



An unusual coordination polymer containing  $\text{Cu}^+$  ions and featuring possible  $\text{Cu} \cdots \text{Cu}$  'cuprophilic' interactions:  
poly[di- $\mu$ -chlorido-( $\mu_4$ -3,5-diaminobenzoato- $\kappa^4\text{O}:\text{O}':\text{N}:\text{N}'$ )tricopper(I)(3  $\text{Cu}-\text{Cu}$ )]

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# An unusual coordination polymer containing $\text{Cu}^+$ ions and featuring possible $\text{Cu} \cdots \text{Cu}$ 'cuprophilic' interactions: poly[di- $\mu$ -chlorido-( $\mu_4$ -3,5-diaminobenzoato- $\kappa^4\text{O}:\text{O}':\text{N}:\text{N}'$ )tricopper(I)(3 $\text{Cu}-\text{Cu}$ )]

Muhammad Kaleem Khosa,<sup>a</sup> Paul T. Wood,<sup>b</sup> Simon M. Humphrey<sup>c</sup> and William T. A. Harrison<sup>d\*</sup>

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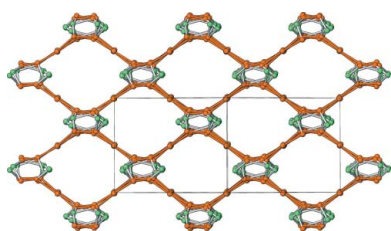
<sup>a</sup>Department of Chemistry, Government College University, Faisalabad 38000, Pakistan, <sup>b</sup>Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England, <sup>c</sup>Department of Chemistry and Biochemistry, The University of Texas at Austin, 1 University Station, Austin, Texas 78712, USA, and <sup>d</sup>Department of Chemistry, University of Aberdeen, Aberdeen AB24 3UE, Scotland. \*Correspondence e-mail: w.harrison@abdn.ac.uk

Compounds containing copper(I) are of interest for their role in biological processes. The nature of short ( $< \sim 3.2 \text{ \AA}$ )  $\text{Cu} \cdots \text{Cu}$  contacts within these compounds has been debated, being either described as weakly attractive (bonding) 'cuprophilic' interactions, or simply as short metal–metal distances constrained by ligand geometry or largely ionic in nature. The title three-dimensional  $\text{Cu}^+$ -containing coordination polymer,  $[\text{Cu}_3(\text{C}_7\text{H}_7\text{N}_2\text{O}_2)\text{Cl}_2]_n$ , was formed from the *in situ* reduction of  $\text{CuCl}_2$  in the presence of 3,5-diaminobenzoic acid and KOH under hydrothermal conditions. Its complex crystal structure contains ten distinct  $\text{Cu}^{\text{I}}$  atoms, two of which lie on crystallographic inversion centres. The copper coordination geometries include near-linear  $\text{CuOCl}$  and  $\text{CuN}_2$ , T-shaped  $\text{CuOCl}_2$  and distorted tetrahedral  $\text{CuOCl}_3$  groups. Each  $\text{Cu}^{\text{I}}$  atom is also associated with two adjacent metal atoms, with  $\text{Cu} \cdots \text{Cu}$  distances varying from 2.7350 (14) to 3.2142 (13)  $\text{ \AA}$ ; if all these are regarded as 'cuprophilic' interactions, then infinite  $[\bar{1}01]$  zigzag chains of  $\text{Cu}^{\text{I}}$  atoms occur in the crystal. The structure is consolidated by  $\text{N}-\text{H} \cdots \text{Cl}$  hydrogen bonds.

## 1. Introduction

Compounds containing copper(I) (electronic configuration  $[\text{Ar}]3d^{10}$ ) are of interest for their role in biological processes (Tsukihara *et al.*, 1995) and the presence of short ( $< \sim 3.2 \text{ \AA}$ )  $\text{Cu} \cdots \text{Cu}$  contacts in their crystal structures (Arkhireeva *et al.*, 1990; Zheng *et al.*, 2005; Sundararaman *et al.*, 2005; Doshi *et al.*, 2012, Cotton *et al.*, 1998; Carvajal *et al.*, 2004). The nature of these contacts has been debated, with some authors (Zheng *et al.*, 2005; Sundararaman *et al.*, 2005; Doshi *et al.*, 2012) describing them as weakly attractive (bonding) 'cuprophilic' interactions akin to the well-established argentophilic  $\text{Ag} \cdots \text{Ag}$  (Barreiro *et al.*, 2013) and aurophilic  $\text{Au} \cdots \text{Au}$  (Schmidbaur & Schier, 2012) weak bonds in silver(I) and gold(I) compounds, respectively. However, other workers have questioned whether these  $\text{Cu} \cdots \text{Cu}$  contacts represent bonds at all and suggested that the short metal–metal distances observed are either constrained by the ligand geometry (Cotton *et al.*, 1998) or are largely ionic in nature (Carvajal *et al.*, 2004).

Here, we describe the hydrothermal synthesis and crystal structure of the three-dimensional coordination polymer poly[di- $\mu$ -chlorido-( $\mu_4$ -3,5-diaminobenzoato- $\kappa^4\text{O}:\text{O}':\text{N}:\text{N}'$ )tricopper(I)(3  $\text{Cu}-\text{Cu}$ )], (1), which arose from the unexpected reduction of the  $\text{CuCl}_2$  starting material to  $\text{Cu}^+$  under basic conditions.



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**Table 1**  
Experimental details.

Crystal data	
Chemical formula	[Cu <sub>3</sub> (C <sub>7</sub> H <sub>7</sub> CN <sub>2</sub> O <sub>2</sub> )Cl <sub>2</sub> ]
<i>M<sub>r</sub></i>	412.67
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>
Temperature (K)	180
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.4127 (2), 10.8942 (2), 20.2348 (4)
$\beta$ (°)	104.8395 (7)
<i>V</i> (Å <sup>3</sup> )	3071.20 (9)
<i>Z</i>	12
Radiation type	Mo <i>K</i> α
$\mu$ (mm <sup>-1</sup> )	6.68
Crystal size (mm)	0.39 × 0.16 × 0.14
Data collection	
Diffractometer	Bruker APEXII CCD diffractometer
Absorption correction	Multi-scan ( <i>SADABS</i> ; Bruker, 2004)
<i>T<sub>min</sub></i> , <i>T<sub>max</sub></i>	0.181, 0.455
No. of measured, independent and observed [ <i>I</i> > 2σ( <i>I</i> )] reflections	16907, 5987, 4798
<i>R<sub>int</sub></i>	0.069
(sin θ/λ) <sub>max</sub> (Å <sup>-1</sup> )	0.617
Refinement	
<i>R</i> [ <i>F</i> <sup>2</sup> > 2σ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	0.069, 0.202, 1.04
No. of reflections	5987
No. of parameters	436
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$ , $\Delta\rho_{\min}$ (e Å <sup>-3</sup> )	3.40, -2.71

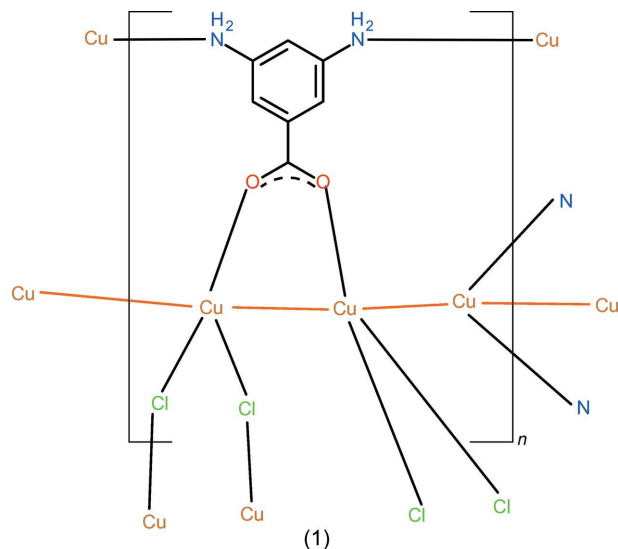
Computer programs: *APEX2* (Bruker, 2004), *SAINTE* (Bruker, 2004), *SHELXS97* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *ATOMS* (Dowty, 2004).

## 2. Experimental

### 2.1. Synthesis and crystallization

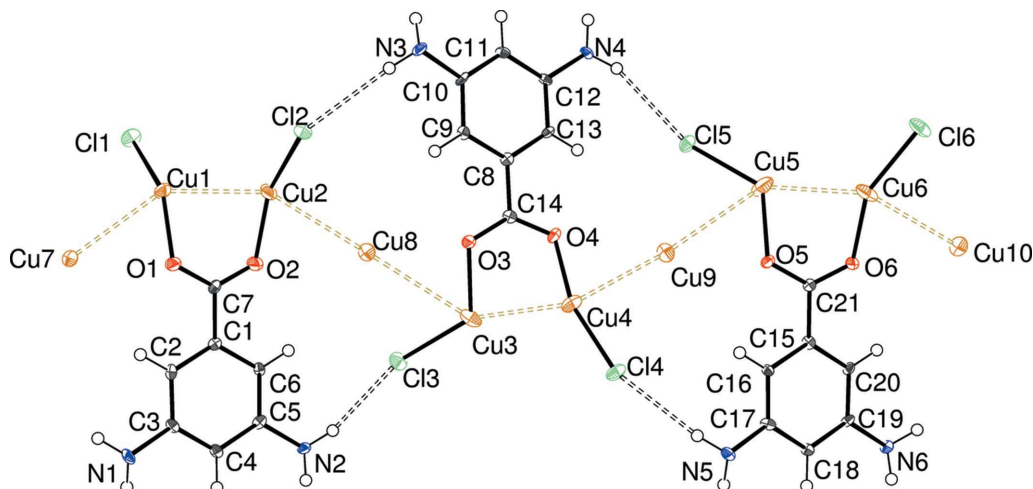
A mixture of CuCl<sub>2</sub> (134 mg, 1.0 mmol) and 3,5-diaminobenzoic acid (304 mg, 2.0 mmol) was added to 1 M KOH

(2.0 ml) with stirring to yield a pale-blue solution. This mixture was heated to 423 K in a 23 ml Teflon-lined autoclave for 15 h and then cooled to room temperature over a period of several hours. Colourless blocks of (1) were recovered from the reaction by filtration and rinsing with water and acetone.



### 2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The crystal quality was only fair, which may correlate with the rather high residuals and the larger than expected difference-map features ( $\Delta\rho_{\min}$  and  $\Delta\rho_{\max} = -2.71$  and  $3.40 \text{ e \AA}^{-3}$ , respectively). The H atoms were placed geometrically (C–H = 0.95 Å and N–H = 0.92 Å) and refined as riding atoms, with the constraint  $U_{\text{iso}}(\text{H}) = U_{\text{eq}}(\text{carrier})$ . This structure has a strong subcell (*C*2/*c*, *a* = 13.077, *b* = 10.894, *c* = 7.209 Å,  $\beta = 94.64^\circ$  and *V* =



**Figure 1**

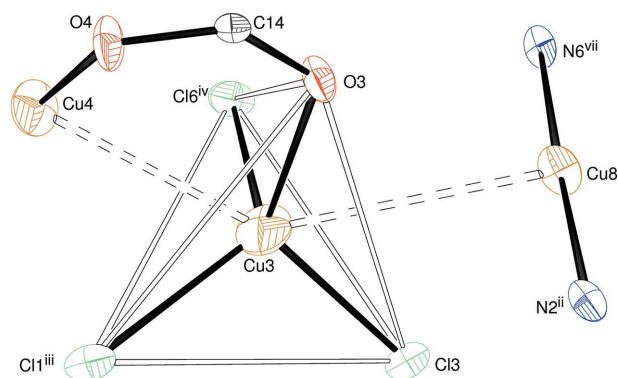
The asymmetric unit of (1), showing displacement ellipsoids at the 50% probability level. The N–H...Cl hydrogen bonds are indicated by double-dashed lines. The Cu...Cu separations (bronze double-dashed lines, Å) are as follows: Cu1...Cu2 = 2.7454 (13), Cu3...Cu4 = 2.7350 (14), Cu5...Cu6 = 2.7551 (15), Cu1...Cu7 = 3.0169 (9), Cu2...Cu8 = 3.0174 (12), Cu3...Cu8 = 3.2142 (13), Cu4...Cu9 = 2.8145 (12), Cu5...Cu9 = 3.1067 (12) and Cu6...Cu10 = 2.845 (10). The Cu...Cu...Cu angles (°) are as follows: Cu7...Cu1...Cu2 = 142.08 (3), Cu1...Cu2...Cu8 = 147.34 (4), Cu2...Cu8...Cu3 = 175.11 (4), Cu8...Cu3...Cu4 = 136.27 (4), Cu3...Cu4...Cu9 = 149.88 (5), Cu4...Cu9...Cu5 = 174.23 (4), Cu9...Cu5...Cu6 = 135.11 (4), Cu5...Cu6...Cu10 = 143.90 (4), Cu1...Cu7...Cu1<sup>i</sup> = 180 and Cu6...Cu10...Cu6<sup>ii</sup> = 180 [symmetry codes: (i)  $-x + 1, -y, -z$ ; (ii)  $-x, -y, -z + 2$ ].

1023.6 Å<sup>3</sup>), but refinements in this space group, in which the asymmetric unit contains two Cu<sup>I</sup> atoms (one with symmetry  $\bar{1}$ ), two Cl atoms and half a ligand molecule, led to much higher residuals [ $R(F) \sim 0.20$ ], large difference Fourier peaks ( $\sim \pm 6 \text{ e Å}^{-3}$ ) in the vicinity of the Cu<sup>I</sup> atoms and many systematic absence violations and was therefore rejected. The structural models were analysed and verified with *PLATON* (Spek, 2009).

### 3. Results and discussion

The lack of colour of the crystals of (1) is consistent with the  $3d^{10}$  electron configuration of the Cu<sup>+</sup> ion (Doshi *et al.*, 2012; Kappenstein & Hugel, 1978). The precise nature of the redox reaction that generated the cuprous ions is unknown, but similar reductions of  $\text{Cu}^{2+} \rightarrow \text{Cu}^+$  in the presence of a nitrogen-containing ligand under hydrothermal conditions have been reported by other workers (Xin *et al.*, 2013) and indeed this type of reduction has been described as a ‘recommended route’ (Peng *et al.*, 2010) to cuprous–halide compounds from  $\text{Cu}^{2+}$ -containing starting materials. The asymmetric unit of (1), which contains no fewer than ten crystallographically independent Cu<sup>I</sup> atoms (eight of which lie on general positions and two on crystallographic inversion centres), as well as three benzoate ligands and six chloride ions, is shown in Fig. 1.

The copper coordination geometries in (1) can be split into several distinct types. Atoms Cu1–Cu6 are bonded to various combinations of benzoate O atoms and chloride ions (Table 1). In this complex structure, all these Cu<sup>I</sup> atoms are surrounded by a number of O and Cl atoms at distances around or slightly shorter than the Bondi (1964) van der Waals radii sum of  $\text{Cu} \cdots \text{O} = 2.92 \text{ Å}$  and  $\text{Cu} \cdots \text{Cl} = 3.15 \text{ Å}$ , but by using the Brown criterion of 0.04 of a bond-valence unit to indicate a significant chemical bond to a univalent cation (Brown, 2002), the following conclusions can be drawn: Cu1 and Cu2 are bonded to a benzoate O atom and two chloride ions in a distorted T-shape, whereas Cu3 and Cu5 are bonded to one O



**Figure 2**

The coordination environment of atom Cu3 in (1), showing its  $\text{CuOCl}_3$  tetrahedron (solid lines for Cu–O and Cu–Cl bonds and open lines connecting vertices) and dashed lines indicating short  $\text{Cu} \cdots \text{Cu}$  contacts to Cu4 (‘semi-supported’ *via* the bridging  $-\text{CO}_2$  group) and Cu8 (unsupported); note how these pass through the tetrahedral faces. For symmetry codes, see Table 1.

**Table 2**

Selected geometric parameters (Å, °).

Cu1–O1	1.943 (4)	Cu6–Cl6	2.1583 (18)
Cu1–Cl1	2.1921 (17)	Cu6–Cl4 <sup>vi</sup>	2.7735 (19)
Cu1–Cl5 <sup>i</sup>	2.3928 (17)	Cu6–Cl2 <sup>v</sup>	2.7828 (18)
Cu2–O2	1.929 (5)	Cu7–N4 <sup>i</sup>	1.929 (5)
Cu2–Cl2	2.1964 (16)	Cu8–N2 <sup>ii</sup>	1.938 (5)
Cu2–Cl3 <sup>ii</sup>	2.4246 (18)	Cu8–N6 <sup>vii</sup>	1.939 (6)
Cu3–O3	2.033 (5)	Cu8–O3	2.697 (4)
Cu3–Cl3	2.2788 (18)	Cu9–N5 <sup>vi</sup>	1.953 (5)
Cu3–Cl1 <sup>iii</sup>	2.439 (2)	Cu9–N1 <sup>viii</sup>	1.957 (5)
Cu3–Cl6 <sup>iv</sup>	2.485 (2)	Cu9–O5	2.661 (4)
Cu4–O4	1.896 (5)	Cu10–N3 <sup>v</sup>	1.946 (5)
Cu4–Cl4	2.1415 (17)	Cu10–O6	2.798 (4)
Cu4–Cl1 <sup>iii</sup>	2.7981 (19)	C7–O2	1.261 (7)
Cu5–O5	2.024 (4)	C7–O1	1.270 (7)
Cu5–Cl5	2.2672 (17)	C14–O4	1.257 (7)
Cu5–Cl2 <sup>v</sup>	2.4009 (18)	C14–O3	1.263 (7)
Cu5–Cl4 <sup>vi</sup>	2.5373 (18)	C21–O6	1.258 (7)
Cu6–O6	1.916 (4)	C21–O5	1.260 (7)
O1–Cu1–Cl1	143.31 (15)	O4–Cu4–Cl4	161.90 (15)
O1–Cu1–Cl5 <sup>i</sup>	103.78 (15)	O5–Cu5–Cl5	124.08 (14)
Cl1–Cu1–Cl5 <sup>i</sup>	108.94 (6)	O5–Cu5–Cl2 <sup>v</sup>	113.99 (14)
O2–Cu2–Cl2	147.00 (16)	Cl5–Cu5–Cl2 <sup>v</sup>	109.72 (7)
O2–Cu2–Cl3 <sup>ii</sup>	103.86 (15)	O5–Cu5–Cl4 <sup>vi</sup>	91.90 (14)
Cl2–Cu2–Cl3 <sup>ii</sup>	106.14 (6)	Cl5–Cu5–Cl4 <sup>vi</sup>	99.86 (6)
O3–Cu3–Cl3	120.86 (15)	Cl2 <sup>v</sup> –Cu5–Cl4 <sup>vi</sup>	114.90 (7)
O3–Cu3–Cl1 <sup>iii</sup>	113.26 (14)	O6–Cu6–Cl6	151.94 (15)
Cl3–Cu3–Cl1 <sup>iii</sup>	107.42 (7)	N4 <sup>i</sup> –Cu7–N4 <sup>iii</sup>	180.0
O3–Cu3–Cl6 <sup>iv</sup>	93.82 (16)	N2 <sup>ii</sup> –Cu8–N6 <sup>vii</sup>	177.8 (2)
Cl3–Cu3–Cl6 <sup>iv</sup>	99.08 (7)	N5 <sup>vi</sup> –Cu9–N1 <sup>viii</sup>	176.6 (2)
Cl1 <sup>iii</sup> –Cu3–Cl6 <sup>iv</sup>	122.15 (7)	N3 <sup>v</sup> –Cu10–N3 <sup>iv</sup>	180.0 (3)

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

atom and three chloride ions in very distorted tetrahedral arrangements (Fig. 2). The Cu4 and Cu6 coordination geometries are ambiguous; they have two well-defined short bonds to one O atom and one chloride ion in an approximately linear arrangement [ $\text{O} - \text{Cu} - \text{Cl} = 161.90 (15)$  and  $151.94 (15)^\circ$  for Cu4 and Cu6, respectively], but also one (for Cu4) and two (for Cu6) very long Cu–Cl contacts, which are right on the borderline of being considered as bonds.

In every case, the Cu<sup>I</sup> atom also has two short  $\text{Cu} \cdots \text{Cu}$  contacts to adjacent metal atoms, with the separations indicated in the caption of Fig. 1; these are further discussed below. Bond-valence sums (BSV; Brown & Altermatt, 1985) for atoms Cu1 (1.05), Cu2 (1.04), Cu3 (1.03), Cu4 (1.01), Cu5 (1.05) and Cu6 (1.05) are in excellent agreement with the expected value of 1.00 for the cuprous ion, confirming that reduction from  $\text{Cu}^{2+}$  has occurred.

The other group of metal atoms, Cu7–Cu10 (Cu7 and Cu10 lie on crystallographic inversion centres), are bonded to two ligand N atoms ( $\text{Cu} - \text{N} < 2.00 \text{ Å}$ ) in a linear or near-linear geometry [ $\text{N} - \text{Cu} - \text{N} = 180, 177.8 (2), 176.6 (2)$  and  $180^\circ$  for Cu7, Cu8, Cu9 and Cu10, respectively]. Again, these atoms have a number of  $\text{Cu} \cdots \text{O}$  and  $\text{Cu} \cdots \text{Cl}$  contacts slightly shorter than the van der Waals radii sums noted above, with some of the former being *just* significant as bonds based on the Brown bond-valence criterion (Table 1). Even when the long Cu–O bonds are included, these Cu<sup>I</sup> atoms appear to be substantially ‘under-bonded’ (Saines *et al.*, 2006), with their BVS values of 0.66 (Cu7), 0.74 (Cu8), 0.72 (Cu9) and 0.71



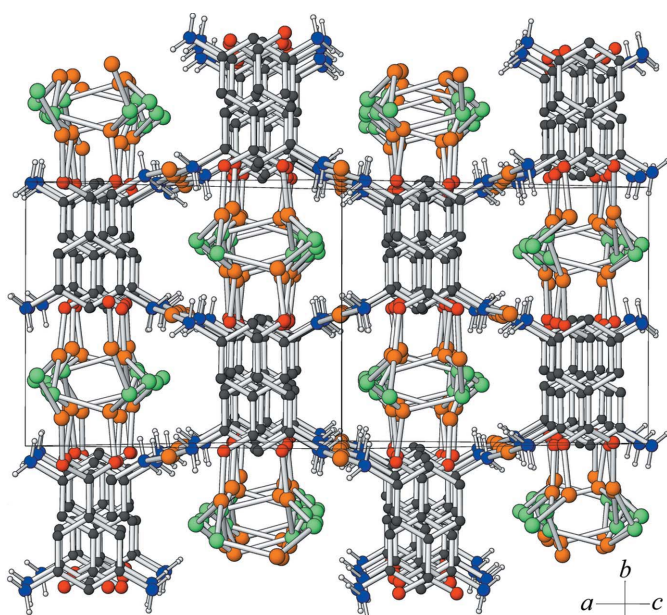
**Table 3**  
 Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1A $\cdots$ Cl1 <sup>ix</sup>	0.92	2.64	3.517 (6)	160
N1—H1B $\cdots$ Cl1 <sup>x</sup>	0.92	2.74	3.657 (6)	176
N2—H2A $\cdots$ Cl2 <sup>ix</sup>	0.92	2.53	3.422 (5)	164
N2—H2B $\cdots$ Cl3	0.92	2.54	3.440 (5)	165
N3—H3A $\cdots$ Cl2	0.92	2.75	3.661 (6)	173
N3—H3B $\cdots$ Cl3 <sup>xi</sup>	0.92	2.57	3.471 (5)	168
N4—H4A $\cdots$ Cl5	0.92	2.73	3.612 (5)	160
N4—H4B $\cdots$ Cl4 <sup>xi</sup>	0.92	2.49	3.354 (5)	156
N5—H5A $\cdots$ Cl5 <sup>ix</sup>	0.92	2.52	3.423 (5)	168
N5—H5B $\cdots$ Cl4	0.92	2.65	3.557 (6)	168
N6—H6A $\cdots$ Cl6 <sup>ix</sup>	0.92	2.51	3.382 (6)	159
N6—H6B $\cdots$ Cl6 <sup>xii</sup>	0.92	2.73	3.634 (6)	167

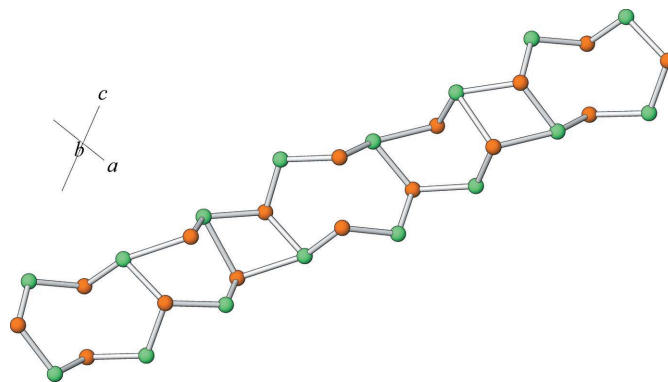
Symmetry codes: (ix)  $x, y + 1, z$ ; (x)  $-x + 1, -y, -z$ ; (xi)  $x, y - 1, z$ ; (xii)  $-x, -y, -z + 2$ .

(Cu10) all significantly smaller than the expected value of 1.00. Considering just the Cu—N bonds and Cu $\cdots$ Cu contacts, each of atoms Cu7—Cu10 has an approximate ‘square-planar’ *trans*-Cu<sub>2</sub>N<sub>2</sub> coordination geometry.

The carboxylate group of the Cl1-containing benzoate ligand is slightly rotated from the plane of the aromatic ring, by 1.3 (5)°; the equivalent values for the C8- and C15-containing anions are much larger, at 18.4 (4) and 18.5 (4)°, respectively. The C—O carboxylate bond lengths indicate substantial delocalization in each case such that the two C—O bond lengths are almost equal (Table 2). For each ligand, the Cu<sup>I</sup> atoms bonded to the O atoms are displaced in an opposite sense from the CO<sub>2</sub> plane: for the C7/O1/O2 group, atoms Cu1 and Cu2 are displaced by  $-0.36$  (2) and  $0.44$  (2) Å, respectively; for C14/O3/O4, Cu3 and Cu4 are displaced by  $-0.58$  (2) and  $0.44$  (2) Å, respectively; for C21/O5/O6, Cu5 and Cu6 are displaced by  $-0.57$  (2) and  $0.48$  (2) Å, respectively. Neglecting



**Figure 3**  
 The packing in (1), viewed approximately down [101], showing the Cu/Cl chains. Colour key: Cu orange, Cl green, C dark grey, H white, N blue and O red. C-bound H atoms have been omitted for clarity.

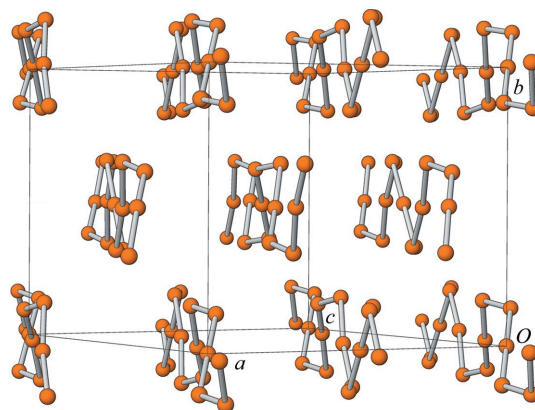


**Figure 4**  
 A fragment of a [101] Cu/Cl chain (key: Cu orange and Cl green) in (1), showing the constituent four-, six- and eight-membered rings.

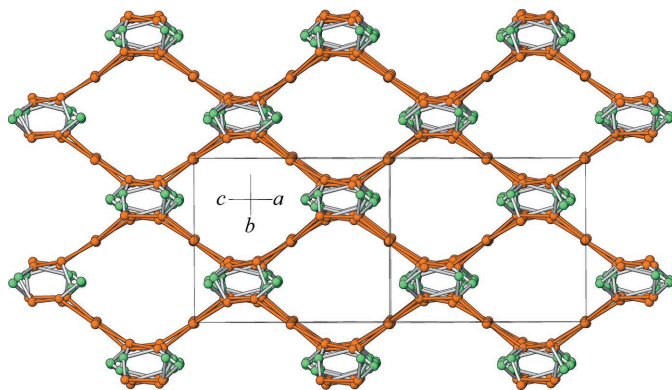
the borderline long Cu—O bonds, each benzoate ligand bonds to four nearby Cu<sup>I</sup> atoms in a  $\mu_4$ -N:N':O:O'-mode. The same  $\mu_4$  ligand-bonding mode (but with a totally different overall structure) has been seen in [Mn(C<sub>7</sub>H<sub>7</sub>N<sub>2</sub>O<sub>2</sub>)(N<sub>3</sub>)] (Chen *et al.*, 2009). Each chloride ion in (1) is bonded to two Cu<sup>I</sup> atoms, with Cu—Cl < 2.5 Å and Cl—Cu—Cl < 125°, but a third metal atom is also present within 3.1 Å.

The packing in (1) is a dense three-dimensional polymeric network without any identifiable channels or voids. When viewed down the [101] direction (Fig. 3), chains of Cu<sup>I</sup> atoms (involving Cu1—Cu6) and chloride ions are apparent, which are shown in more detail in Fig. 4, where four-, six- and eight-atom loops (Peng *et al.*, 2010) are apparent in the chains. The packing is consolidated by N—H $\cdots$ Cl hydrogen bonds (Table 3), with all 12 N—H groups participating in such an interaction (mean H $\cdots$ Cl = 2.62 Å and mean N—H $\cdots$ Cl = 165°). Any possible aromatic  $\pi$ — $\pi$  stacking in the crystal of (1) must be extremely weak, as the shortest separation of the centroids of the benzene rings is greater than 4.0 Å.

The Cu $\cdots$ Cu contacts (or bonds?) in (1) merit some further discussion. As might be expected, the shortest separations occur between pairs of metal atoms bridged by a benzoate ligand: this type of interaction has been termed ‘semi-supported’ by Schmidbaur & Schier (2012): the relevant data



**Figure 5**  
 Zigzag Cu $\cdots$ Cu chains, which propagate in the [101] direction, in the crystal of (1).



**Figure 6**  
The  $[\text{Cu}_3\text{Cl}_2]^+$  network in (1), showing the formation of  $[101]$  channels.

for (1) are  $\text{Cu}1 \cdots \text{Cu}2 = 2.7454(13) \text{ \AA}$ ,  $\text{Cu}3 \cdots \text{Cu}4 = 2.7350(14) \text{ \AA}$  and  $\text{Cu}5 \cdots \text{Cu}6 = 2.7551(15) \text{ \AA}$ . These separations are significantly shorter than those in the recently reported semi-supported (by one bulky benzoate ligand) linear polymer  $[\text{Cu}(2,4,6\text{-triisopropylbenzoate})]_n$  (Hietsoi *et al.*, 2011), with  $\text{Cu} \cdots \text{Cu} = 2.9397(5) \text{ \AA}$ , but are much longer than the 'fully supported' (by two bridging benzoate ligands)  $\text{Cu} \cdots \text{Cu}$  distance of  $2.4934(3) \text{ \AA}$  in the dimeric compound  $[\text{Cu}_2(2,4,6\text{-triisopropylbenzoate})_2(1,2\text{-dichlorobenzene})_2]$  (Hietsoi *et al.*, 2011).

The 'unsupported' (no bridging ligands)  $\text{Cu} \cdots \text{Cu}$  contacts in (1) between the  $\text{Cu}^I$  atoms associated with the benzoate ligands ( $\text{Cu}1\text{--Cu}6$ ) and the  $\text{Cu}^I$  atoms showing a local linear  $\text{N--Cu--N}$  geometry ( $\text{Cu}7\text{--Cu}10$ ) show considerable variation in their lengths, with the  $\text{Cu}4 \cdots \text{Cu}9 [2.8145(12) \text{ \AA}]$  and  $\text{Cu}6 \cdots \text{Cu}10 [2.8455(10) \text{ \AA}]$  separations being almost as short as the semi-supported bonds. Conversely, the  $\text{Cu}1 \cdots \text{Cu}7 [3.0169(9) \text{ \AA}]$  and  $\text{Cu}2 \cdots \text{Cu}8 [3.0174(12) \text{ \AA}]$  links are of intermediate length, and the  $\text{Cu}5 \cdots \text{Cu}9 [3.1067(12) \text{ \AA}]$  and  $\text{Cu}3 \cdots \text{Cu}8 [3.2142(13) \text{ \AA}]$  contacts are the longest. If *all* of these contacts, which are significantly shorter than twice the van der Waals radius of  $1.92 \text{ \AA}$  for  $\text{Cu}^+$  according to Batsanov (2001), are regarded as cuprophilic  $\text{Cu} \cdots \text{Cu}$  interactions/bonds, then infinite  $[\bar{1}01]$  zigzag chains of  $\text{Cu}^I$  atoms occur (Fig. 5). Yet another way to visualize the structure is in terms of the  $\text{Cu}^+$  and  $\text{Cl}^-$  ions: when these are considered together, an unusual three-dimensional cationic open framework of stoichiometry  $[\text{Cu}_3\text{Cl}_2]^+$  results (including the  $\text{Cu} \cdots \text{Cu}$  links), which surrounds  $[101]$  channels (Fig. 6).

#### 4. Conclusions

The serendipitous redox synthesis and crystal structure of  $[\text{Cu}_3(3,5\text{-diaminobenzoate})\text{Cl}_2]$  have been described. A wide

variety of copper coordination polyhedra occur, including  $\text{CuOCl}_2$  (T-shape),  $\text{CuOCl}_3$  (tetrahedral) and  $\text{CuN}_2$  (linear), which obviously correlate with the different functional groups (carboxylate and amine) of the ligand. Every  $\text{Cu}^I$  atom has two near neighbours and if all these are regarded as cuprophilic bonds, then infinite zigzag  $\text{Cu} \cdots \text{Cu}$  chains occur in the crystal.

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#### References

- Arkhireeva, T. M., Bulychev, B. M., Sizov, A. I., Sokolova, T. A., Belsky, V. K. & Soloveichik, G. L. (1990). *Inorg. Chim. Acta*, **169**, 109–118.
- Barreiro, E., Casas, J. S., Couce, M. D., Laguna, A., López-de-Luzuriaga, J. M., Monge, M., Sánchez, A., Sordo, J. & Vázquez López, E. M. (2013). *Dalton Trans.* **42**, 5916–5923.
- Batsanov, S. S. (2001). *Inorg. Mater.* **37**, 871–885.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Brown, I. D. (2002). In *The Chemical Bond in Inorganic Chemistry: The Bond Valence Model*. Oxford University Press.
- Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* **B41**, 244–247.
- Bruker (2004). *APEX2, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Carvajal, M. A., Alvarez, S. & Novoa, J. J. (2004). *Chem. Eur. J.* **10**, 2117–2132.
- Chen, Z.-L., Jiang, C.-F., Yan, W.-H., Liang, F.-P. & Batten, S. R. (2009). *Inorg. Chem.* **48**, 4674–4684.
- Cotton, F. A., Feng, X. & Timmons, D. J. (1998). *Inorg. Chem.* **37**, 4066–4069.
- Doshi, A., Sundararaman, A., Venkatasubbaiah, K., Zakharov, L. N., Rheingold, A. L., Myahkostupov, M., Piotrowiak, P. & Jäkle, F. (2012). *Organometallics*, **31**, 1546–1558.
- Dowty, E. W. (2004). *ATOMS*. Shape Software, Kingsport, Tennessee, USA.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Hietsoi, O., Dubcaec, C., Filatov, A. S. & Petrukhina, M. A. (2011). *Chem. Commun.* **47**, 6939–6941.
- Kappenstein, C. & Hugel, R. P. (1978). *Inorg. Chem.* **17**, 1945–1949.
- Peng, R., Li, M. & Li, D. (2010). *Coord. Chem. Rev.* **254**, 1–18.
- Saines, P. J., Elcombe, M. M. & Kennedy, B. J. (2006). *J. Solid State Chem.* **179**, 613–622.
- Schmidbaur, H. & Schier, A. (2012). *Chem. Soc. Rev.* **41**, 370–412.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2015). *Acta Cryst.* **C71**, 3–8.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Sundararaman, A., Zakharov, L. N., Rheingold, A. L. & Jäkle, F. (2005). *Chem. Commun.* pp. 1708–1710.
- Tsukihara, T., Aoyama, H., Yamashita, E., Tomizaki, T., Yamaguchi, H., Shinzawa-Itoh, K., Nakashima, R., Yaono, R. & Yoshikawa, S. (1995). *Science*, **269**, 1069–1074.
- Xin, B., Zeng, G., Gao, L., Li, Y., Xing, S., Hua, J., Li, G., Shi, Z. & Feng, S. (2013). *Dalton Trans.* **42**, 7562–7568.
- Zheng, S. L., Messerschmidt, M. & Coppens, P. (2005). *Angew. Chem. Int. Ed.* **44**, 4614–4617.

## supporting information

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## An unusual coordination polymer containing Cu<sup>+</sup> ions and featuring possible Cu...Cu 'cuprophilic' interactions: poly[di- $\mu$ -chlorido-( $\mu_4$ -3,5-diaminobenzoato- $\kappa^4$ O:O':N:N')tricopper(I)(3 Cu—Cu)]

**Muhammad Kaleem Khosa, Paul T. Wood, Simon M. Humphrey and William T. A. Harrison**

### Computing details

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINTE* (Bruker, 2004); data reduction: *SAINTE* (Bruker, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *ATOMS* (Dowty, 2004); software used to prepare material for publication: *SHELXL2014* (Sheldrick, 2015).

### Poly[di- $\mu$ -chlorido-( $\mu_4$ -3,5-diaminobenzoato- $\kappa^4$ O:O')tricopper(I)(3 Cu—Cu)]

#### Crystal data

[Cu<sub>3</sub>(C<sub>7</sub>H<sub>7</sub>CN<sub>2</sub>O<sub>2</sub>)Cl<sub>2</sub>]  
 $M_r = 412.67$   
 Monoclinic,  $P2_1/n$   
 $a = 14.4127$  (2) Å  
 $b = 10.8942$  (2) Å  
 $c = 20.2348$  (4) Å  
 $\beta = 104.8395$  (7)°  
 $V = 3071.20$  (9) Å<sup>3</sup>  
 $Z = 12$

$F(000) = 2400$   
 $D_x = 2.677$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 23785 reflections  
 $\theta = 1.0$ – $30.0$ °  
 $\mu = 6.68$  mm<sup>-1</sup>  
 $T = 180$  K  
 Block, colourless  
 $0.39 \times 0.16 \times 0.14$  mm

#### Data collection

Bruker APEXII CCD  
 diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan  
 (*SADABS*; Bruker, 2004)  
 $T_{\min} = 0.181$ ,  $T_{\max} = 0.455$   
 16907 measured reflections

5987 independent reflections  
 4798 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.069$   
 $\theta_{\max} = 26.0$ °,  $\theta_{\min} = 2.1$ °  
 $h = -17 \rightarrow 17$   
 $k = -12 \rightarrow 13$   
 $l = -22 \rightarrow 24$

#### Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.069$   
 $wR(F^2) = 0.202$   
 $S = 1.04$   
 5987 reflections  
 436 parameters  
 0 restraints

Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.1163P)^2 + 23.2868P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.001$   
 $\Delta\rho_{\max} = 3.40$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -2.71$  e Å<sup>-3</sup>

*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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.46131 (6)	-0.15788 (7)	0.11250 (4)	0.0217 (2)
Cu2	0.37595 (6)	-0.15297 (7)	0.21918 (5)	0.0228 (2)
Cu3	0.26100 (8)	0.15557 (9)	0.44481 (5)	0.0351 (3)
Cu4	0.25123 (7)	0.12385 (8)	0.57694 (5)	0.0286 (3)
Cu5	0.08697 (7)	-0.14980 (8)	0.77262 (5)	0.0325 (3)
Cu6	0.08418 (7)	-0.12935 (8)	0.90781 (5)	0.0275 (3)
Cu7	0.5000	0.0000	0.0000	0.0177 (3)
Cu8	0.32887 (5)	-0.00559 (7)	0.33262 (4)	0.0199 (2)
Cu9	0.17070 (5)	0.00558 (7)	0.67278 (4)	0.0206 (2)
Cu10	0.0000	0.0000	1.0000	0.0205 (3)
C1	0.4207 (4)	0.2083 (6)	0.1627 (3)	0.0097 (12)
C2	0.4815 (4)	0.2722 (5)	0.1312 (3)	0.0104 (11)
H2	0.5227	0.2291	0.1094	0.013*
C3	0.4813 (4)	0.3997 (5)	0.1322 (3)	0.0106 (11)
C4	0.4220 (4)	0.4639 (6)	0.1635 (3)	0.0113 (12)
H4	0.4218	0.5511	0.1634	0.014*
C5	0.3622 (4)	0.3990 (5)	0.1954 (3)	0.0107 (11)
C6	0.3601 (4)	0.2720 (5)	0.1953 (3)	0.0096 (11)
H6	0.3185	0.2288	0.2168	0.012*
C7	0.4201 (4)	0.0721 (6)	0.1633 (3)	0.0110 (12)
N1	0.5492 (4)	0.4670 (5)	0.1044 (3)	0.0145 (10)
H1A	0.5233	0.5407	0.0883	0.017*
H1B	0.5606	0.4243	0.0686	0.017*
N2	0.2977 (4)	0.4666 (5)	0.2273 (3)	0.0147 (11)
H2A	0.3248	0.5405	0.2419	0.018*
H2B	0.2915	0.4243	0.2647	0.018*
C8	0.2549 (4)	-0.2226 (5)	0.4944 (3)	0.0092 (11)
C9	0.3132 (4)	-0.2847 (5)	0.4599 (3)	0.0104 (11)
H9	0.3537	-0.2406	0.4379	0.013*
C10	0.3110 (4)	-0.4128 (5)	0.4583 (3)	0.0106 (11)
C11	0.2500 (4)	-0.4779 (5)	0.4887 (3)	0.0109 (11)
H11	0.2471	-0.5649	0.4857	0.013*
C12	0.1938 (4)	-0.4154 (5)	0.5231 (3)	0.0095 (11)
C13	0.1960 (4)	-0.2881 (5)	0.5268 (3)	0.0112 (11)
H13	0.1577	-0.2459	0.5514	0.013*
C14	0.2570 (4)	-0.0856 (5)	0.4979 (3)	0.0099 (11)
N3	0.3797 (4)	-0.4791 (5)	0.4304 (3)	0.0142 (11)
H3A	0.3906	-0.4368	0.3943	0.017*
H3B	0.3554	-0.5539	0.4152	0.017*



N4	0.1299 (4)	-0.4819 (5)	0.5553 (3)	0.0134 (10)
H4A	0.1282	-0.4423	0.5946	0.016*
H4B	0.1548	-0.5580	0.5670	0.016*
C15	0.0841 (3)	0.2246 (6)	0.8298 (3)	0.0093 (12)
C16	0.1397 (4)	0.2878 (5)	0.7943 (3)	0.0093 (11)
H16	0.1787	0.2441	0.7710	0.011*
C17	0.1380 (4)	0.4154 (5)	0.7931 (3)	0.0106 (11)
C18	0.0782 (4)	0.4802 (6)	0.8243 (3)	0.0100 (12)
H18	0.0752	0.5672	0.8217	0.012*
C19	0.0224 (4)	0.4157 (5)	0.8595 (3)	0.0101 (11)
C20	0.0262 (4)	0.2895 (5)	0.8635 (3)	0.0102 (11)
H20	-0.0103	0.2467	0.8891	0.012*
C21	0.0866 (3)	0.0876 (6)	0.8327 (3)	0.0089 (12)
N5	0.2042 (4)	0.4809 (5)	0.7630 (3)	0.0146 (11)
H5A	0.1786	0.5553	0.7479	0.018*
H5B	0.2121	0.4382	0.7262	0.018*
N6	-0.0426 (4)	0.4826 (5)	0.8907 (3)	0.0142 (11)
H6A	-0.0168	0.5576	0.9039	0.017*
H6B	-0.0469	0.4417	0.9290	0.017*
O1	0.4743 (3)	0.0166 (4)	0.1325 (2)	0.0180 (10)
O2	0.3656 (3)	0.0181 (4)	0.1938 (2)	0.0206 (10)
O3	0.2921 (4)	-0.0264 (4)	0.4563 (2)	0.0199 (10)
O4	0.2252 (4)	-0.0391 (4)	0.5446 (2)	0.0216 (10)
O5	0.1191 (3)	0.0303 (4)	0.7893 (2)	0.0167 (9)
O6	0.0561 (3)	0.0371 (4)	0.8790 (2)	0.0172 (9)
Cl1	0.39320 (11)	-0.29137 (15)	0.03396 (8)	0.0225 (4)
Cl2	0.43913 (10)	-0.29010 (13)	0.29733 (8)	0.0172 (3)
Cl3	0.27191 (12)	0.25776 (14)	0.34882 (8)	0.0214 (4)
Cl4	0.26239 (11)	0.28564 (14)	0.63859 (8)	0.0202 (4)
Cl5	0.10718 (11)	-0.25623 (14)	0.68104 (7)	0.0186 (3)
Cl6	0.08403 (13)	-0.28007 (15)	0.97701 (8)	0.0267 (4)

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0264 (5)	0.0164 (4)	0.0250 (5)	-0.0048 (3)	0.0116 (4)	-0.0076 (3)
Cu2	0.0257 (5)	0.0185 (4)	0.0285 (5)	0.0069 (3)	0.0145 (4)	0.0101 (3)
Cu3	0.0522 (7)	0.0215 (5)	0.0343 (6)	0.0021 (4)	0.0159 (5)	0.0124 (4)
Cu4	0.0384 (6)	0.0200 (5)	0.0280 (5)	-0.0033 (4)	0.0099 (4)	-0.0105 (4)
Cu5	0.0354 (6)	0.0252 (5)	0.0399 (6)	-0.0039 (4)	0.0151 (5)	-0.0167 (4)
Cu6	0.0326 (5)	0.0203 (5)	0.0271 (5)	-0.0019 (4)	0.0027 (4)	0.0122 (4)
Cu7	0.0091 (6)	0.0185 (6)	0.0275 (6)	0.0053 (4)	0.0085 (5)	0.0021 (5)
Cu8	0.0108 (5)	0.0220 (5)	0.0294 (5)	-0.0067 (3)	0.0096 (4)	-0.0035 (3)
Cu9	0.0117 (5)	0.0254 (5)	0.0267 (5)	0.0080 (3)	0.0084 (4)	0.0065 (3)
Cu10	0.0109 (6)	0.0262 (6)	0.0254 (6)	-0.0074 (4)	0.0066 (5)	-0.0058 (5)
C1	0.007 (3)	0.011 (3)	0.008 (3)	0.0022 (19)	-0.002 (2)	0.000 (2)
C2	0.005 (2)	0.017 (3)	0.009 (3)	0.001 (2)	0.001 (2)	0.000 (2)
C3	0.008 (3)	0.013 (3)	0.010 (3)	-0.004 (2)	0.000 (2)	0.001 (2)

C4	0.009 (3)	0.013 (3)	0.012 (3)	-0.004 (2)	0.002 (2)	0.000 (2)
C5	0.006 (3)	0.014 (3)	0.009 (3)	0.000 (2)	-0.003 (2)	-0.004 (2)
C6	0.007 (3)	0.013 (3)	0.008 (3)	-0.005 (2)	0.001 (2)	-0.003 (2)
C7	0.009 (3)	0.013 (3)	0.011 (3)	0.002 (2)	0.002 (2)	-0.002 (2)
N1	0.010 (2)	0.016 (2)	0.020 (3)	-0.003 (2)	0.008 (2)	0.004 (2)
N2	0.017 (3)	0.009 (2)	0.023 (3)	0.000 (2)	0.012 (2)	-0.002 (2)
C8	0.005 (2)	0.012 (3)	0.010 (3)	0.001 (2)	-0.001 (2)	0.000 (2)
C9	0.005 (3)	0.013 (3)	0.013 (3)	-0.003 (2)	0.003 (2)	-0.001 (2)
C10	0.008 (3)	0.012 (3)	0.011 (3)	0.005 (2)	0.001 (2)	-0.004 (2)
C11	0.008 (3)	0.009 (3)	0.016 (3)	0.002 (2)	0.002 (2)	0.003 (2)
C12	0.005 (2)	0.009 (3)	0.014 (3)	-0.002 (2)	0.001 (2)	0.003 (2)
C13	0.012 (3)	0.009 (3)	0.013 (3)	0.003 (2)	0.004 (2)	-0.002 (2)
C14	0.004 (2)	0.012 (3)	0.012 (3)	-0.002 (2)	-0.001 (2)	0.000 (2)
N3	0.014 (3)	0.011 (2)	0.020 (3)	0.002 (2)	0.008 (2)	-0.004 (2)
N4	0.015 (3)	0.010 (2)	0.017 (3)	-0.0028 (19)	0.008 (2)	0.002 (2)
C15	0.002 (3)	0.013 (3)	0.012 (3)	0.0006 (19)	0.000 (2)	0.001 (2)
C16	0.008 (3)	0.009 (3)	0.011 (3)	0.001 (2)	0.003 (2)	0.002 (2)
C17	0.005 (2)	0.010 (3)	0.016 (3)	0.000 (2)	0.001 (2)	0.002 (2)
C18	0.006 (3)	0.010 (3)	0.014 (3)	0.0021 (19)	0.003 (2)	0.002 (2)
C19	0.004 (2)	0.011 (3)	0.014 (3)	-0.001 (2)	0.001 (2)	-0.006 (2)
C20	0.009 (3)	0.011 (3)	0.012 (3)	0.000 (2)	0.005 (2)	-0.003 (2)
C21	0.005 (3)	0.011 (3)	0.011 (3)	0.0014 (18)	0.001 (2)	0.000 (2)
N5	0.017 (3)	0.012 (2)	0.018 (3)	-0.003 (2)	0.009 (2)	0.002 (2)
N6	0.015 (3)	0.011 (2)	0.021 (3)	0.0056 (19)	0.013 (2)	0.000 (2)
O1	0.018 (2)	0.013 (2)	0.026 (2)	0.0008 (17)	0.0106 (19)	-0.0006 (18)
O2	0.023 (2)	0.014 (2)	0.028 (3)	0.0032 (18)	0.013 (2)	0.0036 (19)
O3	0.027 (3)	0.012 (2)	0.026 (2)	0.0021 (18)	0.018 (2)	0.0005 (19)
O4	0.034 (3)	0.015 (2)	0.022 (2)	-0.002 (2)	0.018 (2)	-0.0061 (19)
O5	0.023 (2)	0.011 (2)	0.020 (2)	-0.0025 (18)	0.0128 (19)	-0.0040 (18)
O6	0.027 (2)	0.011 (2)	0.019 (2)	0.0030 (18)	0.0140 (19)	0.0021 (17)
Cl1	0.0208 (8)	0.0233 (8)	0.0202 (8)	-0.0011 (6)	-0.0007 (6)	-0.0058 (6)
Cl2	0.0145 (7)	0.0169 (7)	0.0179 (7)	0.0024 (5)	0.0000 (6)	0.0044 (6)
Cl3	0.0226 (8)	0.0234 (8)	0.0159 (7)	0.0000 (6)	0.0008 (6)	0.0040 (6)
Cl4	0.0204 (8)	0.0179 (7)	0.0178 (7)	0.0031 (6)	-0.0031 (6)	-0.0070 (6)
Cl5	0.0181 (7)	0.0209 (7)	0.0147 (7)	0.0019 (6)	0.0005 (6)	-0.0047 (6)
Cl6	0.0313 (9)	0.0233 (8)	0.0182 (8)	-0.0106 (7)	-0.0070 (7)	0.0095 (6)

*Geometric parameters (Å, °)*

Cu1—O1	1.943 (4)	C7—O2	1.261 (7)
Cu1—Cl1	2.1921 (17)	C7—O1	1.270 (7)
Cu1—Cl5 <sup>i</sup>	2.3928 (17)	N1—Cu9 <sup>viii</sup>	1.957 (5)
Cu1—Cu2	2.7454 (13)	N1—H1A	0.9200
Cu1—Cu7	3.0169 (9)	N1—H1B	0.9200
Cu2—O2	1.929 (5)	N2—Cu8 <sup>iii</sup>	1.938 (5)
Cu2—Cl2	2.1964 (16)	N2—H2A	0.9200
Cu2—Cl3 <sup>ii</sup>	2.4246 (18)	N2—H2B	0.9200
Cu2—Cu8	3.0174 (12)	C8—Cl3	1.395 (8)

Cu3—O3	2.033 (5)	C8—C9	1.398 (8)
Cu3—C13	2.2788 (18)	C8—C14	1.494 (8)
Cu3—C11 <sup>iii</sup>	2.439 (2)	C9—C10	1.395 (8)
Cu3—C16 <sup>iv</sup>	2.485 (2)	C9—H9	0.9500
Cu3—Cu4	2.7350 (14)	C10—C11	1.390 (8)
Cu4—O4	1.896 (5)	C10—N3	1.453 (7)
Cu4—C14	2.1415 (17)	C11—C12	1.376 (8)
Cu4—C11 <sup>iii</sup>	2.7981 (19)	C11—H11	0.9500
Cu4—Cu9	2.8145 (12)	C12—C13	1.389 (8)
Cu5—O5	2.024 (4)	C12—N4	1.452 (7)
Cu5—C15	2.2672 (17)	C13—H13	0.9500
Cu5—C12 <sup>v</sup>	2.4009 (18)	C14—O4	1.257 (7)
Cu5—C14 <sup>vi</sup>	2.5373 (18)	C14—O3	1.263 (7)
Cu5—Cu6	2.7551 (15)	N3—Cu10 <sup>vi</sup>	1.946 (5)
Cu6—O6	1.916 (4)	N3—H3A	0.9200
Cu6—C16	2.1583 (18)	N3—H3B	0.9200
Cu6—C14 <sup>vi</sup>	2.7735 (19)	N4—Cu7 <sup>ii</sup>	1.929 (5)
Cu6—C12 <sup>v</sup>	2.7828 (18)	N4—H4A	0.9200
Cu6—Cu10	2.8455 (10)	N4—H4B	0.9200
Cu7—N4 <sup>i</sup>	1.929 (5)	C15—C16	1.387 (8)
Cu7—N4 <sup>iii</sup>	1.929 (5)	C15—C20	1.398 (8)
Cu7—Cu1 <sup>vii</sup>	3.0168 (9)	C15—C21	1.494 (9)
Cu8—N2 <sup>ii</sup>	1.938 (5)	C16—C17	1.391 (8)
Cu8—N6 <sup>viii</sup>	1.939 (6)	C16—H16	0.9500
Cu8—O3	2.697 (4)	C17—C18	1.385 (8)
Cu9—N5 <sup>vi</sup>	1.953 (5)	C17—N5	1.444 (7)
Cu9—N1 <sup>ix</sup>	1.957 (5)	C18—C19	1.394 (8)
Cu9—O5	2.661 (4)	C18—H18	0.9500
Cu10—N3 <sup>v</sup>	1.946 (5)	C19—C20	1.377 (8)
Cu10—N3 <sup>iv</sup>	1.946 (5)	C19—N6	1.453 (7)
Cu10—O6	2.798 (4)	C20—H20	0.9500
Cu10—O6 <sup>x</sup>	2.798 (4)	C21—O6	1.258 (7)
Cu10—Cu6 <sup>x</sup>	2.8455 (10)	C21—O5	1.260 (7)
C1—C2	1.395 (8)	N5—Cu9 <sup>iv</sup>	1.953 (5)
C1—C6	1.406 (8)	N5—H5A	0.9200
C1—C7	1.484 (9)	N5—H5B	0.9200
C2—C3	1.389 (8)	N6—Cu8 <sup>ix</sup>	1.939 (6)
C2—H2	0.9500	N6—H6A	0.9200
C3—C4	1.378 (8)	N6—H6B	0.9200
C3—N1	1.448 (7)	C11—Cu3 <sup>ii</sup>	2.439 (2)
C4—C5	1.394 (8)	C12—Cu5 <sup>i</sup>	2.4010 (18)
C4—H4	0.9500	C13—Cu2 <sup>iii</sup>	2.4246 (18)
C5—C6	1.384 (8)	C14—Cu5 <sup>iv</sup>	2.5373 (18)
C5—N2	1.458 (7)	C15—Cu1 <sup>v</sup>	2.3929 (17)
C6—H6	0.9500	C16—Cu3 <sup>vi</sup>	2.485 (2)
O1—Cu1—C11	143.31 (15)	C10—C11—H11	120.3
O1—Cu1—C15 <sup>i</sup>	103.78 (15)	C11—C12—C13	120.9 (5)

C11—Cu1—C15 <sup>i</sup>	108.94 (6)	C11—C12—N4	120.3 (5)
O2—Cu2—C12	147.00 (16)	C13—C12—N4	118.8 (5)
O2—Cu2—C13 <sup>ii</sup>	103.86 (15)	C12—C13—C8	119.6 (5)
C12—Cu2—C13 <sup>ii</sup>	106.14 (6)	C12—C13—H13	120.2
O3—Cu3—C13	120.86 (15)	C8—C13—H13	120.2
O3—Cu3—C11 <sup>iii</sup>	113.26 (14)	O4—C14—O3	125.4 (6)
C13—Cu3—C11 <sup>iii</sup>	107.42 (7)	O4—C14—C8	115.5 (5)
O3—Cu3—C16 <sup>iv</sup>	93.82 (16)	O3—C14—C8	119.0 (5)
C13—Cu3—C16 <sup>iv</sup>	99.08 (7)	C10—N3—Cu10 <sup>vi</sup>	110.3 (4)
C11 <sup>iii</sup> —Cu3—C16 <sup>iv</sup>	122.15 (7)	C10—N3—H3A	109.6
O4—Cu4—C14	161.90 (15)	Cu10 <sup>vi</sup> —N3—H3A	109.6
O5—Cu5—C15	124.08 (14)	C10—N3—H3B	109.6
O5—Cu5—C12 <sup>v</sup>	113.99 (14)	Cu10 <sup>vi</sup> —N3—H3B	109.6
C15—Cu5—C12 <sup>v</sup>	109.72 (7)	H3A—N3—H3B	108.1
O5—Cu5—C14 <sup>vi</sup>	91.90 (14)	C12—N4—Cu7 <sup>ii</sup>	115.0 (4)
C15—Cu5—C14 <sup>vi</sup>	99.86 (6)	C12—N4—H4A	108.5
C12 <sup>v</sup> —Cu5—C14 <sup>vi</sup>	114.90 (7)	Cu7 <sup>ii</sup> —N4—H4A	108.5
O6—Cu6—C16	151.94 (15)	C12—N4—H4B	108.5
N4 <sup>i</sup> —Cu7—N4 <sup>iii</sup>	180.0	Cu7 <sup>ii</sup> —N4—H4B	108.5
N2 <sup>ii</sup> —Cu8—N6 <sup>viii</sup>	177.8 (2)	H4A—N4—H4B	107.5
N5 <sup>vi</sup> —Cu9—N1 <sup>ix</sup>	176.6 (2)	C16—C15—C20	119.9 (6)
N3 <sup>v</sup> —Cu10—N3 <sup>iv</sup>	180.0 (3)	C16—C15—C21	120.3 (5)
C2—C1—C6	120.4 (6)	C20—C15—C21	119.8 (5)
C2—C1—C7	120.6 (5)	C15—C16—C17	119.7 (5)
C6—C1—C7	119.0 (5)	C15—C16—H16	120.2
C3—C2—C1	119.2 (5)	C17—C16—H16	120.2
C3—C2—H2	120.4	C18—C17—C16	120.8 (5)
C1—C2—H2	120.4	C18—C17—N5	119.7 (5)
C4—C3—C2	121.2 (5)	C16—C17—N5	119.4 (5)
C4—C3—N1	118.9 (5)	C17—C18—C19	119.0 (6)
C2—C3—N1	119.7 (5)	C17—C18—H18	120.5
C3—C4—C5	119.0 (6)	C19—C18—H18	120.5
C3—C4—H4	120.5	C20—C19—C18	120.9 (5)
C5—C4—H4	120.5	C20—C19—N6	119.7 (5)
C6—C5—C4	121.4 (5)	C18—C19—N6	119.3 (5)
C6—C5—N2	119.3 (5)	C19—C20—C15	119.7 (5)
C4—C5—N2	119.2 (5)	C19—C20—H20	120.2
C5—C6—C1	118.6 (5)	C15—C20—H20	120.2
C5—C6—H6	120.7	O6—C21—O5	124.4 (6)
C1—C6—H6	120.7	O6—C21—C15	117.2 (5)
O2—C7—O1	123.7 (6)	O5—C21—C15	118.4 (5)
O2—C7—C1	118.5 (5)	C17—N5—Cu9 <sup>iv</sup>	112.6 (4)
O1—C7—C1	117.8 (5)	C17—N5—H5A	109.1
C3—N1—Cu9 <sup>viii</sup>	111.9 (4)	Cu9 <sup>iv</sup> —N5—H5A	109.1
C3—N1—H1A	109.2	C17—N5—H5B	109.1
Cu9 <sup>viii</sup> —N1—H1A	109.2	Cu9 <sup>iv</sup> —N5—H5B	109.1
C3—N1—H1B	109.2	H5A—N5—H5B	107.8
Cu9 <sup>viii</sup> —N1—H1B	109.2	C19—N6—Cu8 <sup>ix</sup>	115.1 (4)

H1A—N1—H1B	107.9	C19—N6—H6A	108.5
C5—N2—Cu8 <sup>iii</sup>	114.0 (4)	Cu8 <sup>ix</sup> —N6—H6A	108.5
C5—N2—H2A	108.8	C19—N6—H6B	108.5
Cu8 <sup>iii</sup> —N2—H2A	108.8	Cu8 <sup>ix</sup> —N6—H6B	108.5
C5—N2—H2B	108.8	H6A—N6—H6B	107.5
Cu8 <sup>iii</sup> —N2—H2B	108.8	C7—O1—Cu1	122.0 (4)
H2A—N2—H2B	107.6	C7—O2—Cu2	124.5 (4)
C13—C8—C9	120.2 (5)	C14—O3—Cu3	117.4 (4)
C13—C8—C14	119.8 (5)	C14—O4—Cu4	124.0 (4)
C9—C8—C14	120.0 (5)	C21—O5—Cu5	119.1 (4)
C10—C9—C8	118.8 (5)	C21—O6—Cu6	123.6 (4)
C10—C9—H9	120.6	Cu1—C11—Cu3 <sup>ii</sup>	106.78 (7)
C8—C9—H9	120.6	Cu2—C12—Cu5 <sup>i</sup>	105.19 (7)
C11—C10—C9	120.9 (5)	Cu3—C13—Cu2 <sup>iii</sup>	115.93 (8)
C11—C10—N3	119.3 (5)	Cu4—C14—Cu5 <sup>iv</sup>	124.31 (8)
C9—C10—N3	119.5 (5)	Cu5—C15—Cu1 <sup>v</sup>	113.33 (7)
C12—C11—C10	119.5 (5)	Cu6—C16—Cu3 <sup>vi</sup>	118.53 (8)
C12—C11—H11	120.3		
C6—C1—C2—C3	-0.2 (8)	C20—C19—N6—Cu8 <sup>ix</sup>	-88.0 (6)
C7—C1—C2—C3	-179.2 (5)	C18—C19—N6—Cu8 <sup>ix</sup>	90.3 (6)
C1—C2—C3—C4	-0.1 (8)	O2—C7—O1—Cu1	12.7 (7)
C1—C2—C3—N1	175.3 (5)	C1—C7—O1—Cu1	-166.7 (4)
C2—C3—C4—C5	0.8 (8)	C11—Cu1—O1—C7	93.3 (5)
N1—C3—C4—C5	-174.7 (5)	C15 <sup>i</sup> —Cu1—O1—C7	-114.0 (4)
C3—C4—C5—C6	-1.1 (8)	Cu2—Cu1—O1—C7	-22.7 (4)
C3—C4—C5—N2	-178.6 (5)	Cu7—Cu1—O1—C7	139.2 (5)
C4—C5—C6—C1	0.7 (8)	O1—C7—O2—Cu2	16.1 (8)
N2—C5—C6—C1	178.2 (5)	C1—C7—O2—Cu2	-164.5 (4)
C2—C1—C6—C5	0.0 (8)	C12—Cu2—O2—C7	89.9 (5)
C7—C1—C6—C5	179.0 (5)	C13 <sup>ii</sup> —Cu2—O2—C7	-115.3 (5)
C2—C1—C7—O2	178.4 (5)	Cu1—Cu2—O2—C7	-24.6 (5)
C6—C1—C7—O2	-0.6 (8)	Cu8—Cu2—O2—C7	140.2 (5)
C2—C1—C7—O1	-2.2 (8)	O4—C14—O3—Cu3	-18.7 (8)
C6—C1—C7—O1	178.8 (5)	C8—C14—O3—Cu3	163.5 (4)
C4—C3—N1—Cu9 <sup>viii</sup>	87.5 (6)	C13—Cu3—O3—C14	-158.1 (4)
C2—C3—N1—Cu9 <sup>viii</sup>	-88.0 (6)	C11 <sup>iii</sup> —Cu3—O3—C14	-28.6 (5)
C6—C5—N2—Cu8 <sup>iii</sup>	-85.6 (6)	C16 <sup>iv</sup> —Cu3—O3—C14	98.9 (4)
C4—C5—N2—Cu8 <sup>iii</sup>	92.0 (5)	Cu4—Cu3—O3—C14	28.9 (4)
C13—C8—C9—C10	0.3 (8)	O3—C14—O4—Cu4	-16.1 (8)
C14—C8—C9—C10	179.1 (5)	C8—C14—O4—Cu4	161.7 (4)
C8—C9—C10—C11	1.8 (8)	C14—Cu4—O4—C14	-166.7 (4)
C8—C9—C10—N3	-172.2 (5)	Cu3—Cu4—O4—C14	29.5 (5)
C9—C10—C11—C12	-2.5 (9)	Cu9—Cu4—O4—C14	-167.2 (5)
N3—C10—C11—C12	171.4 (5)	O6—C21—O5—Cu5	18.9 (7)
C10—C11—C12—C13	1.1 (9)	C15—C21—O5—Cu5	-161.4 (4)
C10—C11—C12—N4	-179.8 (5)	C15—Cu5—O5—C21	164.7 (4)
C11—C12—C13—C8	1.1 (9)	C12 <sup>v</sup> —Cu5—O5—C21	26.4 (5)



N4—C12—C13—C8	-178.1 (5)	C14 <sup>vi</sup> —Cu5—O5—C21	-92.0 (4)
C9—C8—C13—C12	-1.8 (8)	Cu6—Cu5—O5—C21	-29.9 (4)
C14—C8—C13—C12	179.5 (5)	O5—C21—O6—Cu6	17.4 (7)
C13—C8—C14—O4	18.2 (8)	C15—C21—O6—Cu6	-162.3 (4)
C9—C8—C14—O4	-160.5 (5)	C16—Cu6—O6—C21	169.6 (3)
C13—C8—C14—O3	-163.8 (5)	Cu5—Cu6—O6—C21	-30.6 (4)
C9—C8—C14—O3	17.5 (8)	Cu10—Cu6—O6—C21	168.2 (5)
C11—C10—N3—Cu10 <sup>vi</sup>	-89.8 (6)	O1—Cu1—Cl1—Cu3 <sup>ii</sup>	-90.7 (2)
C9—C10—N3—Cu10 <sup>vi</sup>	84.3 (6)	Cl5 <sup>i</sup> —Cu1—Cl1—Cu3 <sup>ii</sup>	117.39 (7)
C11—C12—N4—Cu7 <sup>ii</sup>	-93.8 (6)	Cu2—Cu1—Cl1—Cu3 <sup>ii</sup>	15.68 (8)
C13—C12—N4—Cu7 <sup>ii</sup>	85.3 (6)	Cu7—Cu1—Cl1—Cu3 <sup>ii</sup>	-131.23 (6)
C20—C15—C16—C17	0.5 (8)	O2—Cu2—Cl2—Cu5 <sup>i</sup>	-90.0 (3)
C21—C15—C16—C17	-178.8 (5)	Cl3 <sup>ii</sup> —Cu2—Cl2—Cu5 <sup>i</sup>	115.39 (7)
C15—C16—C17—C18	-3.0 (9)	Cu1—Cu2—Cl2—Cu5 <sup>i</sup>	15.51 (8)
C15—C16—C17—N5	172.9 (5)	Cu8—Cu2—Cl2—Cu5 <sup>i</sup>	-136.75 (6)
C16—C17—C18—C19	2.7 (8)	O3—Cu3—Cl3—Cu2 <sup>iii</sup>	118.45 (18)
N5—C17—C18—C19	-173.1 (5)	Cl1 <sup>iii</sup> —Cu3—Cl3—Cu2 <sup>iii</sup>	-13.58 (10)
C17—C18—C19—C20	0.0 (8)	Cl6 <sup>iv</sup> —Cu3—Cl3—Cu2 <sup>iii</sup>	-141.53 (7)
C17—C18—C19—N6	-178.3 (5)	Cu4—Cu3—Cl3—Cu2 <sup>iii</sup>	-80.2 (2)
C18—C19—C20—C15	-2.4 (8)	O4—Cu4—Cl4—Cu5 <sup>iv</sup>	95.9 (5)
N6—C19—C20—C15	175.9 (5)	Cu3—Cu4—Cl4—Cu5 <sup>iv</sup>	-102.07 (9)
C16—C15—C20—C19	2.1 (8)	Cu9—Cu4—Cl4—Cu5 <sup>iv</sup>	96.38 (9)
C21—C15—C20—C19	-178.6 (5)	O5—Cu5—Cl5—Cu1 <sup>v</sup>	-120.24 (18)
C16—C15—C21—O6	161.7 (5)	Cl2 <sup>v</sup> —Cu5—Cl5—Cu1 <sup>v</sup>	19.58 (10)
C20—C15—C21—O6	-17.6 (7)	Cl4 <sup>vi</sup> —Cu5—Cl5—Cu1 <sup>v</sup>	140.66 (7)
C16—C15—C21—O5	-18.1 (7)	Cu6—Cu5—Cl5—Cu1 <sup>v</sup>	92.79 (15)
C20—C15—C21—O5	162.6 (5)	O6—Cu6—Cl6—Cu3 <sup>vi</sup>	-107.5 (3)
C18—C17—N5—Cu9 <sup>iv</sup>	91.0 (6)	Cu5—Cu6—Cl6—Cu3 <sup>vi</sup>	97.29 (9)
C16—C17—N5—Cu9 <sup>iv</sup>	-84.9 (6)	Cu10—Cu6—Cl6—Cu3 <sup>vi</sup>	-106.27 (8)

Symmetry codes: (i)  $x+1/2, -y-1/2, z-1/2$ ; (ii)  $-x+1/2, y-1/2, -z+1/2$ ; (iii)  $-x+1/2, y+1/2, -z+1/2$ ; (iv)  $-x+1/2, y+1/2, -z+3/2$ ; (v)  $x-1/2, -y-1/2, z+1/2$ ; (vi)  $-x+1/2, y-1/2, -z+3/2$ ; (vii)  $-x+1, -y, -z$ ; (viii)  $x+1/2, -y+1/2, z-1/2$ ; (ix)  $x-1/2, -y+1/2, z+1/2$ ; (x)  $-x, -y, -z+2$ .

#### Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
N1—H1 <i>A</i> $\cdots$ C11 <sup>xi</sup>	0.92	2.64	3.517 (6)	160
N1—H1 <i>B</i> $\cdots$ C11 <sup>vii</sup>	0.92	2.74	3.657 (6)	176
N2—H2 <i>A</i> $\cdots$ C12 <sup>xi</sup>	0.92	2.53	3.422 (5)	164
N2—H2 <i>B</i> $\cdots$ C13	0.92	2.54	3.440 (5)	165
N3—H3 <i>A</i> $\cdots$ C12	0.92	2.75	3.661 (6)	173
N3—H3 <i>B</i> $\cdots$ C13 <sup>xiii</sup>	0.92	2.57	3.471 (5)	168
N4—H4 <i>A</i> $\cdots$ C15	0.92	2.73	3.612 (5)	160
N4—H4 <i>B</i> $\cdots$ C14 <sup>xii</sup>	0.92	2.49	3.354 (5)	156
N5—H5 <i>A</i> $\cdots$ C15 <sup>xi</sup>	0.92	2.52	3.423 (5)	168
N5—H5 <i>B</i> $\cdots$ C14	0.92	2.65	3.557 (6)	168

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N6—H6A...C16 <sup>xi</sup>	0.92	2.51	3.382 (6)	159
N6—H6B...C16 <sup>x</sup>	0.92	2.73	3.634 (6)	167

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Symmetry codes: (vii)  $-x+1, -y, -z$ ; (x)  $-x, -y, -z+2$ ; (xi)  $x, y+1, z$ ; (xii)  $x, y-1, z$ .