# Crystal structures of two CuII compounds: catena-poly[[chloridocopper(II)]-μ-N-[ethoxy(pyridin-2-yl)methylidene]-N′-[oxido(pyridin-3-yl)methylidene]hydrazine-$\kappa^4N,N',O:N''$] and di-μ-chlorido-1:4κ^2Cl:Cl-2:3κ^2Cl:Cl-dichlorido-2κCl,4κCl-bis[μ3-ethoxy(pyridin-2-yl)methanolato-1:2:3κ^3O:N,O:O;1:3:4κ^3O:O:N,O]bis[μ2-ethoxy(pyridin-2-yl)methanolato-1:2κ^3N,O:O;3:4κ^3N,O:O]tetracopper(II)

Ousmane Sall,[a] **Farba Bouyagui Tamboura,**[b] **Adama Sy,**[a] **Aliou Hamady Barry,**[c] **Elhadj Ibrahima Thiam,**[a] **Mohamed Gaye**[a]* **and Javier Ellena**[d]

[a]Département de Chimie, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Senegal, [b]Département de Chimie, Faculté des Sciences et Techniques, Université Alioune Diop, Bambey, Senegal, [c]Département de Chimie, Faculté des Sciences et Techniques, Université de Nouakchott, Nouakchott, Mauritania, and [d]Instituto de Física de São Carlos, Universidade de São Paulo, CP 369, 13.560-970 – São Carlos, SP, Brazil. *Correspondence e-mail: mlgayeastou@yahoo.fr

Two CuII complexes [Cu(C$_{14}$H$_{13}$N$_4$O$_2$)Cl]$_n$, **I**, and [Cu$_4$(C$_8$H$_{10}$NO$_2$)$_4$Cl$_4$]$_n$, **II**, have been synthesized. In the structure of the mononuclear complex **I**, each ligand is coordinated to two metal centers. The basal plane around the CuII cation is formed by one chloride anion, one oxygen atom, one imino and one pyridine nitrogen atom. The apical position of the distorted square-pyramidal geometry is occupied by a pyridine nitrogen atom from a neighbouring unit, leading to infinite one-dimensional polymeric chains along the *b*-axis direction. Each chain is connected to adjacent chains by intermolecular C—H···O and C—H···Cl interactions, leading to a three-dimensional network structure. The tetranuclear complex **II** lies about a crystallographic inversion centre and has one core in which two CuII metal centers are mutually interconnected *via* two enolato oxygen atoms while the other two CuII cations are linked by a chloride anion and an enolato oxygen. An open-cube structure is generated in which the two open-cube units, with seven vertices each, share a side composed of two CuII ions bridged by two enolato oxygen atoms acting in a μ_3-mode. The CuII atoms in each of the two CuO$_3$NCl units are connected by one μ_2-O and two μ_3-O atoms from deprotonated hydroxyl groups and one chloride anion to the three other CuII centres. Each of the pentacoordinated CuII cations has a distorted NO$_3$Cl square-pyramidal environment. The CuII atoms in each of the two CuO$_2$NCl$_2$ units are connected by μ_2-O and μ_3-O atoms from deprotonated alcohol hydroxy groups and one chloride anion to two other CuII ions. Each of the pentacoordinated CuII cations has a distorted NO$_2$Cl$_2$ square-pyramidal environment. In the crystal, a series of intramolecular C—H···O and C—H···Cl hydrogen bonds are observed in each tetranuclear monomeric unit, which is connected to four tetranuclear monomeric units by intermolecular C—H···O hydrogen bonds, thus forming a planar two-dimensional structure in the ($\bar{1}$01) plane.
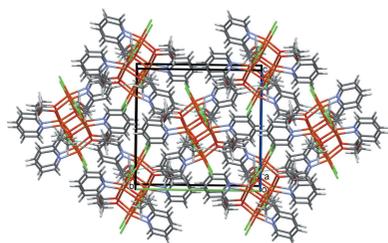
1. Chemical context

Picolinic acid esters (González-Duarte *et al.*, 1996, 1998; Hay & Clark, 1979; Luo *et al.*, 2002; Paul *et al.*, 1974) as well as

nicotinic acid hydrazide (Bharati *et al.*, 2015; Galić *et al.*, 2011; Nakanishi & Sato, 2017) are widely used in coordination chemistry for their ability to bind metals through the amino and/or the ester functional groups (Hay & Clark, 1979). Complexes formed by ethyl picolinate (EP) with various divalent metal thiocyanates (Paul *et al.*, 1975), chlorides (González-Duarte *et al.*, 1996) and perchlorates (Natun *et al.*, 1995) have been prepared and characterized. Several modes of coordination are observed, depending on the conformation of the molecule. Ethyl picolinate acts as a bidentate ligand coordinating through the ring nitrogen and the carbonyl oxygen. The carboxylic ester function can coordinate in several ways, while the pyridine nitrogen atom can also coordinate in a unidentate fashion. The nicotinic acid hydrazide can coordinate through the hydrazino moiety as well as through the pyridine nitrogen atom (Lumme *et al.*, 1984; Shahverdizadeh *et al.*, 2011a,b). These facts make these ligands and their analogues very attractive and they have been used in several studies. Many polynuclear complexes of transition metals with various structures can be generated, depending on the disposition of the metal ions and the donor sites (N or O). Trimers (Zhang *et al.*, 2009), square shapes (Aouaidjia *et al.*, 2017), cyclic forms (Acevedo-Chávez *et al.*, 2002) and cubans (Shit *et al.*, 2013) have been reported that have potential applications in the field of magnetism (Shit *et al.*, 2013), catalysis (Okeke *et al.*, 2018) and biomimetic synthesis (Wu *et al.*, 2004). By extension, the introduction of an ethoxy-carbonyl group in the *ortho* position of the pyridine gives a ligand that can have a similar behavior to α-amino acid esters. It has been shown that the presence of metal ions promotes the hydrolysis of the ester function of the picolinic ester (Xue *et al.*, 2016). A condensation can then occur between nicotinic acid hydrazide and the hydrolysed picolinic ester, to generate two organic ligands with a large number of coordination sites *in situ*, in the presence of copper(II) ions. These ligands then coordinate to the copper(II) cations to yield the two complexes that are reported here.

I

II
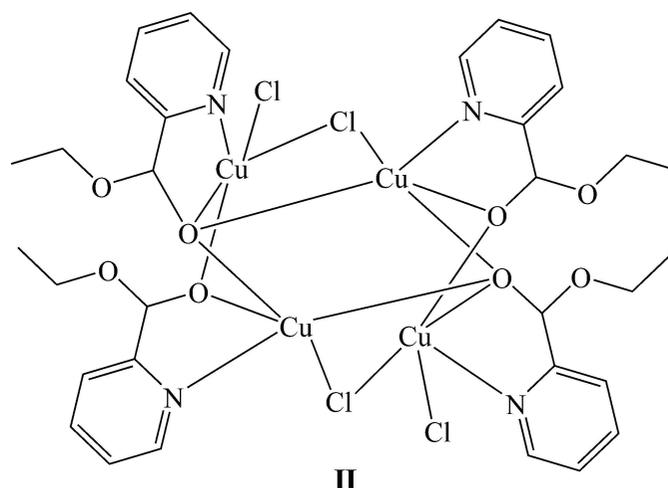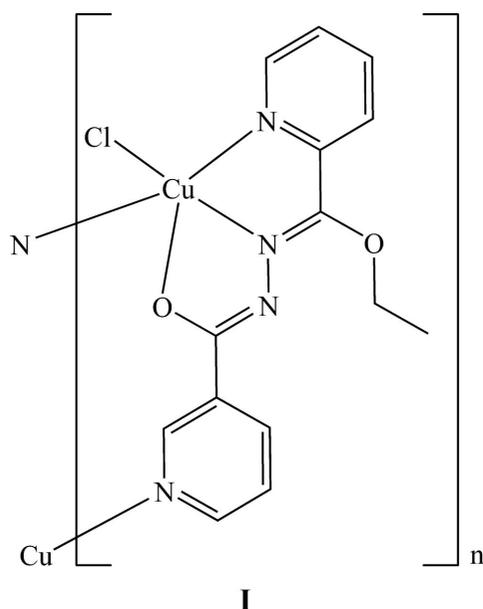
2. Structural commentary

The condensation reaction of pyridine-2-carbaldehyde and nicotinic acid hydrazide in ethanol in the presence of copper acetate yields two different complexes whose ligands are respectively a hemiacetal [ethoxy(pyridine-2-yl)methanol] and a condensation product [({1-[1-ethoxy-1-(pyridin-2-yl)-methylene]}-2-(oxonicotinyl))hydrazine]. It has been shown (Papaefstathiou *et al.*, 2000; Boudalis *et al.*, 2008; Mautner *et al.*, 2010) that the presence of a metal can induce a nucleophilic attack of the ethanol molecule on the carbonyl group to give a hemiacetal. This reaction can also occur when a fragment such as a pyridyl nitrogen atom is present that is capable of inducing the polarization of the carbonyl function (Papaefstathiou *et al.*, 2000). It is under these conditions that the complexes **I** and **II** were formed *in situ*.

In the crystal structure of the coordination polymer $[CuCl(C_{14}H_{13}N_4O_2)]_n$, **I**, the repeat unit of which is shown in (Fig. 1), the Cu^{II} center is pentacoordinated by one chloride atom, one enolate oxygen atom of the mono deprotonated organic ligand, one pyridine, one imino nitrogen atom, and by a pyridine nitrogen atom of a ligand from an adjacent complex
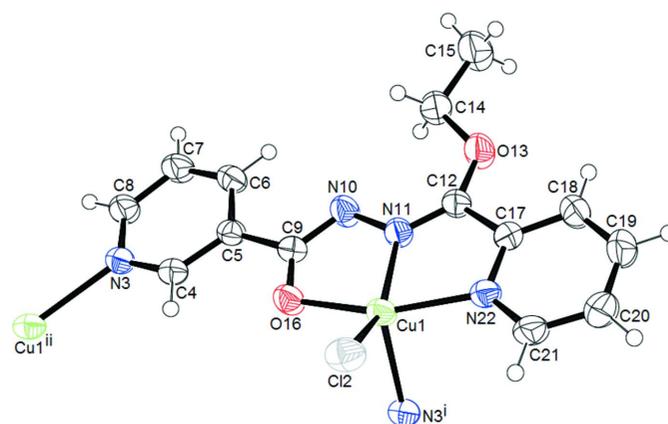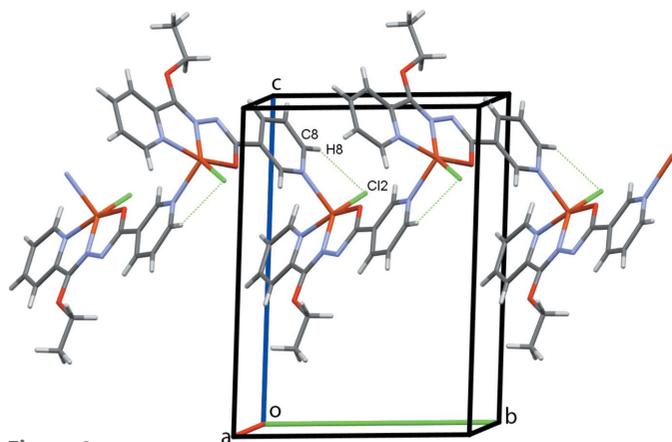

Figure 1
An *ORTEP* view of the repeat unit of the coordination polymer **I**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) $\frac{3}{2} - x$, $-\frac{1}{2} + y$, $\frac{3}{2} - z$; (ii) $\frac{3}{2} - x$, $\frac{1}{2} + y$, $\frac{3}{2} - z$.
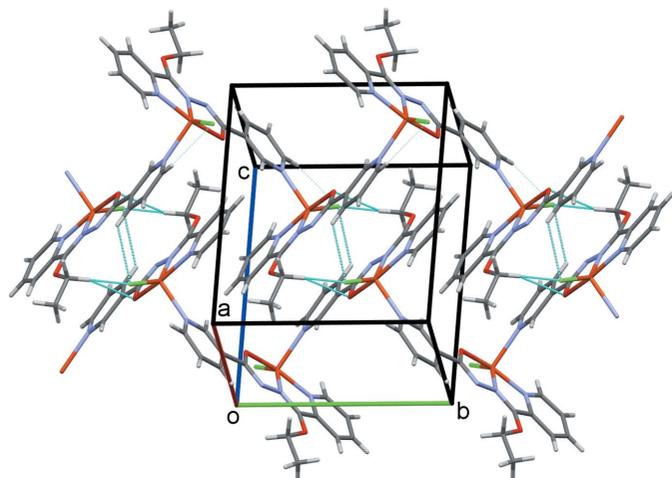
Table 1
Hydrogen-bond geometry (Å, °) for **I**.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C8—H8⋯Cl2[ii]	0.93	2.71	3.354 (2)	128
C20—H20⋯Cl2[iii]	0.93	2.93	3.527 (3)	124
C14—H14B⋯Cl2[iv]	0.97	2.83	3.534 (3)	130
C14—H14B⋯O16[iv]	0.97	2.56	3.441 (3)	151

Symmetry codes: (ii) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{3}{2}$; (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$; (iv) $-x + 1, -y + 1, -z + 1$.

Table 2
Selected geometric parameters (Å, °) for **I**.

Cu1—N11	1.9437 (17)	Cu1—N3[i]	2.2009 (17)
Cu1—O16	1.9808 (15)	Cu1—Cl2	2.2707 (6)
Cu1—N22	2.0444 (17)		
N11—Cu1—O16	79.11 (7)	O16—Cu1—N3[i]	96.39 (7)
N11—Cu1—N22	79.40 (7)	N22—Cu1—N3[i]	92.70 (7)
O16—Cu1—N22	158.51 (7)	N11—Cu1—Cl2	146.17 (6)
N11—Cu1—N3[i]	116.09 (7)	O16—Cu1—Cl2	100.05 (5)

Symmetry code: (i) $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

molecule. This latter contact bridges the Cu^{II} cations to form a one-dimensional coordination polymer along the *b*-axis direction (Fig. 2). Intermolecular C—H⋯O and C—H⋯Cl hydrogen bonds, (Table 1), link the polymers into a three-dimensional network (Fig. 3). The coordination environment can be best described as strongly distorted square pyramidal. The basal plane around the Cu^{II} ion is formed by the Cl2 anion with a Cu1—Cl2 distance of 2.2707 (6) Å, an O16 atom with a Cu1—O16 distance of 1.9808 (15) Å and the N11 and N22 atoms from the same ligand with a Cu—N distances of 1.9437 (17) and 2.0444 (17) Å (Table 2). These bond lengths

Figure 2
The polymer expansion of complex **I**, showing an infinite chain propagating along the *b*-axis direction. In this and subsequent figures, hydrogen bonds are drawn as dashed lines.
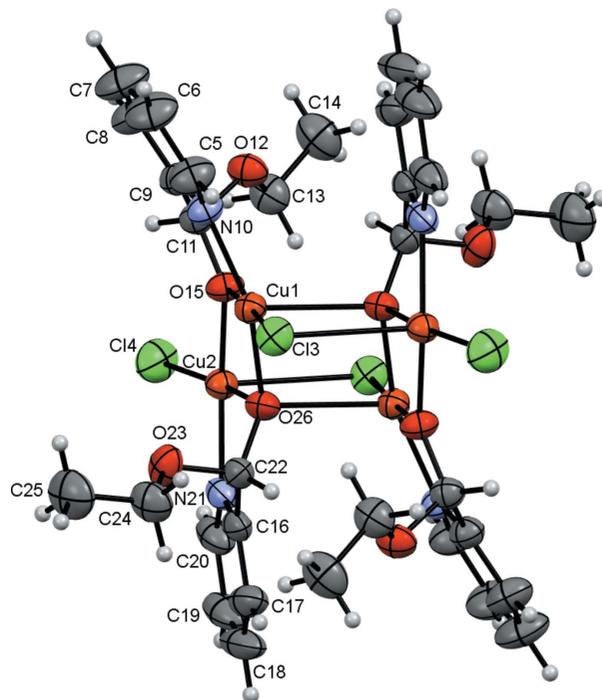

Figure 3
A view of the crystal packing of complex **I**.

are similar to the values found in related complexes (Datta *et al.*, 2011*a*,*b*; Da Silva *et al.*, 2013). The apical position of the distorted square pyramid is occupied by one pyridine N3 atom of a neighbouring unit with a Cu—N distance of 2.2009 (17) Å. This distance is shorter than that found in similar compound (Roztocki *et al.*, 2015). The ligand, which acts in a tridentate fashion, forms two five-membered rings upon coordination with the Cu^{II} centre: OCNNCu and NCCNCu, with the N11 atom common to both. The five-membered chelate rings impose large distortions on the ideal angles of a regular square pyramid, with bite angles in the range 79.11 (7)–79.40 (7)°, which are slightly smaller than those found in similar compounds (Roztocki *et al.*, 2015). The *transoid* angles in the basal plane O16—Cu1—N22 and N11—Cu1—Cl2 deviate severely from linearity with values of 158.51 (7)° and 146.17 (6)° (Table 2). These two largest angles around the Cu^{II} ion give a τ parameter of 0.206, which is indicative of a distorted square-pyramidal environment around the Cu^{II} ion (Addison *et al.*, 1984).
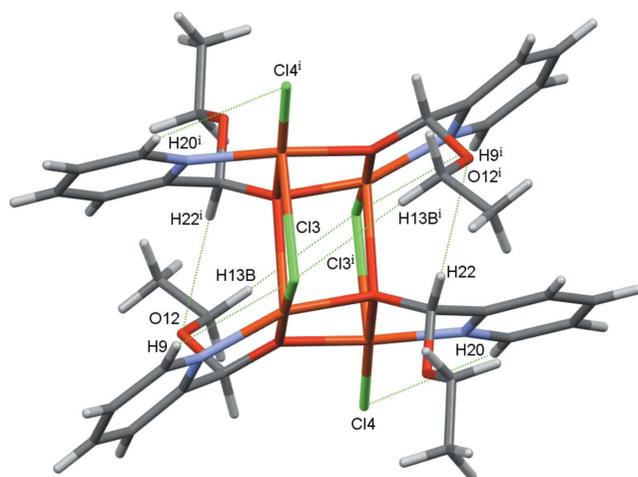

Figure 4
The structure of **II** with ellipsoids drawn at the 50% probability level. Unlabelled atoms are generated by the symmetry operation $1 - x, 1 - y, 1 - z$.

Table 3
Hydrogen-bond geometry (Å, °) for **II**.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C9—H9$\cdots$Cl3	0.93	2.78	3.333 (3)	119
C20—H20$\cdots$Cl4	0.93	2.90	3.393 (3)	115
C13—H13$B\cdots$Cl3^i	0.97	2.82	3.787 (3)	173
C22—H22$\cdots$O12^i	0.98	2.66	3.578 (3)	156
C18—H18$\cdots$O23^{ii}	0.93	2.44	3.367 (3)	177

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$.

Table 4
Selected geometric parameters (Å, °) for **II**.

Cu1—O15	1.9170 (13)	Cu2—O15	1.9324 (13)
Cu1—O26	1.9684 (13)	Cu2—O26	1.9707 (14)
Cu1—N10	1.9886 (17)	Cu2—N21	1.9827 (17)
Cu1—Cl3	2.2181 (6)	Cu2—Cl4	2.1987 (7)
Cu1—O26^i	2.4280 (14)		
O26—Cu1—N10	156.02 (7)	O15—Cu2—N21	157.61 (7)
O15—Cu1—Cl3	176.95 (5)	O26—Cu2—Cl4	170.05 (5)

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

In **II**, the tetranuclear open-cube complex lies about a crystallographic inversion centre, with each mono deprotonated ethoxy(pyridin-2-yl)methanolate ligand coordinating to each Cu atom through its imine nitrogen atom and its alcoholate oxygen atom, forming five-membered chelate rings (Fig. 4). The molecule also forms intramolecular hydrogen bonds between a terminal chloride atom and an aromatic hydrogen atom (C20—H20$\cdots$Cl4) and between a bridging chloride and both an aromatic and a methylene hydrogen atom (C9—H9$\cdots$Cl3 and C13—H13$B\cdots$Cl3^i). Intramolecular C—H$\cdots$O contacts are also found (Table 3, Fig. 5). There are two discrete Cu^{II} environments, Cu1NO$_3$Cl and Cu2NO$_2$Cl$_2$. Two molecules of the ligand act as bridges between two neighbouring Cu atoms through their alcoholate atoms in a μ_2 mode while the other two ligand molecules bridge in a μ_3 fashion. The structure consists of two Cu$_3$O$_3$Cl cores. The first core comprises Cu1, Cu1^i, Cu2 atoms μ_3-bridging atoms O26, O26^i, a μ_2-bridging O15 atom and a μ_2-bridging Cl3^i ion [symmetry code: (i) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$]. The second comprises Cu1, Cu1^i, Cu2^i atoms, μ_3-bridging atoms O26, O26^i, a μ_2-bridging O15^i atom and a μ_2-bridging Cl3 ion. The result is a is a distorted open-cube, defined as a distorted cube missing one corner. This can be seen by considering that the range of Cu—O—Cu angles is [99.76 (6)–102.98 (6)°] and the Cu1—Cl3—Cu2^i angle is 84.39 (2)°. These differ extensively from the 90° angles of an ideal cube. The two Cu$_3$O$_3$Cl open-cubes are joined by a perfectly rectangular side defined by the Cu1, O26, and Cu^i, O26^i atoms. The values of the two different

lengths of the edges of the rectangular sides are 2.4280 (14) and 1.9684 (13) Å. The other faces of the two open-cubes are irregular with different distances *i.e.* Cu1—O26^i = 2.4280 (14) Å, Cu2—O26 = 1.9707 (14) Å, Cu1—Cl3 = 2.2181 (6) Å and Cu2—Cl3 = 2.8134 (6) Å. The Cu1 (Cu1^i) atoms in each of the two CuO$_3$NCl units are connected by one μ_2-O and two μ_3-O atoms from the deprotonated hydroxyl groups and one chloride ion to three other Cu^{II} cations. In the CuO$_2$NCl$_2$ units, the Cu2 (Cu2^i) atoms are linked to one μ_2-O and one μ_3-O atoms from a deprotonated hydroxyl groups and one chloride ion to two other Cu^{II} cations with Cu1—Cu2 and Cu1—Cu2^i distances of approximately 3.012 and 3.408 Å, respectively. These are in good agreement with literature values (Qin *et al.*, 2014). The distances of the oxygen atoms in the μ_3- and μ_2-bridging positions to the copper atoms are assymmetrical with Cu1—O26^i, Cu1—O26 and Cu2—O26 distances of 2.4280 (14), 1.9684 (13), 1.9707 (14) Å, respectively, while Cu1—O15 and Cu2—O15 are 1.9170 (13) and 1.9324 (13) Å, respectively (Table 4). These distances agree with those in related structures (Lazarou *et al.*, 2018; Tabassum *et al.*, 2017). The environment of both Cu^{II} cations is again best described as distorted square pyramidal. The largest angles around Cu1 and Cu2 are O15—Cu1—Cl3 [176.95 (5)°], O26—Cu1—N10 [156.02 (7)°], O26—Cu2—Cl4 [170.05 (5)°] and O15—Cu2—N21 [157.61 (7)°] (Table 2). The Addison τ parameters are 0.348 for Cu1 and 0.207 for Cu2 (Addison *et al.*, 1984), indicating considerable distortion. The basal plane around each of the Cu1 and Cu2 atoms is formed by one chloride anion, one pyridine nitrogen atom and two enolate oxygen atoms while the apical positions are occupied by an enolate oxygen atom for Cu1 and a chloride anion for Cu2. The copper–halogen distances Cu1—Cl3 and Cu2—Cl3 of 2.2181 (6) and 2.8134 (6) Å, respectively, agree with those for a chloride ion in bridging position (Choubey *et al.*, 2015). The Cu2—Cl4 distance of 2.1987 (7) Å is indicative of a unidentate terminal chloride ion (Kalinowska-Lis *et al.*, 2011). The four copper atoms occupy the vertices of a parallelogram with angles Cu1—Cu2—Cu1^i and Cu2—Cu1—Cu2^i of approximately 63.59° and 116.41°. The sum of the angle in the parallelogram is 360° and the lengths of the two diagonals, Cu1—Cu1^i and Cu2—Cu2^i, are 3.399 and 5.461 Å respectively and are comparable to the values found in a similar complex reported in the literature (Monfared *et al.*, 2009). All the Cu—O—Cu angles in the open-cube are in the range 99.76 (6)—102.96 (6)° and the Cu1—Cl3—Cu2^i angles of 84.39 (2)° are different from those of ideal cube. This bridging angle is also

Figure 5
Intramolecular hydrogen bonds in the structure of **II**. Symmetry code: (i) $1-x, 1-y, 1-z$.
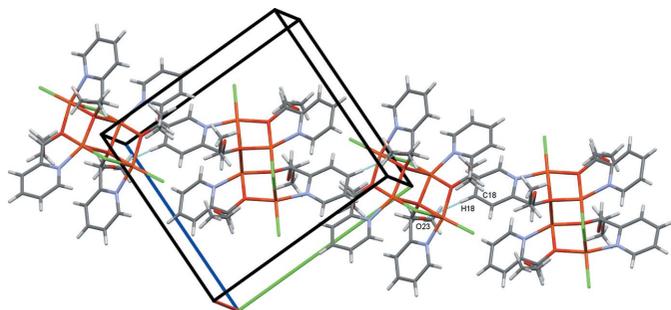
Figure 6
Chains of molecules of **II** along the *bc* diagonal.

smaller than those reported for similar complexes (Banerjee *et al.*, 2013; Swank *et al.*, 1979) but they are nearly equal to those in the complex [Cu₂(qsalBr)₂Cl₂](DMF) where qsalBr = 8-aminoquinoline with 5-bromo-salicylaldehyde (Liu *et al.*, 2009). An immediate consequence is a small Cu1···Cu2 separation [3.4082 (4) Å] compared to those found in another dichlorido-bridged copper (II) complex (Banerjee *et al.*, 2013).

3. Supramolecular features

The crystal structure of **I** is determined by a coordination synthon in which each ligand is coordinated to two metal centers, giving rise to infinite one-dimensional polymeric chains along the *b*-axis direction (Fig. 2). Adjacent chains are linked to one another by intermolecular C—H···O and C—H···Cl hydrogen bonds (Table 1), leading to a three-dimensional network structure (Fig. 3). In the crystal structure of **II**, C18—H18···O23 hydrogen bonds link the complex molecules into chains along the *bc* diagonal (Fig. 6). Additional C18—H18···O23 contacts generate two-dimensional sheets of molecules also along the *bc* diagonal (Fig. 7). π–π-stacking interactions occur between the two unique N10/C5–C9 and N21/C16–C20 pyridine rings with a centroid-to-centroid separation of 3.6800 (16) Å (symmetry operation $\frac{3}{2} - x, -\frac{1}{2} + y, \frac{3}{2} - z$). These contacts combine with the C—H···O hydrogen bonds to stack the molecules in a three-dimensional network along the *a*-axis direction (Fig. 8).
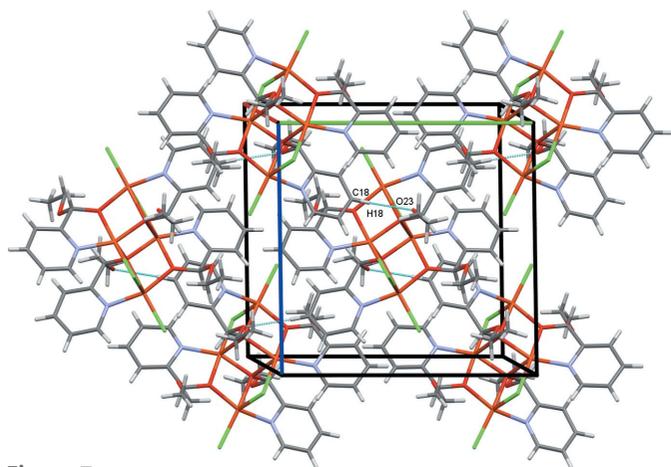

Figure 7
Two-dimensional sheet of molecules of **II** along the *bc* diagonal.
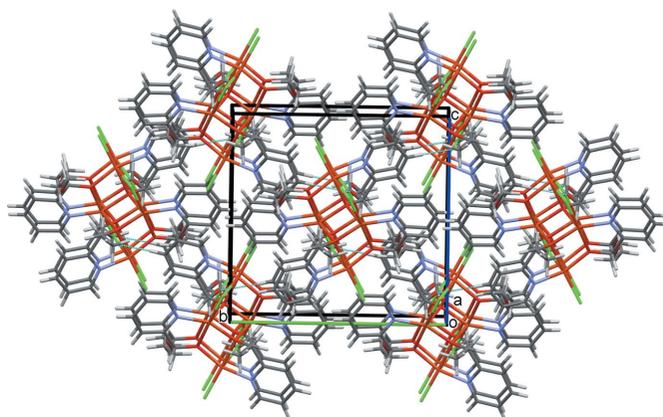

Figure 8
A view along the *a* axis of the crystal packing of **II**.

4. Database survey

A search of the CSD database (Version 5.38; Groom *et al.*, 2016) for the structures **I** and **II** using the fragment [1-ethoxy-1-(pyridin-2-yl)]methylenehydrazine yielded no hits, indicating that compound **I** is reasonably unique. However, a search for ethoxy(pyridin-2-yl)methanolate, the ligand found in **II** gave ten hits, although none of these was closely related to **II**. The matches included the Cu^II complexes HAXBEN (Baggio *et al.*, 1993), HUXDOU (Mautner *et al.*, 2010), TOGLAC (Deveson *et al.*, 1996) and VIMCAX (Efthymiou *et al.*, 2013) that involve the ethoxydipyridin-2-ylmethanol ligand, which differs from the ligand reported here by substitution of the hydrogen atom on the carbon of the alcohol unit by a pyridine ring. A similar substitution with phenyl or by a 2-hydroxypyridine ring leads to the Cu^II complexes JUYYEJ (Kitos *et al.*, 2016) and COHQIA (Boudalis *et al.*, 2008), respectively. The three related hits QANPUQ, QANQAX and QANQEB (Papaefstathiou *et al.*, 2000) are complexes of the symmetrical ligand 1,2-diethoxy-1,2-di(pyridin-2-yl)ethane-1,2-diol, which is a dimer of the ligand found in **II**. KAJKAJ (Georgopoulou *et al.*, 2010) involves a Cu complex of a ligand that is the least similar to that found in **II**. The ligand used, 2,6-bis[1-ethoxy-1-hydroxy-1-(pyridin-2-yl)methyl]pyridin, has a central pyridine ring that is substituted by 1-ethoxy-1-hydroxy-1-(pyridin-2-yl)methyl fragments in the 2- and 6-positions.

5. Synthesis and crystallization

To a solution of 2-pyridine carbaldehyde (0.1070 g, 1 mmol) in 30 ml of ethanol was added a solution of nicotinic hydrazide (0.1371 g, 1 mmol) in 10 ml of ethanol. The mixture was stirred for 5 min. A solution of Cu(OOCH₃)₂·H₂O (0.1996 g, 1 mmol) in 5 ml of ethanol was added at room temperature. The initial yellow solution immediately turned deep blue and was stirred under reflux for 2 h. The mixture was filtered and the solution evaporated to near dryness. The solid was isolated by filtration and recrystallized from a minimum of ethanol. On standing for five days, two types of crystals suitable for X-ray analysis were formed, light-yellow blocks of **I** and light-green plates of **II**.

Table 5
Experimental details.

	I	II
Crystal data		
Chemical formula	$[Cu(C_{14}H_{13}N_4O_2)Cl]$	$[Cu_4(C_8H_{10}NO_2)_4Cl_4]$
M_r	368.27	1004.68
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	293	293
a, b, c (Å)	11.1472 (9), 9.9573 (6), 14.4904 (11)	11.5150 (4), 13.1051 (5), 12.8066 (6)
β (°)	111.595 (9)	100.066 (4)
V (Å^3)	1495.5 (2)	1902.83 (13)
Z	4	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	1.65	2.54
Crystal size (mm)	$0.3 \times 0.2 \times 0.1$	$0.22 \times 0.2 \times 0.05$
Data collection		
Diffractometer	Rigaku Oxford Diffraction XtaLAB Mini (ROW)	Rigaku Oxford Diffraction XtaLAB Mini (ROW)
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2017)	Multi-scan (*CrysAlis PRO*; Rigaku OD, 2017)
T_{min}, T_{max}	0.967, 1.000	0.727, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	8476, 5569, 3671	31609, 7541, 4946
R_{int}	0.021	0.035
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.797	0.797
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.041, 0.109, 1.02	0.035, 0.093, 1.02
No. of reflections	5569	7540
No. of parameters	200	237
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.40, −0.42	0.46, −0.43

Computer programs: *CrysAlis PRO* (Rigaku OD, 2017), *SHELXT2018/3* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008).

For **I**: analysis calculated: $C_{14}H_{13}N_4ClO_2Cu$: C, 45.46; H, 3.56; N, 15.21; Cl; 9.63. Found: C, 45.44; H, 3.53; N, 15.16; Cl; 9.60. IR (ν, cm^{-1}): 2982, 1628, 1583, 1423, 1343, 1245, 941, 816, 630. For **II:** analysis calculated: $C_{16}H_{20}N_2Cl_2O_4Cu_2$: C, 38.26; H, 4.01; N, 5.58; Cl; 14.12. Found: C, 38.23; H, 3.98; N, 5.55; Cl; 14.08. IR (ν, cm^{-1}): 2982, 1585, 1423, 1243, 1145, 940, 812.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. All H atoms were refined using a riding model with d(C—H) = 0.93 Å for aromatic, d(C—H) = 0.97 Å for methylene and d(C—H) = 0.98 Å for methine H atoms with U_{iso}(H) = $1.2U_{eq}$(C) and d(C—H) = 0.96 Å and U_{iso}(H) = $1.5U_{eq}$(C) for methyl H atoms. One reflection with $F_o \lll F_c$ that was likely to have been affected by the beamstop was omitted from the final refinement cycles.

Acknowledgements

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supporting information

Crystal structures of two Cu^{II} compounds: *catena*-poly[[chloridocopper(II)]-*μ*-*N*-[ethoxy(pyridin-2-yl)methylidene]-*N′*-[oxido(pyridin-3-yl)methylidene]hydrazine-*κ*^{4}*N,N′,O:N″*] and di-*μ*-chlorido-1:4*κ*^{2}*Cl:Cl*-2:3*κ*^{2}*Cl:Cl*-dichlorido-2*κCl*,4*κCl*-bis[*μ*$_3$-ethoxy(pyridin-2-yl)methanolato-1:2:3*κ*^{3}*O:N,O:O*;1:3:4*κ*^{3}*O:O:N,O*]bis[*μ*$_2$-ethoxy(pyridin-2-yl)methanolato-1:2*κ*^{3}*N,O:O*;3:4*κ*^{3}*N,O:O*]tetracopper(II)

Ousmane Sall, Farba Bouyagui Tamboura, Adama Sy, Aliou Hamady Barry, Elhadj Ibrahima Thiam, Mohamed Gaye and Javier Ellena

Computing details

For both structures, data collection: *CrysAlis PRO* (Rigaku OD, 2017); cell refinement: *CrysAlis PRO* (Rigaku OD, 2017); data reduction: *CrysAlis PRO* (Rigaku OD, 2017); program(s) used to solve structure: *SHELXT2018/3* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b). Molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009) and *Mercury* (Macrae *et al.*, 2008) for (I); *OLEX2* (Dolomanov *et al.*, 2009) for (II). For both structures, software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

catena-Poly[[chloridocopper(II)]-*μ*-N-[ethoxy(pyridin-2-yl)methylidene]-*N′*-[oxido(pyridin-3-yl)methylidene]hydrazine-*κ*^{4}N,N′,O:N″] (I)

Crystal data

[Cu(C$_{14}$H$_{13}$N$_4$O$_2$)Cl]	*F*(000) = 748
M$_r$ = 368.27	*D$_x$* = 1.636 Mg m^{-3}
Monoclinic, *P*2$_1$/*n*	Mo *Kα* radiation, *λ* = 0.71073 Å
a = 11.1472 (9) Å	Cell parameters from 2449 reflections
b = 9.9573 (6) Å	*θ* = 3.5–28.8°
c = 14.4904 (11) Å	*μ* = 1.65 mm^{-1}
β = 111.595 (9)°	*T* = 293 K
V = 1495.5 (2) Å^3	Block, clear light yellow
Z = 4	0.3 × 0.2 × 0.1 mm

Data collection

Rigaku Oxford Diffraction XtaLAB Mini (ROW) diffractometer	Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2017)
	T$_{min}$ = 0.967, *T*$_{max}$ = 1.000
Radiation source: fine-focus sealed X-ray tube, Rigaku (Mo) X-ray Source	8476 measured reflections
	5569 independent reflections
Graphite monochromator	3671 reflections with *I* > 2*σ*(*I*)
ω scans	*R*$_{int}$ = 0.021

$\theta_{max} = 34.5°$, $\theta_{min} = 2.8°$

$h = -5 \rightarrow 17$

$k = -14 \rightarrow 12$

$l = -21 \rightarrow 20$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.041$	$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 0.1803P]$
$wR(F^2) = 0.109$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
5569 reflections	$\Delta\rho_{max} = 0.40$ e Å^{-3}
200 parameters	$\Delta\rho_{min} = -0.41$ e Å^{-3}
0 restraints	

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.47474 (2)	0.32922 (3)	0.65558 (2)	0.03498 (9)
Cl2	0.34273 (6)	0.44640 (6)	0.71389 (4)	0.04555 (14)
O16	0.61729 (15)	0.46011 (15)	0.68180 (11)	0.0409 (3)
N11	0.52597 (16)	0.29579 (17)	0.54312 (13)	0.0351 (4)
O13	0.47178 (19)	0.17375 (17)	0.39271 (13)	0.0548 (5)
N3	0.93076 (16)	0.70447 (17)	0.71207 (13)	0.0347 (4)
N22	0.34839 (17)	0.17999 (17)	0.58487 (13)	0.0360 (4)
N10	0.62800 (18)	0.3710 (2)	0.53850 (14)	0.0408 (4)
C5	0.77400 (18)	0.5424 (2)	0.62038 (14)	0.0316 (4)
C9	0.66495 (18)	0.4523 (2)	0.61446 (14)	0.0325 (4)
C17	0.3576 (2)	0.1438 (2)	0.49841 (15)	0.0350 (4)
C4	0.82919 (19)	0.6265 (2)	0.70085 (15)	0.0337 (4)
H4	0.793616	0.628682	0.749681	0.040*
C12	0.4615 (2)	0.2121 (2)	0.47694 (15)	0.0356 (4)
C6	0.8249 (2)	0.5432 (2)	0.54629 (16)	0.0392 (4)
H6	0.789474	0.489398	0.490347	0.047*
C8	0.9789 (2)	0.7018 (2)	0.64056 (16)	0.0414 (5)
H8	1.050395	0.754901	0.647646	0.050*
C7	0.9278 (2)	0.6241 (3)	0.55673 (17)	0.0450 (5)
H7	0.962947	0.626743	0.507670	0.054*
C18	0.2755 (2)	0.0507 (2)	0.43614 (18)	0.0479 (6)
H18	0.281599	0.028794	0.375622	0.057*
C21	0.2599 (2)	0.1209 (3)	0.61202 (17)	0.0455 (5)
H21	0.253554	0.145443	0.671970	0.055*
C20	0.1774 (3)	0.0248 (3)	0.5549 (2)	0.0551 (6)
H20	0.117711	−0.016619	0.576519	0.066*
C14	0.5530 (3)	0.2442 (3)	0.34999 (18)	0.0490 (6)
H14A	0.643386	0.228648	0.389388	0.059*

H14B	0.536575	0.339998	0.347922	0.059*
C19	0.1847 (3)	−0.0087 (3)	0.4658 (2)	0.0573 (7)
H19	0.128097	−0.071808	0.425264	0.069*
C15	0.5207 (3)	0.1908 (3)	0.2480 (2)	0.0725 (9)
H15A	0.429643	0.199448	0.211706	0.109*
H15B	0.544680	0.097758	0.251411	0.109*
H15C	0.566903	0.240523	0.214954	0.109*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.03827 (14)	0.04034 (15)	0.02896 (13)	−0.00397 (10)	0.01546 (10)	−0.00355 (11)
Cl2	0.0534 (3)	0.0477 (3)	0.0432 (3)	0.0115 (2)	0.0267 (3)	0.0022 (2)
O16	0.0442 (8)	0.0487 (8)	0.0340 (7)	−0.0114 (7)	0.0194 (6)	−0.0095 (7)
N11	0.0368 (8)	0.0381 (9)	0.0340 (8)	−0.0065 (7)	0.0173 (7)	−0.0053 (7)
O13	0.0726 (12)	0.0579 (11)	0.0474 (10)	−0.0254 (9)	0.0381 (9)	−0.0184 (8)
N3	0.0373 (8)	0.0373 (9)	0.0298 (8)	−0.0047 (7)	0.0126 (7)	−0.0014 (7)
N22	0.0375 (8)	0.0412 (9)	0.0303 (8)	−0.0038 (7)	0.0138 (7)	0.0020 (7)
N10	0.0422 (9)	0.0468 (10)	0.0380 (10)	−0.0118 (8)	0.0201 (8)	−0.0099 (8)
C5	0.0321 (9)	0.0334 (9)	0.0275 (9)	0.0014 (7)	0.0089 (7)	0.0013 (8)
C9	0.0333 (9)	0.0349 (9)	0.0283 (9)	0.0006 (8)	0.0103 (8)	0.0011 (8)
C17	0.0403 (10)	0.0331 (10)	0.0324 (10)	−0.0021 (8)	0.0142 (8)	0.0012 (8)
C4	0.0369 (10)	0.0363 (10)	0.0294 (9)	−0.0006 (8)	0.0139 (8)	0.0004 (8)
C12	0.0410 (10)	0.0380 (10)	0.0319 (10)	−0.0045 (8)	0.0182 (8)	−0.0034 (8)
C6	0.0435 (11)	0.0439 (11)	0.0297 (10)	−0.0041 (9)	0.0129 (9)	−0.0045 (9)
C8	0.0451 (12)	0.0464 (12)	0.0367 (11)	−0.0099 (9)	0.0197 (9)	−0.0042 (9)
C7	0.0526 (13)	0.0542 (13)	0.0357 (11)	−0.0082 (11)	0.0250 (10)	−0.0049 (10)
C18	0.0556 (14)	0.0505 (13)	0.0389 (12)	−0.0151 (11)	0.0189 (11)	−0.0105 (11)
C21	0.0471 (12)	0.0583 (14)	0.0352 (11)	−0.0097 (11)	0.0198 (10)	0.0025 (11)
C20	0.0527 (14)	0.0652 (16)	0.0499 (14)	−0.0203 (12)	0.0219 (12)	0.0025 (13)
C14	0.0583 (14)	0.0520 (14)	0.0460 (13)	−0.0135 (11)	0.0299 (11)	−0.0080 (11)
C19	0.0589 (15)	0.0622 (16)	0.0515 (15)	−0.0280 (13)	0.0212 (13)	−0.0107 (13)
C15	0.091 (2)	0.087 (2)	0.0555 (16)	−0.0389 (18)	0.0467 (16)	−0.0246 (16)

Geometric parameters (Å, º)

Cu1—N11	1.9437 (17)	C4—H4	0.9300
Cu1—O16	1.9808 (15)	C6—C7	1.363 (3)
Cu1—N22	2.0444 (17)	C6—H6	0.9300
Cu1—N3ⁱ	2.2009 (17)	C8—C7	1.374 (3)
Cu1—Cl2	2.2707 (6)	C8—H8	0.9300
O16—C9	1.274 (2)	C7—H7	0.9300
N11—C12	1.274 (3)	C18—C19	1.371 (3)
N11—N10	1.384 (2)	C18—H18	0.9300
O13—C12	1.323 (3)	C21—C20	1.374 (3)
O13—C14	1.452 (3)	C21—H21	0.9300
N3—C8	1.331 (3)	C20—C19	1.364 (4)
N3—C4	1.333 (3)	C20—H20	0.9300

N22—C21	1.326 (3)	C14—C15	1.485 (3)
N22—C17	1.344 (3)	C14—H14A	0.9700
N10—C9	1.305 (3)	C14—H14B	0.9700
C5—C4	1.382 (3)	C19—H19	0.9300
C5—C6	1.387 (3)	C15—H15A	0.9600
C5—C9	1.488 (3)	C15—H15B	0.9600
C17—C18	1.380 (3)	C15—H15C	0.9600
C17—C12	1.472 (3)		
N11—Cu1—O16	79.11 (7)	N11—C12—C17	114.38 (18)
N11—Cu1—N22	79.40 (7)	O13—C12—C17	113.79 (18)
O16—Cu1—N22	158.51 (7)	C7—C6—C5	119.0 (2)
N11—Cu1—N3^i	116.09 (7)	C7—C6—H6	120.5
O16—Cu1—N3^i	96.39 (7)	C5—C6—H6	120.5
N22—Cu1—N3^i	92.70 (7)	N3—C8—C7	123.0 (2)
N11—Cu1—Cl2	146.17 (6)	N3—C8—H8	118.5
O16—Cu1—Cl2	100.05 (5)	C7—C8—H8	118.5
N22—Cu1—Cl2	97.97 (5)	C6—C7—C8	119.3 (2)
N3^i—Cu1—Cl2	97.68 (5)	C6—C7—H7	120.4
C9—O16—Cu1	110.13 (13)	C8—C7—H7	120.4
C12—N11—N10	124.29 (17)	C19—C18—C17	118.3 (2)
C12—N11—Cu1	119.01 (14)	C19—C18—H18	120.9
N10—N11—Cu1	116.63 (13)	C17—C18—H18	120.9
C12—O13—C14	122.21 (18)	N22—C21—C20	122.4 (2)
C8—N3—C4	117.47 (18)	N22—C21—H21	118.8
C8—N3—Cu1^{ii}	119.26 (14)	C20—C21—H21	118.8
C4—N3—Cu1^{ii}	123.23 (14)	C19—C20—C21	118.7 (2)
C21—N22—C17	118.57 (19)	C19—C20—H20	120.6
C21—N22—Cu1	128.61 (16)	C21—C20—H20	120.6
C17—N22—Cu1	112.78 (13)	O13—C14—C15	106.9 (2)
C9—N10—N11	107.74 (17)	O13—C14—H14A	110.3
C4—C5—C6	117.88 (19)	C15—C14—H14A	110.3
C4—C5—C9	120.96 (18)	O13—C14—H14B	110.3
C6—C5—C9	121.15 (18)	C15—C14—H14B	110.3
O16—C9—N10	126.39 (19)	H14A—C14—H14B	108.6
O16—C9—C5	118.76 (17)	C20—C19—C18	119.9 (2)
N10—C9—C5	114.86 (18)	C20—C19—H19	120.0
N22—C17—C18	122.0 (2)	C18—C19—H19	120.0
N22—C17—C12	114.18 (18)	C14—C15—H15A	109.5
C18—C17—C12	123.8 (2)	C14—C15—H15B	109.5
N3—C4—C5	123.38 (19)	H15A—C15—H15B	109.5
N3—C4—H4	118.3	C14—C15—H15C	109.5
C5—C4—H4	118.3	H15A—C15—H15C	109.5
N11—C12—O13	131.82 (19)	H15B—C15—H15C	109.5

Symmetry codes: (i) −*x*+3/2, *y*−1/2, −*z*+3/2; (ii) −*x*+3/2, *y*+1/2, −*z*+3/2.

Hydrogen-bond geometry (Å, º)

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C8—H8⋯Cl2[ii]	0.93	2.71	3.354 (2)	128
C20—H20⋯Cl2[iii]	0.93	2.93	3.527 (3)	124
C14—H14B⋯Cl2[iv]	0.97	2.83	3.534 (3)	130
C14—H14B⋯O16[iv]	0.97	2.56	3.441 (3)	151

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

Di-*µ*-chlorido-1:4*κ*²*Cl:Cl*-2:3*κ*²*Cl:Cl*-dichlorido-2*κCl*,4*κCl*-bis[*µ*₃-ethoxy(pyridin-2-yl)methanolato-1:2:3*κ*³*O:N,O:O*;1:3:4*κ*³*O:O:N,O*]bis[*µ*₂-ethoxy(pyridin-2-yl)methanolato-1:2*κ*³*N,O:O*;3:4*κ*³*N,O:O*]tetracopper(II) (II)

Crystal data

[Cu₄(C₈H₁₀NO₂)₄Cl₄]
$M_r = 1004.68$
Monoclinic, $P2_1/n$
$a = 11.5150 (4)$ Å
$b = 13.1051 (5)$ Å
$c = 12.8066 (6)$ Å
$β = 100.066 (4)°$
$V = 1902.83 (13)$ Å³
$Z = 2$

$F(000) = 1016$
$D_x = 1.753$ Mg m⁻³
Mo $Kα$ radiation, $λ = 0.71073$ Å
Cell parameters from 9290 reflections
$θ = 3.0–32.4°$
$µ = 2.54$ mm⁻¹
$T = 293$ K
Plate, clear light green
$0.22 × 0.2 × 0.05$ mm

Data collection

Rigaku Oxford Diffraction XtaLAB Mini (ROW) diffractometer
Radiation source: fine-focus sealed X-ray tube, Rigaku (Mo) X-ray Source
Graphite monochromator
$ω$ scans
Absorption correction: multi-scan (CrysAlisPro; Rigaku OD, 2017)

$T_{min} = 0.727$, $T_{max} = 1.000$
31609 measured reflections
7541 independent reflections
4946 reflections with $I > 2σ(I)$
$R_{int} = 0.035$
$θ_{max} = 34.5°$, $θ_{min} = 2.6°$
$h = −17→18$
$k = −20→14$
$l = −18→18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2σ(F^2)] = 0.035$
$wR(F^2) = 0.093$
$S = 1.02$
7540 reflections
237 parameters
0 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[σ^2(F_o^2) + (0.0422P)^2 + 0.4202P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(Δ/σ)_{max} = 0.001$
$Δρ_{max} = 0.46$ e Å⁻³
$Δρ_{min} = −0.43$ e Å⁻³

Special details

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

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	0.59802 (2)	0.59673 (2)	0.49846 (2)	0.03411 (7)
Cu2	0.55029 (2)	0.53449 (2)	0.71340 (2)	0.03564 (7)
Cl3	0.67941 (4)	0.53396 (4)	0.36744 (4)	0.04527 (12)
Cl4	0.53662 (7)	0.61216 (5)	0.86295 (5)	0.06187 (17)
O15	0.53512 (12)	0.64894 (10)	0.61683 (11)	0.0386 (3)
O26	0.59121 (12)	0.47291 (10)	0.58419 (11)	0.0370 (3)
O12	0.40663 (13)	0.78727 (11)	0.59492 (12)	0.0454 (3)
O23	0.78892 (13)	0.44737 (12)	0.63858 (14)	0.0503 (4)
N21	0.60042 (14)	0.39764 (13)	0.77014 (15)	0.0418 (4)
N10	0.61957 (15)	0.74464 (13)	0.47288 (14)	0.0410 (4)
C5	0.58862 (18)	0.80472 (15)	0.54740 (18)	0.0409 (4)
C11	0.52350 (17)	0.75255 (15)	0.62500 (17)	0.0381 (4)
H11	0.555202	0.774842	0.697424	0.046*
C16	0.65162 (16)	0.34167 (15)	0.70334 (18)	0.0423 (5)
C22	0.67794 (16)	0.39909 (14)	0.60830 (17)	0.0385 (4)
H22	0.678628	0.353075	0.548094	0.046*
C17	0.6800 (2)	0.24007 (17)	0.7229 (2)	0.0581 (6)
H17	0.714861	0.202010	0.675423	0.070*
C20	0.5775 (2)	0.3558 (2)	0.8600 (2)	0.0551 (6)
H20	0.543030	0.395046	0.906778	0.066*
C13	0.3299 (2)	0.7534 (2)	0.6640 (2)	0.0521 (5)
H13A	0.360939	0.773547	0.736401	0.062*
H13B	0.323321	0.679615	0.661564	0.062*
C18	0.6556 (2)	0.1970 (2)	0.8141 (3)	0.0747 (9)
H18	0.673261	0.128697	0.828962	0.090*
C9	0.6739 (2)	0.78622 (19)	0.3992 (2)	0.0555 (6)
H9	0.695863	0.744342	0.347368	0.067*
C6	0.6124 (2)	0.90782 (17)	0.5516 (2)	0.0579 (6)
H6	0.591579	0.948143	0.605219	0.069*
C19	0.6050 (2)	0.2547 (2)	0.8833 (3)	0.0725 (9)
H19	0.589245	0.226032	0.945725	0.087*
C24	0.8820 (2)	0.4028 (2)	0.5958 (2)	0.0584 (6)
H24A	0.866484	0.409094	0.519149	0.070*
H24B	0.888107	0.330848	0.613617	0.070*
C7	0.6680 (3)	0.95004 (19)	0.4743 (3)	0.0725 (8)
H7	0.684357	1.019542	0.474791	0.087*
C8	0.6984 (3)	0.8886 (2)	0.3974 (3)	0.0692 (8)
H8	0.735208	0.915673	0.344567	0.083*
C14	0.2125 (2)	0.8005 (2)	0.6285 (2)	0.0666 (7)
H14A	0.186088	0.785882	0.554729	0.100*
H14B	0.218259	0.873080	0.638596	0.100*
H14C	0.157202	0.773196	0.669194	0.100*
C25	0.9948 (2)	0.4557 (3)	0.6401 (3)	0.0798 (9)
H25A	1.059000	0.422938	0.614746	0.120*
H25B	1.007511	0.452442	0.716177	0.120*

H25C	0.990264	0.525820	0.618003	0.120*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.03381 (11)	0.03383 (12)	0.03553 (13)	−0.00077 (8)	0.00838 (9)	0.00260 (9)
Cu2	0.03732 (12)	0.03519 (12)	0.03414 (13)	−0.00004 (9)	0.00550 (9)	0.00475 (9)
Cl3	0.0420 (2)	0.0496 (3)	0.0477 (3)	−0.0006 (2)	0.0175 (2)	−0.0010 (2)
Cl4	0.0881 (5)	0.0601 (4)	0.0372 (3)	−0.0049 (3)	0.0104 (3)	−0.0043 (3)
O15	0.0476 (7)	0.0318 (6)	0.0389 (7)	0.0029 (5)	0.0149 (6)	0.0051 (5)
O26	0.0372 (6)	0.0343 (6)	0.0399 (7)	0.0060 (5)	0.0081 (6)	0.0062 (5)
O12	0.0410 (7)	0.0460 (8)	0.0517 (9)	0.0077 (6)	0.0150 (7)	0.0080 (7)
O23	0.0342 (7)	0.0515 (9)	0.0674 (11)	−0.0063 (6)	0.0150 (7)	−0.0100 (8)
N21	0.0325 (8)	0.0443 (9)	0.0460 (10)	−0.0026 (7)	−0.0003 (7)	0.0135 (8)
N10	0.0453 (9)	0.0367 (8)	0.0426 (10)	−0.0035 (7)	0.0123 (7)	0.0045 (7)
C5	0.0393 (9)	0.0357 (9)	0.0488 (12)	−0.0004 (7)	0.0101 (8)	0.0052 (8)
C11	0.0383 (9)	0.0359 (9)	0.0411 (11)	0.0021 (7)	0.0098 (8)	0.0013 (8)
C16	0.0269 (8)	0.0386 (10)	0.0575 (13)	−0.0015 (7)	−0.0040 (8)	0.0096 (9)
C22	0.0311 (8)	0.0343 (9)	0.0489 (12)	0.0014 (7)	0.0032 (8)	−0.0001 (8)
C17	0.0393 (11)	0.0399 (11)	0.093 (2)	0.0034 (9)	0.0047 (12)	0.0143 (12)
C20	0.0395 (11)	0.0660 (15)	0.0574 (14)	−0.0040 (10)	0.0022 (10)	0.0271 (12)
C13	0.0453 (11)	0.0615 (14)	0.0524 (14)	0.0019 (10)	0.0167 (10)	0.0075 (11)
C18	0.0442 (13)	0.0533 (14)	0.122 (3)	0.0035 (11)	0.0014 (15)	0.0442 (17)
C9	0.0680 (15)	0.0502 (13)	0.0547 (14)	−0.0039 (11)	0.0282 (12)	0.0074 (11)
C6	0.0669 (15)	0.0369 (11)	0.0760 (18)	−0.0008 (10)	0.0297 (14)	0.0012 (11)
C19	0.0481 (13)	0.0775 (19)	0.089 (2)	−0.0041 (13)	0.0039 (13)	0.0503 (17)
C24	0.0408 (11)	0.0664 (16)	0.0699 (17)	0.0078 (10)	0.0151 (11)	0.0060 (13)
C7	0.090 (2)	0.0383 (12)	0.099 (2)	−0.0064 (12)	0.0429 (18)	0.0112 (13)
C8	0.084 (2)	0.0541 (15)	0.078 (2)	−0.0072 (13)	0.0398 (16)	0.0180 (14)
C14	0.0495 (13)	0.090 (2)	0.0631 (17)	0.0111 (13)	0.0178 (12)	0.0067 (15)
C25	0.0396 (13)	0.094 (2)	0.108 (3)	−0.0015 (13)	0.0194 (15)	0.0143 (19)

Geometric parameters (Å, º)

Cu1—O15	1.9170 (13)	C17—C18	1.369 (4)
Cu1—O26	1.9684 (13)	C17—H17	0.9300
Cu1—N10	1.9886 (17)	C20—C19	1.383 (4)
Cu1—Cl3	2.2181 (6)	C20—H20	0.9300
Cu1—O26ⁱ	2.4280 (14)	C13—C14	1.484 (3)
Cu1—Cu2	3.0122 (4)	C13—H13A	0.9700
Cu2—O15	1.9324 (13)	C13—H13B	0.9700
Cu2—O26	1.9707 (14)	C18—C19	1.370 (5)
Cu2—N21	1.9827 (17)	C18—H18	0.9300
Cu2—Cl4	2.1987 (7)	C9—C8	1.371 (3)
O15—C11	1.370 (2)	C9—H9	0.9300
O26—C22	1.386 (2)	C6—C7	1.385 (4)
O12—C11	1.409 (2)	C6—H6	0.9300
O12—C13	1.426 (3)	C19—H19	0.9300

O23—C24	1.413 (3)	C24—C25	1.494 (4)
O23—C22	1.418 (2)	C24—H24A	0.9700
N21—C16	1.339 (3)	C24—H24B	0.9700
N21—C20	1.341 (3)	C7—C8	1.365 (4)
N10—C5	1.333 (3)	C7—H7	0.9300
N10—C9	1.336 (3)	C8—H8	0.9300
C5—C6	1.378 (3)	C14—H14A	0.9600
C5—C11	1.509 (3)	C14—H14B	0.9600
C11—H11	0.9800	C14—H14C	0.9600
C16—C17	1.384 (3)	C25—H25A	0.9600
C16—C22	1.506 (3)	C25—H25B	0.9600
C22—H22	0.9800	C25—H25C	0.9600
O15—Cu1—O26	78.21 (6)	O26—C22—O23	109.23 (15)
O15—Cu1—N10	81.81 (6)	O26—C22—C16	106.85 (16)
O26—Cu1—N10	156.02 (7)	O23—C22—C16	107.52 (17)
O15—Cu1—Cl3	176.95 (5)	O26—C22—H22	111.0
O26—Cu1—Cl3	100.34 (4)	O23—C22—H22	111.0
N10—Cu1—Cl3	98.95 (5)	C16—C22—H22	111.0
O15—Cu1—O26ⁱ	92.55 (5)	C18—C17—C16	118.3 (3)
O26—Cu1—O26ⁱ	79.23 (6)	C18—C17—H17	120.9
N10—Cu1—O26ⁱ	115.02 (6)	C16—C17—H17	120.9
Cl3—Cu1—O26ⁱ	89.80 (4)	N21—C20—C19	120.3 (3)
O15—Cu1—Cu2	38.69 (4)	N21—C20—H20	119.8
O26—Cu1—Cu2	40.15 (4)	C19—C20—H20	119.8
N10—Cu1—Cu2	117.54 (5)	O12—C13—C14	108.1 (2)
Cl3—Cu1—Cu2	139.425 (18)	O12—C13—H13A	110.1
O26ⁱ—Cu1—Cu2	90.19 (3)	C14—C13—H13A	110.1
O15—Cu2—O26	77.80 (6)	O12—C13—H13B	110.1
O15—Cu2—N21	157.61 (7)	C14—C13—H13B	110.1
O26—Cu2—N21	80.81 (7)	H13A—C13—H13B	108.4
O15—Cu2—Cl4	100.71 (5)	C17—C18—C19	119.8 (2)
O26—Cu2—Cl4	170.05 (5)	C17—C18—H18	120.1
N21—Cu2—Cl4	99.21 (6)	C19—C18—H18	120.1
O15—Cu2—Cu1	38.33 (4)	N10—C9—C8	122.3 (2)
O26—Cu2—Cu1	40.09 (4)	N10—C9—H9	118.9
N21—Cu2—Cu1	119.47 (6)	C8—C9—H9	118.9
Cl4—Cu2—Cu1	136.30 (2)	C5—C6—C7	118.5 (2)
C11—O15—Cu1	118.00 (12)	C5—C6—H6	120.8
C11—O15—Cu2	136.01 (13)	C7—C6—H6	120.8
Cu1—O15—Cu2	102.98 (6)	C18—C19—C20	119.8 (3)
C22—O26—Cu1	127.03 (12)	C18—C19—H19	120.1
C22—O26—Cu2	111.56 (12)	C20—C19—H19	120.1
Cu1—O26—Cu2	99.76 (6)	O23—C24—C25	109.2 (2)
C22—O26—Cu1ⁱ	113.05 (11)	O23—C24—H24A	109.8
Cu1—O26—Cu1ⁱ	100.77 (6)	C25—C24—H24A	109.8
Cu2—O26—Cu1ⁱ	101.06 (5)	O23—C24—H24B	109.8
C11—O12—C13	113.30 (16)	C25—C24—H24B	109.8

C24—O23—C22	114.72 (18)	H24A—C24—H24B	108.3
C16—N21—C20	119.9 (2)	C8—C7—C6	119.3 (2)
C16—N21—Cu2	113.18 (14)	C8—C7—H7	120.4
C20—N21—Cu2	126.56 (17)	C6—C7—H7	120.4
C5—N10—C9	118.78 (19)	C7—C8—C9	119.1 (2)
C5—N10—Cu1	113.66 (13)	C7—C8—H8	120.5
C9—N10—Cu1	126.96 (16)	C9—C8—H8	120.5
N10—C5—C6	122.1 (2)	C13—C14—H14A	109.5
N10—C5—C11	115.44 (17)	C13—C14—H14B	109.5
C6—C5—C11	122.4 (2)	H14A—C14—H14B	109.5
O15—C11—O12	113.60 (16)	C13—C14—H14C	109.5
O15—C11—C5	109.41 (16)	H14A—C14—H14C	109.5
O12—C11—C5	103.56 (16)	H14B—C14—H14C	109.5
O15—C11—H11	110.0	C24—C25—H25A	109.5
O12—C11—H11	110.0	C24—C25—H25B	109.5
C5—C11—H11	110.0	H25A—C25—H25B	109.5
N21—C16—C17	121.9 (2)	C24—C25—H25C	109.5
N21—C16—C22	114.57 (17)	H25A—C25—H25C	109.5
C17—C16—C22	123.6 (2)	H25B—C25—H25C	109.5

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9···Cl3	0.93	2.78	3.333 (3)	119
C20—H20···Cl4	0.93	2.90	3.393 (3)	115
C13—H13*B*···Cl3[i]	0.97	2.82	3.787 (3)	173
C22—H22···O12[i]	0.98	2.66	3.578 (3)	156
C18—H18···O23[ii]	0.93	2.44	3.367 (3)	177

Symmetry codes: (i) −*x*+1, −*y*+1, −*z*+1; (ii) −*x*+3/2, *y*−1/2, −*z*+3/2.