

A new stepped tetranuclear copper(II) complex: synthesis, crystal structure and photoluminescence properties

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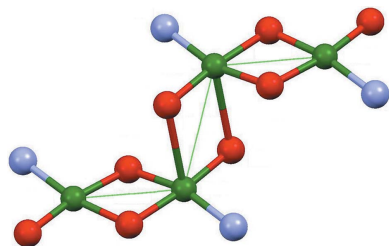
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Binuclear and tetranuclear copper(II) complexes are of interest because of their structural, magnetic and photoluminescence properties. Of the several important configurations of tetranuclear copper(II) complexes, there are limited reports on the crystal structures and solid-state photoluminescence properties of 'stepped' tetranuclear copper(II) complexes. A new Cu^{II} complex, namely bis{ μ_3 -3-[(4-methoxy-2-oxidobenzylidene)amino]propanolato}bis{ μ_2 -3-[(4-methoxy-2-oxidobenzylidene)amino]propanolato}tetra-copper(II), [Cu₄(C₁₁H₁₃NO₃)₄], has been synthesized and characterized using elemental analysis, FT-IR, solid-state UV-Vis spectroscopy and single-crystal X-ray diffraction. The crystal structure determination shows that the complex is a stepped tetranuclear structure consisting of two dinuclear [Cu₂(L)₂] units {L is 3-[(4-methoxy-2-oxidobenzylidene)amino]propanolato}. The two terminal Cu^{II} atoms are four-coordinated in square-planar environments, while the two central Cu^{II} atoms are five-coordinated in square-pyramidal environments. The solid-state photoluminescence properties of both the complex and 3-[(2-hydroxy-4-methoxybenzylidene)amino]propanol (H₂L) have been investigated at room temperature in the visible region. When the complex and H₂L are excited under UV light at 349 nm, the complex displays a strong blue emission at 469 nm and H₂L displays a green emission at 515 nm.

1. Introduction

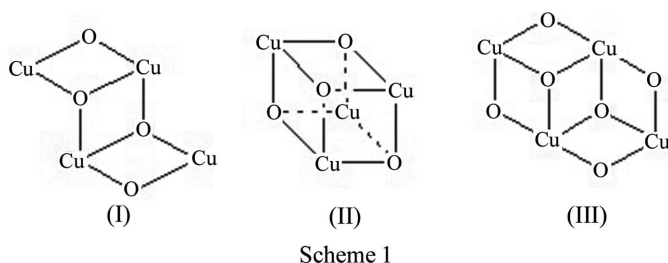
Recently, extensive research has been carried with Schiff base ligands and their metal complexes in the fields of coordination polymers (Kara, 2008*b*; Adams *et al.*, 2008; Lu, 2003), magnetochemistry (Kara, 2008*a*; Gungor *et al.*, 2015; Yahsi & Kara, 2013; Kahn, 1993; Kara, 2007), bioinorganic chemistry (Massoud *et al.*, 2014; Bhat *et al.*, 2011) and catalysis (Halvagar *et al.*, 2014; Kirillov *et al.*, 2012). Many transition metal complexes have been prepared using tridentate Schiff base ligands with NNO or ONO types of donor sets and hydroxide, alkoxide, azide, sulfide or iminate bridging groups (Yahsi, Gungor *et al.*, 2016; Kara, 2008*a,b*; Halcrow, Sun *et al.*, 1995; Fomina *et al.*, 2010; Halcrow *et al.*, 1995*a,b*). Of all of these, binuclear and linked binuclear, *i.e.* tetranuclear, copper(II) complexes have attracted most attention because of their structural, magnetic and photoluminescence properties (Zhang *et al.*, 2006; Gao *et al.*, 2015; Yraola *et al.*, 2008).

A search of the Cambridge Structural Database indicates the existence of several important configurations of tetranuclear copper(II) complexes. These motifs, *i.e.* stepped or ladder/chair-like, (I), cubane-like, (II), and double open cubane-like, (III), are shown in Scheme 1. A number of 'cubane-like' and 'double open cubane-like' tetranuclear copper(II) complexes have been studied intensively due to



their structural and magnetic properties. However, to the best of our knowledge, there are limited reports on the crystal structure and solid-state photoluminescence properties of ‘stepped’ tetranuclear copper(II) complexes (Zhang *et al.*, 2006; Mathews & Manohar, 1991; Biswas *et al.*, 2009; Balboa *et al.*, 2008).

Our research group and others have successfully synthesized mononuclear, binuclear and tetranuclear copper(II) complexes (Hopa & Cokay, 2016*a,b*; Gungor & Kara, 2012, 2015; Gungor *et al.*, 2014; Celen *et al.*, 2016; Yahsi, 2016; Yahsi & Kara, 2013; Yardan *et al.*, 2014) and investigated their magnetostructural properties. We describe here the synthesis, crystal structure, spectroscopic and photoluminescence properties of a new stepped tetranuclear copper(II) complex, namely bis{ μ_3 -3-[(4-methoxy-2-oxidobenzylidene)amino]propanolato}bis{ μ_2 -3-[(4-methoxy-2-oxidobenzylidene)amino]propanolato}tetracopper(II), (1) (Scheme 2).



2. Experimental

All chemical reagents and solvents were purchased from Merck or Aldrich and used without further purification. Elemental (C, H and N) analyses was carried out using standard methods with a LECO, CHNS-932 analyzer. Solid-state UV–Vis spectra were measured using an Ocean Optics Maya 2000-PRO spectrometer. IR spectra were recorded on a PerkinElmer Spectrum 65 instrument. Solid-state photoluminescence spectra in the visible region were measured at room temperature using an ANDOR SR500i-BL Photoluminescence Spectrometer, equipped with a triple grating and an air-cooled CCD camera as detector. The measurements were carried out using excitation at 349 nm from a Spectra-Physics Nd:YLF laser as the source with a 5 ns pulse width and 1.3 mJ of energy per pulse. The synthetic route used for the preparation of 3-[(2-hydroxy-4-methoxybenzylidene)amino]propanol (H_2L) and complex (1) is outlined in Scheme 2.

2.1. Synthesis and crystallization

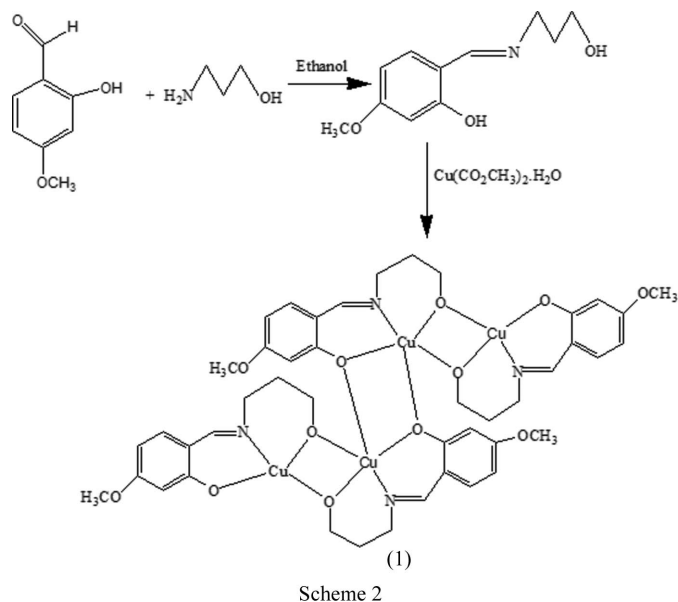
The tridentate Schiff base H_2L was prepared from the reaction between 3-aminopropan-1-ol (1 mmol) and 4-methoxysalicylaldehyde (1 mmol) in hot ethanol (60 ml). The solution obtained was stirred at 338 K for 10 min and a yellow precipitate was obtained on cooling. Complex (1) was prepared by the addition of a solution of copper(II) acetate monohydrate (1 mmol, 0.199 g) in hot methanol (20 ml) to a solution of H_2L (1 mmol, 0.195 g) in hot ethanol (30 ml). The resulting solution was warmed to 351 K and stirred for 15 min. The solution was filtered rapidly and allowed to stand at room temperature. Green crystals of complex (1), which were

Table 1
Experimental details.

Crystal data	
Chemical formula	[Cu ₄ (C ₁₁ H ₁₃ NO ₃) ₄]
M_r	1083.05
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	16.2592 (3), 14.2078 (3), 9.2560 (2)
β (°)	92.527 (1)
V (Å ³)	2136.13 (8)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	2.03
Crystal size (mm)	0.17 × 0.16 × 0.06
Data collection	
Diffractometer	Bruker APEXII with a CCD area detector
Absorption correction	Multi-scan (<i>TWINABS</i> ; Sheldrick, 2008 <i>b</i>)
T_{\min}, T_{\max}	0.767, 0.885
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8050, 8050, 5655
R_{int}	0.038
$(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹)	0.775
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.051, 0.123, 1.21
No. of reflections	8050
No. of parameters	348
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (e Å ⁻³)	0.74, -0.58

Computer programs: *APEX2* (Bruker, 2007), *SAINT* (Bruker, 2007), *SHELXS97* (Sheldrick, 2008*a*), *SHELXL2016* (Sheldrick, 2015), *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2006).

suitable for X-ray analysis, had grown after several weeks. Analysis calculated for H_2L (C₁₁H₁₅NO₃, yield 85%): C 63.14, H 7.23, N 6.69%; found: C 63.18, H 7.32, N 6.78%. Analysis calculated for C₄₄H₅₂Cu₄N₄O₁₂ (yield 75%): C 48.79, H 4.84, N 5.17%; found: C 48.95, H 4.71, N 5.25%.



2.2. Refinement

The crystallographic data and structure refinement details are summarized in Table 1. The crystal of (1) used for data

collection was found to display nonmerohedral twinning. Both components of the twin were indexed with the program *CELL_NOW* (Sheldrick, 2008*b*) and the intensity data for each domain was then integrated and reduced using the program *SAINTE* (Bruker, 2007). The combined data were scaled and an absorption correction performed using *TWINABS* (Sheldrick, 2008*b*). Integrated intensities for the reflections from the two components were written into a *SHELXL* HKLF 5 reflection file with *TWINABS*, using all reflection data (exactly overlapped, partially overlapped and nonoverlapped). H atoms were included in idealized positions, with isotropic displacement parameters constrained to 1.5 times the U_{eq} values of their attached C atoms for methyl H atoms, and 1.2 times U_{eq} of their attached C atoms for all other H atoms. The 3-aminopropan-1-ol portion of the ligand is disordered over two positions (*A* and *B*). Atoms C1*A*, C2*A*, C3*A*, N1*A* and C4*A* were refined with occupancies of 0.498 (10), C1*B*, C2*B*, C3*B*, N1*B* and C4*B* with occupancies of 0.502 (10), C12*A*, C13*A*, C14*A*, N2*A* and C15*A* with occupancies of 0.685 (9), and C12*B*, C13*B*, C14*B*, N2*B* and C15*B* with occupancies of 0.315 (9). Disordered atoms C1*A*/C1*B*, C4*A*/C4*B*, C12*A*/C12*B* and C15*A*/C15*B* were constrained to occupy the same site.

3. Results and discussion

3.1. Crystal structure

The asymmetric unit of tetranuclear complex (1) includes half of the centrosymmetric $[\text{Cu}_2(\text{L})_2]_2$ molecule. The results of the crystal structure determination indicate that complex (1) has a stepped tetranuclear structure consisting of two dinuclear $[\text{Cu}_2(\text{L})_2]$ subunits, as shown in Fig. 1(*a*). In the crystal structure of complex (1), atom Cu1 is in a square-planar environment, consisting of one imine N atom (N1), and one alkoxy O atom (O1), one phenoxy O atom (O2) and a bridging alkoxy O atom (O4) from the Schiff base *L* ligands. Atom Cu2 is in a square-pyramidal environment; the four

Table 2
Selected geometric parameters (Å, °).

Cu1—O1	1.916 (2)	Cu2—O5	1.9242 (19)
Cu1—O2	1.900 (2)	Cu2—O5 ⁱ	2.641 (2)
Cu1—O4	1.928 (2)	Cu2—N2 <i>A</i>	1.982 (9)
Cu1—N1 <i>A</i>	1.959 (8)	Cu2—N2 <i>B</i>	1.91 (2)
Cu1—N1 <i>B</i>	1.942 (8)	Cu1···Cu2	3.0251 (5)
Cu2—O1	1.941 (2)	Cu2···Cu2 ⁱ	3.4586 (6)
Cu2—O4	1.930 (2)		
O1—Cu1—N1 <i>A</i>	95.9 (2)	O4—Cu2—N2 <i>A</i>	95.3 (3)
O2—Cu1—N1 <i>A</i>	94.7 (3)	O5—Cu2—N2 <i>A</i>	93.8 (3)
O4—Cu1—N1 <i>A</i>	169.7 (3)	N2 <i>B</i> —Cu2—O1	155.3 (4)
O1—Cu1—N1 <i>B</i>	95.5 (3)	N2 <i>B</i> —Cu2—O4	91.4 (5)
O2—Cu1—N1 <i>B</i>	95.0 (3)	N2 <i>B</i> —Cu2—O5	97.1 (5)
O4—Cu1—N1 <i>B</i>	167.0 (3)	O4—Cu2—O1	76.01 (8)
O2—Cu1—O1	169.33 (9)	O5—Cu2—O1	94.66 (8)
O2—Cu1—O4	92.70 (8)	O5—Cu2—O4	170.65 (8)
O1—Cu1—O4	76.63 (8)	Cu1—O1—Cu2	103.34 (9)
O1—Cu2—N2 <i>A</i>	167.4 (2)	Cu1—O4—Cu2	103.27 (9)

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

basal donor atoms include one imine N atom (N2), one alkoxy O atom (O4), one phenoxy O atom (O5) and one bridging alkoxy O atom (O1) from the Schiff base *L* ligands. The apical donor is a bridging phenoxy O atom [O5ⁱ; symmetry code: (i) $-x + 1, -y + 1, -z$] from an *L* ligand of the symmetry-related $[\text{Cu}_2(\text{L})_2]$ half molecule. Atom Cu1 (Cu1ⁱ) bridges to Cu2 (Cu2ⁱ) through two alkoxy O atoms, yielding two $[\text{Cu}(\mu\text{-O}_{\text{alkoxy}})_2\text{Cu}]$ pairs in which the Cu···Cuⁱ distance is 3.0251 (5) Å (Fig. 1*b*). In addition, atom Cu2 bridges to Cu2ⁱ through two phenoxy O atoms (O5 and O5ⁱ) from each of the two Schiff base ligands, yielding one $\text{Cu}(\mu\text{-O}_{\text{phenoxy}})_2\text{Cu}$ pair in which the Cu2···Cu2ⁱ distance is 3.4586 (6) Å (Fig. 1*b*). While the $[\text{Cu}(\mu\text{-O}_{\text{alkoxy}})_2\text{Cu}]$ cores are practically perfect lozenges, with Cu—O—Cu bridging angles of 103.27 (9) and 103.34 (9)°, the $\text{Cu}(\mu\text{-O}_{\text{phenoxy}})_2\text{Cu}$ core is a symmetry-imposed rectangle. The selected Cu—O and Cu—N bond lengths and Cu—O—Cu bond angles for complex (1) given in Table 2 are comparable to those of similar complexes reported in the literature (Louhibi *et al.*, 2007; Zhang *et al.*, 2006).

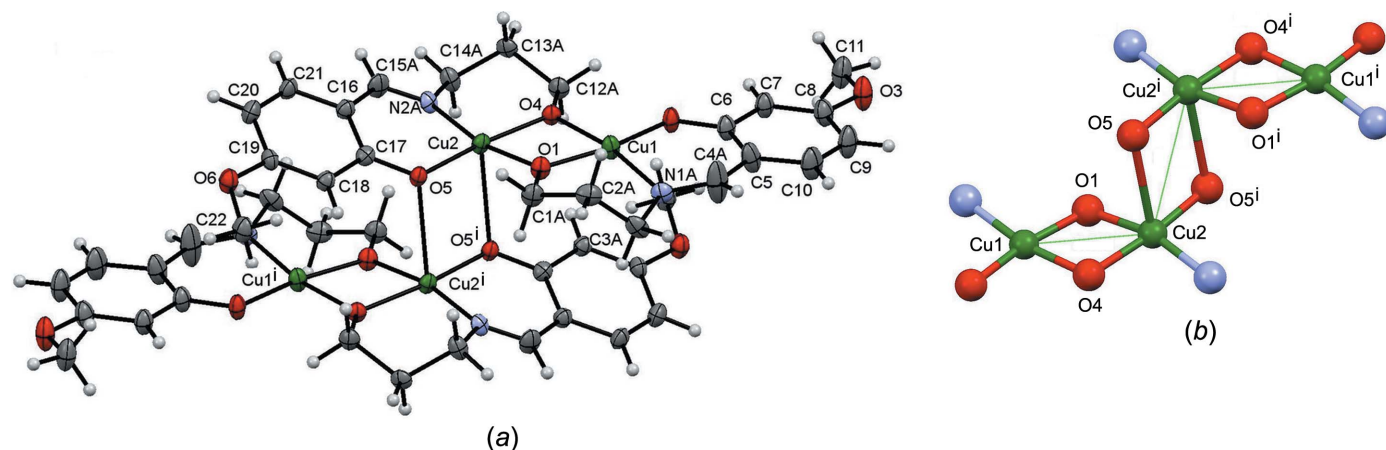


Figure 1

(*a*) The molecular structure of (1), showing the atom labelling and with displacement ellipsoids drawn at the 50% probability level. The disordered atoms have been omitted for clarity. (*b*) A view of the Cu_4O_6 core of (1). See Table 2 for the Cu···Cu distances (dotted lines). [Symmetry code: (i) $-x + 1, -y + 1, -z$.]

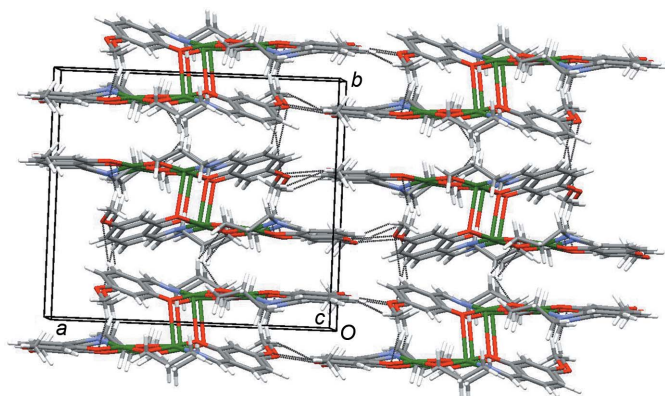


Figure 2
The packing structure of complex (1). Dashed lines represent weak C–H...O interactions.

Complex (1) reveals the presence of intermolecular C–H...O interactions between the interconnected tetranuclear complex units (Table 3). This hydrogen-bonded network lies in the *ab* plane and stacks along the *c* axis (Fig. 2).

3.2. FT-IR spectroscopy

The IR spectrum of (1) was compared with that of free H_2L in the region 4000–400 cm^{-1} (Fig. 3). The IR spectra of H_2L shows a broad band in the region 3455–3394 cm^{-1} due to O–H stretching, which disappears in complex (1), indicating deprotonation of the Schiff base ligand upon complexation. The presence of several weak peaks observed in the range 3054–2833 cm^{-1} is likely to originate from aromatic and aliphatic C–H stretches. The strong absorption band at 1648 cm^{-1} in the spectrum of (1) can be assigned to the C=N stretching frequency of the coordinated Schiff base ligand (Rahaman *et al.*, 2005). The shift of this band towards lower frequency compared with that of the free Schiff base (1637 cm^{-1}) indicates the coordination of the imine N atom to the metal centre. The phenolic C–O group of free H_2L exhibits a strong band at 1265–1205 cm^{-1} , whereas in the complex, this band is observed in the lower frequency region 1222–1150 cm^{-1} , providing evidence for coordination to the

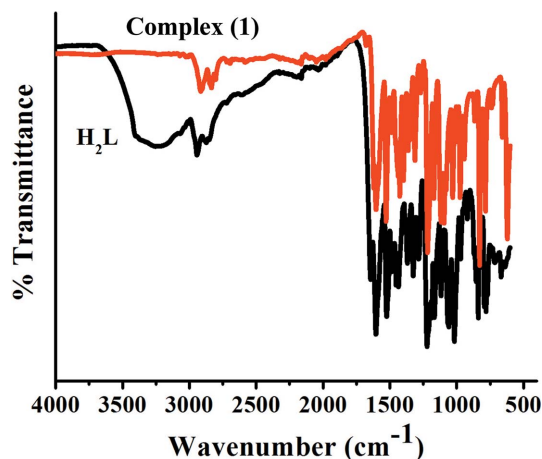


Figure 3
The IR spectra of H_2L and complex (1).

Table 3
Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C3B-H3BB\cdots O2^{ii}$	0.99	2.48	3.385 (12)	152
$C11-H11B\cdots O6^{iii}$	0.98	2.56	3.359 (4)	138
$C21-H21\cdots O6^{iv}$	0.95	2.54	3.279 (4)	135
$C22-H22C\cdots O2^i$	0.98	2.52	3.362 (4)	144

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

metal ions through the deprotonated phenolic O atoms (You & Zhu, 2004).

3.3. Solid-state UV-Vis spectra

The solid-state UV-Vis spectrum of (1) was obtained and compared with that of free H_2L (Fig. 4). The UV-Vis spectrum of H_2L displays a band at 369 nm, whereas complex (1) shows two bands at 280 and 407 nm. The first band can be attributed to a $\pi-\pi^*$ transition within the aromatic ring, while the second band would be due to an $n-\pi^*$ transition within the $-C=N$ group. The bands at the high-energy region are probably obscured by the intense charge-transfer transitions (Lever, 1984).

3.4. Photoluminescence properties

Photoluminescence properties of transition metal complexes have attracted considerable attention because of their potential applications in many areas, such as light-emitting devices (LED) and as probes in fluorescence lifetime imaging microscopy (FLIM) and sensors (Keefe *et al.*, 2000; Lo *et al.*, 2012; Suhling *et al.*, 2005; Svensson *et al.*, 2011). In this context, Schiff base ligands are used as molecular and electrochemical sensors since they include C=N double bonds and this offers electron-pair enrichment to the sensor and an easy way to bind metals (Erkarlan *et al.*, 2016; Obali & Ucan, 2015; Yang *et al.*, 2013; Spichiger-Keller, 1998).

The solid-state photoluminescence properties of H_2L and complex (1) were investigated at room temperature in the visible region with excitation at $\lambda_{ex} = 349$ nm (Fig. 5). Free

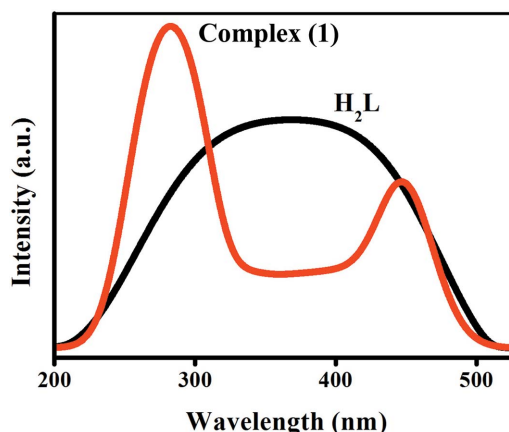


Figure 4
The absorption spectra of H_2L and complex (1).

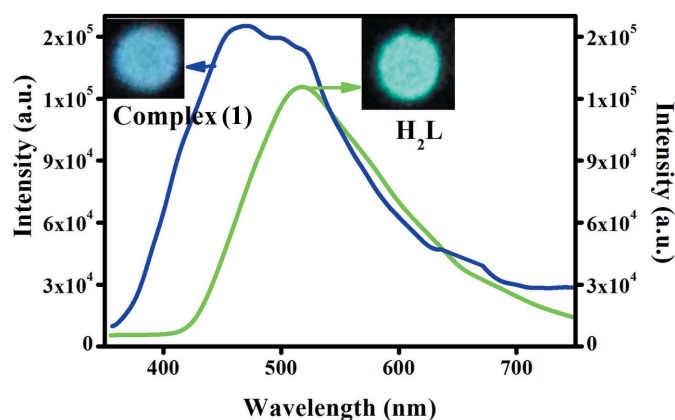


Figure 5
The emission spectra of H_2L and complex (1) in solid samples at room temperature ($\lambda_{ex} = 349$ nm).

H_2L shows a strong green emission band at $\lambda_{max} = 515$ nm, which may be assigned to the $n-\pi$ or $\pi-\pi^*$ electronic transition (ILCT) (Hopa & Cokay, 2016a; Feng *et al.*, 2015). When free H_2L is combined with Cu^{II} in complex (1), a stronger blue emission band is exhibited at $\lambda_{max} = 469$ nm. The observed emissions of complex (1) probably originate from the $n-\pi$ or $\pi-\pi^*$ intraligand fluorescence, since a similar emission was also observed for the ligand (Yahsi, Ozbek *et al.*, 2016; Wu *et al.*, 2006; Manjunatha *et al.*, 2011). The intensity of the emission of (1) is found to be greater than that of free H_2L . The observed emission spectrum of (1) is blue shifted when compared with that of H_2L . The reason for this shift can be explained by the influence of the coordinated metal atom on the ligand (Feng *et al.*, 2015; Manjunatha *et al.*, 2011). The enhancement of luminescence may be attributed to the chelation of the ligand to the central metal atom. The chelation enhances the 'rigidity' of the ligand and thus reduces the loss of energy through a radiationless pathway (Erkarlan *et al.*, 2016; Paira *et al.*, 2007; Zheng *et al.*, 2001).

4. Conclusions

A new stepped tetranuclear copper(II) complex, $[Cu_2(L)_2]_2$ [H_2L is 3-[(2-hydroxy-4-methoxybenzylidene)amino]propanol], (1), has been synthesized and characterized using single-crystal X-ray diffraction analysis, and spectroscopic and photoluminescence measurements. The photoluminescence studies indicate a blue shift compared with free H_2L and the emission intensity of (1) is stronger than that of the ligand. The enhancement of luminescence may be attributed to the chelation of the ligand to the central metal atom. The luminescence properties showed that the photoluminescence arose as a result of intraligand emission from the excited state and that the compound is a novel potential candidate for applications in optoelectronic devices.

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supporting information

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A new stepped tetranuclear copper(II) complex: synthesis, crystal structure and photoluminescence properties

Elif Gungor

Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *APEX2* (Bruker, 2007); data reduction: *S SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008a); program(s) used to refine structure: *SHELXL2016* (Sheldrick, 2015); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2006).

Bis{ μ_3 -3-[(4-methoxy-2-oxidobenzylidene)amino]propanolato}bis{ μ_2 -3-[(4-methoxy-2-oxidobenzylidene)amino]propanolato}tetra-copper(II)

Crystal data

[Cu₄(C₁₁H₁₃NO₃)₄]
 $M_r = 1083.05$
 Monoclinic, $P2_1/c$
 $a = 16.2592$ (3) Å
 $b = 14.2078$ (3) Å
 $c = 9.2560$ (2) Å
 $\beta = 92.527$ (1)°
 $V = 2136.13$ (8) Å³
 $Z = 2$

$F(000) = 1112$
 $D_x = 1.684$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 846 reflections
 $\theta = 2.6$ – 25.5 °
 $\mu = 2.03$ mm⁻¹
 $T = 100$ K
 Plate, violet
 $0.17 \times 0.16 \times 0.06$ mm

Data collection

Bruker APEXII with a CCD area detector
 diffractometer
 Radiation source: fine-focus sealed tube
 phi and ω scans
 Absorption correction: multi-scan
 (TWINABS; Sheldrick, 2008b)
 $T_{\min} = 0.767$, $T_{\max} = 0.885$
 8050 measured reflections

8050 independent reflections
 5655 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.038$
 $\theta_{\max} = 33.4$ °, $\theta_{\min} = 1.3$ °
 $h = 0 \rightarrow 24$
 $k = -21 \rightarrow 0$
 $l = -14 \rightarrow 14$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.123$
 $S = 1.21$
 8050 reflections
 348 parameters
 0 restraints

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0276P)^2 + 3.965P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.74$ e Å⁻³
 $\Delta\rho_{\min} = -0.58$ 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.

Refinement. Refined as a 2-component twin.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cu1	0.28607 (2)	0.38313 (3)	0.07394 (4)	0.02378 (9)	
Cu2	0.47193 (2)	0.39545 (3)	0.07983 (4)	0.02041 (9)	
O1	0.37587 (12)	0.39379 (16)	-0.0522 (2)	0.0234 (4)	
O2	0.21254 (12)	0.36940 (17)	0.2266 (2)	0.0259 (5)	
O3	-0.04308 (14)	0.3618 (2)	0.4600 (3)	0.0395 (6)	
O4	0.38181 (12)	0.36959 (15)	0.2028 (2)	0.0212 (4)	
O5	0.54848 (12)	0.42022 (15)	-0.0683 (2)	0.0209 (4)	
O6	0.80182 (13)	0.38723 (17)	-0.3068 (2)	0.0281 (5)	
C1A	0.37454 (19)	0.4003 (3)	-0.2044 (3)	0.0276 (6)	0.498 (10)
H1AA	0.416811	0.357716	-0.241990	0.033*	0.498 (10)
H1AB	0.388372	0.465387	-0.232620	0.033*	0.498 (10)
C2A	0.2896 (4)	0.3737 (6)	-0.2724 (6)	0.0269 (16)	0.498 (10)
H2AA	0.291195	0.377903	-0.378958	0.032*	0.498 (10)
H2AB	0.276681	0.307856	-0.246951	0.032*	0.498 (10)
C3A	0.2224 (4)	0.4381 (6)	-0.2204 (6)	0.0272 (18)	0.498 (10)
H3AA	0.241544	0.504146	-0.223851	0.033*	0.498 (10)
H3AB	0.173068	0.432218	-0.286385	0.033*	0.498 (10)
N1A	0.1998 (5)	0.4155 (6)	-0.0720 (9)	0.0237 (15)	0.498 (10)
C4A	0.1229 (2)	0.3951 (4)	-0.0512 (4)	0.0562 (14)	0.498 (10)
H4A	0.088119	0.385597	-0.135181	0.067*	0.498 (10)
C1B	0.37454 (19)	0.4003 (3)	-0.2044 (3)	0.0276 (6)	0.502 (10)
H1BA	0.387289	0.337842	-0.245317	0.033*	0.502 (10)
H1BB	0.417698	0.444838	-0.233035	0.033*	0.502 (10)
C2B	0.2933 (4)	0.4326 (7)	-0.2652 (7)	0.032 (2)	0.502 (10)
H2BA	0.296411	0.439536	-0.371249	0.039*	0.502 (10)
H2BB	0.281232	0.495365	-0.224827	0.039*	0.502 (10)
C3B	0.2240 (4)	0.3672 (8)	-0.2342 (7)	0.039 (3)	0.502 (10)
H3BA	0.175549	0.382937	-0.298151	0.047*	0.502 (10)
H3BB	0.240552	0.301775	-0.255513	0.047*	0.502 (10)
N1B	0.2012 (5)	0.3740 (7)	-0.0797 (9)	0.0277 (17)	0.502 (10)
C4B	0.1229 (2)	0.3951 (4)	-0.0512 (4)	0.0562 (14)	0.502 (10)
H4B	0.088958	0.418564	-0.129298	0.067*	0.502 (10)
C5	0.0860 (2)	0.3856 (3)	0.0843 (3)	0.0350 (8)	
C6	0.13247 (18)	0.3733 (2)	0.2178 (3)	0.0262 (6)	
C7	0.08859 (18)	0.3640 (2)	0.3459 (3)	0.0266 (6)	
H7	0.117980	0.354849	0.435751	0.032*	
C8	0.0033 (2)	0.3682 (3)	0.3419 (4)	0.0314 (7)	
C9	-0.0422 (2)	0.3796 (3)	0.2103 (4)	0.0387 (9)	

H9	-0.100637	0.381171	0.208214	0.046*	
C10	-0.0011 (2)	0.3882 (3)	0.0860 (4)	0.0419 (9)	
H10	-0.031936	0.396385	-0.002756	0.050*	
C11	-0.0017 (2)	0.3665 (3)	0.5997 (4)	0.0381 (9)	
H11A	0.034693	0.311966	0.613042	0.057*	
H11B	-0.042486	0.366416	0.674618	0.057*	
H11C	0.030915	0.424460	0.607071	0.057*	
C12A	0.38366 (19)	0.3635 (2)	0.3554 (3)	0.0243 (6)	0.685 (9)
H12A	0.335667	0.326734	0.385629	0.029*	0.685 (9)
H12B	0.379671	0.427521	0.396816	0.029*	0.685 (9)
C13A	0.4644 (3)	0.3157 (3)	0.4149 (4)	0.0220 (11)	0.685 (9)
H13A	0.461564	0.307797	0.520789	0.026*	0.685 (9)
H13B	0.468442	0.252237	0.371564	0.026*	0.685 (9)
C14A	0.5412 (3)	0.3707 (5)	0.3836 (5)	0.0247 (11)	0.685 (9)
H14A	0.534321	0.436425	0.416470	0.030*	0.685 (9)
H14B	0.588457	0.343250	0.439901	0.030*	0.685 (9)
N2A	0.5596 (5)	0.3712 (5)	0.2307 (9)	0.0200 (12)	0.685 (9)
C15A	0.62992 (19)	0.3384 (3)	0.1943 (3)	0.0295 (7)	0.685 (9)
H15A	0.661471	0.305734	0.267187	0.035*	0.685 (9)
C12B	0.38366 (19)	0.3635 (2)	0.3554 (3)	0.0243 (6)	0.315 (9)
H12C	0.370098	0.298446	0.384172	0.029*	0.315 (9)
H12D	0.341392	0.406034	0.393091	0.029*	0.315 (9)
C13B	0.4644 (6)	0.3892 (7)	0.4192 (9)	0.024 (2)	0.315 (9)
H13C	0.463252	0.386990	0.525997	0.028*	0.315 (9)
H13D	0.478656	0.454041	0.390333	0.028*	0.315 (9)
C14B	0.5283 (7)	0.3209 (11)	0.3675 (10)	0.028 (3)	0.315 (9)
H14C	0.578366	0.324293	0.432046	0.033*	0.315 (9)
H14D	0.506479	0.255901	0.371196	0.033*	0.315 (9)
N2B	0.5494 (11)	0.3433 (11)	0.2190 (19)	0.017 (3)	0.315 (9)
C15B	0.62992 (19)	0.3384 (3)	0.1943 (3)	0.0295 (7)	0.315 (9)
H15B	0.666680	0.328994	0.275680	0.035*	0.315 (9)
C16	0.66532 (17)	0.3459 (2)	0.0556 (3)	0.0220 (5)	
C17	0.62523 (17)	0.3916 (2)	-0.0659 (3)	0.0200 (5)	
C18	0.67166 (17)	0.4068 (2)	-0.1896 (3)	0.0211 (5)	
H18	0.647335	0.438772	-0.270845	0.025*	
C19	0.75224 (17)	0.3755 (2)	-0.1934 (3)	0.0215 (5)	
C20	0.79026 (19)	0.3267 (2)	-0.0757 (3)	0.0268 (6)	
H20	0.844686	0.302990	-0.081051	0.032*	
C21	0.74726 (18)	0.3143 (2)	0.0454 (3)	0.0245 (6)	
H21	0.773215	0.283350	0.126147	0.029*	
C22	0.7697 (2)	0.4359 (3)	-0.4321 (3)	0.0306 (7)	
H22A	0.719692	0.404220	-0.469695	0.046*	
H22B	0.810852	0.436109	-0.506282	0.046*	
H22C	0.756497	0.500918	-0.406097	0.046*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.01875 (17)	0.0373 (2)	0.01511 (15)	-0.00328 (15)	-0.00174 (12)	0.00247 (14)
Cu2	0.01825 (16)	0.02807 (19)	0.01484 (14)	0.00302 (14)	0.00010 (11)	0.00193 (13)
O1	0.0210 (9)	0.0340 (12)	0.0150 (8)	0.0007 (9)	0.0003 (7)	0.0001 (8)
O2	0.0151 (9)	0.0426 (13)	0.0198 (9)	-0.0014 (9)	-0.0014 (7)	0.0038 (9)
O3	0.0197 (11)	0.0725 (19)	0.0263 (11)	-0.0028 (11)	0.0006 (9)	-0.0019 (12)
O4	0.0196 (9)	0.0286 (11)	0.0153 (8)	0.0004 (8)	-0.0003 (7)	0.0039 (8)
O5	0.0165 (9)	0.0272 (11)	0.0191 (9)	0.0030 (7)	0.0015 (7)	0.0019 (8)
O6	0.0213 (10)	0.0393 (13)	0.0239 (10)	0.0025 (9)	0.0034 (8)	0.0025 (9)
C1A	0.0273 (15)	0.0387 (18)	0.0167 (12)	0.0018 (13)	0.0003 (10)	0.0051 (12)
C2A	0.037 (4)	0.028 (4)	0.016 (2)	-0.002 (3)	-0.005 (2)	-0.001 (2)
C3A	0.031 (3)	0.036 (5)	0.014 (2)	-0.010 (3)	-0.004 (2)	0.007 (2)
N1A	0.026 (3)	0.029 (4)	0.016 (2)	-0.001 (3)	0.000 (2)	0.002 (3)
C4A	0.0244 (16)	0.123 (5)	0.0200 (15)	-0.010 (2)	-0.0071 (13)	0.008 (2)
C1B	0.0273 (15)	0.0387 (18)	0.0167 (12)	0.0018 (13)	0.0003 (10)	0.0051 (12)
C2B	0.033 (4)	0.049 (6)	0.015 (3)	-0.007 (3)	-0.003 (2)	0.006 (3)
C3B	0.024 (3)	0.075 (7)	0.019 (3)	-0.022 (4)	-0.007 (2)	0.007 (3)
N1B	0.026 (3)	0.041 (5)	0.015 (2)	-0.005 (4)	-0.004 (2)	0.000 (4)
C4B	0.0244 (16)	0.123 (5)	0.0200 (15)	-0.010 (2)	-0.0071 (13)	0.008 (2)
C5	0.0222 (14)	0.061 (2)	0.0211 (13)	-0.0102 (15)	-0.0040 (11)	0.0069 (15)
C6	0.0180 (12)	0.0384 (18)	0.0218 (12)	-0.0037 (12)	-0.0029 (10)	0.0003 (12)
C7	0.0190 (13)	0.0402 (18)	0.0205 (12)	-0.0015 (12)	-0.0017 (10)	0.0017 (12)
C8	0.0213 (14)	0.046 (2)	0.0265 (14)	-0.0058 (13)	-0.0023 (11)	0.0015 (14)
C9	0.0196 (14)	0.067 (3)	0.0295 (16)	-0.0015 (16)	-0.0045 (12)	0.0004 (16)
C10	0.0246 (15)	0.071 (3)	0.0291 (16)	-0.0043 (17)	-0.0092 (13)	0.0050 (17)
C11	0.0206 (14)	0.069 (3)	0.0252 (14)	0.0034 (15)	0.0018 (12)	0.0017 (16)
C12A	0.0237 (14)	0.0331 (16)	0.0161 (11)	0.0001 (12)	0.0010 (10)	0.0045 (11)
C13A	0.025 (2)	0.027 (3)	0.0135 (16)	-0.0014 (17)	0.0015 (14)	0.0048 (15)
C14A	0.022 (2)	0.037 (3)	0.0148 (18)	-0.008 (2)	-0.0009 (15)	0.0012 (19)
N2A	0.018 (3)	0.025 (4)	0.017 (2)	-0.006 (2)	-0.0037 (17)	-0.002 (2)
C15A	0.0240 (14)	0.0435 (19)	0.0205 (13)	0.0037 (13)	-0.0043 (11)	0.0085 (13)
C12B	0.0237 (14)	0.0331 (16)	0.0161 (11)	0.0001 (12)	0.0010 (10)	0.0045 (11)
C13B	0.029 (5)	0.026 (6)	0.015 (4)	-0.006 (4)	0.001 (3)	-0.002 (3)
C14B	0.034 (6)	0.041 (7)	0.008 (3)	-0.001 (5)	-0.004 (3)	0.004 (4)
N2B	0.012 (5)	0.025 (8)	0.013 (4)	-0.007 (5)	-0.002 (3)	-0.006 (5)
C15B	0.0240 (14)	0.0435 (19)	0.0205 (13)	0.0037 (13)	-0.0043 (11)	0.0085 (13)
C16	0.0200 (13)	0.0252 (14)	0.0205 (12)	0.0022 (11)	0.0002 (10)	0.0027 (11)
C17	0.0206 (12)	0.0205 (13)	0.0186 (11)	0.0004 (11)	-0.0015 (9)	-0.0024 (10)
C18	0.0201 (12)	0.0241 (14)	0.0189 (11)	0.0024 (10)	0.0008 (10)	0.0006 (10)
C19	0.0183 (12)	0.0247 (14)	0.0220 (12)	-0.0009 (10)	0.0052 (10)	-0.0008 (10)
C20	0.0187 (13)	0.0317 (17)	0.0299 (14)	0.0046 (12)	-0.0012 (11)	-0.0002 (12)
C21	0.0177 (12)	0.0297 (16)	0.0257 (13)	0.0039 (11)	-0.0028 (10)	0.0035 (12)
C22	0.0261 (15)	0.0434 (19)	0.0226 (13)	0.0030 (14)	0.0056 (11)	0.0028 (13)

Geometric parameters (Å, °)

Cu1—O1	1.916 (2)	C5—C10	1.418 (5)
Cu1—O2	1.900 (2)	C6—C7	1.416 (4)
Cu1—O4	1.928 (2)	C7—H7	0.9500
Cu1—N1A	1.959 (8)	C7—C8	1.387 (4)
Cu1—N1B	1.942 (8)	C8—C9	1.406 (5)
Cu2—O1	1.941 (2)	C9—H9	0.9500
Cu2—O4	1.930 (2)	C9—C10	1.361 (5)
Cu2—O5	1.9242 (19)	C10—H10	0.9500
Cu2—O5 ⁱ	2.641 (2)	C11—H11A	0.9800
Cu2—N2A	1.982 (9)	C11—H11B	0.9800
Cu2—N2B	1.91 (2)	C11—H11C	0.9800
Cu1—Cu2	3.0251 (5)	C12A—H12A	0.9900
Cu2—Cu2 ⁱ	3.459 (5)	C12A—H12B	0.9900
O1—C1A	1.410 (3)	C12A—C13A	1.558 (5)
O1—C1B	1.410 (3)	C13A—H13A	0.9900
O2—C6	1.302 (4)	C13A—H13B	0.9900
O3—C8	1.359 (4)	C13A—C14A	1.511 (7)
O3—C11	1.433 (4)	C14A—H14A	0.9900
O4—C12A	1.414 (3)	C14A—H14B	0.9900
O4—C12B	1.414 (3)	C14A—N2A	1.459 (10)
O5—C17	1.312 (3)	N2A—C15A	1.293 (10)
O6—C19	1.362 (3)	C15A—H15A	0.9500
O6—C22	1.429 (4)	C15A—C16	1.434 (4)
C1A—H1AA	0.9900	C12B—H12C	0.9900
C1A—H1AB	0.9900	C12B—H12D	0.9900
C1A—C2A	1.539 (7)	C12B—C13B	1.462 (10)
C2A—H2AA	0.9900	C13B—H13C	0.9900
C2A—H2AB	0.9900	C13B—H13D	0.9900
C2A—C3A	1.519 (11)	C13B—C14B	1.514 (16)
C3A—H3AA	0.9900	C14B—H14C	0.9900
C3A—H3AB	0.9900	C14B—H14D	0.9900
C3A—N1A	1.473 (10)	C14B—N2B	1.47 (2)
N1A—C4A	1.306 (9)	N2B—C15B	1.341 (18)
C4A—H4A	0.9500	C15B—H15B	0.9500
C4A—C5	1.420 (5)	C15B—C16	1.434 (4)
C1B—H1BA	0.9900	C16—C17	1.430 (4)
C1B—H1BB	0.9900	C16—C21	1.413 (4)
C1B—C2B	1.486 (8)	C17—C18	1.416 (4)
C2B—H2BA	0.9900	C18—H18	0.9500
C2B—H2BB	0.9900	C18—C19	1.385 (4)
C2B—C3B	1.497 (12)	C19—C20	1.410 (4)
C3B—H3BA	0.9900	C20—H20	0.9500
C3B—H3BB	0.9900	C20—C21	1.359 (4)
C3B—N1B	1.497 (10)	C21—H21	0.9500
N1B—C4B	1.345 (10)	C22—H22A	0.9800
C4B—H4B	0.9500	C22—H22B	0.9800

C4B—C5	1.420 (5)	C22—H22C	0.9800
C5—C6	1.430 (4)		
O1—Cu1—Cu2	38.62 (6)	O2—C6—C5	123.2 (3)
O1—Cu1—N1A	95.9 (2)	O2—C6—C7	118.9 (3)
O2—Cu1—Cu2	130.78 (6)	C7—C6—C5	117.9 (3)
O2—Cu1—N1A	94.7 (3)	C6—C7—H7	119.5
O4—Cu1—Cu2	38.38 (6)	C8—C7—C6	120.9 (3)
O4—Cu1—N1A	169.7 (3)	C8—C7—H7	119.5
O1—Cu1—N1B	95.5 (3)	O3—C8—C7	124.4 (3)
O2—Cu1—N1B	95.0 (3)	O3—C8—C9	114.5 (3)
O4—Cu1—N1B	167.0 (3)	C7—C8—C9	121.0 (3)
O2—Cu1—O1	169.33 (9)	C8—C9—H9	120.5
O2—Cu1—O4	92.70 (8)	C10—C9—C8	118.9 (3)
O1—Cu1—O4	76.63 (8)	C10—C9—H9	120.5
N1A—Cu1—Cu2	133.1 (2)	C5—C10—H10	118.9
N1B—Cu1—Cu2	134.0 (3)	C9—C10—C5	122.3 (3)
O1—Cu2—Cu1	38.03 (6)	C9—C10—H10	118.9
O1—Cu2—N2A	167.4 (2)	O3—C11—H11A	109.5
O4—Cu2—Cu1	38.35 (6)	O3—C11—H11B	109.5
O4—Cu2—N2A	95.3 (3)	O3—C11—H11C	109.5
O5—Cu2—Cu1	132.43 (6)	H11A—C11—H11B	109.5
O5—Cu2—N2A	93.8 (3)	H11A—C11—H11C	109.5
N2B—Cu2—O1	155.3 (4)	H11B—C11—H11C	109.5
N2B—Cu2—O4	91.4 (5)	O4—C12A—H12A	109.4
N2B—Cu2—O5	97.1 (5)	O4—C12A—H12B	109.4
O4—Cu2—O1	76.01 (8)	O4—C12A—C13A	111.1 (3)
O5—Cu2—O1	94.66 (8)	H12A—C12A—H12B	108.0
O5—Cu2—O4	170.65 (8)	C13A—C12A—H12A	109.4
N2A—Cu2—Cu1	133.6 (3)	C13A—C12A—H12B	109.4
N2B—Cu2—Cu1	128.2 (5)	C12A—C13A—H13A	108.9
Cu1—O1—Cu2	103.34 (9)	C12A—C13A—H13B	108.9
C1A—O1—Cu1	129.45 (18)	H13A—C13A—H13B	107.7
C1A—O1—Cu2	127.20 (18)	C14A—C13A—C12A	113.4 (4)
C1B—O1—Cu1	129.45 (18)	C14A—C13A—H13A	108.9
C1B—O1—Cu2	127.20 (18)	C14A—C13A—H13B	108.9
C6—O2—Cu1	127.56 (19)	C13A—C14A—H14A	108.9
C8—O3—C11	117.9 (3)	C13A—C14A—H14B	108.9
Cu1—O4—Cu2	103.27 (9)	H14A—C14A—H14B	107.7
C12A—O4—Cu1	127.22 (18)	N2A—C14A—C13A	113.3 (4)
C12A—O4—Cu2	128.12 (18)	N2A—C14A—H14A	108.9
C12B—O4—Cu1	127.22 (18)	N2A—C14A—H14B	108.9
C12B—O4—Cu2	128.12 (18)	C14A—N2A—Cu2	120.8 (6)
C17—O5—Cu2	125.17 (18)	C15A—N2A—Cu2	119.7 (6)
C19—O6—C22	118.5 (2)	C15A—N2A—C14A	118.2 (7)
O1—C1A—H1AA	109.3	N2A—C15A—H15A	116.5
O1—C1A—H1AB	109.3	N2A—C15A—C16	126.9 (5)
O1—C1A—C2A	111.5 (3)	C16—C15A—H15A	116.5

H1AA—C1A—H1AB	108.0	O4—C12B—H12C	109.3
C2A—C1A—H1AA	109.3	O4—C12B—H12D	109.3
C2A—C1A—H1AB	109.3	O4—C12B—C13B	111.6 (4)
C1A—C2A—H2AA	109.3	H12C—C12B—H12D	108.0
C1A—C2A—H2AB	109.3	C13B—C12B—H12C	109.3
H2AA—C2A—H2AB	108.0	C13B—C12B—H12D	109.3
C3A—C2A—C1A	111.6 (6)	C12B—C13B—H13C	109.8
C3A—C2A—H2AA	109.3	C12B—C13B—H13D	109.8
C3A—C2A—H2AB	109.3	C12B—C13B—C14B	109.2 (8)
C2A—C3A—H3AA	109.2	H13C—C13B—H13D	108.3
C2A—C3A—H3AB	109.2	C14B—C13B—H13C	109.8
H3AA—C3A—H3AB	107.9	C14B—C13B—H13D	109.8
N1A—C3A—C2A	112.2 (6)	C13B—C14B—H14C	109.6
N1A—C3A—H3AA	109.2	C13B—C14B—H14D	109.6
N1A—C3A—H3AB	109.2	H14C—C14B—H14D	108.1
C3A—N1A—Cu1	119.6 (6)	N2B—C14B—C13B	110.4 (11)
C4A—N1A—Cu1	120.5 (5)	N2B—C14B—H14C	109.6
C4A—N1A—C3A	117.8 (7)	N2B—C14B—H14D	109.6
N1A—C4A—H4A	116.7	C14B—N2B—Cu2	122.8 (12)
N1A—C4A—C5	126.5 (5)	C15B—N2B—Cu2	121.7 (12)
C5—C4A—H4A	116.7	C15B—N2B—C14B	114.8 (14)
O1—C1B—H1BA	109.2	N2B—C15B—H15B	117.2
O1—C1B—H1BB	109.2	N2B—C15B—C16	125.6 (8)
O1—C1B—C2B	111.9 (3)	C16—C15B—H15B	117.2
H1BA—C1B—H1BB	107.9	C17—C16—C15A	123.4 (3)
C2B—C1B—H1BA	109.2	C17—C16—C15B	123.4 (3)
C2B—C1B—H1BB	109.2	C21—C16—C15A	116.9 (3)
C1B—C2B—H2BA	108.9	C21—C16—C15B	116.9 (3)
C1B—C2B—H2BB	108.9	C21—C16—C17	119.3 (3)
C1B—C2B—C3B	113.5 (7)	O5—C17—C16	123.6 (3)
H2BA—C2B—H2BB	107.7	O5—C17—C18	118.7 (2)
C3B—C2B—H2BA	108.9	C18—C17—C16	117.7 (3)
C3B—C2B—H2BB	108.9	C17—C18—H18	119.7
C2B—C3B—H3BA	109.4	C19—C18—C17	120.7 (3)
C2B—C3B—H3BB	109.4	C19—C18—H18	119.7
H3BA—C3B—H3BB	108.0	O6—C19—C18	124.9 (3)
N1B—C3B—C2B	111.3 (6)	O6—C19—C20	113.7 (3)
N1B—C3B—H3BA	109.4	C18—C19—C20	121.4 (3)
N1B—C3B—H3BB	109.4	C19—C20—H20	120.8
C3B—N1B—Cu1	120.4 (6)	C21—C20—C19	118.5 (3)
C4B—N1B—Cu1	119.4 (5)	C21—C20—H20	120.8
C4B—N1B—C3B	118.6 (6)	C16—C21—H21	118.8
N1B—C4B—H4B	116.9	C20—C21—C16	122.4 (3)
N1B—C4B—C5	126.3 (5)	C20—C21—H21	118.8
C5—C4B—H4B	116.9	O6—C22—H22A	109.5
C4A—C5—C6	123.2 (3)	O6—C22—H22B	109.5
C4B—C5—C6	123.2 (3)	O6—C22—H22C	109.5
C10—C5—C4A	117.9 (3)	H22A—C22—H22B	109.5

C10—C5—C4B	117.9 (3)	H22A—C22—H22C	109.5
C10—C5—C6	118.9 (3)	H22B—C22—H22C	109.5

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

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
C3B—H3BB...O2 ⁱⁱ	0.99	2.48	3.385 (12)	152
C11—H11B...O6 ⁱⁱⁱ	0.98	2.56	3.359 (4)	138
C12A—H12A...O2	0.99	2.51	2.979 (4)	109
C21—H21...O6 ^{iv}	0.95	2.54	3.279 (4)	135
C22—H22C...O2 ⁱ	0.98	2.52	3.362 (4)	144

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