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# Poly[tetra-$\mu_{1,1}$-azido-bis($\mu_2$-pyrimidine-2-carboxylato)tricopper(II)]

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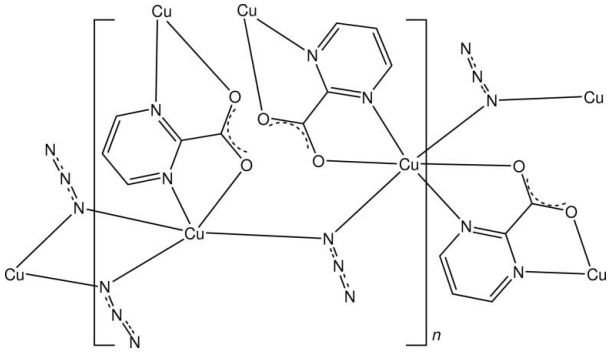
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.011 Å; $R$ factor = 0.052; $wR$ factor = 0.134; data-to-parameter ratio = 10.4.

In the title compound, $[Cu_3(C_5H_3N_2O_2)_2(N_3)_4]_n$, one of the $Cu^{II}$ atoms lies on an inversion centre and is octahedrally coordinated by two bidentate chelating pyrimidine-2-carboxylate ligands and two azide anions, each of which gives an *N*:*N*-bridge to the second inversion-related $Cu^{II}$ centre in the formula unit. The second $Cu^{II}$ atom is five-coordinated with a distorted square-pyramidal coordination sphere comprising a single bidentate chelating pyrimidine-2-carboxylate anion and three azide N anions, two of which doubly bridge centrosymmetric $Cu^{II}$ centres, giving a two-dimensional network structure extending parallel to (010).

## Related literature

Copper azide complexes have attracted much attention in recent years because the azide anions can mediate magnetic interactions effectively between the copper ions, see: Zhao *et al.* (2009). The structures of the complexes are dependant on the co-ligand and conditions employed in the synthesis, see: Zeng *et al.* (2009). For azide complexes with 2,2′-bipyrimidine or oxalate as co-ligands, see: Cortes *et al.* (1996); Escuer *et al.* (1994) and for an azide complex with a pyrimidine-2-carboxylate ligand, see: Suarez-Varela *et al.* (2008).



## Experimental

### Crystal data

$[Cu_3(C_5H_3N_2O_2)_2(N_3)_4]$
$M_r$ = 604.96
Monoclinic, $P2_1/c$
$a$ = 7.4743 (15) Å
$b$ = 14.997 (3) Å
$c$ = 9.479 (4) Å
$\beta$ = 122.31 (2)°
$V$ = 898.0 (5) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 3.59 mm$^{-1}$
$T$ = 293 K
0.20 × 0.18 × 0.18 mm

### Data collection

Rigaku SCXmini CCD diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min}$ = 0.625, $T_{max}$ = 1.000
7028 measured reflections
1572 independent reflections
1305 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.061

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.134
$S$ = 1.24
1572 reflections
151 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.71 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.46 e Å$^{-3}$

Data collection: *SCXmini Benchtop Crystallography System Software* (Rigaku, 2006); cell refinement: *PROCESS-AUTO* (Rigaku, 1998); data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *PLATON* (Spek, 2009); 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: ZS2045).

## References

Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Cortes, R., Lezama, L., Pizarro, J. L., Arriortua, M. A. & Rojo, T. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 1810–1812.
Escuer, A., Vicente, R., Solans, X. & Font-Bardia, M. (1994). *Inorg. Chem.* **33**, 6007–6011.
Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
Rigaku (1998). *PROCESS-AUTO*. Rigaku Americas Corporation, The Woodlands, Texas, USA.
Rigaku (2006). *SCXmini Benchtop Crystallography System Software*. Rigaku Americas Corporation, The Woodlands, Texas, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.
Suarez-Varela, J., Mota, A. J., Aouryaghal, H., Cano, J., Rodriguez-Dieguez, A., Luneau, D., Colacio, E. (2008). *Inorg. Chem.* **47**, 8143–8158.
Zeng, Y.-F., Hu, X., Liu, F.-C. & Bu, X.-H. (2009). *Chem. Soc. Rev.* **38** 469–480.
Zhao, J.-P., Hu, B.-W., Yang, Q., Liu, F.-C., Hu, T.-L. & Bu, X.-H. (2009). *Chin. Sci. Bull.* **54**, 2461–2466.

# supporting information

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## Poly[tetra-$\mu_{1,1}$-azido-bis($\mu_2$-pyrimidine-2-carboxylato)tricopper(II)]

**Jiong-Peng Zhao and Fu-Chen Liu**

### S1. Comment

Copper azide complexes have attracted much attention in recent years because the azide anions can mediate magnetic interactions effectively between the copper ions (Zhao *et al.*, 2009). The structures of those complexes are dependant on the co-ligand and conditions employed in the synthesis (Zeng *et al.*, 2009). Some azide complexes with 2,2′-bipyrimidine or oxalate as co-ligands have been reported (Cortes *et al.*, 1996); Escuer *et al.*, 1994). The pyrimidine-2-carboxylate ligand can be considered as the combination of 2,2′-bipyrimidine and oxalate, and a new metal azide complex with it as ligand has been reported (Suarez-Varela *et al.*, 2008). In this work we report a new copper(II) azide complex with pyrimidine-2-carboxylate as co-ligand, $[Cu_3(C_5H_3N_2O_2)_2(N_3)_4]_n$ (I), prepared under hydrothermal conditions and its structure is reported here.

In the asymmetric units of the title compound, there are one and a half copper(II) cations, two azido anions and two pyrimidine-2-carboxylate ligands (Fig. 1). One of the cations (Cu2) lies on an inversion centre and is octahedrally coordinated by two bidentate chelate pyrimidine-2-carboxylato-N,O ligands and two azido anions, each giving an N bridge to the inversion-related Cu1 centres in the formula unit [Cu2—Cu1, 3.4652 (14) Å]. A second weak contact between a carboxyl O (O1) to Cu1 is also present [Cu1···O1, 2.950 (4) Å] but is too long to be considered a bridging (Cu–O) bond. The coordination sphere about Cu1 is five-coordinate with a distorted square pyramidal coordination sphere comprising a single bidentate chelate pyrimidine-2-carboxylate anion and three azido N anions, one bridging to Cu2, the other two giving double N bridges to centrosymmetrically related Cu centres [Cu1—Cu1$^{iii}$, 3.329 (2) Å] [symmetry code: (iii) *x* -1, *y*, *z*]. Structure extension results in a two-dimensional network (Figs. 2, 3).

### S2. Experimental

A mixture of copper(II) nitrate (1.5mmol) and sodium azide (2 mmol), and pyrimidine-2-carboxylic acid (0.5 mmol) in 10 ml of water was sealed in a Teflon-lined stainless-steel Parr bomb that was heated at 413 K for 48 h. Black crystals of the title complex were collected after the bomb was allowed to cool to room temperature (yield 20% based on Cu). Caution: azides may be explosive: although we have had no problems in this work, only small quantities should be prepared and should be handled with great caution.

### S3. Refinement

Hydrogen atoms were included in calculated positions and treated as riding on their parent C atoms with C—H = 0.93Å and $U_{iso}$(H) = 1.2$U_{eq}$(C).

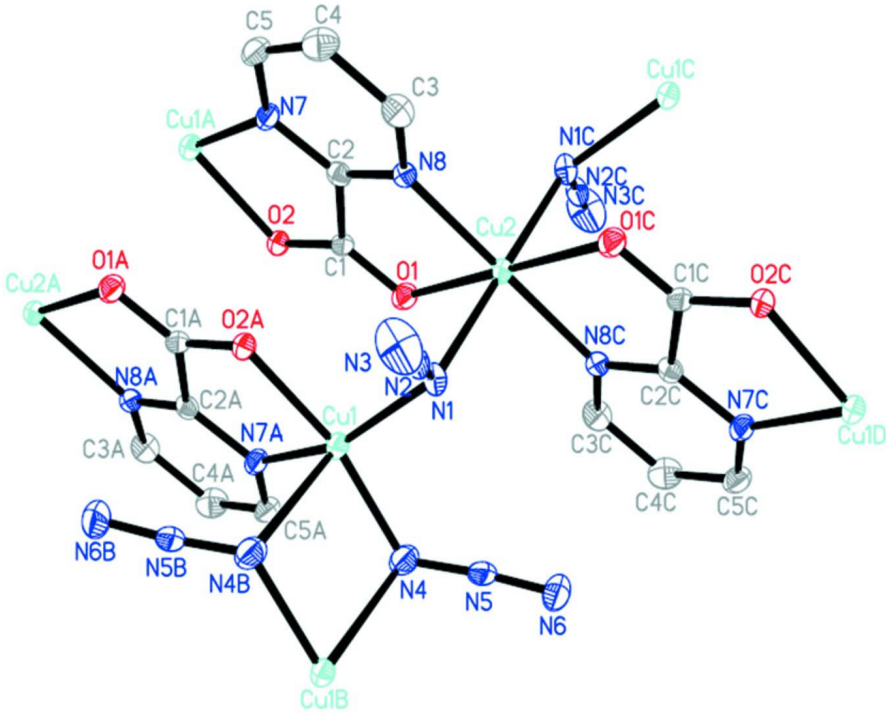


**Figure 1**

The coordination mode and linkage of the metal ions and ligands in (I). Ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity. [Symmetry codes: (A) -*x* + 2, -*y*, -*z*; (B) -*x* + 1, -*y*, -*z* - 1; (C) -*x* + 1, -*y*, -*z*; (D) *x* - 1, *y*, *z*].

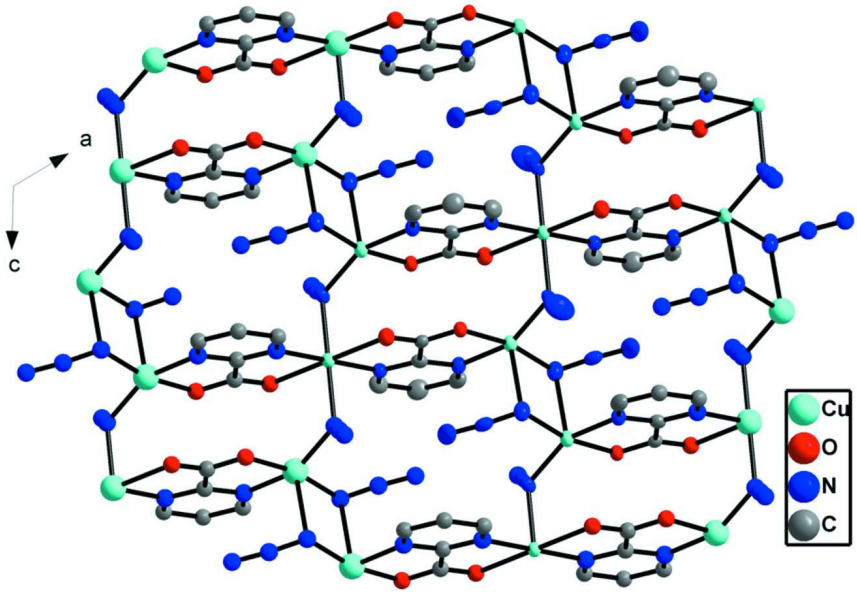


**Figure 2**

The two-dimensional network structure of (I).

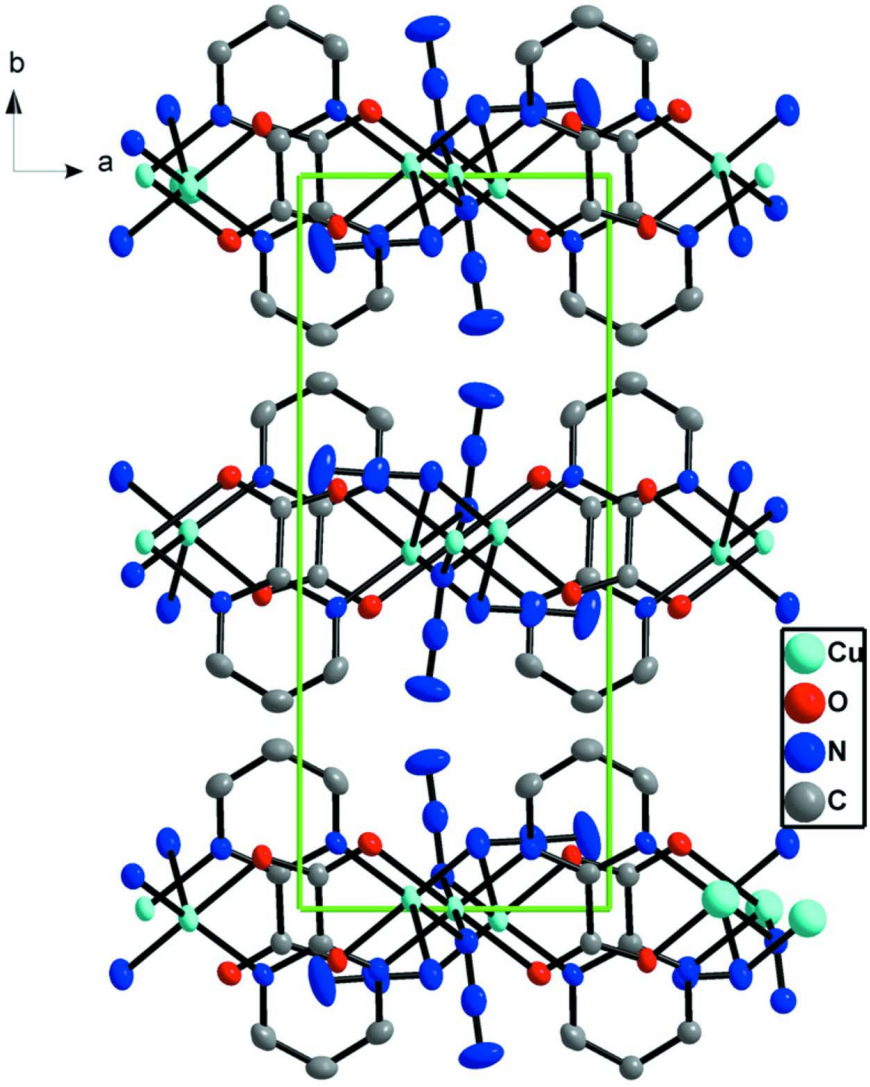


**Figure 3**

The packing mode of the complex in the unit cell.

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*Crystal data*

$[Cu_3(C_5H_3N_2O_2)_2(N_3)_4]$
$M_r = 604.96$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 7.4743\ (15)$ Å
$b = 14.997\ (3)$ Å
$c = 9.479\ (4)$ Å
$\beta = 122.31\ (2)°$
$V = 898.0\ (5)$ Å$^3$
$Z = 2$

$F(000) = 594$
$D_x = 2.237$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 7433 reflections
$\theta = 3.2–27.5°$
$\mu = 3.59$ mm$^{-1}$
$T = 293$ K
Block, black
0.20 × 0.18 × 0.18 mm

*Data collection*

Rigaku SCXmini CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\omega$ scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min}$ = 0.625, $T_{max}$ = 1.000
7028 measured reflections
1572 independent reflections
1305 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.061
$\theta_{max}$ = 25.0°, $\theta_{min}$ = 3.2°
$h = -8 \rightarrow 8$
$k = -17 \rightarrow 17$
$l = -11 \rightarrow 11$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.134
$S$ = 1.24
1572 reflections
151 parameters
0 restraints
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
$w = 1/[\sigma^2(F_o^2) + (0.0543P)^2 + 2.0516P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.71 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.46 e Å$^{-3}$

*Special details*

**Geometry**. Bond distances, angles etc. have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell esds are taken into account in the estimation of distances, angles and torsion angles

**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 | 0.64025 (11) | −0.01316 (5) | −0.29370 (10) | 0.0259 (3) |
| Cu2 | 0.50000 | 0.00000 | 0.00000 | 0.0221 (3) |
| O1 | 0.7728 (6) | −0.0882 (3) | 0.0359 (5) | 0.0278 (12) |
| O2 | 1.1215 (6) | −0.0703 (3) | 0.1528 (5) | 0.0234 (12) |
| N1 | 0.4612 (8) | 0.0444 (4) | −0.2223 (7) | 0.0279 (17) |
| N2 | 0.4377 (9) | 0.1253 (4) | −0.2455 (7) | 0.0344 (19) |
| N3 | 0.4134 (13) | 0.2001 (5) | −0.2695 (10) | 0.063 (3) |
| N4 | 0.4241 (9) | −0.0895 (4) | −0.4673 (7) | 0.0365 (19) |
| N5 | 0.2454 (9) | −0.0933 (4) | −0.4977 (6) | 0.035 (2) |
| N6 | 0.0719 (11) | −0.0987 (6) | −0.5367 (8) | 0.064 (3) |
| N7 | 1.1181 (8) | 0.0896 (3) | 0.2648 (6) | 0.0245 (17) |
| N8 | 0.7462 (8) | 0.0827 (3) | 0.1309 (6) | 0.0224 (17) |
| C1 | 0.9407 (9) | −0.0464 (4) | 0.1173 (7) | 0.0214 (17) |
| C2 | 0.9320 (9) | 0.0481 (4) | 0.1760 (7) | 0.0221 (17) |
| C3 | 0.7414 (11) | 0.1682 (4) | 0.1722 (9) | 0.033 (2) |
| C4 | 0.9286 (12) | 0.2167 (5) | 0.2647 (9) | 0.038 (3) |
| C5 | 1.1161 (11) | 0.1746 (4) | 0.3094 (8) | 0.032 (2) |

| | | | | |
|---|---|---|---|---|
| H3A | 0.61250 | 0.19510 | 0.13880 | 0.0390* |
| H4A | 0.92720 | 0.27550 | 0.29530 | 0.0460* |
| H5A | 1.24310 | 0.20550 | 0.37130 | 0.0390* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0184 (4) | 0.0326 (5) | 0.0258 (5) | −0.0030 (3) | 0.0112 (4) | −0.0039 (3) |
| Cu2 | 0.0168 (6) | 0.0274 (6) | 0.0215 (6) | −0.0014 (4) | 0.0099 (5) | −0.0009 (4) |
| O1 | 0.026 (2) | 0.026 (2) | 0.030 (2) | −0.0038 (19) | 0.014 (2) | −0.0047 (19) |
| O2 | 0.018 (2) | 0.028 (2) | 0.023 (2) | −0.0004 (17) | 0.0102 (18) | −0.0010 (18) |
| N1 | 0.025 (3) | 0.031 (3) | 0.034 (3) | −0.001 (2) | 0.020 (3) | 0.001 (3) |
| N2 | 0.029 (3) | 0.048 (4) | 0.035 (3) | −0.001 (3) | 0.023 (3) | −0.001 (3) |
| N3 | 0.091 (6) | 0.032 (4) | 0.092 (6) | 0.014 (4) | 0.066 (5) | 0.011 (4) |
| N4 | 0.026 (3) | 0.045 (4) | 0.035 (3) | −0.003 (3) | 0.014 (3) | −0.010 (3) |
| N5 | 0.035 (4) | 0.050 (4) | 0.018 (3) | −0.012 (3) | 0.012 (3) | −0.002 (3) |
| N6 | 0.034 (4) | 0.114 (7) | 0.040 (4) | −0.025 (4) | 0.018 (3) | −0.001 (4) |
| N7 | 0.021 (3) | 0.024 (3) | 0.026 (3) | −0.005 (2) | 0.011 (2) | −0.003 (2) |
| N8 | 0.021 (3) | 0.025 (3) | 0.022 (3) | −0.001 (2) | 0.012 (2) | −0.002 (2) |
| C1 | 0.021 (3) | 0.026 (3) | 0.016 (3) | −0.001 (3) | 0.009 (3) | 0.000 (3) |
| C2 | 0.027 (3) | 0.020 (3) | 0.022 (3) | 0.000 (3) | 0.015 (3) | 0.002 (2) |
| C3 | 0.035 (4) | 0.029 (4) | 0.037 (4) | 0.007 (3) | 0.021 (3) | 0.002 (3) |
| C4 | 0.047 (5) | 0.025 (4) | 0.041 (4) | 0.000 (3) | 0.022 (4) | −0.004 (3) |
| C5 | 0.030 (4) | 0.035 (4) | 0.026 (4) | −0.011 (3) | 0.012 (3) | −0.004 (3) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Cu1—N1 | 1.991 (7) | N2—N3 | 1.140 (10) |
| Cu1—N4 | 1.946 (6) | N4—N5 | 1.208 (10) |
| Cu1—N4$^{i}$ | 2.563 (6) | N5—N6 | 1.146 (12) |
| Cu1—O2$^{ii}$ | 1.995 (5) | N7—C2 | 1.334 (9) |
| Cu1—N7$^{ii}$ | 2.030 (6) | N7—C5 | 1.346 (8) |
| Cu2—O1 | 2.298 (5) | N8—C2 | 1.321 (10) |
| Cu2—N1 | 2.077 (6) | N8—C3 | 1.347 (8) |
| Cu2—N8 | 2.006 (6) | C1—C2 | 1.537 (9) |
| Cu2—O1$^{iii}$ | 2.298 (5) | C3—C4 | 1.394 (12) |
| Cu2—N1$^{iii}$ | 2.077 (6) | C4—C5 | 1.381 (13) |
| Cu2—N8$^{iii}$ | 2.006 (5) | C3—H3A | 0.9300 |
| O1—C1 | 1.236 (8) | C4—H4A | 0.9300 |
| O2—C1 | 1.258 (9) | C5—H5A | 0.9300 |
| N1—N2 | 1.229 (8) | | |
| | | | |
| N1—Cu1—N4 | 97.9 (3) | Cu1—N1—N2 | 115.2 (5) |
| N1—Cu1—N4$^{i}$ | 101.4 (2) | Cu2—N1—N2 | 115.3 (5) |
| O2$^{ii}$—Cu1—N1 | 91.3 (2) | N1—N2—N3 | 178.9 (8) |
| N1—Cu1—N7$^{ii}$ | 155.5 (2) | Cu1—N4—N5 | 122.8 (5) |
| N4—Cu1—N4$^{i}$ | 85.8 (2) | Cu1—N4—Cu1$^{i}$ | 94.2 (2) |
| O2$^{ii}$—Cu1—N4 | 167.4 (2) | Cu1$^{i}$—N4—N5 | 99.0 (4) |

| | | | |
|---|---|---|---|
| N4—Cu1—N7$^{ii}$ | 93.4 (3) | N4—N5—N6 | 175.6 (7) |
| O2$^{ii}$—Cu1—N4$^{i}$ | 83.89 (19) | C2—N7—C5 | 117.2 (6) |
| N4$^{i}$—Cu1—N7$^{ii}$ | 101.0 (2) | Cu1$^{ii}$—N7—C2 | 112.0 (4) |
| O2$^{ii}$—Cu1—N7$^{ii}$ | 81.5 (2) | Cu1$^{ii}$—N7—C5 | 130.6 (5) |
| O1—Cu2—N1 | 88.1 (2) | Cu2—N8—C2 | 114.5 (4) |
| O1—Cu2—N8 | 79.4 (2) | Cu2—N8—C3 | 127.6 (6) |
| O1—Cu2—O1$^{iii}$ | 180.00 | C2—N8—C3 | 117.8 (6) |
| O1—Cu2—N1$^{iii}$ | 91.9 (2) | O1—C1—O2 | 127.6 (6) |
| O1—Cu2—N8$^{iii}$ | 100.6 (2) | O1—C1—C2 | 117.9 (6) |
| N1—Cu2—N8 | 90.8 (2) | O2—C1—C2 | 114.4 (6) |
| O1$^{iii}$—Cu2—N1 | 91.9 (2) | N7—C2—N8 | 125.6 (6) |
| N1—Cu2—N1$^{iii}$ | 180.00 | N7—C2—C1 | 115.3 (6) |
| N1—Cu2—N8$^{iii}$ | 89.2 (2) | N8—C2—C1 | 119.1 (6) |
| O1$^{iii}$—Cu2—N8 | 100.6 (2) | N8—C3—C4 | 120.4 (8) |
| N1$^{iii}$—Cu2—N8 | 89.2 (2) | C3—C4—C5 | 117.9 (7) |
| N8—Cu2—N8$^{iii}$ | 180.00 | N7—C5—C4 | 121.1 (7) |
| O1$^{iii}$—Cu2—N1$^{iii}$ | 88.1 (2) | N8—C3—H3A | 120.00 |
| O1$^{iii}$—Cu2—N8$^{iii}$ | 79.4 (2) | C4—C3—H3A | 120.00 |
| N1$^{iii}$—Cu2—N8$^{iii}$ | 90.8 (2) | C3—C4—H4A | 121.00 |
| Cu2—O1—C1 | 109.0 (4) | C5—C4—H4A | 121.00 |
| Cu1$^{ii}$—O2—C1 | 116.6 (4) | N7—C5—H5A | 119.00 |
| Cu1—N1—Cu2 | 116.8 (3) | C4—C5—H5A | 119.00 |

| | | | |
|---|---|---|---|
| O1—Cu1—N1—N2 | 136.0 (5) | N8—Cu2—N1—Cu1 | 84.3 (3) |
| N4—Cu1—N1—Cu2 | 103.7 (3) | N8—Cu2—N1—N2 | −55.7 (6) |
| N4—Cu1—N1—N2 | −116.3 (5) | O1$^{iii}$—Cu2—N1—Cu1 | −175.1 (3) |
| N4$^{i}$—Cu1—N1—Cu2 | −169.0 (3) | O1$^{iii}$—Cu2—N1—N2 | 44.9 (6) |
| N4$^{i}$—Cu1—N1—N2 | −28.9 (5) | N8$^{iii}$—Cu2—N1—Cu1 | −95.7 (3) |
| O2$^{ii}$—Cu1—N1—Cu2 | −84.9 (3) | N8$^{iii}$—Cu2—N1—N2 | 124.3 (6) |
| O2$^{ii}$—Cu1—N1—N2 | 55.1 (5) | O1—Cu2—N8—C2 | −2.2 (4) |
| N7$^{ii}$—Cu1—N1—Cu2 | −12.9 (8) | O1—Cu2—N8—C3 | 175.8 (6) |
| N7$^{ii}$—Cu1—N1—N2 | 127.2 (6) | N1—Cu2—N8—C2 | −90.1 (5) |
| O1—Cu1—N4—N5 | 72.4 (6) | N1—Cu2—N8—C3 | 87.9 (6) |
| O1—Cu1—N4—Cu1$^{i}$ | 175.86 (15) | O1$^{iii}$—Cu2—N8—C2 | 177.8 (4) |
| N1—Cu1—N4—N5 | −2.6 (6) | O1$^{iii}$—Cu2—N8—C3 | −4.3 (6) |
| N1—Cu1—N4—Cu1$^{i}$ | 100.9 (2) | N1$^{iii}$—Cu2—N8—C2 | 89.9 (5) |
| N4$^{i}$—Cu1—N4—N5 | −103.5 (6) | N1$^{iii}$—Cu2—N8—C3 | −92.2 (6) |
| N4$^{i}$—Cu1—N4—Cu1$^{i}$ | 0.0 (2) | Cu1—O1—C1—O2 | −91.6 (6) |
| N7$^{ii}$—Cu1—N4—N5 | 155.7 (6) | Cu1—O1—C1—C2 | 84.7 (5) |
| N7$^{ii}$—Cu1—N4—Cu1$^{i}$ | −100.8 (2) | Cu2—O1—C1—O2 | −175.2 (5) |
| N1—Cu1—N4$^{i}$—Cu1$^{i}$ | −97.2 (3) | Cu2—O1—C1—C2 | 1.2 (6) |
| N1—Cu1—N4$^{i}$—N5$^{i}$ | 138.6 (4) | Cu1$^{ii}$—O2—C1—O1 | −178.1 (5) |
| N4—Cu1—N4$^{i}$—Cu1$^{i}$ | 0.0 (3) | Cu1$^{ii}$—O2—C1—C2 | 5.5 (6) |
| N4—Cu1—N4$^{i}$—N5$^{i}$ | −124.2 (5) | C5—N7—C2—N8 | −1.4 (9) |
| O1—Cu1—O2$^{ii}$—C1$^{ii}$ | 87.9 (4) | C5—N7—C2—C1 | 175.8 (5) |
| N1—Cu1—O2$^{ii}$—C1$^{ii}$ | 160.8 (4) | Cu1$^{ii}$—N7—C2—N8 | −176.8 (5) |
| O1—Cu1—N7$^{ii}$—C2$^{ii}$ | −84.5 (4) | Cu1$^{ii}$—N7—C2—C1 | 0.4 (6) |
| O1—Cu1—N7$^{ii}$—C5$^{ii}$ | 90.1 (6) | C2—N7—C5—C4 | 0.0 (10) |

| | | | |
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| N1—Cu1—N7$^{ii}$—C2$^{ii}$ | −75.9 (7) | Cu1$^{ii}$—N7—C5—C4 | 174.4 (5) |
| N1—Cu1—N7$^{ii}$—C5$^{ii}$ | 98.7 (7) | Cu2—N8—C2—N7 | −179.3 (5) |
| N4—Cu1—N7$^{ii}$—C2$^{ii}$ | 166.6 (4) | Cu2—N8—C2—C1 | 3.6 (7) |
| N4—Cu1—N7$^{ii}$—C5$^{ii}$ | −18.8 (6) | C3—N8—C2—N7 | 2.6 (9) |
| N1—Cu2—O1—Cu1 | −2.98 (18) | C3—N8—C2—C1 | −174.6 (6) |
| N1—Cu2—O1—C1 | 91.6 (4) | Cu2—N8—C3—C4 | 179.9 (5) |
| N8—Cu2—O1—Cu1 | −94.14 (17) | C2—N8—C3—C4 | −2.2 (10) |
| N8—Cu2—O1—C1 | 0.4 (4) | O1—C1—C2—N7 | 179.3 (5) |
| N1$^{iii}$—Cu2—O1—Cu1 | 177.02 (18) | O1—C1—C2—N8 | −3.3 (8) |
| N1$^{iii}$—Cu2—O1—C1 | −88.4 (4) | O2—C1—C2—N7 | −3.9 (8) |
| N8$^{iii}$—Cu2—O1—Cu1 | 85.86 (17) | O2—C1—C2—N8 | 173.5 (5) |
| N8$^{iii}$—Cu2—O1—C1 | −179.6 (4) | N8—C3—C4—C5 | 1.0 (11) |
| O1—Cu2—N1—Cu1 | 4.9 (3) | C3—C4—C5—N7 | 0.2 (11) |
| O1—Cu2—N1—N2 | −135.1 (6) | | |

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