinuclear component of (II) including Cu2 and Cu3, with the main differences resulting from one nitrate ligand that is bridging between the two copper ions in complex (I) being rotated so that in complex (II) it instead bridges one of these copper ions to the third that has no counterpart in complex (I). The two copper ions that are bridged by a nitrate ion in complex (I) are thus not bridged in complex (II) (featuring a methanol molecule and a nitrate bridging to the third copper instead), leading to a larger distance between the copper ions in complex (II) and a different tilt angle of the fully protonated dhbp ligand (left dhbp in Fig. 5).

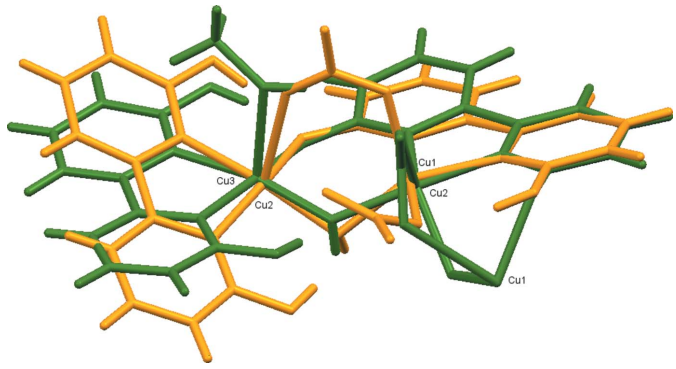


Figure 5
Complex (I) in yellow is overlaid on the Cu2—Cu3 dimer portion of the asymmetric unit of complex (II) in green.

The bridging oxygen species for both complexes (I) and (II) are correctly assigned as hydroxides to balance the overall neutral charge of the complex. Complex (I) with two Cu^{II} ions is charge balanced with one terminal and one bridging nitrate each with a single negative charge, one deprotonated hydroxyl group of dhbp, and one bridging hydroxide. The bond lengths to the bridging hydroxide from Cu1 to O5 is 1.964 (3) Å and Cu2 to O5 is 1.939 (3) Å where the proton of O5 hydrogen bonds to one acceptor. A comparable bond length is 1.946 (3) Å from Cu2 to O2 of the deprotonated dhbp ligand. The remaining oxygen atoms of the dhbp ligands are each protonated and engaged in hydrogen bonding as described above. The asymmetric unit of complex (II) balances similarly with three Cu (II) ions against one bridging nitrate, one nitrate bridging the two asymmetric units, two deprotonated dhbp hydroxyl groups, and two bridging hydroxides. The bond lengths to the bridging hydroxide, Cu2 and Cu3 to O13: 1.933 (2) and 1.951 (2) Å, respectively, are comparable to those observed in complex (I) where each of these hydroxides have one hydrogen bond. Alternatively, the bond lengths to the bridging hydroxide are longer where Cu1 and Cu2 to O14 are 1.970 (2) and 2.062 (3) Å, respectively, likely due to the two hydrogen-bonding interactions described above weakening the orbital overlap with the copper and lengthening these bonds. The two copper–hydroxyl dhbp bonds in complex (II) are comparable to this bond in complex (I) at 1.966 (3) Å from Cu1 to O3 of dhbp and 1.960 (2) Å from Cu3 to O4 of dhbp.

3. Supramolecular features

Some intermolecular hydrogen-bonding interactions in both complexes have already been discussed, *vide supra*. The dinuclear complex (I) also features intermolecular parallel offset π-stacking of both dhbp ligands. The dhbp ligand coordinating to Cu1 is π-stacked with its symmetry counterpart alternating across two inversion centers, one for each ring of this dhbp ligand. These alternating π–π interactions form chains in the [010] direction. The pyridine ring containing N2 interacts with the symmetry-equivalent ring of a neighboring

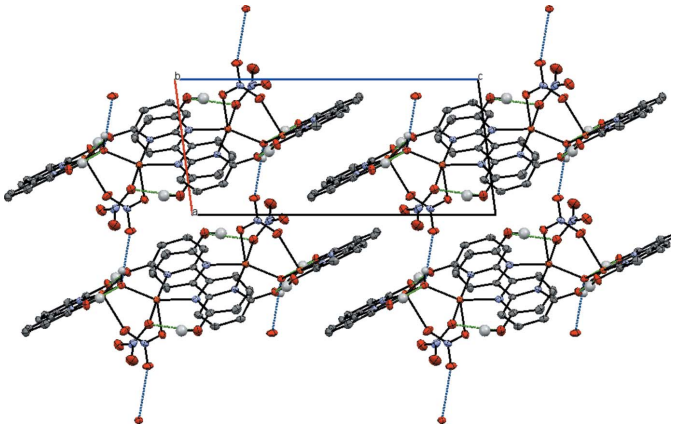


Figure 6
The packing arrangement of complex (I) propagates along [100] *via* intermolecular hydrogen bonding (blue) and in the *bc* plane by π-stacking of the dhbp pyridyl rings.

molecule across the symmetry operation $1 - x, -y, -z$ at a distance of 3.894 (3) Å between the centroids of the rings. The pyridine ring containing N1 interacts with its symmetry-equivalent ring across the symmetry operation $1 - x, 1 - y, -z$ with a centroid-to-centroid distance of 3.969 (3) Å. The dhbp ligand coordinating to Cu2 also shows π-stacking *via* two alternating inversion-symmetry operations, forming chains along [100]. The pyridine rings containing N3 and N4 intercross by the symmetry operation $1 - x, -y, 1 - z$ where the centroid of the ring defined by N3 is at a distance of 3.604 (2) Å from the centroid of the ring defined as N4 on side of the dhbp plane with the bridging hydroxide. These rings also π-stack on the opposite face of the plane at a distance of 3.768 (2) Å from the centroid of the ring defined by N3 to N4 through the symmetry operation $-x, -y, 1 - z$. Intermolecular hydrogen bonding from the bridging hydroxide ligand to the terminal oxygen of the bridging nitrate ligand interlinks neighboring molecules primarily along [100]. See Fig. 6 for extended intermolecular interactions of complex (I).

The hexanuclear complex (II) progresses along [010] through two symmetry-related hydrogen bonds between O15 of the bound methanol molecule of Cu3 to O10 of the Cu1–Cu2 bridging nitrate (Fig. 7). The dhbp ligands are primarily within the *ac* plane and exhibit π-stacking but in a less regular fashion than for complex (I), primarily in the [010] direction without forming chains. Off-set π-stacking of the dhbp ligand bound to Cu1 are related through the symmetry operation $1 - x, -y, -z$ with a centroid-to-centroid distance of 3.784 (2) Å of the pyridine rings containing N1 to the ring containing N2 and *vice versa*. A single ring of each dhbp ligand bound to Cu2 and Cu3 π-stack *via* translation at a distance of 3.551 (2) Å between the centroids of the pyridine rings defined by N3 and N5, respectively. Additionally, the Cu3 dhbp ligand π-stacks *via* the symmetry-equivalent ring defined by N5 of a neighboring molecule across the symmetry operation $-x, -y, 1 - z$ at a centroid-to-centroid distance of 3.887 (2) Å. Close proximity occurs in plane between the pyridine ring containing N4 of the dhbp ligand bound to Cu2

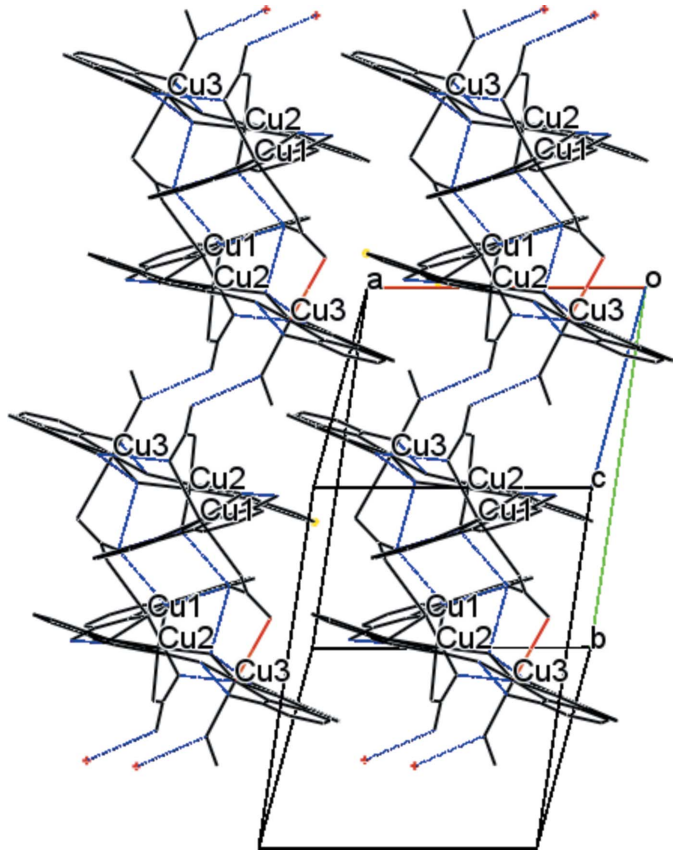


Figure 7
The packing arrangement of complex (II) propagates along [010] *via* intermolecular hydrogen bonding (blue) and in the *ac* plane by π-stacking of the dhbp pyridyl rings.

at a distance of 3.818 (2) Å between C18 to C19 and *vice versa* across the symmetry operation $1 - x, 1 - y, -z$.

4. Database survey

Although many structures have been reported featuring a hydroxide anion bridging two copper(II) ions each bound by 2,2′-bipyridine, no analogous structure has been reported with a 6,6′-dihydroxy-2,2′-bipyridine ligand. A search of the Cambridge Structural Database (Version 5.36, May 2015; Groom & Allen, 2014) for the substructure of copper ligated by 6-hydroxy-2,2′-bipyridine, where the hydroxyl group (–OH) further ligates to a second copper atom, resulted in several structures. These primarily planar structures are reported either with co-crystallized metal-containing counterions: CSD refcode QEXHUX (Guo *et al.*, 2007), VIHZIX (Zhong, Li *et al.*, 2013), WUJGUE (Wang *et al.*, 2009), XIQGAH (Zhong, Feng *et al.*, 2013); or with a bridging molecule linking two of these planar copper dimers: IYOWOI (He & Lu, 2004), MISPUZ (Zhang, Tong & Chen, 2002), REMMAY (Luo *et al.*, 2006), SESDAW (Sun *et al.*, 2006), XOVTEH (Zhang, Tong, Gong *et al.*, 2002).

The most relevant structure reported in the database contains a dinuclear copper 6-hydroxybipyridine complex with

Table 3
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$[Cu_2(C_{10}H_7N_2O_2)(OH)(NO_3)_2(C_{10}H_8N_2O_2)]$	$[Cu_6(C_{10}H_6N_2O_2)_2(CH_4O)_2(OH)_4(NO_3)_4(C_{10}H_8N_2O_2)_4]$
M_r	643.47	1886.53
Crystal system, space group	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$
Temperature (K)	100	100
a, b, c (Å)	7.358 (2), 10.447 (3), 15.744 (4)	10.2135 (7), 13.3707 (8), 14.0565 (10)
α, β, γ (°)	77.610 (4), 78.927 (4), 69.938 (4)	64.591 (4), 75.659 (5), 82.262 (5)
V (Å^3)	1101.1 (5)	1679.0 (2)
Z	2	1
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	2.01	1.97
Crystal size (mm)	0.17 × 0.12 × 0.03	0.26 × 0.22 × 0.07
Data collection		
Diffractometer	Bruker SMART APEX CCD	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2009)	Multi-scan (*TWINABS*; Sheldrick, 2009)
T_{min}, T_{max}	0.605, 0.746	0.622, 0.746
No. of measured, independent and observed $[I > 2\sigma(I)]$ reflections	14887, 6413, 4302	20719, 10920, 7847
R_{int}	0.050	0.068
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.717	0.746
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.052, 0.125, 1.04	0.044, 0.119, 1.00
No. of reflections	6413	10920
No. of parameters	365	529
No. of restraints	3	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.11, −0.69	0.90, −1.08

Computer programs: *APEX2* and *SAINT* (Bruker, 2009, 2012), *SHELXS97* and *SHELXTL* (Sheldrick, 2008), *SHELXL2012* and *SHELXL2014/7* (Sheldrick, 2015), *SHELXLE* (Hübschle *et al.*, 2011) and *Mercury* (Macrae *et al.*, 2008).

a nitrate ligand bridging the copper ions, IBOXAZ (Zhang *et al.*, 2004). No examples of hydroxybipyridine-ligated copper compounds with oxide or hydroxide bridges have been reported.

5. Synthesis and crystallization

The neutral copper dinuclear complex **(I)** Copper(II) nitrate trihydrate (128 mg, 0.530 mmol) and 6,6′-dhbp (100 mg, 0.531 mmol) were combined in 50/50 ethanol and water solvent (10 mL) and stirred two days. Green plate crystals were grown from an ethanol solution in a freezer. This complex was analyzed exclusively by X-ray diffraction.

The neutral copper hexanuclear complex **(II)** Copper(II) nitrate hemipentahydrate (124 mg, 0.533 mmol) and 6,6′-dhbp (100 mg, 0.531 mmol) were combined in 10 mL of 0.1 M NaOAc adjusted to pH 3 by acetic acid. The mixture was stirred for three days at room temperature. The resulting solution was dried under high vacuum and recrystallized twice from methanol to afford green prismatic crystals. This complex was analyzed exclusively by x-ray diffraction.

6. Refinement

Crystal data, data collection, and structure refinement details are summarized in Table 3.

The crystal under investigation for complex (II) was found to be split with two major domains not related by any obvious twin operation. The orientation matrices for the two components were identified using the program *Cell Now* (Sheldrick, 2008), with the two components being related by a 2.9° rotation about either the reciprocal axis 1.000 − 0.363 − 0.339 or the real axis 1.000 − 0.178 − 0.265. The two components were integrated using *SAINT* (Bruker, 2012), resulting in the following statistics: 17535 data (5769 unique) involve domain 1 only, mean I/σ 8.6, 17271 data (5689 unique) involve domain 2 only, mean I/σ 8.2, 34813 data (9811 unique) involve 2 domains, mean I/sigma 9.5, 11 data (11 unique) involve 3 domains, mean I/σ 8.7 and 4 data (2 unique) involve 4 domains, mean I/σ 57.6 The exact correlation matrix as identified by the integration program was found to be 1.00336 0.02923 −0.02720, −0.01894 1.02272 −0.04903, 0.02520 0.05747 0.97055. The data were corrected for absorption using *TWINABS* (Sheldrick, 2009), and the structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the HKLF5 routine with all reflections of component 1 (including the overlapping ones), resulting in a BASF value of 0.486 (1). The R_{int} value given is for all reflections and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (*TWINABS*; Sheldrick, 2009).

C- and O-bound H atoms were placed in calculated positions and allowed to ride on their carrier atoms: aromatic C—H_{arom} = 0.95 Å with $U_{iso}(H) = 1.2U_{eq}(C)$, C—$H_{methyl}$ = 0.98 Å with $U_{iso}(H) = 1.5U_{eq}(C)$. O—H were refined for complex (I) and for hydroxide and methanol H atoms of complex (II), with O—H distances restrained to 0.84 (2) Å for O1, O3 and O4 of complex (I), and O13 and O14 of complex (II) yielding O—H distances of 0.748–0.828 Å. The remainder of the hydroxyl atoms were placed in calculated positions with O—H = 0.84 Å, and all $U_{iso}(H_{OH})$ were set to $1.5U_{eq}(O)$.

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supporting information

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Crystal structures of bis- and hexakis[(6,6′-dihydroxybipyridine)copper(II)] nitrate coordination complexes

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Computing details

Data collection: *APEX2* (Bruker, 2009) for (I); *APEX2* (Bruker, 2012) for (II). Cell refinement: *SAINT* (Bruker, 2009) for (I); *SAINT* (Bruker, 2012) for (II). Data reduction: *SAINT* (Bruker, 2009) for (I); *SAINT* (Bruker, 2012) for (II). For both compounds, program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008). Program(s) used to refine structure: *SHELXL2014*/7 (Sheldrick, 2015), *SHELXLE* (Hübschle *et al.*, 2011) for (I); *SHELXL2012* (Sheldrick, 2015), *SHELXLE* (Hübschle *et al.*, 2011) for (II). For both compounds, molecular graphics: *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

(I) (6,6′-Dihydroxybipyridine-2κ^2N,N')[μ-6-(6-hydroxypyridin-2-yl)pyridin-2-olato-1:2$\kappa^3N,N':O^2$](μ-hydroxido-1:2$\kappa^2O:O'$)(μ-nitrato-1:2$\kappa^2O:O'$)(nitrato-1κO)dicopper(II)

Crystal data

$[Cu_2(C_{10}H_7N_2O_2)(OH)(NO_3)_2(C_{10}H_8N_2O_2)]$
M_r = 643.47
Triclinic, $P\overline{1}$
a = 7.358 (2) Å
b = 10.447 (3) Å
c = 15.744 (4) Å
α = 77.610 (4)°
β = 78.927 (4)°
γ = 69.938 (4)°
V = 1101.1 (5) Å^3
Z = 2
$F(000)$ = 648
D_x = 1.941 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 390 reflections
θ = 2.3–24.8°
μ = 2.01 mm^{-1}
T = 100 K
Plate, green
0.17 × 0.12 × 0.03 mm

Data collection

Bruker SMART APEX CCD diffractometer
Radiation source: fine-focus sealed tube
ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2009)
T_{min} = 0.605, T_{max} = 0.746
14887 measured reflections
6413 independent reflections
4302 reflections with $I > 2\sigma(I)$
R_{int} = 0.050
θ_{max} = 30.7°, θ_{min} = 1.3°
h = −10→10
k = −14→14
l = −22→21

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.125$
$S = 1.04$
6413 reflections
365 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0555P)^2 + 0.1969P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.11$ e Å^{-3}
$\Delta\rho_{min} = -0.69$ 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.

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

	x	y	z	U_{iso}*/U_{eq}
C1	0.2710 (5)	0.4849 (4)	−0.0150 (3)	0.0185 (8)
C2	0.2962 (6)	0.5280 (4)	−0.1049 (3)	0.0216 (8)
H2	0.2206	0.6168	−0.1305	0.026*
C3	0.4322 (6)	0.4401 (4)	−0.1562 (3)	0.0220 (8)
H3	0.4521	0.4670	−0.2180	0.026*
C4	0.5418 (5)	0.3099 (4)	−0.1166 (2)	0.0190 (8)
H4	0.6379	0.2480	−0.1510	0.023*
C5	0.5083 (5)	0.2731 (4)	−0.0271 (2)	0.0144 (7)
C6	0.6100 (5)	0.1354 (4)	0.0196 (2)	0.0147 (7)
C7	0.7447 (5)	0.0339 (4)	−0.0228 (3)	0.0190 (8)
H7	0.7805	0.0511	−0.0845	0.023*
C8	0.8294 (5)	−0.0964 (4)	0.0263 (3)	0.0187 (8)
H8	0.9244	−0.1676	−0.0018	0.022*
C9	0.7735 (5)	−0.1193 (4)	0.1146 (3)	0.0174 (8)
H9	0.8290	−0.2065	0.1486	0.021*
C10	0.6315 (5)	−0.0113 (4)	0.1552 (2)	0.0140 (7)
C11	0.2728 (5)	0.2782 (4)	0.4525 (2)	0.0169 (7)
C12	0.1854 (5)	0.3244 (4)	0.5324 (3)	0.0186 (8)
H12	0.1660	0.4165	0.5392	0.022*
C13	0.1285 (5)	0.2346 (4)	0.6005 (3)	0.0201 (8)
H13	0.0705	0.2638	0.6553	0.024*
C14	0.1560 (5)	0.0991 (4)	0.5894 (2)	0.0175 (7)
H14	0.1177	0.0355	0.6362	0.021*
C15	0.2398 (5)	0.0608 (4)	0.5090 (2)	0.0138 (7)
H15	0.584 (6)	0.211 (4)	0.257 (3)	0.016 (12)*
C16	0.2731 (5)	−0.0791 (4)	0.4908 (2)	0.0147 (7)
C17	0.2193 (5)	−0.1803 (4)	0.5517 (2)	0.0164 (7)
H17	0.1568	−0.1622	0.6085	0.020*

C18	0.2577 (5)	−0.3093 (4)	0.5287 (2)	0.0172 (7)
H18	0.2232	−0.3806	0.5702	0.021*
C19	0.3449 (5)	−0.3331 (4)	0.4465 (3)	0.0191 (8)
H19	0.3704	−0.4204	0.4299	0.023*
C20	0.3961 (5)	−0.2269 (4)	0.3869 (2)	0.0172 (7)
N1	0.3732 (4)	0.3613 (3)	0.0244 (2)	0.0156 (6)
N2	0.5553 (4)	0.1137 (3)	0.10808 (19)	0.0129 (6)
N3	0.2987 (4)	0.1489 (3)	0.44065 (19)	0.0126 (6)
N4	0.3616 (4)	−0.1019 (3)	0.40843 (19)	0.0139 (6)
N5	0.0443 (5)	0.4545 (4)	0.2519 (2)	0.0217 (7)
N6	0.0449 (4)	0.1339 (3)	0.2131 (2)	0.0149 (6)
O1	0.1390 (4)	0.5753 (3)	0.03228 (18)	0.0244 (6)
H1	0.140 (7)	0.552 (5)	0.0859 (14)	0.037*
O2	0.5740 (4)	−0.0383 (3)	0.23919 (17)	0.0181 (5)
O3	0.3321 (4)	0.3654 (3)	0.38846 (17)	0.0194 (6)
H3B	0.380 (6)	0.334 (5)	0.3421 (19)	0.029*
O4	0.4801 (4)	−0.2525 (3)	0.30803 (18)	0.0217 (6)
H4B	0.532 (6)	−0.195 (4)	0.280 (3)	0.033*
O5	0.4755 (4)	0.2277 (3)	0.26553 (17)	0.0159 (5)
O6	0.1872 (4)	0.4522 (3)	0.19101 (18)	0.0208 (6)
O7	0.0328 (4)	0.3455 (3)	0.29893 (19)	0.0294 (7)
O8	−0.0797 (4)	0.5672 (3)	0.2623 (2)	0.0367 (8)
O9	0.1131 (4)	0.2090 (3)	0.15141 (17)	0.0205 (6)
O10	0.1392 (4)	0.0637 (3)	0.2725 (2)	0.0290 (7)
O11	−0.1223 (4)	0.1285 (3)	0.21196 (19)	0.0260 (7)
Cu1	0.36658 (6)	0.27682 (5)	0.15407 (3)	0.01478 (12)
Cu2	0.41333 (6)	0.06500 (5)	0.33097 (3)	0.01386 (12)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0167 (17)	0.0172 (19)	0.024 (2)	−0.0082 (15)	−0.0056 (15)	−0.0011 (16)
C2	0.0243 (19)	0.0138 (19)	0.027 (2)	−0.0079 (15)	−0.0079 (16)	0.0036 (16)
C3	0.027 (2)	0.023 (2)	0.0168 (19)	−0.0125 (17)	−0.0023 (15)	0.0030 (16)
C4	0.0224 (19)	0.020 (2)	0.0154 (18)	−0.0094 (16)	−0.0001 (15)	−0.0017 (15)
C5	0.0112 (15)	0.0162 (19)	0.0183 (18)	−0.0070 (14)	−0.0005 (13)	−0.0045 (15)
C6	0.0107 (15)	0.0180 (19)	0.0172 (18)	−0.0076 (14)	−0.0024 (13)	−0.0010 (15)
C7	0.0167 (17)	0.020 (2)	0.0198 (19)	−0.0075 (15)	0.0012 (14)	−0.0027 (16)
C8	0.0131 (16)	0.0170 (19)	0.025 (2)	−0.0026 (14)	−0.0009 (14)	−0.0059 (16)
C9	0.0140 (16)	0.0138 (18)	0.025 (2)	−0.0032 (14)	−0.0032 (14)	−0.0045 (15)
C10	0.0134 (16)	0.0148 (18)	0.0160 (18)	−0.0070 (14)	0.0003 (13)	−0.0045 (14)
C11	0.0169 (17)	0.0137 (18)	0.0212 (19)	−0.0045 (14)	−0.0071 (14)	−0.0013 (15)
C12	0.0181 (17)	0.0148 (19)	0.024 (2)	−0.0034 (14)	−0.0059 (15)	−0.0064 (16)
C13	0.0196 (18)	0.024 (2)	0.0180 (19)	−0.0063 (16)	−0.0011 (14)	−0.0077 (16)
C14	0.0155 (17)	0.019 (2)	0.0184 (18)	−0.0062 (15)	−0.0027 (14)	−0.0034 (15)
C15	0.0117 (15)	0.0145 (18)	0.0155 (17)	−0.0044 (13)	−0.0026 (13)	−0.0015 (14)
C16	0.0110 (15)	0.0150 (18)	0.0178 (18)	−0.0027 (13)	−0.0032 (13)	−0.0028 (14)
C17	0.0165 (17)	0.0191 (19)	0.0142 (17)	−0.0083 (15)	−0.0011 (13)	−0.0003 (15)

C18	0.0154 (17)	0.0164 (19)	0.0203 (19)	−0.0080 (14)	−0.0030 (14)	0.0014 (15)
C19	0.0198 (18)	0.0096 (18)	0.028 (2)	−0.0055 (14)	−0.0022 (15)	−0.0036 (15)
C20	0.0170 (17)	0.0154 (19)	0.0189 (19)	−0.0037 (14)	−0.0045 (14)	−0.0027 (15)
N1	0.0141 (14)	0.0139 (15)	0.0193 (16)	−0.0065 (12)	−0.0032 (12)	0.0006 (13)
N2	0.0117 (13)	0.0128 (15)	0.0139 (15)	−0.0040 (11)	−0.0006 (11)	−0.0025 (12)
N3	0.0120 (13)	0.0114 (15)	0.0143 (14)	−0.0028 (11)	−0.0021 (11)	−0.0030 (12)
N4	0.0126 (14)	0.0133 (15)	0.0156 (15)	−0.0035 (11)	−0.0029 (11)	−0.0020 (12)
N5	0.0220 (16)	0.0194 (18)	0.0257 (18)	−0.0022 (14)	−0.0097 (14)	−0.0092 (15)
N6	0.0140 (14)	0.0127 (15)	0.0178 (16)	−0.0039 (12)	0.0004 (12)	−0.0050 (13)
O1	0.0309 (15)	0.0146 (14)	0.0209 (15)	0.0007 (12)	−0.0024 (12)	−0.0024 (12)
O2	0.0208 (13)	0.0147 (13)	0.0151 (13)	−0.0051 (10)	0.0007 (10)	0.0016 (11)
O3	0.0295 (15)	0.0160 (14)	0.0154 (13)	−0.0103 (11)	−0.0021 (11)	−0.0036 (11)
O4	0.0325 (15)	0.0169 (14)	0.0171 (14)	−0.0110 (12)	0.0049 (11)	−0.0076 (11)
O5	0.0151 (13)	0.0151 (13)	0.0186 (14)	−0.0067 (11)	−0.0021 (10)	−0.0019 (11)
O6	0.0240 (14)	0.0142 (14)	0.0225 (14)	−0.0041 (11)	−0.0024 (11)	−0.0027 (11)
O7	0.0319 (16)	0.0290 (17)	0.0274 (16)	−0.0131 (13)	0.0039 (13)	−0.0061 (14)
O8	0.0320 (17)	0.0305 (18)	0.0410 (19)	0.0030 (14)	0.0008 (14)	−0.0180 (15)
O9	0.0215 (13)	0.0256 (15)	0.0160 (13)	−0.0125 (12)	0.0007 (10)	−0.0013 (12)
O10	0.0244 (15)	0.0310 (17)	0.0330 (17)	−0.0126 (13)	−0.0151 (13)	0.0083 (14)
O11	0.0140 (13)	0.0296 (16)	0.0354 (17)	−0.0104 (12)	−0.0033 (12)	−0.0012 (14)
Cu1	0.0146 (2)	0.0141 (2)	0.0145 (2)	−0.00367 (17)	−0.00074 (16)	−0.00225 (18)
Cu2	0.0155 (2)	0.0128 (2)	0.0137 (2)	−0.00583 (17)	−0.00062 (16)	−0.00191 (17)

Geometric parameters (Å, º)

C1—O1	1.335 (5)	C15—C16	1.478 (5)
C1—N1	1.336 (5)	C16—N4	1.366 (4)
C1—C2	1.388 (6)	C16—C17	1.378 (5)
C2—C3	1.369 (6)	C17—C18	1.391 (5)
C2—H2	0.9500	C17—H17	0.9500
C3—C4	1.402 (5)	C18—C19	1.363 (5)
C3—H3	0.9500	C18—H18	0.9500
C4—C5	1.376 (5)	C19—C20	1.399 (5)
C4—H4	0.9500	C19—H19	0.9500
C5—N1	1.370 (4)	C20—O4	1.316 (4)
C5—C6	1.480 (5)	C20—N4	1.346 (5)
C6—N2	1.366 (5)	N1—Cu1	2.042 (3)
C6—C7	1.372 (5)	N2—Cu1	1.969 (3)
C7—C8	1.411 (5)	N3—Cu2	2.011 (3)
C7—H7	0.9500	N4—Cu2	2.009 (3)
C8—C9	1.366 (5)	N5—O8	1.238 (4)
C8—H8	0.9500	N5—O7	1.239 (4)
C9—C10	1.420 (5)	N5—O6	1.276 (4)
C9—H9	0.9500	N6—O10	1.225 (4)
C10—O2	1.310 (4)	N6—O9	1.251 (4)
C10—N2	1.346 (5)	N6—O11	1.254 (4)
C11—O3	1.322 (5)	O1—H1	0.827 (19)
C11—N3	1.347 (5)	O2—Cu2	1.946 (3)

C11—C12	1.402 (5)	O3—H3B	0.829 (19)
C12—C13	1.367 (5)	O4—H4B	0.827 (19)
C12—H12	0.9500	O5—Cu2	1.939 (3)
C13—C14	1.404 (5)	O5—Cu1	1.964 (3)
C13—H13	0.9500	O5—H15	0.75 (4)
C14—C15	1.374 (5)	O6—Cu1	1.985 (3)
C14—H14	0.9500	O9—Cu1	2.221 (3)
C15—N3	1.365 (5)	O10—Cu2	2.377 (3)

O1—C1—N1	120.4 (3)	C18—C19—C20	119.0 (4)
O1—C1—C2	116.4 (3)	C18—C19—H19	120.5
N1—C1—C2	123.2 (4)	C20—C19—H19	120.5
C3—C2—C1	118.7 (4)	O4—C20—N4	120.3 (3)
C3—C2—H2	120.7	O4—C20—C19	117.8 (3)
C1—C2—H2	120.7	N4—C20—C19	121.9 (3)
C2—C3—C4	119.3 (4)	C1—N1—C5	118.0 (3)
C2—C3—H3	120.3	C1—N1—Cu1	130.4 (3)
C4—C3—H3	120.3	C5—N1—Cu1	111.6 (2)
C5—C4—C3	119.1 (4)	C10—N2—C6	119.6 (3)
C5—C4—H4	120.5	C10—N2—Cu1	126.3 (2)
C3—C4—H4	120.5	C6—N2—Cu1	114.1 (2)
N1—C5—C4	121.7 (3)	C11—N3—C15	118.6 (3)
N1—C5—C6	115.6 (3)	C11—N3—Cu2	127.8 (2)
C4—C5—C6	122.7 (3)	C15—N3—Cu2	113.6 (2)
N2—C6—C7	121.8 (3)	C20—N4—C16	118.6 (3)
N2—C6—C5	115.4 (3)	C20—N4—Cu2	127.7 (2)
C7—C6—C5	122.7 (3)	C16—N4—Cu2	113.7 (2)
C6—C7—C8	119.1 (3)	O8—N5—O7	121.6 (4)
C6—C7—H7	120.4	O8—N5—O6	118.6 (4)
C8—C7—H7	120.4	O7—N5—O6	119.8 (3)
C9—C8—C7	119.4 (3)	O10—N6—O9	121.6 (3)
C9—C8—H8	120.3	O10—N6—O11	119.9 (3)
C7—C8—H8	120.3	O9—N6—O11	118.5 (3)
C8—C9—C10	119.3 (4)	C1—O1—H1	114 (3)
C8—C9—H9	120.4	C10—O2—Cu2	137.1 (2)
C10—C9—H9	120.4	C11—O3—H3B	114 (3)
O2—C10—N2	121.2 (3)	C20—O4—H4B	114 (3)
O2—C10—C9	117.9 (3)	Cu2—O5—Cu1	108.02 (13)
N2—C10—C9	120.9 (3)	Cu2—O5—H15	108 (3)
O3—C11—N3	120.3 (3)	Cu1—O5—H15	110 (3)
O3—C11—C12	117.9 (3)	N5—O6—Cu1	121.9 (2)
N3—C11—C12	121.8 (3)	N6—O9—Cu1	124.9 (2)
C13—C12—C11	118.9 (4)	N6—O10—Cu2	135.9 (2)
C13—C12—H12	120.5	O5—Cu1—N2	92.97 (12)
C11—C12—H12	120.5	O5—Cu1—O6	89.59 (11)
C12—C13—C14	119.9 (4)	N2—Cu1—O6	174.53 (12)
C12—C13—H13	120.0	O5—Cu1—N1	150.90 (12)
C14—C13—H13	120.0	N2—Cu1—N1	82.98 (12)

C15—C14—C13	118.3 (4)	O6—Cu1—N1	92.44 (12)
C15—C14—H14	120.8	O5—Cu1—O9	116.83 (10)
C13—C14—H14	120.8	N2—Cu1—O9	92.96 (11)
N3—C15—C14	122.4 (3)	O6—Cu1—O9	90.19 (11)
N3—C15—C16	115.4 (3)	N1—Cu1—O9	92.20 (11)
C14—C15—C16	122.2 (3)	O5—Cu2—O2	89.00 (11)
N4—C16—C17	121.7 (3)	O5—Cu2—N4	174.31 (12)
N4—C16—C15	115.1 (3)	O2—Cu2—N4	93.75 (11)
C17—C16—C15	123.2 (3)	O5—Cu2—N3	94.05 (12)
C16—C17—C18	119.0 (3)	O2—Cu2—N3	167.14 (11)
C16—C17—H17	120.5	N4—Cu2—N3	82.20 (12)
C18—C17—H17	120.5	O5—Cu2—O10	104.96 (11)
C19—C18—C17	119.8 (3)	O2—Cu2—O10	86.67 (11)
C19—C18—H18	120.1	N4—Cu2—O10	80.20 (11)
C17—C18—H18	120.1	N3—Cu2—O10	104.54 (11)

O1—C1—C2—C3	178.8 (3)	C4—C5—N1—C1	1.1 (5)
N1—C1—C2—C3	0.0 (6)	C6—C5—N1—C1	−177.1 (3)
C1—C2—C3—C4	−0.2 (6)	C4—C5—N1—Cu1	−178.2 (3)
C2—C3—C4—C5	0.7 (6)	C6—C5—N1—Cu1	3.6 (4)
C3—C4—C5—N1	−1.2 (5)	O2—C10—N2—C6	−176.0 (3)
C3—C4—C5—C6	176.9 (3)	C9—C10—N2—C6	2.4 (5)
N1—C5—C6—N2	0.3 (5)	O2—C10—N2—Cu1	4.4 (5)
C4—C5—C6—N2	−177.8 (3)	C9—C10—N2—Cu1	−177.2 (3)
N1—C5—C6—C7	177.9 (3)	C7—C6—N2—C10	−1.5 (5)
C4—C5—C6—C7	−0.3 (6)	C5—C6—N2—C10	176.0 (3)
N2—C6—C7—C8	−0.2 (5)	C7—C6—N2—Cu1	178.1 (3)
C5—C6—C7—C8	−177.5 (3)	C5—C6—N2—Cu1	−4.3 (4)
C6—C7—C8—C9	1.0 (5)	O3—C11—N3—C15	178.4 (3)
C7—C8—C9—C10	−0.1 (5)	C12—C11—N3—C15	−0.8 (5)
C8—C9—C10—O2	176.8 (3)	O3—C11—N3—Cu2	−2.6 (5)
C8—C9—C10—N2	−1.6 (5)	C12—C11—N3—Cu2	178.2 (3)
O3—C11—C12—C13	−177.9 (3)	C14—C15—N3—C11	−0.3 (5)
N3—C11—C12—C13	1.3 (5)	C16—C15—N3—C11	180.0 (3)
C11—C12—C13—C14	−0.7 (6)	C14—C15—N3—Cu2	−179.4 (3)
C12—C13—C14—C15	−0.3 (5)	C16—C15—N3—Cu2	0.9 (4)
C13—C14—C15—N3	0.8 (5)	O4—C20—N4—C16	179.6 (3)
C13—C14—C15—C16	−179.5 (3)	C19—C20—N4—C16	−0.3 (5)
N3—C15—C16—N4	1.1 (4)	O4—C20—N4—Cu2	2.8 (5)
C14—C15—C16—N4	−178.6 (3)	C19—C20—N4—Cu2	−177.1 (3)
N3—C15—C16—C17	−178.7 (3)	C17—C16—N4—C20	0.0 (5)
C14—C15—C16—C17	1.6 (5)	C15—C16—N4—C20	−179.8 (3)
N4—C16—C17—C18	0.6 (5)	C17—C16—N4—Cu2	177.3 (3)
C15—C16—C17—C18	−179.6 (3)	C15—C16—N4—Cu2	−2.5 (4)
C16—C17—C18—C19	−0.9 (5)	N2—C10—O2—Cu2	−9.7 (5)
C17—C18—C19—C20	0.7 (6)	C9—C10—O2—Cu2	171.9 (3)
C18—C19—C20—O4	180.0 (3)	O8—N5—O6—Cu1	−168.6 (3)
C18—C19—C20—N4	−0.1 (6)	O7—N5—O6—Cu1	11.6 (5)

O1—C1—N1—C5	−179.2 (3)	O10—N6—O9—Cu1	−18.1 (5)
C2—C1—N1—C5	−0.4 (5)	O11—N6—O9—Cu1	163.9 (2)
O1—C1—N1—Cu1	−0.2 (5)	O9—N6—O10—Cu2	20.0 (5)
C2—C1—N1—Cu1	178.6 (3)	O11—N6—O10—Cu2	−162.0 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H15···O11^{i}	0.75 (4)	2.08 (4)	2.802 (4)	164 (4)
O1—H1···O6	0.83 (2)	1.78 (2)	2.583 (4)	163 (5)
O3—H3*B*···O5	0.83 (2)	1.70 (2)	2.510 (4)	164 (5)
O4—H4*B*···O2	0.83 (2)	1.73 (2)	2.528 (4)	161 (5)

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

(II) Bis(μ_3-bipyridine-2,2′-diolato-κ^3O:*N*,*N*′:*O*′)tetrakis(6,6′-dihydroxybipyridine-κ^2N,*N*′)tetrakis(μ-hydroxido-κ^2O:*O*′)bis(methanol-κO)tetrakis(μ-nitrato-κ^2O:*O*′)hexacopper(II)

Crystal data

$[Cu_6(C_{10}H_6N_2O_2)_2(CH_4O)_2(OH)_4(NO_3)_4(C_{10}H_8N_2O_2)_4]$
M_r = 1886.53
Triclinic, $P\overline{1}$
a = 10.2135 (7) Å
b = 13.3707 (8) Å
c = 14.0565 (10) Å
α = 64.591 (4)°
β = 75.659 (5)°
γ = 82.262 (5)°
V = 1679.0 (2) Å^3
Z = 1
$F(000)$ = 954
D_x = 1.866 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 1117 reflections
θ = 3.0–29.1°
μ = 1.97 mm^{-1}
T = 100 K
Prism, green
0.26 × 0.22 × 0.07 mm

Data collection

Bruker APEXII CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*TWINABS*; Sheldrick, 2009)
T_{min} = 0.622, T_{max} = 0.746
20719 measured reflections
10920 independent reflections
7847 reflections with $I > 2\sigma(I)$
R_{int} = 0.068
θ_{max} = 32.0°, θ_{min} = 1.6°
h = −14→14
k = −16→19
l = 0→20

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.119
S = 1.00
10920 reflections
529 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.068P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.90 e Å^{-3}
$\Delta\rho_{min}$ = −1.08 e Å^{-3}

Special details

Experimental. The crystal under investigation was found to be split with two major domains not related by any obvious twin operation. The orientation matrices for the two components were identified using the program Cell_Now, with the two components being related by a 2.9 degrees rotation about either the reciprocal axis 1.000 - 0.363 - 0.339 or the real axis 1.000 - 0.178 - 0.265 degree. The two components were integrated using Saint, resulting in in the following statistics:
17535 data (5769 unique) involve domain 1 only, mean I/sigma 8.6 17271 data (5689 unique) involve domain 2 only, mean I/sigma 8.2 34813 data (9811 unique) involve 2 domains, mean I/sigma 9.5 11 data (11 unique) involve 3 domains, mean I/sigma 8.7 4 data (2 unique) involve 4 domains, mean I/sigma 57.6
The exact correlation matrix was identified by the integration program was found to be
Transforms h1.1(1)->h1.2(2) 1.00336 0.02923 - 0.02720 - 0.01894 1.02272 - 0.04903 0.02520 0.05747 0.97055.
The data were corrected for absorption using twinabs, and the structure was solved using direct methods with only the non-overlapping reflections of component 1. The structure was refined using the hklf 5 routine with all reflections of component 1 (including the overlapping ones), resulting in a BASF value of 0.486 (1).
The R_{int} value given is for all reflections and is based on agreement between observed single and composite intensities and those calculated from refined unique intensities and twin fractions (TWINABS (Sheldrick, 2009)).

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. Refined as a 2-component twin.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.41028 (4)	0.22335 (3)	0.75942 (3)	0.01004 (9)
Cu2	0.48719 (4)	0.28424 (3)	0.49234 (3)	0.01009 (9)
Cu3	0.79681 (4)	0.28550 (3)	0.32300 (3)	0.00978 (9)
O1	0.6858 (2)	0.3553 (2)	0.66647 (18)	0.0149 (5)
H1	0.6187	0.3498	0.6447	0.022*
O2	0.1351 (2)	0.0820 (2)	0.89259 (19)	0.0210 (6)
H2A	0.1769	0.1133	0.8284	0.031*
O3	0.2766 (2)	0.17719 (19)	0.70803 (17)	0.0108 (4)
O4	0.6689 (2)	0.3846 (2)	0.23790 (17)	0.0154 (5)
O5	0.8343 (2)	0.1430 (2)	0.56936 (18)	0.0162 (5)
H5	0.7765	0.1877	0.5382	0.024*
O6	0.8053 (2)	0.3901 (2)	0.06196 (18)	0.0174 (5)
H6	0.7504	0.3859	0.1189	0.026*
O7	0.2336 (2)	0.3684 (2)	0.77329 (18)	0.0169 (5)
O8	0.1064 (2)	0.5167 (2)	0.71865 (19)	0.0172 (5)
O9	0.2815 (2)	0.49085 (19)	0.60670 (18)	0.0166 (5)
O10	0.5101 (3)	−0.0537 (2)	0.6858 (2)	0.0244 (6)
O11	0.5594 (2)	0.0977 (2)	0.68885 (19)	0.0160 (5)
O12	0.4932 (2)	0.1038 (2)	0.55029 (19)	0.0164 (5)
O13	0.6824 (2)	0.28679 (18)	0.45612 (17)	0.0103 (4)
H13A	0.695 (4)	0.347 (2)	0.455 (3)	0.015*
O14	0.4843 (2)	0.33310 (19)	0.61349 (17)	0.0105 (4)
H14A	0.432 (3)	0.387 (2)	0.598 (3)	0.016*
O15	0.7227 (3)	0.1269 (2)	0.3314 (2)	0.0262 (6)
H15	0.647 (4)	0.121 (4)	0.375 (4)	0.039*

N1	0.5541 (2)	0.2397 (2)	0.8244 (2)	0.0105 (5)
N2	0.3295 (3)	0.1288 (2)	0.9159 (2)	0.0111 (5)
N3	0.2886 (2)	0.2882 (2)	0.5293 (2)	0.0104 (5)
N4	0.4511 (2)	0.3683 (2)	0.3394 (2)	0.0102 (5)
N5	0.9518 (3)	0.2047 (2)	0.3927 (2)	0.0110 (5)
N6	0.9403 (3)	0.3065 (2)	0.1862 (2)	0.0108 (5)
N7	0.2064 (3)	0.4580 (2)	0.7012 (2)	0.0125 (5)
N8	0.5208 (3)	0.0495 (2)	0.6423 (2)	0.0134 (6)
C1	0.6682 (3)	0.2959 (3)	0.7701 (3)	0.0132 (6)
C2	0.7689 (3)	0.2919 (3)	0.8239 (3)	0.0148 (7)
H2	0.8502	0.3303	0.7848	0.018*
C3	0.7495 (3)	0.2321 (3)	0.9335 (3)	0.0174 (7)
H3	0.8176	0.2287	0.9703	0.021*
C4	0.6293 (3)	0.1761 (3)	0.9908 (3)	0.0168 (7)
H4	0.6131	0.1359	1.0668	0.020*
C5	0.5354 (3)	0.1810 (3)	0.9336 (3)	0.0115 (6)
C6	0.4062 (3)	0.1227 (3)	0.9856 (3)	0.0124 (7)
C7	0.3656 (3)	0.0679 (3)	1.0958 (3)	0.0157 (7)
H7	0.4210	0.0644	1.1423	0.019*
C8	0.2402 (3)	0.0176 (3)	1.1371 (3)	0.0177 (7)
H8	0.2100	−0.0214	1.2127	0.021*
C9	0.1613 (3)	0.0243 (3)	1.0695 (3)	0.0173 (7)
H9	0.0750	−0.0079	1.0971	0.021*
C10	0.2101 (3)	0.0798 (3)	0.9580 (3)	0.0148 (7)
C11	0.2146 (3)	0.2432 (3)	0.6310 (3)	0.0118 (6)
C12	0.0747 (3)	0.2651 (3)	0.6532 (3)	0.0147 (7)
H12	0.0230	0.2328	0.7248	0.018*
C13	0.0135 (3)	0.3340 (3)	0.5699 (3)	0.0162 (7)
H13	−0.0806	0.3515	0.5841	0.019*
C14	0.0893 (3)	0.3782 (3)	0.4647 (3)	0.0134 (6)
H14	0.0480	0.4249	0.4063	0.016*
C15	0.2260 (3)	0.3523 (3)	0.4478 (3)	0.0107 (6)
C16	0.3161 (3)	0.3916 (3)	0.3392 (3)	0.0107 (6)
C17	0.2675 (3)	0.4448 (3)	0.2472 (3)	0.0136 (7)
H17	0.1728	0.4556	0.2506	0.016*
C18	0.3584 (3)	0.4833 (3)	0.1480 (3)	0.0170 (7)
H18	0.3268	0.5215	0.0829	0.020*
C19	0.4939 (3)	0.4648 (3)	0.1461 (3)	0.0155 (7)
H19	0.5575	0.4926	0.0795	0.019*
C20	0.5395 (3)	0.4043 (3)	0.2436 (2)	0.0124 (6)
C21	0.9476 (3)	0.1470 (3)	0.4981 (3)	0.0132 (6)
C22	1.0618 (3)	0.0891 (3)	0.5372 (3)	0.0150 (7)
H22	1.0561	0.0473	0.6124	0.018*
C23	1.1811 (3)	0.0938 (3)	0.4656 (3)	0.0163 (7)
H23	1.2598	0.0562	0.4906	0.020*
C24	1.1870 (3)	0.1542 (3)	0.3551 (3)	0.0152 (7)
H24	1.2693	0.1577	0.3044	0.018*
C25	1.0716 (3)	0.2084 (3)	0.3209 (3)	0.0120 (6)

C26	1.0664 (3)	0.2698 (3)	0.2063 (3)	0.0121 (6)
C27	1.1783 (3)	0.2865 (3)	0.1232 (3)	0.0169 (7)
H27	1.2658	0.2639	0.1385	0.020*
C28	1.1625 (3)	0.3365 (3)	0.0176 (3)	0.0175 (7)
H28	1.2391	0.3471	−0.0398	0.021*
C29	1.0370 (3)	0.3706 (3)	−0.0045 (3)	0.0165 (7)
H29	1.0243	0.4034	−0.0765	0.020*
C30	0.9276 (3)	0.3557 (3)	0.0827 (3)	0.0136 (7)
C31	0.7846 (4)	0.0935 (4)	0.2443 (3)	0.0308 (9)
H31A	0.8829	0.1003	0.2282	0.046*
H31B	0.7492	0.1413	0.1800	0.046*
H31C	0.7636	0.0164	0.2659	0.046*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.00874 (18)	0.0129 (2)	0.00790 (18)	−0.00220 (14)	−0.00128 (13)	−0.00351 (15)
Cu2	0.00726 (17)	0.0145 (2)	0.00810 (18)	−0.00063 (13)	−0.00178 (13)	−0.00408 (15)
Cu3	0.00937 (18)	0.0123 (2)	0.00782 (18)	0.00178 (14)	−0.00247 (13)	−0.00451 (15)
O1	0.0088 (10)	0.0228 (14)	0.0133 (11)	−0.0060 (9)	−0.0021 (8)	−0.0062 (10)
O2	0.0149 (12)	0.0354 (17)	0.0115 (12)	−0.0138 (11)	−0.0006 (9)	−0.0061 (12)
O3	0.0098 (10)	0.0145 (12)	0.0072 (10)	−0.0033 (8)	−0.0019 (8)	−0.0028 (9)
O4	0.0101 (11)	0.0237 (14)	0.0083 (10)	0.0025 (9)	−0.0031 (8)	−0.0030 (10)
O5	0.0126 (11)	0.0195 (13)	0.0129 (11)	0.0018 (9)	−0.0040 (9)	−0.0033 (10)
O6	0.0135 (11)	0.0266 (15)	0.0115 (11)	0.0047 (10)	−0.0033 (9)	−0.0084 (11)
O7	0.0218 (12)	0.0130 (13)	0.0113 (11)	0.0030 (9)	−0.0016 (9)	−0.0027 (10)
O8	0.0127 (11)	0.0189 (13)	0.0217 (13)	0.0050 (9)	−0.0035 (9)	−0.0115 (11)
O9	0.0205 (12)	0.0140 (12)	0.0109 (11)	0.0007 (9)	0.0025 (9)	−0.0046 (10)
O10	0.0251 (13)	0.0103 (13)	0.0334 (15)	−0.0018 (10)	−0.0150 (11)	0.0000 (12)
O11	0.0130 (11)	0.0183 (13)	0.0194 (12)	−0.0009 (9)	−0.0042 (9)	−0.0098 (11)
O12	0.0171 (12)	0.0158 (13)	0.0159 (12)	0.0013 (9)	−0.0061 (9)	−0.0051 (10)
O13	0.0088 (10)	0.0124 (12)	0.0098 (10)	0.0007 (8)	−0.0029 (8)	−0.0047 (9)
O14	0.0096 (10)	0.0110 (11)	0.0111 (10)	0.0008 (8)	−0.0029 (8)	−0.0046 (9)
O15	0.0306 (15)	0.0195 (15)	0.0308 (16)	−0.0048 (12)	−0.0132 (12)	−0.0076 (13)
N1	0.0096 (12)	0.0133 (14)	0.0089 (12)	0.0012 (10)	−0.0016 (10)	−0.0055 (11)
N2	0.0104 (12)	0.0113 (14)	0.0097 (12)	−0.0029 (10)	−0.0018 (10)	−0.0022 (11)
N3	0.0096 (12)	0.0122 (14)	0.0117 (13)	−0.0002 (9)	−0.0020 (10)	−0.0074 (11)
N4	0.0100 (12)	0.0109 (13)	0.0103 (12)	0.0008 (10)	−0.0044 (10)	−0.0042 (11)
N5	0.0111 (12)	0.0104 (13)	0.0115 (13)	0.0007 (10)	−0.0023 (10)	−0.0049 (11)
N6	0.0130 (13)	0.0100 (14)	0.0099 (12)	0.0015 (10)	−0.0026 (10)	−0.0051 (11)
N7	0.0151 (13)	0.0130 (14)	0.0111 (13)	−0.0017 (10)	−0.0009 (10)	−0.0073 (11)
N8	0.0107 (13)	0.0095 (14)	0.0179 (14)	−0.0001 (10)	−0.0046 (11)	−0.0029 (12)
C1	0.0140 (15)	0.0133 (17)	0.0138 (15)	0.0006 (12)	−0.0024 (12)	−0.0077 (13)
C2	0.0085 (14)	0.0195 (19)	0.0196 (17)	−0.0022 (12)	−0.0028 (12)	−0.0108 (15)
C3	0.0151 (16)	0.0193 (19)	0.0204 (18)	−0.0002 (13)	−0.0081 (13)	−0.0085 (15)
C4	0.0187 (17)	0.021 (2)	0.0120 (15)	0.0006 (14)	−0.0055 (13)	−0.0075 (14)
C5	0.0102 (14)	0.0146 (17)	0.0126 (15)	0.0018 (12)	−0.0039 (12)	−0.0082 (13)
C6	0.0125 (15)	0.0115 (17)	0.0118 (15)	0.0019 (12)	−0.0033 (12)	−0.0039 (13)

C7	0.0185 (17)	0.0177 (19)	0.0101 (15)	0.0015 (13)	−0.0032 (12)	−0.0055 (14)
C8	0.0225 (18)	0.0147 (18)	0.0115 (15)	−0.0025 (13)	0.0008 (13)	−0.0031 (14)
C9	0.0147 (16)	0.020 (2)	0.0141 (16)	−0.0062 (13)	0.0032 (13)	−0.0059 (15)
C10	0.0126 (15)	0.0181 (18)	0.0141 (16)	−0.0011 (13)	−0.0026 (12)	−0.0069 (14)
C11	0.0106 (14)	0.0118 (16)	0.0122 (15)	−0.0034 (11)	−0.0001 (11)	−0.0045 (13)
C12	0.0116 (15)	0.0191 (18)	0.0152 (16)	−0.0013 (12)	−0.0005 (12)	−0.0097 (14)
C13	0.0102 (14)	0.0206 (18)	0.0197 (17)	0.0006 (12)	−0.0013 (12)	−0.0113 (15)
C14	0.0130 (15)	0.0147 (17)	0.0136 (15)	0.0017 (12)	−0.0051 (12)	−0.0061 (13)
C15	0.0101 (14)	0.0117 (16)	0.0123 (15)	−0.0001 (11)	−0.0043 (11)	−0.0059 (13)
C16	0.0118 (14)	0.0093 (15)	0.0136 (15)	0.0012 (11)	−0.0039 (11)	−0.0069 (13)
C17	0.0139 (15)	0.0135 (17)	0.0148 (16)	0.0030 (12)	−0.0055 (12)	−0.0067 (14)
C18	0.0197 (17)	0.021 (2)	0.0119 (15)	0.0066 (14)	−0.0076 (13)	−0.0075 (14)
C19	0.0161 (16)	0.0209 (19)	0.0069 (14)	0.0047 (13)	−0.0035 (12)	−0.0042 (14)
C20	0.0129 (15)	0.0151 (17)	0.0091 (14)	0.0026 (12)	−0.0034 (11)	−0.0051 (13)
C21	0.0148 (15)	0.0116 (16)	0.0143 (15)	−0.0009 (12)	−0.0033 (12)	−0.0059 (13)
C22	0.0175 (16)	0.0135 (17)	0.0139 (15)	0.0004 (12)	−0.0079 (12)	−0.0035 (13)
C23	0.0151 (16)	0.0149 (17)	0.0189 (17)	0.0051 (12)	−0.0077 (13)	−0.0063 (14)
C24	0.0112 (15)	0.0180 (18)	0.0194 (17)	0.0028 (12)	−0.0036 (12)	−0.0112 (15)
C25	0.0128 (15)	0.0114 (16)	0.0138 (15)	0.0025 (11)	−0.0025 (12)	−0.0083 (13)
C26	0.0125 (15)	0.0116 (16)	0.0167 (16)	0.0014 (12)	−0.0053 (12)	−0.0093 (13)
C27	0.0137 (16)	0.0205 (19)	0.0196 (17)	0.0022 (13)	−0.0031 (13)	−0.0121 (15)
C28	0.0150 (16)	0.021 (2)	0.0174 (16)	−0.0005 (13)	0.0017 (13)	−0.0118 (15)
C29	0.0191 (17)	0.0209 (19)	0.0107 (15)	0.0016 (14)	−0.0031 (12)	−0.0083 (14)
C30	0.0149 (16)	0.0116 (17)	0.0136 (15)	0.0032 (12)	−0.0021 (12)	−0.0060 (13)
C31	0.036 (2)	0.030 (2)	0.032 (2)	−0.0003 (18)	−0.0100 (18)	−0.016 (2)

Geometric parameters (Å, º)

Cu1—O3	1.966 (2)	C1—C2	1.403 (5)
Cu1—O14	1.970 (2)	C2—C3	1.373 (5)
Cu1—N1	1.991 (3)	C2—H2	0.9500
Cu1—N2	2.028 (3)	C3—C4	1.399 (5)
Cu1—O11	2.474 (2)	C3—H3	0.9500
Cu1—O7	2.503 (2)	C4—C5	1.374 (5)
Cu2—O13	1.933 (2)	C4—H4	0.9500
Cu2—N3	1.964 (2)	C5—C6	1.481 (5)
Cu2—N4	2.056 (3)	C6—C7	1.377 (4)
Cu2—O14	2.062 (2)	C7—C8	1.399 (5)
Cu2—O12	2.188 (2)	C7—H7	0.9500
Cu3—O13	1.951 (2)	C8—C9	1.358 (5)
Cu3—O4	1.960 (2)	C8—H8	0.9500
Cu3—N5	2.008 (3)	C9—C10	1.404 (5)
Cu3—N6	2.044 (2)	C9—H9	0.9500
Cu3—O15	2.292 (3)	C11—C12	1.404 (4)
O1—C1	1.304 (4)	C12—C13	1.376 (5)
O1—H1	0.8400	C12—H12	0.9500
O2—C10	1.324 (4)	C13—C14	1.393 (4)
O2—H2A	0.8400	C13—H13	0.9500

O3—C11	1.312 (4)	C14—C15	1.380 (4)
O4—C20	1.302 (4)	C14—H14	0.9500
O5—C21	1.321 (4)	C15—C16	1.483 (4)
O5—H5	0.8400	C16—C17	1.363 (4)
O6—C30	1.330 (4)	C17—C18	1.394 (5)
O6—H6	0.8400	C17—H17	0.9500
O7—N7	1.244 (3)	C18—C19	1.369 (4)
O8—N7	1.243 (3)	C18—H18	0.9500
O9—N7	1.277 (3)	C19—C20	1.418 (4)
O10—N8	1.255 (4)	C19—H19	0.9500
O11—N8	1.247 (4)	C21—C22	1.404 (4)
O12—N8	1.265 (4)	C22—C23	1.364 (4)
O13—H13A	0.828 (19)	C22—H22	0.9500
O14—H14A	0.823 (18)	C23—C24	1.400 (5)
O15—C31	1.452 (5)	C23—H23	0.9500
O15—H15	0.85 (4)	C24—C25	1.377 (4)
N1—C1	1.345 (4)	C24—H24	0.9500
N1—C5	1.368 (4)	C25—C26	1.472 (4)
N2—C10	1.338 (4)	C26—C27	1.379 (4)
N2—C6	1.369 (4)	C27—C28	1.385 (5)
N3—C11	1.352 (4)	C27—H27	0.9500
N3—C15	1.352 (4)	C28—C29	1.365 (5)
N4—C20	1.349 (4)	C28—H28	0.9500
N4—C16	1.373 (4)	C29—C30	1.401 (4)
N5—C21	1.337 (4)	C29—H29	0.9500
N5—C25	1.372 (4)	C31—H31A	0.9800
N6—C30	1.346 (4)	C31—H31B	0.9800
N6—C26	1.368 (4)	C31—H31C	0.9800

O3—Cu1—O14	92.09 (9)	C5—C4—H4	121.0
O3—Cu1—N1	169.20 (10)	C3—C4—H4	121.0
O14—Cu1—N1	94.74 (10)	N1—C5—C4	122.7 (3)
O3—Cu1—N2	92.42 (10)	N1—C5—C6	114.8 (3)
O14—Cu1—N2	171.80 (10)	C4—C5—C6	122.6 (3)
N1—Cu1—N2	81.86 (11)	N2—C6—C7	122.7 (3)
O3—Cu1—O11	81.68 (8)	N2—C6—C5	114.9 (3)
O14—Cu1—O11	81.22 (8)	C7—C6—C5	122.4 (3)
N1—Cu1—O11	91.10 (9)	C6—C7—C8	118.1 (3)
N2—Cu1—O11	106.22 (9)	C6—C7—H7	121.0
O3—Cu1—O7	83.89 (9)	C8—C7—H7	121.0
O14—Cu1—O7	86.60 (8)	C9—C8—C7	120.3 (3)
N1—Cu1—O7	104.84 (9)	C9—C8—H8	119.8
N2—Cu1—O7	87.07 (9)	C7—C8—H8	119.8
O11—Cu1—O7	160.71 (8)	C8—C9—C10	118.6 (3)
O13—Cu2—N3	177.44 (10)	C8—C9—H9	120.7
O13—Cu2—N4	98.59 (10)	C10—C9—H9	120.7
N3—Cu2—N4	81.24 (10)	O2—C10—N2	119.2 (3)
O13—Cu2—O14	90.04 (9)	O2—C10—C9	118.2 (3)

N3—Cu2—O14	88.22 (9)	N2—C10—C9	122.6 (3)
N4—Cu2—O14	132.65 (10)	O3—C11—N3	118.3 (3)
O13—Cu2—O12	91.19 (9)	O3—C11—C12	121.0 (3)
N3—Cu2—O12	91.20 (10)	N3—C11—C12	120.8 (3)
N4—Cu2—O12	114.24 (10)	C13—C12—C11	119.1 (3)
O14—Cu2—O12	112.01 (9)	C13—C12—H12	120.5
O13—Cu3—O4	91.56 (9)	C11—C12—H12	120.5
O13—Cu3—N5	93.98 (10)	C12—C13—C14	120.1 (3)
O4—Cu3—N5	169.81 (11)	C12—C13—H13	119.9
O13—Cu3—N6	168.03 (10)	C14—C13—H13	119.9
O4—Cu3—N6	91.13 (10)	C15—C14—C13	118.1 (3)
N5—Cu3—N6	81.74 (10)	C15—C14—H14	120.9
O13—Cu3—O15	98.82 (10)	C13—C14—H14	120.9
O4—Cu3—O15	94.90 (10)	N3—C15—C14	122.5 (3)
N5—Cu3—O15	92.70 (10)	N3—C15—C16	114.5 (3)
N6—Cu3—O15	92.58 (11)	C14—C15—C16	122.9 (3)
C1—O1—H1	109.5	C17—C16—N4	123.2 (3)
C10—O2—H2A	109.5	C17—C16—C15	122.3 (3)
C11—O3—Cu1	125.2 (2)	N4—C16—C15	114.5 (3)
C20—O4—Cu3	140.7 (2)	C16—C17—C18	119.2 (3)
C21—O5—H5	109.5	C16—C17—H17	120.4
C30—O6—H6	109.5	C18—C17—H17	120.4
N7—O7—Cu1	128.98 (17)	C19—C18—C17	118.7 (3)
N8—O11—Cu1	123.07 (18)	C19—C18—H18	120.6
N8—O12—Cu2	115.9 (2)	C17—C18—H18	120.6
Cu2—O13—Cu3	125.46 (12)	C18—C19—C20	120.1 (3)
Cu2—O13—H13A	101 (3)	C18—C19—H19	120.0
Cu3—O13—H13A	105 (3)	C20—C19—H19	120.0
Cu1—O14—Cu2	114.21 (11)	O4—C20—N4	121.0 (3)
Cu1—O14—H14A	109 (3)	O4—C20—C19	118.2 (3)
Cu2—O14—H14A	101 (3)	N4—C20—C19	120.9 (3)
C31—O15—Cu3	117.3 (2)	O5—C21—N5	120.4 (3)
C31—O15—H15	137 (3)	O5—C21—C22	117.6 (3)
Cu3—O15—H15	100 (3)	N5—C21—C22	122.0 (3)
C1—N1—C5	119.1 (3)	C23—C22—C21	118.9 (3)
C1—N1—Cu1	125.9 (2)	C23—C22—H22	120.6
C5—N1—Cu1	114.8 (2)	C21—C22—H22	120.6
C10—N2—C6	117.8 (3)	C22—C23—C24	119.7 (3)
C10—N2—Cu1	128.6 (2)	C22—C23—H23	120.1
C6—N2—Cu1	113.5 (2)	C24—C23—H23	120.1
C11—N3—C15	119.4 (3)	C25—C24—C23	119.0 (3)
C11—N3—Cu2	124.0 (2)	C25—C24—H24	120.5
C15—N3—Cu2	116.1 (2)	C23—C24—H24	120.5
C20—N4—C16	117.8 (3)	N5—C25—C24	121.4 (3)
C20—N4—Cu2	129.6 (2)	N5—C25—C26	115.6 (3)
C16—N4—Cu2	112.6 (2)	C24—C25—C26	123.0 (3)
C21—N5—C25	118.9 (3)	N6—C26—C27	121.2 (3)
C21—N5—Cu3	127.1 (2)	N6—C26—C25	115.3 (3)

C25—N5—Cu3	113.9 (2)	C27—C26—C25	123.5 (3)
C30—N6—C26	118.0 (3)	C26—C27—C28	119.7 (3)
C30—N6—Cu3	129.0 (2)	C26—C27—H27	120.2
C26—N6—Cu3	112.9 (2)	C28—C27—H27	120.2
O8—N7—O7	121.4 (3)	C29—C28—C27	120.2 (3)
O8—N7—O9	118.7 (3)	C29—C28—H28	119.9
O7—N7—O9	119.9 (2)	C27—C28—H28	119.9
O11—N8—O10	120.4 (3)	C28—C29—C30	117.8 (3)
O11—N8—O12	120.5 (3)	C28—C29—H29	121.1
O10—N8—O12	119.1 (3)	C30—C29—H29	121.1
O1—C1—N1	120.0 (3)	O6—C30—N6	118.7 (3)
O1—C1—C2	119.4 (3)	O6—C30—C29	118.2 (3)
N1—C1—C2	120.6 (3)	N6—C30—C29	123.1 (3)
C3—C2—C1	119.8 (3)	O15—C31—H31A	109.5
C3—C2—H2	120.1	O15—C31—H31B	109.5
C1—C2—H2	120.1	H31A—C31—H31B	109.5
C2—C3—C4	119.8 (3)	O15—C31—H31C	109.5
C2—C3—H3	120.1	H31A—C31—H31C	109.5
C4—C3—H3	120.1	H31B—C31—H31C	109.5
C5—C4—C3	118.0 (3)		

Cu1—O7—N7—O8	172.8 (2)	C13—C14—C15—C16	178.1 (3)
Cu1—O7—N7—O9	−6.8 (4)	C20—N4—C16—C17	2.7 (5)
Cu1—O11—N8—O10	−111.9 (3)	Cu2—N4—C16—C17	−178.7 (3)
Cu1—O11—N8—O12	68.9 (3)	C20—N4—C16—C15	−178.2 (3)
Cu2—O12—N8—O11	−9.2 (3)	Cu2—N4—C16—C15	0.4 (3)
Cu2—O12—N8—O10	171.6 (2)	N3—C15—C16—C17	171.4 (3)
C5—N1—C1—O1	−177.7 (3)	C14—C15—C16—C17	−8.2 (5)
Cu1—N1—C1—O1	7.1 (4)	N3—C15—C16—N4	−7.7 (4)
C5—N1—C1—C2	1.9 (4)	C14—C15—C16—N4	172.7 (3)
Cu1—N1—C1—C2	−173.2 (2)	N4—C16—C17—C18	−3.5 (5)
O1—C1—C2—C3	178.2 (3)	C15—C16—C17—C18	177.5 (3)
N1—C1—C2—C3	−1.5 (5)	C16—C17—C18—C19	0.9 (5)
C1—C2—C3—C4	−0.3 (5)	C17—C18—C19—C20	2.1 (5)
C2—C3—C4—C5	1.7 (5)	Cu3—O4—C20—N4	19.3 (5)
C1—N1—C5—C4	−0.5 (4)	Cu3—O4—C20—C19	−160.8 (3)
Cu1—N1—C5—C4	175.1 (3)	C16—N4—C20—O4	−179.6 (3)
C1—N1—C5—C6	179.7 (3)	Cu2—N4—C20—O4	2.1 (5)
Cu1—N1—C5—C6	−4.6 (3)	C16—N4—C20—C19	0.5 (5)
C3—C4—C5—N1	−1.3 (5)	Cu2—N4—C20—C19	−177.8 (2)
C3—C4—C5—C6	178.5 (3)	C18—C19—C20—O4	177.2 (3)
C10—N2—C6—C7	0.5 (5)	C18—C19—C20—N4	−2.9 (5)
Cu1—N2—C6—C7	176.2 (2)	C25—N5—C21—O5	179.1 (3)
C10—N2—C6—C5	−178.6 (3)	Cu3—N5—C21—O5	−3.4 (5)
Cu1—N2—C6—C5	−2.8 (3)	C25—N5—C21—C22	−0.8 (5)
N1—C5—C6—N2	4.9 (4)	Cu3—N5—C21—C22	176.7 (2)
C4—C5—C6—N2	−174.8 (3)	O5—C21—C22—C23	−178.6 (3)
N1—C5—C6—C7	−174.1 (3)	N5—C21—C22—C23	1.4 (5)

C4—C5—C6—C7	6.2 (5)	C21—C22—C23—C24	−1.1 (5)
N2—C6—C7—C8	−0.5 (5)	C22—C23—C24—C25	0.3 (5)
C5—C6—C7—C8	178.5 (3)	C21—N5—C25—C24	0.0 (5)
C6—C7—C8—C9	−0.7 (5)	Cu3—N5—C25—C24	−177.8 (3)
C7—C8—C9—C10	1.8 (5)	C21—N5—C25—C26	177.6 (3)
C6—N2—C10—O2	−178.4 (3)	Cu3—N5—C25—C26	−0.2 (4)
Cu1—N2—C10—O2	6.6 (5)	C23—C24—C25—N5	0.2 (5)
C6—N2—C10—C9	0.7 (5)	C23—C24—C25—C26	−177.2 (3)
Cu1—N2—C10—C9	−174.3 (2)	C30—N6—C26—C27	2.6 (5)
C8—C9—C10—O2	177.3 (3)	Cu3—N6—C26—C27	−173.8 (3)
C8—C9—C10—N2	−1.8 (5)	C30—N6—C26—C25	−175.0 (3)
Cu1—O3—C11—N3	67.6 (4)	Cu3—N6—C26—C25	8.6 (3)
Cu1—O3—C11—C12	−113.4 (3)	N5—C25—C26—N6	−5.7 (4)
C15—N3—C11—O3	176.9 (3)	C24—C25—C26—N6	171.9 (3)
Cu2—N3—C11—O3	−12.0 (4)	N5—C25—C26—C27	176.8 (3)
C15—N3—C11—C12	−2.0 (5)	C24—C25—C26—C27	−5.7 (5)
Cu2—N3—C11—C12	169.1 (2)	N6—C26—C27—C28	−3.2 (5)
O3—C11—C12—C13	−179.4 (3)	C25—C26—C27—C28	174.2 (3)
N3—C11—C12—C13	−0.5 (5)	C26—C27—C28—C29	1.0 (6)
C11—C12—C13—C14	2.1 (5)	C27—C28—C29—C30	1.6 (5)
C12—C13—C14—C15	−1.1 (5)	C26—N6—C30—O6	178.8 (3)
C11—N3—C15—C14	3.1 (5)	Cu3—N6—C30—O6	−5.5 (5)
Cu2—N3—C15—C14	−168.7 (3)	C26—N6—C30—C29	0.2 (5)
C11—N3—C15—C16	−176.5 (3)	Cu3—N6—C30—C29	175.9 (3)
Cu2—N3—C15—C16	11.7 (3)	C28—C29—C30—O6	179.1 (3)
C13—C14—C15—N3	−1.5 (5)	C28—C29—C30—N6	−2.2 (5)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O14	0.84	1.61	2.448 (3)	175
O2—H2*A*···O3	0.84	1.66	2.499 (3)	172
O5—H5···O13	0.84	1.70	2.536 (3)	170
O6—H6···O4	0.84	1.67	2.495 (3)	168
O13—H13*A*···O9^{i}	0.83 (2)	1.98 (2)	2.763 (3)	158 (4)
O14—H14*A*···O9	0.82 (2)	1.94 (2)	2.738 (3)	163 (4)
O15—H15···O10^{ii}	0.85 (5)	2.42 (5)	2.790 (4)	107 (4)

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