

Hexa- μ -chlorido- μ_4 -oxido-tetrakis({1-[(pyridin-2-yl)methyl]-1H-benzimidazole- κ N³}copper(II))

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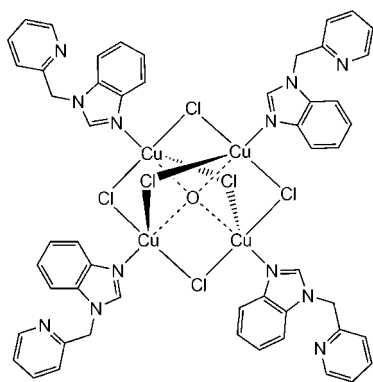
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Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.009$ Å; R factor = 0.028; wR factor = 0.062; data-to-parameter ratio = 14.5.

The title tetranuclear complex, $[\text{Cu}_4\text{Cl}_6\text{O}(\text{C}_{13}\text{H}_{11}\text{N}_3)_4]$, features a tetrahedral arrangement of copper(II) ions bonded to the central O atom (site symmetry $\bar{4}$). Each of the six edges of the Cu_4 tetrahedron is bridged by a chloride ion (one of which has site symmetry 2), so that each copper ion is linked to the other three metal ions through the central O atom and through three separate chloride-ion bridges. The fifth coordination position, located on the central Cu—O axis on the outside of the cluster, is occupied by an N atom of the monodentate 1-(pyridin-2-ylmethyl)-1H-benzimidazole ligand. The resulting coordination geometry of the metal ion is a distorted trigonal bipyramid with the O and N atoms in the axial positions. The dihedral angle between the benzimidazole ring system and the pendant pyridine ring is $61.0(2)^\circ$.

Related literature

For background to polynuclear copper halides, see: Willett (1991); Chivers *et al.* (2005); Li *et al.* (2009).



Experimental

Crystal data

$[\text{Cu}_4\text{Cl}_6\text{O}(\text{C}_{13}\text{H}_{11}\text{N}_3)_4]$
 $M_r = 1319.85$
 Tetragonal, $I\bar{4}$
 $a = 13.8532(12)$ Å
 $c = 14.507(3)$ Å
 $V = 2784.1(6)$ Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 1.85$ mm⁻¹
 $T = 294$ K
 $0.25 \times 0.23 \times 0.20$ mm

Data collection

Rigaku Mercury CCD diffractometer
 Absorption correction: multi-scan (*CrystalClear*; Rigaku/MS, 2005)
 $T_{\min} = 0.637$, $T_{\max} = 0.691$

7149 measured reflections
 2467 independent reflections
 2178 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.028$
 $wR(F^2) = 0.062$
 $S = 1.06$
 2467 reflections
 170 parameters
 H-atom parameters constrained

$\Delta\rho_{\max} = 0.34$ e Å⁻³
 $\Delta\rho_{\min} = -0.17$ e Å⁻³
 Absolute structure: Flack (1983), 1172 Friedel pairs
 Flack parameter: 0.005 (15)

Table 1

Selected bond lengths (Å).

Cu1—O1	1.9199 (4)	Cu1—Cl1	2.4192 (10)
Cu1—N3	1.974 (3)	Cu1—Cl2	2.4263 (10)
Cu1—Cl1 ⁱ	2.3961 (10)		

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

Data collection: *CrystalClear* (Rigaku/MS, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB6384).

References

- Chivers, T., Fu, Z. & Thompson, L. K. (2005). *Chem. Commun.* pp. 2339–2341.
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
 Li, Z. X., Xu, Y., Zuo, Y., Li, L., Pan, Q., Hu, T. L. & Bu, X. H. (2009). *Cryst. Growth Des.* **9**, 3904–3909.
 Rigaku/MS (2005). *CrystalClear*. Rigaku/MS Inc., The Woodlands, Texas, USA.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Willett, R. D. (1991). *Coord. Chem. Rev.* **109**, 181–205.

supplementary materials

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Hexa- μ -chlorido- μ_4 -oxido-tetrakis({1-[(pyridin-2-yl)methyl]-1*H*-benzimidazole- κ N³})copper(II)

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Comment

Copper(II) halide framework materials have attracted much attention for their interesting magnetic properties and structural richness (Willett *et al.*, 1991). The most commonly employed technique to modulate the inorganic network involves the direct addition of an organic ligand as a templating reagent (Chivers *et al.*, 2005). benzimidazole has been well used in crystal engineering, and a large number of benzimidazole ligands have been extensively studied (Li *et al.*, 2009). The reaction of CuCl_2 with the benzimidazole-pyridine ligand (**L**) affords a tetranuclear molecule $[(\text{Cu}_4\text{O})\text{Cl}_6(\text{L})_4]$, (**I**). The crystal structure was elucidated by X-ray diffraction analysis.

Experimental

To a solution of **L** (0.12 mmol, 25 mg) dissolved in CH_3CN (9 ml), a solution of $\text{CuCl}_2 \cdot 6\text{H}_2\text{O}$ (0.12 mmol, 28.9 mg) in H_2O (9 ml) was added under stirring in a few minutes. The solution was left to stand at room temperature. Brown blocks of (**I**) were obtained after several days with solvent evaporation. Yield: ~20% (based on **L**).

Refinement

C-bound H atoms were positioned geometrically and refined in the riding-model approximation, with $\text{C}-\text{H} = 0.93\text{\AA}$ and $U_{\text{iso}}(\text{H}) = 1.2\text{U}_{\text{eq}}$.

Figures

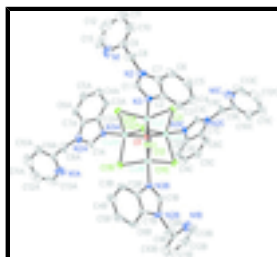


Fig. 1. The molecular structure of (**I**). Displacement ellipsoids are drawn at the 30% probability level and H atoms are removed for clarity. [symmetry code: (A) $-y + 1, x, -z$; (B) $y, -x + 1, -z$; (C) $-x + 1, -y + 1, z$].

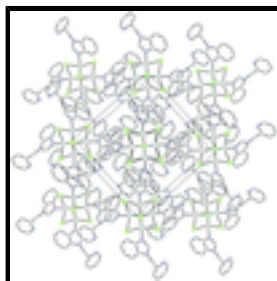


Fig. 2. The crystal packing for (**I**) viewed along the *c* axis.

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Crystal data

$[\text{Cu}_4\text{Cl}_6\text{O}(\text{C}_{13}\text{H}_{11}\text{N}_3)_4]$	$D_x = 1.574 \text{ Mg m}^{-3}$
$M_r = 1319.85$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Tetragonal, $I\bar{4}$	Cell parameters from 3492 reflections
$a = 13.8532 (12) \text{ \AA}$	$\theta = 2.8\text{--}25.3^\circ$
$c = 14.507 (3) \text{ \AA}$	$\mu = 1.85 \text{ mm}^{-1}$
$V = 2784.1 (6) \text{ \AA}^3$	$T = 294 \text{ K}$
$Z = 2$	Block, brown
$F(000) = 1332$	$0.25 \times 0.23 \times 0.20 \text{ mm}$

Data collection

Rigaku Mercury CCD diffractometer	2467 independent reflections
Radiation source: fine-focus sealed tube graphite	2178 reflections with $I > 2\sigma(I)$
Detector resolution: 9 pixels mm^{-1}	$R_{\text{int}} = 0.033$
ω scans	$\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 2.0^\circ$
Absorption correction: multi-scan (<i>CrystalClear</i> ; Rigaku/MSO, 2005)	$h = -14 \rightarrow 16$
$T_{\text{min}} = 0.637$, $T_{\text{max}} = 0.691$	$k = -16 \rightarrow 14$
7149 measured reflections	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.028$	H-atom parameters constrained
$wR(F^2) = 0.062$	$w = 1/[\sigma^2(F_o^2) + (0.0286P)^2]$
$S = 1.06$	where $P = (F_o^2 + 2F_c^2)/3$
2467 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
170 parameters	$\Delta\rho_{\text{max}} = 0.34 \text{ e \AA}^{-3}$
0 restraints	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$
0 constraints	Absolute structure: Flack (1983), 1172 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.005 (15)

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.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.42929 (3)	0.41004 (3)	0.07467 (3)	0.03400 (12)
Cl1	0.28847 (6)	0.47255 (6)	-0.00384 (7)	0.0473 (2)
Cl2	0.5000	0.5000	0.20129 (8)	0.0637 (4)
N3	0.3550 (2)	0.3189 (2)	0.1515 (2)	0.0412 (7)
C1	0.3592 (3)	0.2243 (3)	0.1520 (3)	0.0498 (10)
H1	0.3992	0.1887	0.1133	0.060*
C2	0.2867 (3)	0.3436 (3)	0.2180 (2)	0.0485 (10)
C7	0.2518 (3)	0.2588 (3)	0.2595 (3)	0.0533 (10)
N2	0.2998 (3)	0.1839 (2)	0.2144 (2)	0.0548 (9)
C6	0.1844 (3)	0.2627 (4)	0.3322 (3)	0.0736 (15)
H6	0.1636	0.2068	0.3616	0.088*
C3	0.2513 (3)	0.4325 (3)	0.2461 (3)	0.0663 (13)
H3	0.2726	0.4892	0.2184	0.080*
C4	0.1837 (4)	0.4350 (4)	0.3161 (4)	0.0844 (16)
H4	0.1593	0.4940	0.3359	0.101*
C5	0.1515 (4)	0.3495 (5)	0.3574 (4)	0.0899 (18)
H5	0.1056	0.3532	0.4040	0.108*
C8	0.2900 (4)	0.0806 (3)	0.2368 (3)	0.0755 (15)
H8A	0.2343	0.0721	0.2764	0.091*
H8B	0.3465	0.0601	0.2711	0.091*
O1	0.5000	0.5000	0.0000	0.0292 (9)
C9	0.2789 (3)	0.0170 (3)	0.1543 (3)	0.0563 (10)
C10	0.1944 (4)	-0.0195 (4)	0.1286 (4)	0.0846 (16)
H10	0.1380	-0.0038	0.1600	0.102*
N1	0.3632 (4)	-0.0017 (4)	0.1100 (4)	0.1075 (18)
C12	0.2815 (9)	-0.1018 (5)	0.0115 (5)	0.128 (3)
H12	0.2863	-0.1449	-0.0374	0.154*
C11	0.1926 (7)	-0.0858 (5)	0.0487 (5)	0.116 (2)
H11	0.1364	-0.1138	0.0261	0.139*
C13	0.3600 (8)	-0.0601 (5)	0.0405 (6)	0.140 (4)
H13	0.4172	-0.0730	0.0093	0.168*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0374 (2)	0.0322 (2)	0.03237 (19)	-0.00702 (17)	0.0024 (2)	0.00311 (19)
Cl1	0.0319 (5)	0.0549 (5)	0.0552 (5)	-0.0045 (4)	-0.0026 (4)	0.0094 (5)

supplementary materials

C12	0.0911 (11)	0.0707 (10)	0.0294 (6)	-0.0472 (9)	0.000	0.000
N3	0.0419 (18)	0.0393 (18)	0.0425 (16)	-0.0130 (14)	0.0009 (14)	0.0065 (14)
C1	0.061 (3)	0.045 (2)	0.043 (2)	-0.0162 (19)	-0.006 (2)	0.0044 (19)
C2	0.045 (2)	0.058 (3)	0.042 (2)	-0.0166 (19)	-0.0002 (18)	0.007 (2)
C7	0.054 (2)	0.060 (3)	0.045 (2)	-0.021 (2)	0.001 (2)	0.010 (2)
N2	0.068 (2)	0.048 (2)	0.048 (2)	-0.0231 (17)	-0.0028 (18)	0.0152 (17)
C6	0.064 (3)	0.096 (4)	0.061 (3)	-0.035 (3)	0.005 (2)	0.030 (3)
C3	0.073 (3)	0.060 (3)	0.066 (3)	-0.015 (2)	0.021 (3)	0.003 (2)
C4	0.083 (4)	0.080 (4)	0.091 (4)	-0.003 (3)	0.037 (3)	0.002 (3)
C5	0.084 (4)	0.102 (5)	0.084 (4)	-0.016 (3)	0.040 (3)	0.002 (3)
C8	0.108 (4)	0.054 (3)	0.065 (3)	-0.030 (3)	-0.008 (3)	0.021 (2)
O1	0.0293 (14)	0.0293 (14)	0.029 (2)	0.000	0.000	0.000
C9	0.064 (3)	0.042 (2)	0.064 (3)	-0.002 (2)	0.010 (2)	0.020 (2)
C10	0.093 (4)	0.081 (4)	0.081 (4)	-0.020 (3)	0.010 (3)	0.001 (3)
N1	0.107 (4)	0.085 (3)	0.130 (5)	0.035 (3)	0.033 (3)	0.025 (3)
C12	0.229 (11)	0.066 (4)	0.090 (5)	-0.007 (6)	0.033 (7)	0.000 (4)
C11	0.158 (7)	0.092 (5)	0.097 (5)	-0.030 (5)	-0.005 (5)	0.008 (4)
C13	0.202 (10)	0.064 (5)	0.154 (8)	0.052 (5)	0.079 (7)	0.012 (5)

Geometric parameters (\AA , $^\circ$)

Cu1—O1	1.9199 (4)	C4—C5	1.400 (7)
Cu1—N3	1.974 (3)	C4—H4	0.9300
Cu1—C11 ⁱ	2.3961 (10)	C5—H5	0.9300
Cu1—C11	2.4192 (10)	C8—C9	1.494 (7)
Cu1—C12	2.4263 (10)	C8—H8A	0.9700
C11—Cu1 ⁱⁱ	2.3961 (9)	C8—H8B	0.9700
C12—Cu1 ⁱⁱⁱ	2.4263 (10)	O1—Cu1 ⁱⁱⁱ	1.9199 (4)
N3—C1	1.313 (4)	O1—Cu1 ⁱ	1.9199 (4)
N3—C2	1.394 (5)	O1—Cu1 ⁱⁱ	1.9199 (4)
C1—N2	1.345 (5)	C9—C10	1.328 (6)
C1—H1	0.9300	C9—N1	1.358 (6)
C2—C3	1.386 (6)	C10—C11	1.480 (8)
C2—C7	1.407 (5)	C10—H10	0.9300
C7—N2	1.395 (6)	N1—C13	1.293 (9)
C7—C6	1.409 (6)	C12—C13	1.301 (12)
N2—C8	1.474 (5)	C12—C11	1.362 (10)
C6—C5	1.337 (8)	C12—H12	0.9300
C6—H6	0.9300	C11—H11	0.9300
C3—C4	1.382 (6)	C13—H13	0.9300
C3—H3	0.9300		
O1—Cu1—N3	179.14 (9)	C3—C4—H4	119.7
O1—Cu1—C11 ⁱ	85.68 (3)	C5—C4—H4	119.7
N3—Cu1—C11 ⁱ	95.10 (9)	C6—C5—C4	122.3 (5)
O1—Cu1—C11	85.03 (3)	C6—C5—H5	118.8
N3—Cu1—C11	94.25 (9)	C4—C5—H5	118.8
C11 ⁱ —Cu1—C11	120.483 (17)	N2—C8—C9	113.9 (4)

O1—Cu1—Cl2	83.56 (2)	N2—C8—H8A	108.8
N3—Cu1—Cl2	96.40 (9)	C9—C8—H8A	108.8
Cl1 ⁱ —Cu1—Cl2	117.17 (3)	N2—C8—H8B	108.8
Cl1—Cu1—Cl2	119.88 (3)	C9—C8—H8B	108.8
Cu1 ⁱⁱ —Cl1—Cu1	80.69 (3)	H8A—C8—H8B	107.7
Cu1—Cl2—Cu1 ⁱⁱⁱ	81.58 (4)	Cu1 ⁱⁱⁱ —O1—Cu1 ⁱ	108.564 (12)
C1—N3—C2	105.8 (3)	Cu1 ⁱⁱⁱ —O1—Cu1	111.30 (2)
C1—N3—Cu1	128.2 (3)	Cu1 ⁱ —O1—Cu1	108.564 (12)
C2—N3—Cu1	126.0 (2)	Cu1 ⁱⁱⁱ —O1—Cu1 ⁱⁱ	108.564 (12)
N3—C1—N2	113.1 (4)	Cu1 ⁱ —O1—Cu1 ⁱⁱ	111.30 (2)
N3—C1—H1	123.5	Cu1—O1—Cu1 ⁱⁱ	108.564 (12)
N2—C1—H1	123.5	C10—C9—N1	123.5 (5)
C3—C2—N3	131.4 (3)	C10—C9—C8	122.7 (5)
C3—C2—C7	119.6 (4)	N1—C9—C8	113.8 (5)
N3—C2—C7	108.9 (4)	C9—C10—C11	118.1 (6)
N2—C7—C2	104.9 (4)	C9—C10—H10	121.0
N2—C7—C6	134.1 (4)	C11—C10—H10	121.0
C2—C7—C6	121.0 (5)	C13—N1—C9	117.3 (7)
C1—N2—C7	107.4 (3)	C13—C12—C11	123.7 (8)
C1—N2—C8	127.5 (4)	C13—C12—H12	118.1
C7—N2—C8	125.1 (4)	C11—C12—H12	118.1
C5—C6—C7	117.8 (4)	C12—C11—C10	113.3 (7)
C5—C6—H6	121.1	C12—C11—H11	123.3
C7—C6—H6	121.1	C10—C11—H11	123.3
C4—C3—C2	118.6 (4)	N1—C13—C12	123.9 (8)
C4—C3—H3	120.7	N1—C13—H13	118.0
C2—C3—H3	120.7	C12—C13—H13	118.0
C3—C4—C5	120.6 (5)		
O1—Cu1—Cl1—Cu1 ⁱⁱ	-1.10 (2)	N2—C7—C6—C5	-178.9 (5)
N3—Cu1—Cl1—Cu1 ⁱⁱ	178.42 (9)	C2—C7—C6—C5	3.0 (7)
Cl1 ⁱ —Cu1—Cl1—Cu1 ⁱⁱ	-83.12 (4)	N3—C2—C3—C4	-178.9 (4)
Cl2—Cu1—Cl1—Cu1 ⁱⁱ	78.54 (4)	C7—C2—C3—C4	1.4 (7)
O1—Cu1—Cl2—Cu1 ⁱⁱⁱ	0.0	C2—C3—C4—C5	-0.2 (8)
N3—Cu1—Cl2—Cu1 ⁱⁱⁱ	-179.13 (9)	C7—C6—C5—C4	-1.8 (9)
Cl1 ⁱ —Cu1—Cl2—Cu1 ⁱⁱⁱ	81.77 (3)	C3—C4—C5—C6	0.5 (9)
Cl1—Cu1—Cl2—Cu1 ⁱⁱⁱ	-80.48 (3)	C1—N2—C8—C9	-48.8 (6)
O1—Cu1—N3—C1	150 (6)	C7—N2—C8—C9	135.3 (4)
Cl1 ⁱ —Cu1—N3—C1	-4.5 (3)	N3—Cu1—O1—Cu1 ⁱⁱⁱ	88 (6)
Cl1—Cu1—N3—C1	116.6 (3)	Cl1 ⁱ —Cu1—O1—Cu1 ⁱⁱⁱ	-117.99 (3)
Cl2—Cu1—N3—C1	-122.7 (3)	Cl1—Cu1—O1—Cu1 ⁱⁱⁱ	120.87 (3)
O1—Cu1—N3—C2	-31 (6)	Cl2—Cu1—O1—Cu1 ⁱⁱⁱ	0.0
Cl1 ⁱ —Cu1—N3—C2	174.8 (3)	N3—Cu1—O1—Cu1 ⁱ	-153 (6)
Cl1—Cu1—N3—C2	-64.1 (3)	Cl1 ⁱ —Cu1—O1—Cu1 ⁱ	1.44 (3)
Cl2—Cu1—N3—C2	56.7 (3)	Cl1—Cu1—O1—Cu1 ⁱ	-119.70 (3)

supplementary materials

C2—N3—C1—N2	-0.7 (4)	Cl2—Cu1—O1—Cu1 ⁱ	119.434 (8)
Cu1—N3—C1—N2	178.8 (2)	N3—Cu1—O1—Cu1 ⁱⁱ	-32 (6)
C1—N3—C2—C3	-178.6 (4)	Cl1 ⁱ —Cu1—O1—Cu1 ⁱⁱ	122.58 (3)
Cu1—N3—C2—C3	2.0 (6)	Cl1—Cu1—O1—Cu1 ⁱⁱ	1.43 (3)
C1—N3—C2—C7	1.2 (4)	Cl2—Cu1—O1—Cu1 ⁱⁱ	-119.434 (8)
Cu1—N3—C2—C7	-178.3 (2)	N2—C8—C9—C10	-102.8 (6)
C3—C2—C7—N2	178.6 (4)	N2—C8—C9—N1	78.9 (5)
N3—C2—C7—N2	-1.2 (4)	N1—C9—C10—C11	1.4 (7)
C3—C2—C7—C6	-2.8 (6)	C8—C9—C10—C11	-176.8 (4)
N3—C2—C7—C6	177.4 (4)	C10—C9—N1—C13	-1.6 (7)
N3—C1—N2—C7	-0.1 (4)	C8—C9—N1—C13	176.8 (5)
N3—C1—N2—C8	-176.6 (4)	C13—C12—C11—C10	-2.7 (10)
C2—C7—N2—C1	0.8 (4)	C9—C10—C11—C12	0.6 (8)
C6—C7—N2—C1	-177.6 (5)	C9—N1—C13—C12	-0.5 (10)
C2—C7—N2—C8	177.4 (4)	C11—C12—C13—N1	2.8 (13)
C6—C7—N2—C8	-1.0 (8)		

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

Fig. 1

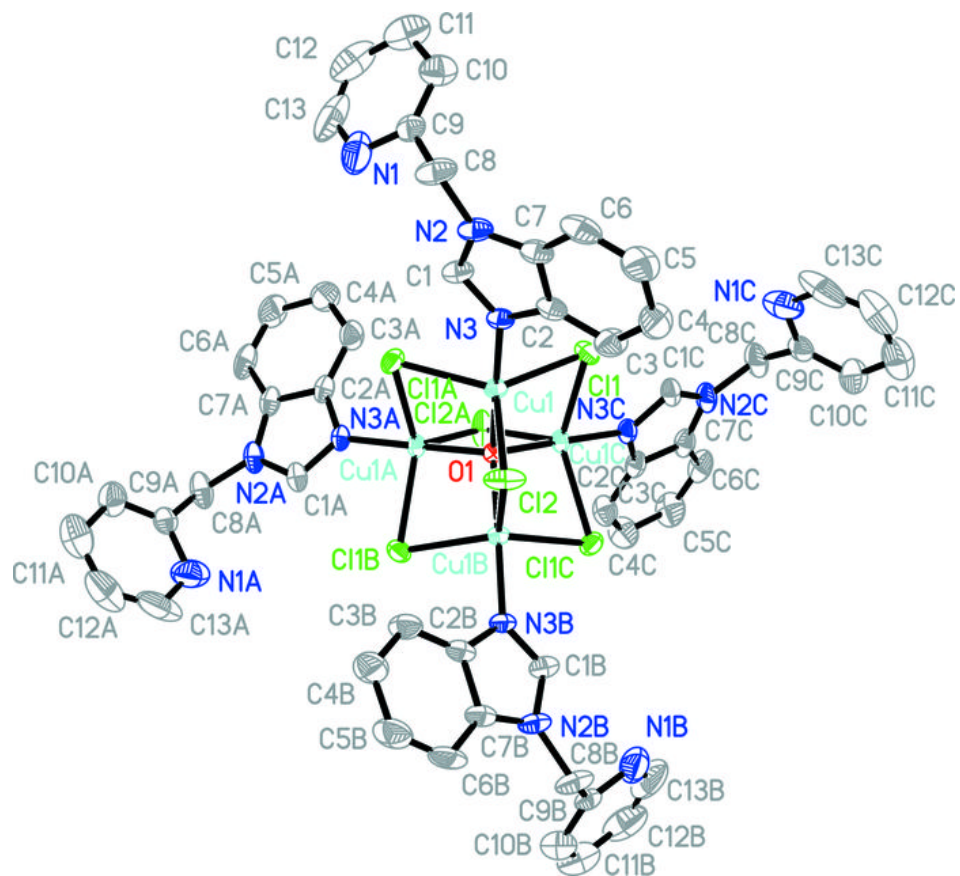


Fig. 2

