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# *catena*-Poly[{di-$\mu$-azido-bis[azido(*N*,*N*-diethylethane-1,2-diamine)copper(II)]} [[azido(*N*,*N*-diethylethane-1,2-diamine)-copper(II)]-$\mu$-azido]]

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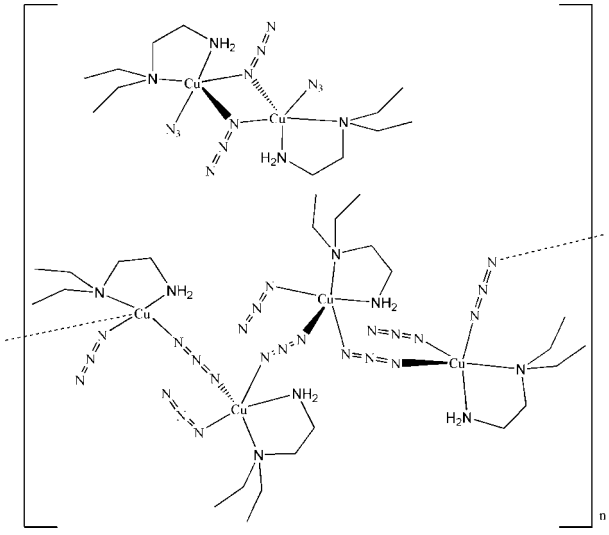
Key indicators: single-crystal X-ray study; $T$ = 298 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.034; $wR$ factor = 0.084; data-to-parameter ratio = 18.5.

The title complex, $\{[Cu_2(N_3)_4(C_6H_{16}N_2)_2][Cu(N_3)_2(C_6H_{16}N_2)]\}_n$, consists of an end-on azide-bridged dinuclear copper(II) complex and an end-to-end azide-bridged polynuclear copper(II) complex. Each Cu atom is five-coordinated by two N atoms of *N*,*N*-diethylethane-1,2-diamine and by three N atoms from three azide ligands, forming a slightly distorted square-pyramidal coordination environment.

## Related literature

For related literature, see: Colacio *et al.* (2005); Meyer *et al.* (2005); Sarkar *et al.* (2004).



## Experimental

### Crystal data

$[Cu_2(N_3)_4(C_6H_{16}N_2)_2][Cu(N_3)_2(C_6H_{16}N_2)]$
$M_r$ = 791.42
Monoclinic, $P2_1/c$
$a$ = 22.722 (2) Å
$b$ = 13.2010 (12) Å
$c$ = 11.6488 (10) Å
$\beta$ = 92.478 (2)°
$V$ = 3490.8 (5) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 1.86 mm$^{-1}$
$T$ = 298 (2) K
0.15 × 0.12 × 0.10 mm

### Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min}$ = 0.768, $T_{max}$ = 0.836
28917 measured reflections
7614 independent reflections
6149 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.031

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.084
$S$ = 1.02
7614 reflections
412 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.44 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.31 e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Cu1—N6 | 1.9663 (19) | Cu2—N11$^{i}$ | 2.006 (2) |
| Cu1—N2 | 1.9792 (18) | Cu2—N13 | 2.0779 (19) |
| Cu1—N3 | 1.983 (2) | Cu3—N17 | 1.975 (2) |
| Cu1—N1 | 2.0827 (19) | Cu3—N24 | 1.9950 (18) |
| Cu1—N9 | 2.562 (2) | Cu3—N20$^{ii}$ | 2.0269 (19) |
| Cu2—N5 | 2.654 (2) | Cu3—N23 | 2.0773 (19) |
| Cu2—N14 | 1.936 (2) | Cu3—N20 | 2.4458 (19) |
| Cu2—N12 | 1.9673 (18) | | |
| N6—Cu1—N2 | 169.89 (9) | N11$^{i}$—Cu2—N13 | 158.19 (9) |
| N6—Cu1—N3 | 91.52 (9) | N17—Cu3—N24 | 175.07 (9) |
| N2—Cu1—N3 | 93.96 (8) | N17—Cu3—N20$^{ii}$ | 91.67 (9) |
| N6—Cu1—N1 | 92.82 (9) | N24—Cu3—N20$^{ii}$ | 92.09 (8) |
| N2—Cu1—N1 | 85.59 (8) | N17—Cu3—N23 | 92.22 (8) |
| N3—Cu1—N1 | 156.09 (8) | N24—Cu3—N23 | 85.03 (8) |
| N14—Cu2—N12 | 171.30 (12) | N20$^{ii}$—Cu3—N23 | 163.83 (8) |
| N14—Cu2—N11$^{i}$ | 93.02 (10) | N17—Cu3—N20 | 90.89 (8) |
| N12—Cu2—N11$^{i}$ | 92.72 (8) | N24—Cu3—N20 | 85.94 (7) |
| N14—Cu2—N13 | 91.96 (10) | N20$^{ii}$—Cu3—N20 | 89.64 (7) |
| N12—Cu2—N13 | 85.10 (7) | N23—Cu3—N20 | 105.99 (7) |

Symmetry codes: (i) $x, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x+1, -y, -z+1$.

**Table 2**
Hydrogen-bond geometry (Å, °).

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2*C*···N11$^{i}$ | 0.89 | 2.41 | 3.095 (3) | 134 |
| N2—H2*D*···N6$^{i}$ | 0.89 | 2.35 | 3.186 (3) | 156 |
| N12—H12*D*···N8$^{iii}$ | 0.89 | 2.28 | 3.087 (3) | 151 |
| N12—H12*E*···N3$^{i}$ | 0.89 | 2.51 | 3.067 (3) | 121 |
| N24—H24*A*···N17$^{ii}$ | 0.89 | 2.37 | 3.189 (3) | 153 |
| N24—H24*A*···N18$^{ii}$ | 0.89 | 2.67 | 3.531 (3) | 163 |
| N24—H24*B*···N19$^{iv}$ | 0.90 | 2.18 | 3.031 (3) | 157 |

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); 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: HG2329).

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# supplementary materials

*Acta Cryst.* (2007). E**63**, m3148-m3149 [ **doi:10.1107/S1600536807061041** ]

# *catena*-Poly[{di-$\mu$-azido-bis[azido(*N*,*N*-diethylethane-1,2-diamine)copper(II)]} [[azido(*N*,*N*-diethylethane-1,2-diamine)copper(II)]-$\mu$-azido]]

**C.-L. Yuan**

## Comment

The azide anion is a versatile ligand that is able to link metal ions with different coordination modes, generating interesting polynuclear complexes (Colacio *et al.*, 2005; Meyer *et al.*, 2005; Sarkar *et al.*, 2004). In this paper, a new azido-bridged copper(II) complex is reported.

The title complex consists of an end-on azido-bridged dinuclear copper(II) molecule (unit 1, Fig. 1) and an end-to-end azido-bridged polynuclear copper(II) molecule (unit 2, Fig. 2). Each Cu atom in unit 1 is in a square pyramidal coordination environment and is five-coordinated by two N atoms of *N*,*N*-diethylethane-1,2-diamine, one N atom of a terminal azido ligand, and one N atom of an end-on azido bridge, defining the basal plane, and by one N atom of another end-on azido bridge occupying the apical position. Each Cu atom in unit 2 is in a square pyramidal coordination environment and is five-coordinated by two N atoms of *N*,*N*-diethylethane-1,2-diamine, one N atom of a terminal azido ligand, and one N atom of an end-to-end azido bridge, defining the basal plane, and by one N atom of another end-to-end azido bridge occupying the apical position. The significant distortion of the square pyramids is revealed by the apical bond lengths (Cu1—N9 = 2.562 (2) Å, Cu2—N5 = 2.654 (2) Å, Cu3—N20 = 2.446 (2) Å), as well as the bond angles between the apical and basal donor atoms (Table 1).

## Experimental

*N*,*N*-Diethylethane-1,2-diamine (0.1 mmol, 11.6 mg), $NaN_3$ (0.2 mmol, 13.0 mg), and $Cu(CH_3COO)_2{\cdot}H_2O$ (0.1 mmol, 20.0 mg) were dissolved in a methanol solution (10 ml). The mixture was stirred at room temperature for 20 min to give a blue solution. The solution was kept in air for about a week, blue block-shaped crystals were formed at the bottom of the vessel on slow evaporation of the solvent.

## Refinement

H atoms were placed in idealized positions and constrained to ride on their parent atoms, with C–H distances in the range 0.96–0.97 Å, N–H distances of 0.90 Å, and with $U_{iso}$(H) set to 1.2$U_{eq}$(C,*N*) and 1.5$U_{eq}$(methyl C).

## Figures

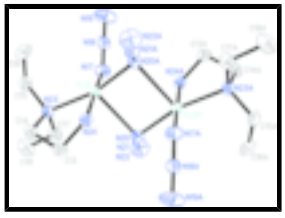


Fig. 1. The structure of the dinuclear copper(II) molecule at the 30% probability level. H atoms have been omitted for clarity. Atoms labeled with the suffix A are at the symmetry position 1 − *x*, −*y*, 1 − *z*.

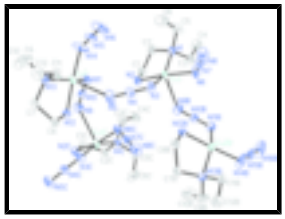


Fig. 2. The structure of the polynuclear copper(II) molecule at the 30% probability level. H atoms have been omitted for clarity. Atoms labeled with the suffix B and C are at the symmetry positions *x*, 1/2 − *y*, 1/2 + *z* and *x*, 1/2 − *y*, −1/2 + *z*, respectively.

**_catena_-Poly[{di-μ-azido-bis[azido(*N*,*N*-diethylethane-1,2-diamine)copper(II)]} [[azido(*N*,*N*-diethylethane-1,2-diamine)copper(II)]-μ-azido]]**

*Crystal data*

| | |
|---|---|
| $[Cu_2(N_3)_4(C_6H_{16}N_2)_2][Cu(N_3)_2(C_6H_{16}N_2)]$ | $F_{000}$ = 1644 |
| $M_r$ = 791.42 | $D_x$ = 1.506 Mg m$^{-3}$ |
| Monoclinic, $P2_1/c$ | Mo $K\alpha$ radiation<br>λ = 0.71073 Å |
| Hall symbol: -P 2ybc | Cell parameters from 8536 reflections |
| $a$ = 22.722 (2) Å | θ = 2.3–25.7º |
| $b$ = 13.2010 (12) Å | μ = 1.86 mm$^{-1}$ |
| $c$ = 11.6488 (10) Å | $T$ = 298 (2) K |
| β = 92.478 (2)º | Block, blue |
| $V$ = 3490.8 (5) Å$^3$ | 0.15 × 0.12 × 0.10 mm |
| $Z$ = 4 | |

*Data collection*

| | |
|---|---|
| Bruker SMART CCD area-detector diffractometer | 7614 independent reflections |
| Radiation source: fine-focus sealed tube | 6149 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int}$ = 0.031 |
| $T$ = 298(2) K | $\theta_{max}$ = 27.0º |
| ω scans | $\theta_{min}$ = 1.8º |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | $h$ = −28→29 |
| $T_{min}$ = 0.768, $T_{max}$ = 0.836 | $k$ = −16→16 |
| 28917 measured reflections | $l$ = −14→14 |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)]$ = 0.034 | H-atom parameters constrained |
| $wR(F^2)$ = 0.084 | $w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + 0.7266P]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S$ = 1.02 | $(\Delta/\sigma)_{max} < 0.001$ |
| 7614 reflections | $\Delta\rho_{max}$ = 0.44 e Å$^{-3}$ |

412 parameters

Primary atom site location: structure-invariant direct methods

$\Delta\rho_{min} = -0.30$ e Å$^{-3}$

Extinction correction: none

*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 (Å$^2$)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Cu1 | 0.126741 (11) | 0.15809 (2) | 0.22935 (2) | 0.03596 (8) |
| Cu2 | 0.213868 (13) | 0.00077 (2) | −0.15330 (3) | 0.04405 (9) |
| Cu3 | 0.463891 (12) | 0.02522 (2) | 0.38321 (2) | 0.03575 (8) |
| N1 | 0.04653 (8) | 0.09273 (15) | 0.26784 (16) | 0.0420 (5) |
| N2 | 0.09839 (8) | 0.14681 (16) | 0.06679 (16) | 0.0421 (5) |
| H2C | 0.1142 | 0.0932 | 0.0344 | 0.051* |
| H2D | 0.1062 | 0.2048 | 0.0313 | 0.051* |
| N3 | 0.21109 (8) | 0.15964 (17) | 0.19209 (18) | 0.0470 (5) |
| N4 | 0.23046 (9) | 0.14004 (16) | 0.10224 (19) | 0.0454 (5) |
| N5 | 0.25194 (11) | 0.1210 (2) | 0.0168 (2) | 0.0762 (8) |
| N6 | 0.14633 (9) | 0.19101 (18) | 0.39114 (17) | 0.0517 (5) |
| N7 | 0.18555 (10) | 0.15046 (17) | 0.44386 (17) | 0.0480 (5) |
| N8 | 0.22317 (13) | 0.1135 (3) | 0.4975 (2) | 0.0846 (9) |
| N9 | 0.09411 (10) | 0.34205 (18) | 0.1973 (2) | 0.0583 (6) |
| N10 | 0.11200 (8) | 0.39817 (15) | 0.26618 (18) | 0.0409 (5) |
| N11 | 0.12909 (9) | 0.45634 (16) | 0.33842 (18) | 0.0459 (5) |
| N12 | 0.23902 (8) | 0.12097 (14) | −0.23815 (16) | 0.0395 (4) |
| H12D | 0.2213 | 0.1257 | −0.3074 | 0.047* |
| H12E | 0.2327 | 0.1785 | −0.2012 | 0.047* |
| N13 | 0.29158 (8) | −0.06397 (15) | −0.20589 (17) | 0.0411 (4) |
| N14 | 0.19881 (12) | −0.1125 (2) | −0.0533 (3) | 0.0941 (11) |
| N15 | 0.15157 (11) | −0.12740 (18) | −0.0216 (2) | 0.0630 (7) |
| N16 | 0.10672 (14) | −0.1438 (3) | 0.0117 (3) | 0.1171 (14) |
| N17 | 0.47984 (10) | −0.11053 (16) | 0.32045 (19) | 0.0525 (5) |
| N18 | 0.51569 (9) | −0.12911 (15) | 0.25446 (18) | 0.0446 (5) |
| N19 | 0.55073 (13) | −0.1515 (2) | 0.1903 (3) | 0.0886 (10) |
| N20 | 0.44968 (8) | −0.04691 (15) | 0.57341 (16) | 0.0394 (4) |
| N21 | 0.43106 (9) | −0.12899 (19) | 0.57895 (18) | 0.0492 (5) |
| N22 | 0.41048 (13) | −0.2094 (2) | 0.5856 (2) | 0.0776 (8) |
| N23 | 0.38086 (8) | 0.03056 (14) | 0.30150 (17) | 0.0396 (4) |

| | | | | |
|---|---|---|---|---|
| N24 | 0.44157 (8) | 0.15731 (14) | 0.45227 (16) | 0.0389 (4) |
| H24A | 0.4567 | 0.1632 | 0.5238 | 0.047* |
| H24B | 0.4547 | 0.2103 | 0.4124 | 0.047* |
| C1 | 0.03390 (10) | 0.1352 (2) | 0.0643 (2) | 0.0472 (6) |
| H1A | 0.0195 | 0.1116 | −0.0106 | 0.057* |
| H1B | 0.0153 | 0.1995 | 0.0801 | 0.057* |
| C2 | 0.02024 (11) | 0.0589 (2) | 0.1552 (2) | 0.0493 (6) |
| H2A | −0.0221 | 0.0521 | 0.1601 | 0.059* |
| H2B | 0.0362 | −0.0066 | 0.1354 | 0.059* |
| C3 | 0.00902 (11) | 0.1712 (2) | 0.3218 (2) | 0.0560 (7) |
| H3A | 0.0064 | 0.2292 | 0.2707 | 0.067* |
| H3B | 0.0292 | 0.1935 | 0.3925 | 0.067* |
| C4 | −0.05267 (14) | 0.1405 (3) | 0.3494 (3) | 0.0835 (11) |
| H4A | −0.0515 | 0.0775 | 0.3907 | 0.125* |
| H4B | −0.0760 | 0.1324 | 0.2793 | 0.125* |
| H4C | −0.0698 | 0.1919 | 0.3957 | 0.125* |
| C5 | 0.05591 (14) | 0.0050 (2) | 0.3475 (3) | 0.0676 (8) |
| H5A | 0.0636 | 0.0307 | 0.4247 | 0.081* |
| H5B | 0.0198 | −0.0343 | 0.3478 | 0.081* |
| C6 | 0.10497 (17) | −0.0633 (3) | 0.3182 (3) | 0.0897 (11) |
| H6A | 0.1414 | −0.0263 | 0.3225 | 0.135* |
| H6B | 0.0981 | −0.0888 | 0.2416 | 0.135* |
| H6C | 0.1072 | −0.1188 | 0.3714 | 0.135* |
| C7 | 0.31562 (11) | 0.00834 (17) | −0.2892 (2) | 0.0409 (5) |
| H7A | 0.2977 | −0.0038 | −0.3650 | 0.049* |
| H7B | 0.3578 | −0.0013 | −0.2930 | 0.049* |
| C8 | 0.30298 (10) | 0.11470 (18) | −0.2523 (2) | 0.0411 (5) |
| H8A | 0.3242 | 0.1300 | −0.1803 | 0.049* |
| H8B | 0.3149 | 0.1626 | −0.3100 | 0.049* |
| C9 | 0.27930 (13) | −0.16364 (19) | −0.2597 (3) | 0.0646 (8) |
| H9A | 0.2714 | −0.2124 | −0.2001 | 0.077* |
| H9B | 0.3141 | −0.1862 | −0.2979 | 0.077* |
| C10 | 0.22794 (16) | −0.1616 (3) | −0.3455 (4) | 0.0951 (13) |
| H10A | 0.1927 | −0.1444 | −0.3071 | 0.143* |
| H10B | 0.2233 | −0.2272 | −0.3804 | 0.143* |
| H10C | 0.2349 | −0.1120 | −0.4036 | 0.143* |
| C11 | 0.33289 (11) | −0.0760 (2) | −0.1028 (2) | 0.0538 (7) |
| H11A | 0.3146 | −0.1212 | −0.0492 | 0.065* |
| H11B | 0.3372 | −0.0106 | −0.0656 | 0.065* |
| C12 | 0.39392 (12) | −0.1163 (3) | −0.1242 (3) | 0.0697 (9) |
| H12A | 0.3906 | −0.1780 | −0.1677 | 0.105* |
| H12B | 0.4145 | −0.1295 | −0.0520 | 0.105* |
| H12C | 0.4153 | −0.0671 | −0.1664 | 0.105* |
| C13 | 0.37677 (11) | 0.16183 (18) | 0.4497 (2) | 0.0450 (6) |
| H13A | 0.3637 | 0.2300 | 0.4662 | 0.054* |
| H13B | 0.3615 | 0.1163 | 0.5066 | 0.054* |
| C14 | 0.35535 (10) | 0.13047 (18) | 0.3304 (2) | 0.0448 (6) |
| H14A | 0.3127 | 0.1262 | 0.3268 | 0.054* |
| H14B | 0.3670 | 0.1808 | 0.2751 | 0.054* |

| | | | | |
|---|---|---|---|---|
| C15 | 0.38632 (13) | 0.0202 (2) | 0.1756 (2) | 0.0585 (7) |
| H15A | 0.3492 | 0.0390 | 0.1373 | 0.070* |
| H15B | 0.3938 | −0.0503 | 0.1578 | 0.070* |
| C16 | 0.43467 (15) | 0.0842 (3) | 0.1286 (2) | 0.0776 (10) |
| H16A | 0.4720 | 0.0630 | 0.1623 | 0.116* |
| H16B | 0.4280 | 0.1540 | 0.1469 | 0.116* |
| H16C | 0.4348 | 0.0762 | 0.0467 | 0.116* |
| C17 | 0.34449 (11) | −0.05372 (19) | 0.3482 (2) | 0.0518 (6) |
| H17A | 0.3410 | −0.0426 | 0.4300 | 0.062* |
| H17B | 0.3656 | −0.1168 | 0.3392 | 0.062* |
| C18 | 0.28313 (13) | −0.0659 (2) | 0.2937 (3) | 0.0734 (9) |
| H18A | 0.2858 | −0.0895 | 0.2161 | 0.110* |
| H18B | 0.2631 | −0.0019 | 0.2936 | 0.110* |
| H18C | 0.2615 | −0.1142 | 0.3369 | 0.110* |

*Atomic displacement parameters (Å$^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.03348 (15) | 0.04709 (17) | 0.02709 (14) | −0.00311 (12) | −0.00114 (10) | −0.00492 (11) |
| Cu2 | 0.03608 (16) | 0.04575 (17) | 0.05113 (19) | 0.00447 (12) | 0.01128 (13) | 0.01752 (14) |
| Cu3 | 0.03740 (16) | 0.03712 (15) | 0.03270 (15) | 0.01020 (11) | 0.00123 (11) | −0.00185 (11) |
| N1 | 0.0427 (11) | 0.0484 (12) | 0.0350 (10) | −0.0087 (9) | 0.0044 (8) | −0.0034 (9) |
| N2 | 0.0395 (11) | 0.0551 (12) | 0.0316 (10) | −0.0058 (9) | −0.0002 (8) | −0.0039 (9) |
| N3 | 0.0366 (11) | 0.0612 (14) | 0.0431 (12) | 0.0001 (9) | 0.0018 (9) | −0.0087 (10) |
| N4 | 0.0348 (11) | 0.0548 (13) | 0.0459 (13) | 0.0093 (9) | −0.0040 (9) | 0.0002 (10) |
| N5 | 0.0594 (16) | 0.119 (2) | 0.0513 (15) | 0.0249 (16) | 0.0086 (12) | −0.0064 (15) |
| N6 | 0.0507 (13) | 0.0723 (15) | 0.0314 (11) | 0.0111 (11) | −0.0075 (9) | −0.0107 (10) |
| N7 | 0.0514 (13) | 0.0641 (14) | 0.0282 (10) | 0.0056 (11) | −0.0014 (9) | −0.0085 (9) |
| N8 | 0.086 (2) | 0.116 (2) | 0.0500 (15) | 0.0403 (18) | −0.0208 (14) | −0.0046 (15) |
| N9 | 0.0524 (14) | 0.0558 (14) | 0.0659 (15) | −0.0081 (11) | −0.0072 (12) | −0.0100 (12) |
| N10 | 0.0314 (10) | 0.0387 (11) | 0.0528 (13) | 0.0008 (8) | 0.0044 (9) | 0.0040 (10) |
| N11 | 0.0385 (11) | 0.0464 (12) | 0.0532 (13) | −0.0030 (9) | 0.0073 (9) | −0.0085 (10) |
| N12 | 0.0408 (11) | 0.0354 (10) | 0.0427 (11) | 0.0016 (8) | 0.0080 (9) | 0.0030 (8) |
| N13 | 0.0401 (11) | 0.0372 (10) | 0.0463 (12) | 0.0032 (8) | 0.0064 (9) | 0.0057 (9) |
| N14 | 0.0556 (16) | 0.101 (2) | 0.128 (3) | 0.0149 (15) | 0.0306 (17) | 0.080 (2) |
| N15 | 0.0566 (15) | 0.0602 (15) | 0.0734 (17) | 0.0057 (12) | 0.0169 (13) | 0.0356 (13) |
| N16 | 0.066 (2) | 0.146 (3) | 0.141 (3) | 0.004 (2) | 0.035 (2) | 0.085 (3) |
| N17 | 0.0585 (14) | 0.0463 (12) | 0.0534 (13) | 0.0087 (10) | 0.0094 (11) | −0.0127 (10) |
| N18 | 0.0475 (12) | 0.0403 (11) | 0.0456 (12) | 0.0081 (9) | −0.0030 (10) | −0.0131 (9) |
| N19 | 0.0780 (19) | 0.079 (2) | 0.112 (2) | −0.0036 (15) | 0.0389 (18) | −0.0457 (17) |
| N20 | 0.0355 (10) | 0.0427 (12) | 0.0402 (11) | 0.0075 (9) | 0.0029 (8) | 0.0026 (9) |
| N21 | 0.0480 (13) | 0.0602 (15) | 0.0398 (12) | 0.0101 (11) | 0.0072 (9) | −0.0040 (11) |
| N22 | 0.091 (2) | 0.0576 (16) | 0.085 (2) | −0.0149 (15) | 0.0117 (16) | −0.0052 (14) |
| N23 | 0.0401 (11) | 0.0404 (11) | 0.0379 (11) | 0.0067 (8) | −0.0033 (8) | 0.0010 (8) |
| N24 | 0.0454 (11) | 0.0373 (10) | 0.0340 (10) | 0.0082 (8) | 0.0005 (8) | 0.0016 (8) |
| C1 | 0.0398 (13) | 0.0652 (16) | 0.0359 (13) | −0.0071 (12) | −0.0069 (10) | −0.0055 (12) |
| C2 | 0.0459 (14) | 0.0552 (16) | 0.0468 (14) | −0.0145 (12) | 0.0025 (11) | −0.0129 (12) |
| C3 | 0.0474 (15) | 0.0690 (18) | 0.0526 (16) | −0.0075 (13) | 0.0125 (12) | −0.0159 (14) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C4 | 0.061 (2) | 0.093 (3) | 0.099 (3) | −0.0067 (18) | 0.0331 (19) | −0.019 (2) |
| C5 | 0.072 (2) | 0.069 (2) | 0.063 (2) | −0.0116 (16) | 0.0071 (16) | 0.0169 (15) |
| C6 | 0.100 (3) | 0.069 (2) | 0.099 (3) | 0.009 (2) | −0.004 (2) | 0.027 (2) |
| C7 | 0.0424 (13) | 0.0462 (13) | 0.0346 (13) | 0.0005 (10) | 0.0074 (10) | 0.0012 (10) |
| C8 | 0.0419 (13) | 0.0407 (13) | 0.0413 (13) | −0.0080 (10) | 0.0075 (10) | 0.0002 (10) |
| C9 | 0.0601 (18) | 0.0366 (14) | 0.097 (2) | −0.0001 (13) | 0.0090 (17) | −0.0085 (14) |
| C10 | 0.085 (3) | 0.070 (2) | 0.129 (3) | −0.0171 (19) | −0.015 (2) | −0.037 (2) |
| C11 | 0.0515 (15) | 0.0625 (17) | 0.0477 (15) | 0.0146 (13) | 0.0056 (12) | 0.0122 (13) |
| C12 | 0.0558 (18) | 0.086 (2) | 0.067 (2) | 0.0210 (16) | 0.0010 (15) | 0.0128 (17) |
| C13 | 0.0462 (14) | 0.0385 (13) | 0.0512 (15) | 0.0104 (10) | 0.0118 (11) | −0.0005 (11) |
| C14 | 0.0394 (13) | 0.0401 (13) | 0.0544 (15) | 0.0080 (10) | −0.0037 (11) | 0.0058 (11) |
| C15 | 0.0596 (17) | 0.075 (2) | 0.0400 (15) | 0.0117 (15) | −0.0098 (13) | −0.0014 (13) |
| C16 | 0.086 (2) | 0.107 (3) | 0.0405 (16) | 0.004 (2) | 0.0072 (15) | 0.0144 (17) |
| C17 | 0.0493 (15) | 0.0390 (13) | 0.0669 (18) | 0.0053 (11) | 0.0023 (13) | 0.0013 (12) |
| C18 | 0.0550 (18) | 0.0513 (17) | 0.113 (3) | −0.0033 (14) | −0.0038 (18) | −0.0035 (17) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cu1—N6 | 1.9663 (19) | C1—H1B | 0.9700 |
| Cu1—N2 | 1.9792 (18) | C2—H2A | 0.9700 |
| Cu1—N3 | 1.983 (2) | C2—H2B | 0.9700 |
| Cu1—N1 | 2.0827 (19) | C3—C4 | 1.507 (4) |
| Cu1—N9 | 2.562 (2) | C3—H3A | 0.9700 |
| Cu2—N5 | 2.654 (2) | C3—H3B | 0.9700 |
| Cu2—N14 | 1.936 (2) | C4—H4A | 0.9600 |
| Cu2—N12 | 1.9673 (18) | C4—H4B | 0.9600 |
| Cu2—N11$^{i}$ | 2.006 (2) | C4—H4C | 0.9600 |
| Cu2—N13 | 2.0779 (19) | C5—C6 | 1.485 (5) |
| Cu3—N17 | 1.975 (2) | C5—H5A | 0.9700 |
| Cu3—N24 | 1.9950 (18) | C5—H5B | 0.9700 |
| Cu3—N20$^{ii}$ | 2.0269 (19) | C6—H6A | 0.9600 |
| Cu3—N23 | 2.0773 (19) | C6—H6B | 0.9600 |
| Cu3—N20 | 2.4458 (19) | C6—H6C | 0.9600 |
| N1—C2 | 1.486 (3) | C7—C8 | 1.500 (3) |
| N1—C5 | 1.494 (3) | C7—H7A | 0.9700 |
| N1—C3 | 1.497 (3) | C7—H7B | 0.9700 |
| N2—C1 | 1.472 (3) | C8—H8A | 0.9700 |
| N2—H2C | 0.9000 | C8—H8B | 0.9700 |
| N2—H2D | 0.9000 | C9—C10 | 1.503 (4) |
| N3—N4 | 1.181 (3) | C9—H9A | 0.9700 |
| N4—N5 | 1.155 (3) | C9—H9B | 0.9700 |
| N6—N7 | 1.188 (3) | C10—H10A | 0.9600 |
| N7—N8 | 1.146 (3) | C10—H10B | 0.9600 |
| N9—N10 | 1.153 (3) | C10—H10C | 0.9600 |
| N10—N11 | 1.192 (3) | C11—C12 | 1.516 (4) |
| N11—Cu2$^{iii}$ | 2.006 (2) | C11—H11A | 0.9700 |
| N12—C8 | 1.472 (3) | C11—H11B | 0.9700 |
| N12—H12D | 0.9000 | C12—H12A | 0.9600 |

| | | | |
|---|---|---|---|
| N12—H12E | 0.9000 | C12—H12B | 0.9600 |
| N13—C9 | 1.479 (3) | C12—H12C | 0.9600 |
| N13—C7 | 1.482 (3) | C13—C14 | 1.511 (3) |
| N13—C11 | 1.500 (3) | C13—H13A | 0.9700 |
| N14—N15 | 1.167 (3) | C13—H13B | 0.9700 |
| N15—N16 | 1.127 (3) | C14—H14A | 0.9700 |
| N17—N18 | 1.170 (3) | C14—H14B | 0.9700 |
| N18—N19 | 1.154 (3) | C15—C16 | 1.507 (4) |
| N20—N21 | 1.166 (3) | C15—H15A | 0.9700 |
| N20—Cu3$^{ii}$ | 2.0269 (19) | C15—H15B | 0.9700 |
| N21—N22 | 1.164 (3) | C16—H16A | 0.9600 |
| N23—C15 | 1.483 (3) | C16—H16B | 0.9600 |
| N23—C14 | 1.485 (3) | C16—H16C | 0.9600 |
| N23—C17 | 1.502 (3) | C17—C18 | 1.516 (4) |
| N24—C13 | 1.473 (3) | C17—H17A | 0.9700 |
| N24—H24A | 0.9000 | C17—H17B | 0.9700 |
| N24—H24B | 0.9000 | C18—H18A | 0.9600 |
| C1—C2 | 1.503 (4) | C18—H18B | 0.9600 |
| C1—H1A | 0.9700 | C18—H18C | 0.9600 |
| N6—Cu1—N2 | 169.89 (9) | C3—C4—H4A | 109.5 |
| N6—Cu1—N3 | 91.52 (9) | C3—C4—H4B | 109.5 |
| N2—Cu1—N3 | 93.96 (8) | H4A—C4—H4B | 109.5 |
| N6—Cu1—N1 | 92.82 (9) | C3—C4—H4C | 109.5 |
| N2—Cu1—N1 | 85.59 (8) | H4A—C4—H4C | 109.5 |
| N3—Cu1—N1 | 156.09 (8) | H4B—C4—H4C | 109.5 |
| N14—Cu2—N12 | 171.30 (12) | C6—C5—N1 | 114.6 (3) |
| N14—Cu2—N11$^{i}$ | 93.02 (10) | C6—C5—H5A | 108.6 |
| N12—Cu2—N11$^{i}$ | 92.72 (8) | N1—C5—H5A | 108.6 |
| N14—Cu2—N13 | 91.96 (10) | C6—C5—H5B | 108.6 |
| N12—Cu2—N13 | 85.10 (7) | N1—C5—H5B | 108.6 |
| N11$^{i}$—Cu2—N13 | 158.19 (9) | H5A—C5—H5B | 107.6 |
| N17—Cu3—N24 | 175.07 (9) | C5—C6—H6A | 109.5 |
| N17—Cu3—N20$^{ii}$ | 91.67 (9) | C5—C6—H6B | 109.5 |
| N24—Cu3—N20$^{ii}$ | 92.09 (8) | H6A—C6—H6B | 109.5 |
| N17—Cu3—N23 | 92.22 (8) | C5—C6—H6C | 109.5 |
| N24—Cu3—N23 | 85.03 (8) | H6A—C6—H6C | 109.5 |
| N20$^{ii}$—Cu3—N23 | 163.83 (8) | H6B—C6—H6C | 109.5 |
| N17—Cu3—N20 | 90.89 (8) | N13—C7—C8 | 109.56 (18) |
| N24—Cu3—N20 | 85.94 (7) | N13—C7—H7A | 109.8 |
| N20$^{ii}$—Cu3—N20 | 89.64 (7) | C8—C7—H7A | 109.8 |
| N23—Cu3—N20 | 105.99 (7) | N13—C7—H7B | 109.8 |
| C2—N1—C5 | 110.9 (2) | C8—C7—H7B | 109.8 |
| C2—N1—C3 | 111.3 (2) | H7A—C7—H7B | 108.2 |
| C5—N1—C3 | 110.1 (2) | N12—C8—C7 | 106.67 (18) |
| C2—N1—Cu1 | 104.86 (14) | N12—C8—H8A | 110.4 |
| C5—N1—Cu1 | 110.64 (17) | C7—C8—H8A | 110.4 |
| C3—N1—Cu1 | 108.84 (15) | N12—C8—H8B | 110.4 |

| | | | |
|---|---|---|---|
| C1—N2—Cu1 | 107.99 (14) | C7—C8—H8B | 110.4 |
| C1—N2—H2C | 109.3 | H8A—C8—H8B | 108.6 |
| Cu1—N2—H2C | 110.3 | N13—C9—C10 | 113.1 (2) |
| C1—N2—H2D | 107.4 | N13—C9—H9A | 109.0 |
| Cu1—N2—H2D | 108.4 | C10—C9—H9A | 109.0 |
| H2C—N2—H2D | 113.3 | N13—C9—H9B | 109.0 |
| N4—N3—Cu1 | 126.31 (17) | C10—C9—H9B | 109.0 |
| N5—N4—N3 | 176.9 (3) | H9A—C9—H9B | 107.8 |
| N7—N6—Cu1 | 121.99 (17) | C9—C10—H10A | 109.5 |
| N8—N7—N6 | 177.8 (3) | C9—C10—H10B | 109.5 |
| N9—N10—N11 | 178.3 (2) | H10A—C10—H10B | 109.5 |
| N10—N11—Cu2$^{iii}$ | 119.92 (16) | C9—C10—H10C | 109.5 |
| C8—N12—Cu2 | 108.69 (14) | H10A—C10—H10C | 109.5 |
| C8—N12—H12D | 108.3 | H10B—C10—H10C | 109.5 |
| Cu2—N12—H12D | 112.5 | N13—C11—C12 | 116.8 (2) |
| C8—N12—H12E | 106.4 | N13—C11—H11A | 108.1 |
| Cu2—N12—H12E | 113.0 | C12—C11—H11A | 108.1 |
| H12D—N12—H12E | 107.7 | N13—C11—H11B | 108.1 |
| C9—N13—C7 | 111.3 (2) | C12—C11—H11B | 108.1 |
| C9—N13—C11 | 110.2 (2) | H11A—C11—H11B | 107.3 |
| C7—N13—C11 | 110.90 (19) | C11—C12—H12A | 109.5 |
| C9—N13—Cu2 | 110.11 (16) | C11—C12—H12B | 109.5 |
| C7—N13—Cu2 | 105.66 (14) | H12A—C12—H12B | 109.5 |
| C11—N13—Cu2 | 108.55 (14) | C11—C12—H12C | 109.5 |
| N15—N14—Cu2 | 120.6 (2) | H12A—C12—H12C | 109.5 |
| N16—N15—N14 | 177.8 (3) | H12B—C12—H12C | 109.5 |
| N18—N17—Cu3 | 125.29 (19) | N24—C13—C14 | 106.84 (19) |
| N19—N18—N17 | 177.3 (3) | N24—C13—H13A | 110.4 |
| N21—N20—Cu3$^{ii}$ | 117.87 (17) | C14—C13—H13A | 110.4 |
| N21—N20—Cu3 | 118.31 (16) | N24—C13—H13B | 110.4 |
| Cu3$^{ii}$—N20—Cu3 | 90.36 (7) | C14—C13—H13B | 110.4 |
| N22—N21—N20 | 177.5 (3) | H13A—C13—H13B | 108.6 |
| C15—N23—C14 | 110.84 (19) | N23—C14—C13 | 109.77 (18) |
| C15—N23—C17 | 111.2 (2) | N23—C14—H14A | 109.7 |
| C14—N23—C17 | 110.46 (19) | C13—C14—H14A | 109.7 |
| C15—N23—Cu3 | 109.68 (16) | N23—C14—H14B | 109.7 |
| C14—N23—Cu3 | 106.38 (14) | C13—C14—H14B | 109.7 |
| C17—N23—Cu3 | 108.16 (14) | H14A—C14—H14B | 108.2 |
| C13—N24—Cu3 | 107.38 (14) | N23—C15—C16 | 113.7 (2) |
| C13—N24—H24A | 111.2 | N23—C15—H15A | 108.8 |
| Cu3—N24—H24A | 111.0 | C16—C15—H15A | 108.8 |
| C13—N24—H24B | 108.2 | N23—C15—H15B | 108.8 |
| Cu3—N24—H24B | 112.1 | C16—C15—H15B | 108.8 |
| H24A—N24—H24B | 107.0 | H15A—C15—H15B | 107.7 |
| N2—C1—C2 | 107.0 (2) | C15—C16—H16A | 109.5 |
| N2—C1—H1A | 110.3 | C15—C16—H16B | 109.5 |
| C2—C1—H1A | 110.3 | H16A—C16—H16B | 109.5 |
| N2—C1—H1B | 110.3 | C15—C16—H16C | 109.5 |

| | | | |
|---|---|---|---|
| C2—C1—H1B | 110.3 | H16A—C16—H16C | 109.5 |
| H1A—C1—H1B | 108.6 | H16B—C16—H16C | 109.5 |
| N1—C2—C1 | 109.48 (19) | N23—C17—C18 | 115.9 (2) |
| N1—C2—H2A | 109.8 | N23—C17—H17A | 108.3 |
| C1—C2—H2A | 109.8 | C18—C17—H17A | 108.3 |
| N1—C2—H2B | 109.8 | N23—C17—H17B | 108.3 |
| C1—C2—H2B | 109.8 | C18—C17—H17B | 108.3 |
| H2A—C2—H2B | 108.2 | H17A—C17—H17B | 107.4 |
| N1—C3—C4 | 117.1 (2) | C17—C18—H18A | 109.5 |
| N1—C3—H3A | 108.0 | C17—C18—H18B | 109.5 |
| C4—C3—H3A | 108.0 | H18A—C18—H18B | 109.5 |
| N1—C3—H3B | 108.0 | C17—C18—H18C | 109.5 |
| C4—C3—H3B | 108.0 | H18A—C18—H18C | 109.5 |
| H3A—C3—H3B | 107.3 | H18B—C18—H18C | 109.5 |

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

*Hydrogen-bond geometry (Å, °)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2C···N11$^{i}$ | 0.89 | 2.41 | 3.095 (3) | 134 |
| N2—H2D···N6$^{i}$ | 0.89 | 2.35 | 3.186 (3) | 156 |
| N12—H12D···N8$^{iv}$ | 0.89 | 2.28 | 3.087 (3) | 151 |
| N12—H12E···N3$^{i}$ | 0.89 | 2.51 | 3.067 (3) | 121 |
| N24—H24A···N17$^{ii}$ | 0.89 | 2.37 | 3.189 (3) | 153 |
| N24—H24A···N18$^{ii}$ | 0.89 | 2.67 | 3.531 (3) | 163 |
| N24—H24B···N19$^{v}$ | 0.90 | 2.18 | 3.031 (3) | 157 |

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

**Fig. 1**

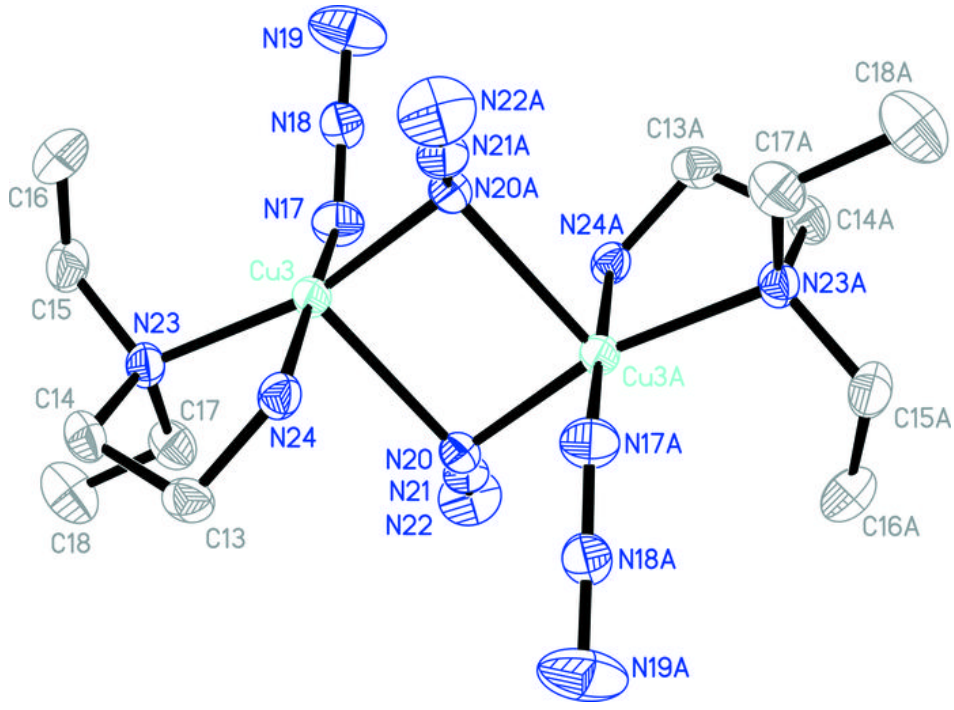
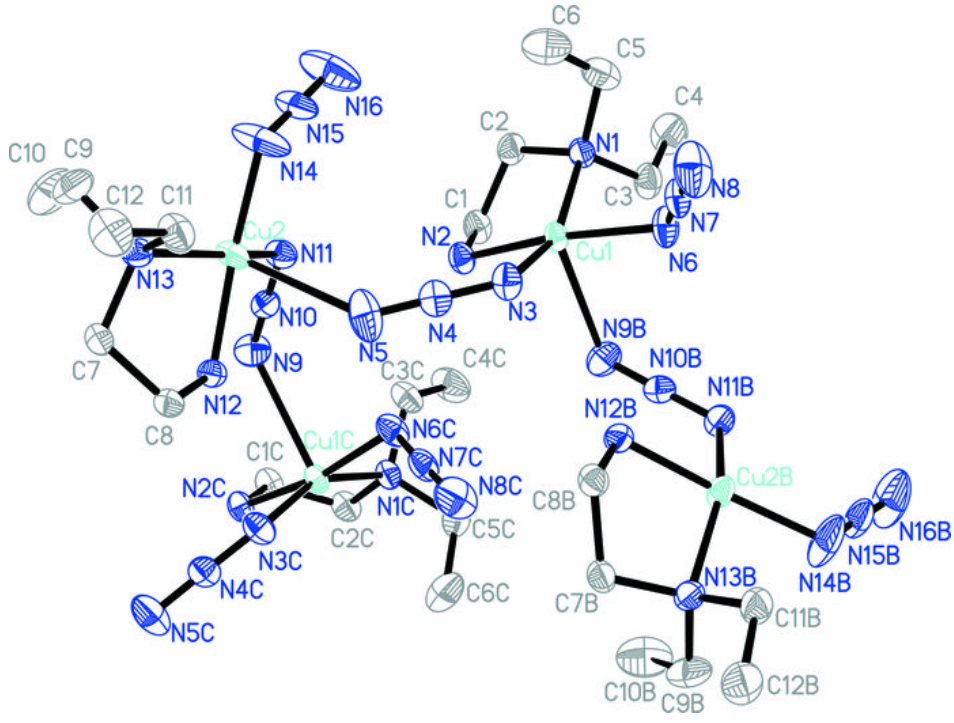

N19
N18
N22A
N21A
N20A
C18A
C13A
C17A
C16
N17
N24A
C14A
Cu3
N23A
C15
N23
Cu3A
C14
C17
N24
C15A
N20
N17A
N21
N22
C16A
C18
C13
N18A
N19A

**Fig. 2**


C6
C5
C4
C2
N1
C1
C3
N8
N7
N2
Cu1
N6
N3
N4
N5
N16
N15
N14
C10
C9
C12
C11
Cu2
N11
N13
N10
N9
C7
N12
C8
C3C
C4C
N6C
N7C
C1C
Cu1C
N2C
N8C
N1C
C2C
C5C
N3C
N4C
C6C
N5C
N9B
N10B
N11B
N12B
Cu2B
C8B
N16B
N15B
N14B
N13B
C7B
C11B
C10B
C9B
C12B