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Hexa-μ-chlorido-μ_4-oxido-tetrakis({1-[(pyridin-2-yl)methyl]-1*H*-benzimidazole-κN^3}copper(II))

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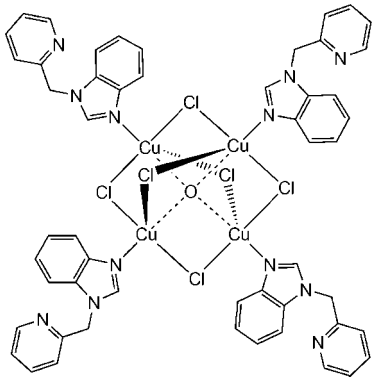
Key indicators: single-crystal X-ray study; T = 294 K; mean σ(C–C) = 0.009 Å; R factor = 0.028; wR factor = 0.062; data-to-parameter ratio = 14.5.

The title tetranuclear complex, $[Cu_4Cl_6O(C_{13}H_{11}N_3)_4]$, features a tetrahedral arrangement of copper(II) ions bonded to the central O atom (site symmetry $\overline{4}$). 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)-1*H*-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)°.

Related literature

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



Experimental

Crystal data

$[Cu_4Cl_6O(C_{13}H_{11}N_3)_4]$
M_r = 1319.85
Tetragonal, $I\overline{4}$
a = 13.8532 (12) Å
c = 14.507 (3) Å
V = 2784.1 (6) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 1.85 mm^{-1}
T = 294 K
0.25 × 0.23 × 0.20 mm

Data collection

Rigaku Mercury CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
T_{min} = 0.637, T_{max} = 0.691
7149 measured reflections
2467 independent reflections
2178 reflections with $I > 2\sigma(I)$
R_{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/MSC, 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).

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supporting information

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S1. 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 $[(Cu_4O)Cl_6(\mathbf{L})_4]$, (I). The crystal structure was elucidated by X-ray diffraction analysis.

S2. Experimental

To a solution of **L** (0.12 mmol, 25 mg) dissolved in CH_3CN (9 ml), a solution of $CuCl_2{\cdot}6H_2O$ (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**).

S3. Refinement

C-bound H atoms were positioned geometrically and refined in the riding-model approximation, with C—H = 0.93Å and U_{iso}(H) = 1.2Ueq.

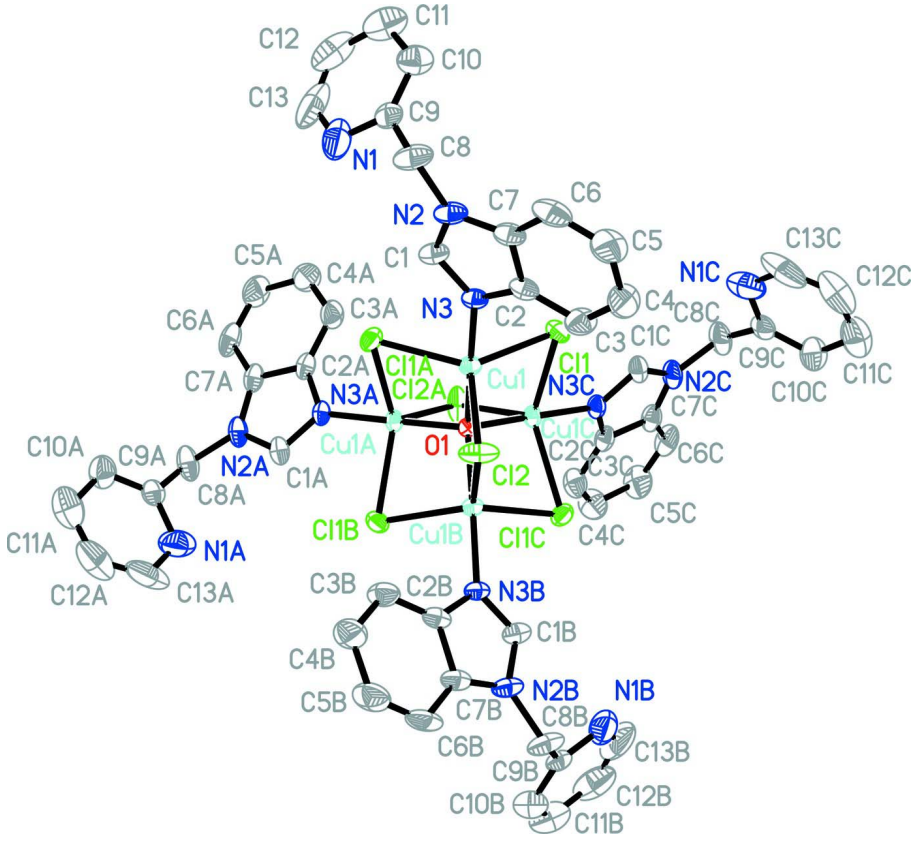

Figure 1

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*].

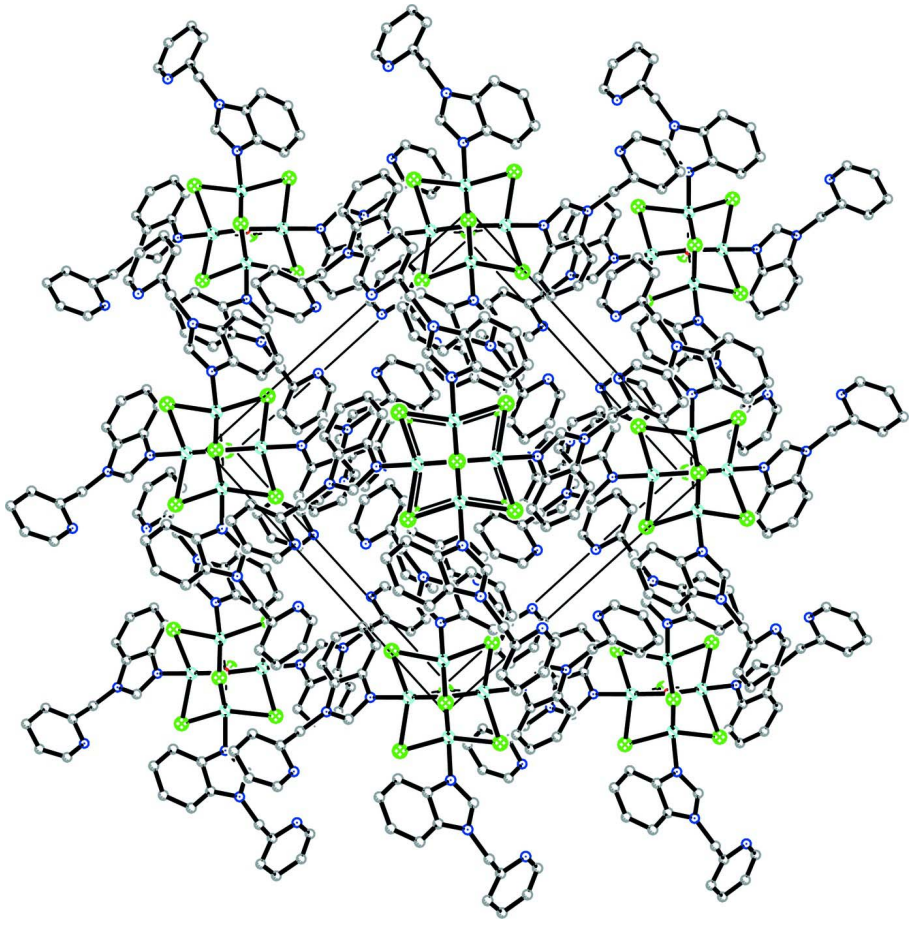

Figure 2

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

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Crystal data

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M_r = 1319.85
Tetragonal, $I\bar{4}$
a = 13.8532 (12) Å
c = 14.507 (3) Å
V = 2784.1 (6) Å^3
Z = 2
$F(000)$ = 1332
D_x = 1.574 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3492 reflections
θ = 2.8–25.3°
μ = 1.85 mm^{-1}
T = 294 K
Block, brown
0.25 × 0.23 × 0.20 mm

Data collection

Rigaku Mercury CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 9 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2005)
T_{min} = 0.637, T_{max} = 0.691
7149 measured reflections
2467 independent reflections
2178 reflections with $I > 2\sigma(I)$
R_{int} = 0.033

θ_{max} = 25.0°, θ_{min} = 2.0°
h = −14→16
k = −16→14
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.062
S = 1.06
2467 reflections
170 parameters
0 restraints
0 constraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0286P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Absolute structure: Flack (1983), 1172 Friedel pairs
Absolute structure 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 (Å²)

	x	y	z	U_{iso}*/U_{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 (Å²)

	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)
Cl2	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 (Å, º)

Cu1—O1	1.9199 (4)	C4—C5	1.400 (7)
Cu1—N3	1.974 (3)	C4—H4	0.9300
Cu1—Cl1^{i}	2.3961 (10)	C5—H5	0.9300
Cu1—Cl1	2.4192 (10)	C8—C9	1.494 (7)
Cu1—Cl2	2.4263 (10)	C8—H8A	0.9700
Cl1—Cu1^{ii}	2.3961 (9)	C8—H8B	0.9700
Cl2—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—Cl1^{i}	85.68 (3)	C5—C4—H4	119.7
N3—Cu1—Cl1^{i}	95.10 (9)	C6—C5—C4	122.3 (5)
O1—Cu1—Cl1	85.03 (3)	C6—C5—H5	118.8
N3—Cu1—Cl1	94.25 (9)	C4—C5—H5	118.8
Cl1^{i}—Cu1—Cl1	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)
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*.