

catena-Poly[[bis(μ -5-bromopyridine-3-carboxylato- κ^2 O:O')dicopper(II)]-bis(μ -5-bromopyridine-3-carboxylato)- κ^3 O,O':N; κ^3 N:O,O']

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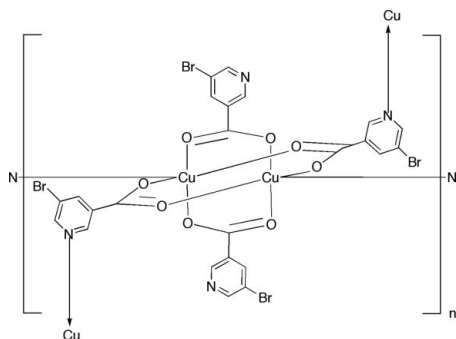
Received 7 October 2010; accepted 19 October 2010

Key indicators: single-crystal X-ray study; $T = 90$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.021; wR factor = 0.054; data-to-parameter ratio = 18.8.

The title compound $[\text{Cu}_2(\text{C}_6\text{H}_3\text{BrNO}_2)_4]_n$, forms sheets in the bc plane. The structure features the dinuclear paddle-wheel cage motif common to copper(II) carboxylates. The polymeric structure is achieved through bridging between binuclear units by the pyridyl donors of two of the four carboxylates of the cage. Each cage engages in axial bonding at each copper atom to a pyridyl nitrogen donor and extends two 5-bromopyridine-3-carboxylate groups to bridge to adjacent binuclear sites in the bc plane. Each cage is linked to four adjacent cages in the plane. The intradimer $\text{Cu} \cdots \text{Cu}$ distance is 2.6465 (5) Å. The remaining 5-bromopyridine-3-carboxylate groups project into the interlamellar domain and interdigitate in pairs from each neighboring layer.

Related literature

For a general review of copper(II) carboxylates, see: Doedens (1976). For polynuclear copper carboxylates with the $[\text{Cu}_2(\text{O}_2\text{CR})_4]$ core, see: Agterberg *et al.* (1997); Valentine *et al.* (1974); Yamanaka *et al.* (1991). For the preparation of copper coordination polymers under hydrothermal conditions, see: Lu (2003). For general discussion of hydrothermal methods, see: Gopalakrishnan (1995); Zubieta (2004).



Experimental

Crystal data

$[\text{Cu}_2(\text{C}_6\text{H}_3\text{BrNO}_2)_4]$
 $M_r = 931.11$
Monoclinic, $P2_1/n$
 $a = 11.1390$ (12) Å
 $b = 11.5866$ (13) Å
 $c = 12.6325$ (14) Å
 $\beta = 115.432$ (2)°

$V = 1472.4$ (3) Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 6.93$ mm⁻¹
 $T = 90$ K
 $0.35 \times 0.30 \times 0.27$ mm

Data collection

Bruker APEX CCD area-detector diffractometer
Absorption correction: multi-scan (SADABS; Bruker, 1998)
 $T_{\min} = 0.196$, $T_{\max} = 0.256$

14281 measured reflections
3571 independent reflections
3218 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.022$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.054$
 $S = 1.05$
3571 reflections

190 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.77$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.51$ e Å⁻³

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *DIAMOND* (Brandenburg & Putz, 1999); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RN2072).

References

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supplementary materials

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***catena*-Poly[[bis(μ -5-bromopyridine-3-carboxylato- $\kappa^2 O:O'$)dicopper(II)]-bis(μ -5-bromopyridine-3-carboxylato)- $\kappa^3 O,O':N;\kappa^3 N:O,O'$]**

P. DeBurgomaster and J. Zubieta

Comment

The dinuclear *paddle-wheel* cage structure of copper(II) carboxylates is well established [Doedens (1976)]. Polymeric structures incorporating this core can be obtained using ligands capable of bridging between the dinuclear units [Agterberg, *et al.* (1997); Valentine, *et al.* (1974); Yamanaka, *et al.* (1991)]. Since hydrothermal methods are most effective for the preparation and crystallization of organic-inorganic coordination polymers [Gopalakrishnan (1995); Zubieta (2004)], the crystal engineering of copper-containing materials under these conditions has witnessed considerable contemporary attention [Lu (2003)]. In the course of our investigations of Cu(II)-ligand substructures in complex metal oxide hybrid materials, the two-dimensional material [Cu₂(O₂CC₅H₃NBr)₄] was isolated.

As shown in Fig. 1, the title compound is two-dimensional, forming sheets oriented parallel to the crystallographic *bc* plane. The fundamental building block of these sheets is the dinuclear *paddle-wheel* cage structure [Cu₂(O₂CR)₄], shown in Fig. 2. The four oxygen donors of the basal plane about the crystallographically unique copper site exhibit Cu—O distances in the range of 1.959 (1) Å to 1.985 (1) Å. There is a crystallographic inversion center at the mid-point of the CuLCu vector relating the two halves of the cage. The Cu...Cu distance is 2.6465 (5) Å.

The cages are linked into the two-dimensional network through the pyridyl nitrogen donors of two of the 5-bromopyridine-3-carboxylato ligands, with a copper-axial nitrogen distance of 2.160 (2) Å. The connectivity pattern links each [Cu₂(O₂CR)₄] cage to four neighboring cages to provide the 2-D extension. Two 5-bromopyridine-3-carboxylato ligands of each cage are pendant and project from either face of the polymeric sheets into the interlamellar domains (Fig. 3). These projecting groups interdigitate in pairs with those of neighboring sheets to provide a relatively densely packed arrangement of sheets.

Experimental

A solution containing Cu(II) acetate hydrate (0.201 g, 1.01 mmol), 5-bromo-2-pyridylcarboxylic acid (0.102, 0.50 mmol), methanol (5.00 ml, 123.56 mmol), and DMF (5.00 ml, 64.58 mmol), in the mole ratio 2.02:1.00:247:129 was stirred briefly before transfer to a 20 ml glass vial. The capped vial was heated at 75 °C for 72 h. Green blocks of the title compound, suitable for X-ray diffraction, were isolated in 50% yield. Initial and final pH values of 4.0 and 4.0, respectively, were recorded. Anal. Calcd. for C₁₂H₆Br₂CuN₂O₄:C, 30.9; H, 1.29; N, 6.01. Found: C, 29.7; H, 1.55; N, 5.93.

Refinement

All hydrogen atoms were discernable in the difference Fourier map. The hydrogen atoms were placed in calculated positions with C—H = 0.95 Å and included in the riding model approximation with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

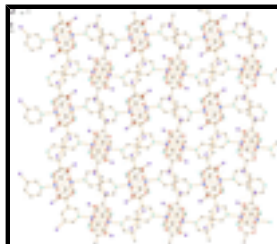


Fig. 1. A view of the two-dimensional structure of $[\text{Cu}_2(\text{O}_2\text{CC}_5\text{H}_3\text{NBr})_4]$ in the bc plane. Color scheme as for Fig. 2.

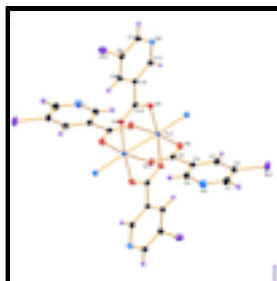


Fig. 2. An *ORTEP* view of the dinuclear *paddle-wheel* cage building block of the title compound, showing the atom-labeling scheme for the asymmetric unit and 50% displacement ellipsoids. Color scheme: Cu, blue; Br, maroon; O, red; N, light blue; C, black; H, pink.

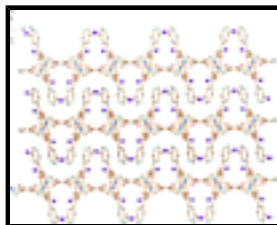


Fig. 3. A view of the packing showing the interdigitation of the pendant 5-bromo-2-pyridyl groups. Color scheme as for Fig. 2.

catena-Poly[[bis(μ -5-bromopyridine-3-carboxylato- $\kappa^2\text{O}:\text{O}'$)dicopper(II)]-bis(μ -5-bromopyridine-3-carboxylato)- $\kappa^3\text{O},\text{O}':\text{N};\kappa^3\text{N}:\text{O},\text{O}'$]

Crystal data

$[\text{Cu}_2(\text{C}_6\text{H}_3\text{BrNO}_2)_4]$

$M_r = 931.11$

Monoclinic, $P2_1/n$

Hall symbol: $-P\ 2_1n$

$a = 11.1390$ (12) Å

$b = 11.5866$ (13) Å

$c = 12.6325$ (14) Å

$\beta = 115.432$ (2)°

$V = 1472.4$ (3) Å³

$Z = 2$

$F(000) = 892$

$D_x = 2.100$ Mg m⁻³

$D_m = 2.09$ (2) Mg m⁻³

D_m measured by flotation

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 3266 reflections

$\theta = 2.4$ – 28.3 °

$\mu = 6.93$ mm⁻¹

$T = 90$ K

Block, blue

$0.35 \times 0.30 \times 0.27$ mm

Data collection

Bruker APEX CCD area-detector diffractometer

3571 independent reflections

| | |
|--|--|
| Radiation source: fine-focus sealed tube graphite | 3218 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.022$ |
| Detector resolution: 512 pixels mm^{-1} | $\theta_{\text{max}} = 28.1^\circ$, $\theta_{\text{min}} = 2.0^\circ$ |
| φ and ω scans | $h = -14 \rightarrow 14$ |
| Absorption correction: multi-scan (SADABS; Bruker, 1998) | $k = -15 \rightarrow 14$ |
| $T_{\text{min}} = 0.196$, $T_{\text{max}} = 0.256$ | $l = -15 \rightarrow 16$ |
| 14281 measured reflections | |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | Primary atom site location: structure-invariant direct methods |
| Least-squares matrix: full | Secondary atom site location: difference Fourier map |
| $R[F^2 > 2\sigma(F^2)] = 0.021$ | Hydrogen site location: inferred from neighbouring sites |
| $wR(F^2) = 0.054$ | H-atom parameters constrained |
| $S = 1.05$ | $w = 1/[\sigma^2(F_o^2) + (0.0258P)^2 + 1.3076P]$ |
| 3571 reflections | where $P = (F_o^2 + 2F_c^2)/3$ |
| 190 parameters | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| 0 restraints | $\Delta\rho_{\text{max}} = 0.77 \text{ e } \text{\AA}^{-3}$ |
| | $\Delta\rho_{\text{min}} = -0.51 \text{ e } \text{\AA}^{-3}$ |

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 | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|--------------|---------------|---------------|----------------------------------|
| Br1 | -0.18056 (2) | 0.76143 (2) | -0.11231 (2) | 0.02559 (7) |
| Br2 | 0.84249 (2) | 0.868086 (18) | 0.603257 (19) | 0.02064 (6) |
| Cu1 | 0.56886 (2) | 1.02600 (2) | 0.11208 (2) | 0.01009 (6) |
| O1 | 0.40781 (14) | 0.98221 (13) | 0.12844 (14) | 0.0179 (3) |
| O2 | 0.29176 (14) | 0.93567 (13) | -0.06153 (13) | 0.0174 (3) |
| O3 | 1.00043 (14) | 1.31393 (12) | 0.57312 (13) | 0.0153 (3) |
| O4 | 0.88355 (15) | 1.36151 (12) | 0.38361 (13) | 0.0176 (3) |
| N1 | 0.08987 (19) | 0.89646 (18) | 0.19994 (17) | 0.0232 (4) |
| N2 | 0.70137 (17) | 1.05035 (15) | 0.29489 (15) | 0.0142 (3) |
| C1 | -0.0161 (2) | 0.8474 (2) | 0.1151 (2) | 0.0214 (5) |

supplementary materials

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|-----|--------------|--------------|--------------|------------|
| H1 | -0.0875 | 0.8233 | 0.1320 | 0.026* |
| C2 | -0.0258 (2) | 0.83017 (19) | 0.00277 (19) | 0.0176 (4) |
| C3 | 0.0770 (2) | 0.86282 (17) | -0.0242 (2) | 0.0161 (4) |
| H3 | 0.0718 | 0.8518 | -0.1006 | 0.019* |
| C4 | 0.1886 (2) | 0.91256 (18) | 0.06474 (19) | 0.0146 (4) |
| C5 | 0.1900 (2) | 0.92849 (19) | 0.17425 (19) | 0.0181 (4) |
| H5 | 0.2657 | 0.9639 | 0.2340 | 0.022* |
| C6 | 0.30570 (19) | 0.94647 (17) | 0.04201 (19) | 0.0139 (4) |
| C7 | 0.7262 (2) | 0.96880 (18) | 0.37741 (18) | 0.0146 (4) |
| H7 | 0.6806 | 0.8971 | 0.3561 | 0.018* |
| C8 | 0.8166 (2) | 0.98675 (17) | 0.49263 (18) | 0.0137 (4) |
| C9 | 0.8847 (2) | 1.09039 (17) | 0.52675 (18) | 0.0138 (4) |
| H9 | 0.9470 | 1.1034 | 0.6056 | 0.017* |
| C10 | 0.85843 (19) | 1.17443 (17) | 0.44120 (18) | 0.0116 (4) |
| C11 | 0.76676 (19) | 1.15074 (17) | 0.32653 (18) | 0.0132 (4) |
| H11 | 0.7500 | 1.2083 | 0.2683 | 0.016* |
| C12 | 0.92049 (19) | 1.29269 (17) | 0.46889 (18) | 0.0124 (4) |

Atomic displacement parameters (\AA^2)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|--------------|--------------|--------------|--------------|---------------|
| Br1 | 0.01981 (11) | 0.03107 (13) | 0.02547 (13) | -0.01189 (9) | 0.00931 (10) | -0.00522 (10) |
| Br2 | 0.03049 (12) | 0.01399 (11) | 0.01496 (11) | -0.00414 (8) | 0.00738 (9) | 0.00332 (8) |
| Cu1 | 0.01025 (11) | 0.00862 (12) | 0.00980 (12) | 0.00020 (8) | 0.00280 (9) | 0.00007 (9) |
| O1 | 0.0152 (7) | 0.0211 (8) | 0.0180 (8) | -0.0049 (6) | 0.0078 (6) | -0.0028 (6) |
| O2 | 0.0140 (7) | 0.0229 (8) | 0.0163 (8) | -0.0013 (6) | 0.0073 (6) | 0.0000 (6) |
| O3 | 0.0183 (7) | 0.0113 (7) | 0.0127 (7) | -0.0035 (6) | 0.0033 (6) | -0.0016 (6) |
| O4 | 0.0220 (8) | 0.0105 (7) | 0.0139 (8) | -0.0030 (6) | 0.0015 (6) | 0.0012 (6) |
| N1 | 0.0233 (10) | 0.0302 (11) | 0.0186 (10) | -0.0033 (8) | 0.0113 (8) | 0.0015 (8) |
| N2 | 0.0163 (8) | 0.0120 (8) | 0.0130 (9) | -0.0012 (6) | 0.0049 (7) | -0.0006 (7) |
| C1 | 0.0197 (10) | 0.0245 (11) | 0.0239 (12) | -0.0031 (9) | 0.0130 (9) | 0.0016 (9) |
| C2 | 0.0142 (9) | 0.0171 (10) | 0.0201 (11) | -0.0033 (8) | 0.0060 (8) | -0.0010 (9) |
| C3 | 0.0176 (10) | 0.0140 (10) | 0.0184 (11) | 0.0002 (8) | 0.0092 (8) | 0.0003 (8) |
| C4 | 0.0143 (9) | 0.0124 (9) | 0.0175 (10) | 0.0008 (7) | 0.0073 (8) | 0.0024 (8) |
| C5 | 0.0169 (10) | 0.0190 (11) | 0.0170 (11) | -0.0025 (8) | 0.0060 (8) | 0.0001 (8) |
| C6 | 0.0132 (9) | 0.0090 (9) | 0.0197 (11) | 0.0008 (7) | 0.0071 (8) | 0.0017 (8) |
| C7 | 0.0168 (10) | 0.0119 (9) | 0.0151 (10) | -0.0038 (7) | 0.0068 (8) | -0.0024 (8) |
| C8 | 0.0174 (9) | 0.0116 (9) | 0.0125 (10) | 0.0005 (7) | 0.0068 (8) | 0.0038 (8) |
| C9 | 0.0145 (9) | 0.0143 (10) | 0.0115 (10) | -0.0005 (7) | 0.0045 (8) | -0.0016 (8) |
| C10 | 0.0130 (9) | 0.0094 (9) | 0.0127 (10) | 0.0000 (7) | 0.0056 (7) | -0.0011 (7) |
| C11 | 0.0142 (9) | 0.0114 (9) | 0.0132 (10) | -0.0007 (7) | 0.0053 (8) | 0.0013 (7) |
| C12 | 0.0125 (9) | 0.0107 (9) | 0.0154 (10) | 0.0004 (7) | 0.0072 (8) | -0.0007 (8) |

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

| | | | |
|--------|-------------|-------|-----------|
| Br1—C2 | 1.888 (2) | C1—C2 | 1.390 (3) |
| Br2—C8 | 1.892 (2) | C1—H1 | 0.9500 |
| Cu1—O1 | 1.9588 (14) | C2—C3 | 1.380 (3) |

| | | | |
|---|-------------|--------------|-------------|
| Cu1—O2 ⁱ | 1.9665 (14) | C3—C4 | 1.393 (3) |
| Cu1—O4 ⁱⁱ | 1.9726 (14) | C3—H3 | 0.9500 |
| Cu1—O3 ⁱⁱⁱ | 1.9852 (14) | C4—C5 | 1.389 (3) |
| Cu1—N2 | 2.1595 (18) | C4—C6 | 1.504 (3) |
| Cu1—Cu1 ⁱ | 2.6465 (5) | C5—H5 | 0.9500 |
| O1—C6 | 1.261 (3) | C7—C8 | 1.384 (3) |
| O2—C6 | 1.255 (3) | C7—H7 | 0.9500 |
| O3—C12 | 1.257 (2) | C8—C9 | 1.387 (3) |
| O4—C12 | 1.259 (2) | C9—C10 | 1.389 (3) |
| N1—C1 | 1.334 (3) | C9—H9 | 0.9500 |
| N1—C5 | 1.340 (3) | C10—C11 | 1.395 (3) |
| N2—C11 | 1.339 (3) | C10—C12 | 1.507 (3) |
| N2—C7 | 1.345 (3) | C11—H11 | 0.9500 |
| O1—Cu1—O2 ⁱ | 168.33 (6) | C2—C3—H3 | 121.2 |
| O1—Cu1—O4 ⁱⁱ | 89.67 (6) | C4—C3—H3 | 121.2 |
| O2 ⁱ —Cu1—O4 ⁱⁱ | 89.25 (7) | C5—C4—C3 | 118.87 (19) |
| O1—Cu1—O3 ⁱⁱⁱ | 89.81 (6) | C5—C4—C6 | 121.06 (19) |
| O2 ⁱ —Cu1—O3 ⁱⁱⁱ | 88.91 (6) | C3—C4—C6 | 120.06 (19) |
| O4 ⁱⁱ —Cu1—O3 ⁱⁱⁱ | 168.37 (6) | N1—C5—C4 | 123.3 (2) |
| O1—Cu1—N2 | 99.05 (7) | N1—C5—H5 | 118.3 |
| O2 ⁱ —Cu1—N2 | 92.60 (6) | C4—C5—H5 | 118.3 |
| O4 ⁱⁱ —Cu1—N2 | 92.56 (6) | O2—C6—O1 | 126.63 (18) |
| O3 ⁱⁱⁱ —Cu1—N2 | 99.00 (6) | O2—C6—C4 | 116.34 (18) |
| O1—Cu1—Cu1 ⁱ | 85.28 (5) | O1—C6—C4 | 117.03 (18) |
| O2 ⁱ —Cu1—Cu1 ⁱ | 83.08 (5) | N2—C7—C8 | 121.60 (18) |
| O4 ⁱⁱ —Cu1—Cu1 ⁱ | 80.50 (4) | N2—C7—H7 | 119.2 |
| O3 ⁱⁱⁱ —Cu1—Cu1 ⁱ | 87.88 (4) | C8—C7—H7 | 119.2 |
| N2—Cu1—Cu1 ⁱ | 171.84 (5) | C7—C8—C9 | 120.71 (18) |
| C6—O1—Cu1 | 121.33 (13) | C7—C8—Br2 | 118.60 (15) |
| C6—O2—Cu1 ⁱ | 123.66 (13) | C9—C8—Br2 | 120.67 (16) |
| C12—O3—Cu1 ^{iv} | 117.81 (13) | C8—C9—C10 | 117.44 (19) |
| C12—O4—Cu1 ^v | 127.10 (14) | C8—C9—H9 | 121.3 |
| C1—N1—C5 | 117.7 (2) | C10—C9—H9 | 121.3 |
| C11—N2—C7 | 118.33 (18) | C9—C10—C11 | 119.06 (18) |
| C11—N2—Cu1 | 117.85 (14) | C9—C10—C12 | 122.30 (18) |
| C7—N2—Cu1 | 123.76 (14) | C11—C10—C12 | 118.57 (17) |
| N1—C1—C2 | 122.4 (2) | N2—C11—C10 | 122.86 (18) |
| N1—C1—H1 | 118.8 | N2—C11—H11 | 118.6 |
| C2—C1—H1 | 118.8 | C10—C11—H11 | 118.6 |
| C3—C2—C1 | 120.2 (2) | O3—C12—O4 | 126.62 (18) |
| C3—C2—Br1 | 120.35 (17) | O3—C12—C10 | 117.99 (18) |
| C1—C2—Br1 | 119.44 (15) | O4—C12—C10 | 115.38 (18) |
| C2—C3—C4 | 117.5 (2) | | |
| O2 ⁱ —Cu1—O1—C6 | 5.4 (4) | Cu1—O1—C6—C4 | 178.63 (13) |

supplementary materials

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|-------------------------------|--------------|-------------------------------|--------------|
| O4 ⁱⁱ —Cu1—O1—C6 | -79.30 (16) | C5—C4—C6—O2 | -175.55 (19) |
| O3 ⁱⁱⁱ —Cu1—O1—C6 | 89.08 (16) | C3—C4—C6—O2 | 5.4 (3) |
| N2—Cu1—O1—C6 | -171.84 (15) | C5—C4—C6—O1 | 4.8 (3) |
| Cu1 ⁱ —Cu1—O1—C6 | 1.20 (15) | C3—C4—C6—O1 | -174.31 (19) |
| O1—Cu1—N2—C11 | -127.00 (15) | C11—N2—C7—C8 | 0.1 (3) |
| O2 ⁱ —Cu1—N2—C11 | 53.57 (15) | Cu1—N2—C7—C8 | 177.04 (15) |
| O4 ⁱⁱ —Cu1—N2—C11 | 142.93 (15) | N2—C7—C8—C9 | 0.1 (3) |
| O3 ⁱⁱⁱ —Cu1—N2—C11 | -35.75 (15) | N2—C7—C8—Br2 | 178.81 (15) |
| O1—Cu1—N2—C7 | 56.05 (17) | C7—C8—C9—C10 | 0.1 (3) |
| O2 ⁱ —Cu1—N2—C7 | -123.39 (16) | Br2—C8—C9—C10 | -178.61 (14) |
| O4 ⁱⁱ —Cu1—N2—C7 | -34.03 (16) | C8—C9—C10—C11 | -0.4 (3) |
| O3 ⁱⁱⁱ —Cu1—N2—C7 | 147.30 (16) | C8—C9—C10—C12 | 176.54 (18) |
| C5—N1—C1—C2 | -0.7 (3) | C7—N2—C11—C10 | -0.5 (3) |
| N1—C1—C2—C3 | 0.8 (4) | Cu1—N2—C11—C10 | -177.61 (15) |
| N1—C1—C2—Br1 | -179.34 (18) | C9—C10—C11—N2 | 0.7 (3) |
| C1—C2—C3—C4 | 0.1 (3) | C12—C10—C11—N2 | -176.43 (18) |
| Br1—C2—C3—C4 | -179.72 (15) | Cu1 ^{iv} —O3—C12—O4 | 4.0 (3) |
| C2—C3—C4—C5 | -1.1 (3) | Cu1 ^{iv} —O3—C12—C10 | -174.39 (12) |
| C2—C3—C4—C6 | 178.03 (19) | Cu1 ^v —O4—C12—O3 | -3.7 (3) |
| C1—N1—C5—C4 | -0.3 (3) | Cu1 ^v —O4—C12—C10 | 174.71 (12) |
| C3—C4—C5—N1 | 1.2 (3) | C9—C10—C12—O3 | 1.3 (3) |
| C6—C4—C5—N1 | -177.9 (2) | C11—C10—C12—O3 | 178.26 (18) |
| Cu1 ⁱ —O2—C6—O1 | -0.2 (3) | C9—C10—C12—O4 | -177.28 (18) |
| Cu1 ⁱ —O2—C6—C4 | -179.81 (13) | C11—C10—C12—O4 | -0.3 (3) |
| Cu1—O1—C6—O2 | -1.0 (3) | | |

Symmetry codes: (i) $-x+1, -y+2, -z$; (ii) $-x+3/2, y-1/2, -z+1/2$; (iii) $x-1/2, -y+5/2, z-1/2$; (iv) $x+1/2, -y+5/2, z+1/2$; (v) $-x+3/2, y+1/2, -z+1/2$.

Fig. 1

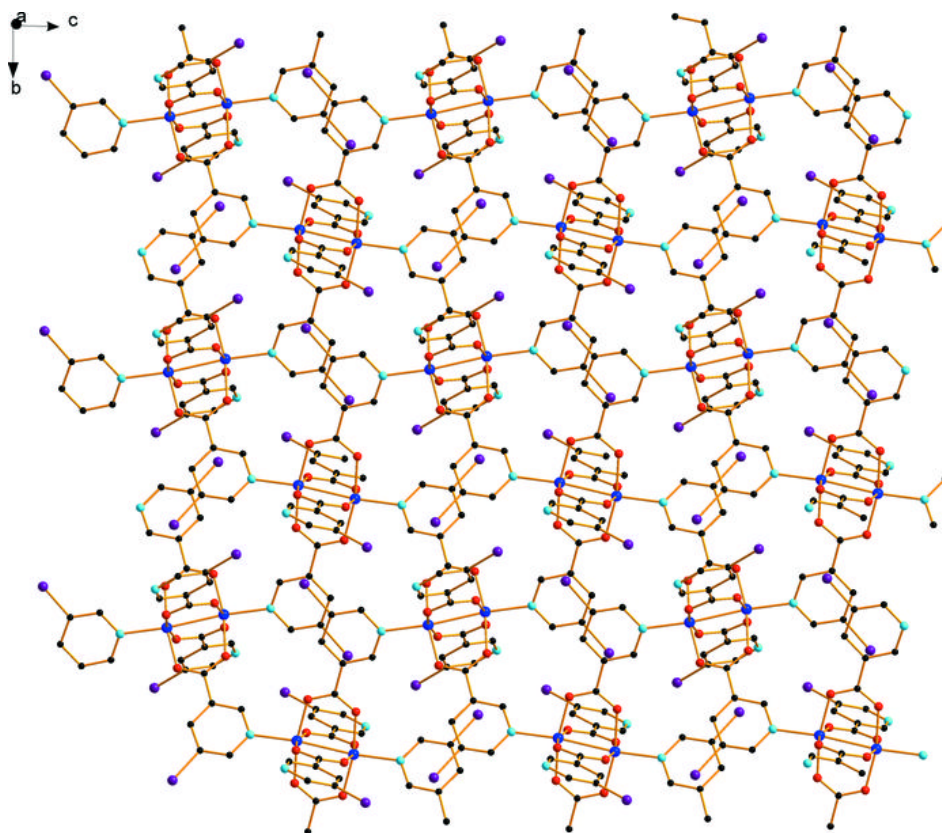


Fig. 2

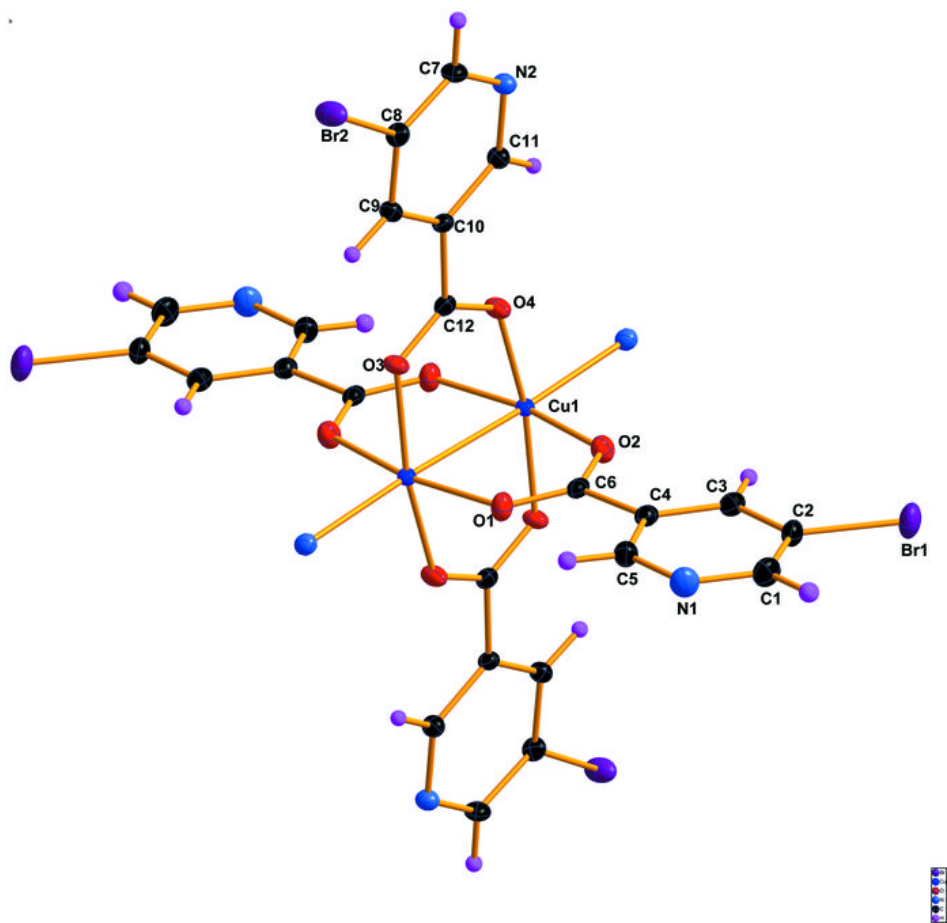


Fig. 3

