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# A triclinic polymorph of bis(2,2′-bipyridine-$\kappa^2N,N'$)(dicyanamido-$\kappa N$)-copper(II) perchlorate

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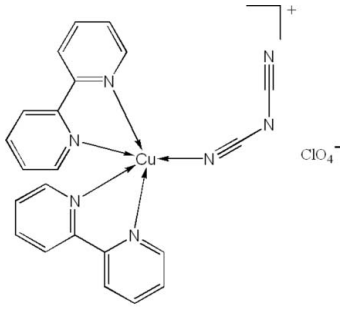
Key indicators: single-crystal X-ray study; $T$ = 293 K; mean $\sigma$(C–C) = 0.010 Å; $R$ factor = 0.069; $wR$ factor = 0.168; data-to-parameter ratio = 12.1.

In the triclinic form of the title compound, $[Cu(C_2N_3)(C_{10}H_8N_2)_2]ClO_4$, the $Cu^{II}$ center is coordinated by five N atoms in a distorted square-pyramidal geometry, which is different from that observed earlier in an orthorhombic polymorph of the same compound.

## Related literature

For the crystal structure of the orthorhombic polymorph, see: Potočňák *et al.* (2002). For the crystal structures of related complexes, see: Huang, Hu *et al.* (2003); Huang, Sun *et al.* (2003); Wang *et al.* (2007); Potočňák *et al.* (2001); Burcak *et al.* (2004). For related literature, see: Addison *et al.* (1984); Garribba *et al.* (2000).




## Experimental

### Crystal data

$[Cu(C_2N_3)(C_{10}H_8N_2)_2]ClO_4$
$M_r$ = 541.41
Triclinic, $P\overline{1}$
$a$ = 7.6881 (12) Å
$b$ = 9.0059 (14) Å
$c$ = 17.737 (3) Å
$\alpha$ = 79.953 (4)°
$\beta$ = 78.131 (3)°
$\gamma$ = 67.468 (3)°
$V$ = 1103.9 (3) Å$^3$
$Z$ = 2
Mo $K\alpha$ radiation
$\mu$ = 1.16 mm$^{-1}$
$T$ = 293 (2) K
0.16 × 0.15 × 0.10 mm

### Data collection

Bruker SMART 1K CCD area-detector diffractometer
Absorption correction: multi-scan *SADABS* (Bruker, 2000)
$T_{min}$ = 0.837, $T_{max}$ = 0.893
5551 measured reflections
3839 independent reflections
2781 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.065

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.069
$wR(F^2)$ = 0.168
$S$ = 1.03
3839 reflections
317 parameters
12 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.65 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.38 e Å$^{-3}$

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

| | | | |
|---|---|---|---|
| Cu1—N4 | 1.978 (4) | Cu1—N3 | 2.019 (5) |
| Cu1—N5 | 1.988 (5) | Cu1—N1 | 2.163 (5) |
| Cu1—N2 | 1.991 (4) | | |
| N4—Cu1—N2 | 177.48 (18) | N4—Cu1—N1 | 102.75 (18) |
| N5—Cu1—N2 | 86.8 (2) | N5—Cu1—N1 | 98.96 (19) |
| N4—Cu1—N3 | 81.29 (18) | N2—Cu1—N1 | 78.38 (18) |
| N5—Cu1—N3 | 161.8 (2) | N3—Cu1—N1 | 99.24 (18) |
| N2—Cu1—N3 | 96.32 (19) | | |

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; 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: CV2256).

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Wang, L., Yang, X.-Y. & Huang, W. (2007). *Acta Cryst.* E**63**, m835–m836.

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# supplementary materials

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# A triclinic polymorph of bis(2,2'-bipyridine-$\kappa^2N,N'$)(dicyanamido-$\kappa N$)copper(II) perchlorate

**R. Jiao, L. Wang, F. Xu and W. Huang**

## Comment

Bis(2,2'-bipyridine-$\kappa^2N,N^1$)copper(II) species is a very useful building block for constructuring coordination complexes and supramolecular frameworks. We have described several bis(2,2'-bipyridine-$\kappa^2N,N^1$)copper(II) based complexes in our early studies (Huang, Hu *et al.*, 2003; Huang, Sun *et al.*, 2003; Wang *et al.*, 2007). The crystal structures of bis(2,2'-bipyridine-$\kappa^2N,N^1$)(dicyanamido-$\kappa N'$)\ copper(II) divalent cation countered by one monodentate dicyanamide anion and another uncoordinated perchlorate, tetrafluoroborate and trifluoromethanesulfonate anions have been previously reported (Potočňák *et al.*, 2001, 2002; Burcak *et al.*, 2004). In this paper, we report a new triclinic polymorph of $[Cu(C_{10}H_8N_2)_2(C_2N_3)]ClO_4$.

The atom-numbering scheme of the title compound (I) is shown in Fig. 1, while selected bond distances and bond angles are given in Table 1. The title compound crystallizes in the triclinic $P\bar{1}$ space group and the coordination configuration of Cu(II) center is distorted five-coordinate square pyramid. Atom N1 occupies the apical position with a longer Cu–N bond length of 2.163 (5) Å, while the other four Cu–N bond lengths vary within 1.978 (4)–2.019 (5) Å. The perchlorate anion is believed to be uncoordinated since the shortest distance between the oxygen atom and the central copper ion is 3.314 (10) Å (Cu1···O4).

The main difference between the title complex and the earlier reported orthorhombic polymorph (Potočňák *et al.*, 2002) comes from the crystal symmetry and coordination geometry of the central metal ion. The reported bis(2,2'-bipyridine-$\kappa^2N,N^1$)(dicyanamido-$\kappa N'$)\ copper(II) perchlorate and bis(2,2'-bipyridine-$\kappa^2N,N^1$)(dicyanamido-$\kappa N'$)\ copper(II) tetrafluoroborate (Potočňák *et al.*, 2001) are isostructural and they both crystallize in the orthorhombic *Pbca* space group. The values of $\tau$ parameter (Addison *et al.*, 1984) for the two complexes are 0.508 and 0.542, respectively, showing distorted trigonal bipyramid geometry. In contrast, for the title complex, the $\tau$ value is 0.262, indicative of a distorted square pyramidal coordination sphere. As a result, the bond angle of Cu1–N5–C21 is 151.6 (5)°, which is significantly larger than that in the above-mentioned two complexes (143.5 (2)° for percholate and 141.7 (3)° for tetrafluoroborate). In addition, the coplanar monodentate dicyanamide ligand has a C21–N6–C22 bond angle of 121.1 (6)°, which is also a little bit larger than 119.4 (2)° in percholate and 119.6 (3)° in tetrafluoroborate.

## Experimental

The title compound (I) was obtained by refluxing an ethanol solution of equal molar ratio of [bis(2,2'-bipyridine-$\kappa^2N,N^1$)(percholate-$\kappa O$) copper(II) percholate (0.575 g, 1.0 mmol) (Garribba *et al.*, 2000) and $Na[N(CN)_2]$ (0.089 g, 1.0 mmol) for 1 h. The blue mixture was cooled to room temperature, and blue single-crystal sample of (I) suitable for X-ray diffraction measurement was grown in one week by slow evaporation in air at room temperature. Anal. Calcd. for $C_{22}H_{16}ClCuN_7O_4$: C, 48.81; H, 2.98; N, 18.11%. Found: C, 48.74; H, 3.04; N, 18.19%. Main FT–IR (KBr plates, $cm^{-1}$): 2279 (*m*), 2219 (*m*), 2173 (*versus*), 2133 (*s*), 1608 (*m*), 1602 (*m*), 1595 (*m*), 1473 (*m*), 1444 (*s*), 1154 (*m*), 1108 (*s*), 1084 (*versus*), 774 (*s*), 766 (*m*) and 622 (*m*).

### Refinement

All H-atoms were placed in geometrically idealized positions (C—H = 0.93 Å) and refined as riding, with $U_{iso}(H) = 1.2_{eq}(C)$.

### Figures

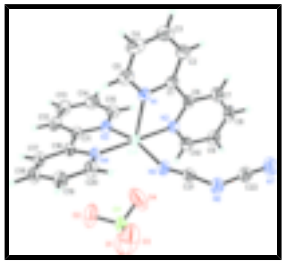


Fig. 1. A drawing of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and the H atoms are shown as small spheres of arbitrary radii.

### bis(2,2'-bipyridine-κ$^2$*N*,*N*')(dicyanamido-κ*N*)copper(II) perchlorate

*Crystal data*

| | |
|---|---|
| $[Cu(C_2N_3)(C_{10}H_8N_2)_2]ClO_4$ | $Z = 2$ |
| $M_r = 541.41$ | $F_{000} = 550$ |
| Triclinic, $P\overline{1}$ | $D_x = 1.629$ Mg m$^{-3}$ |
| Hall symbol: -P 1 | Mo $K\alpha$ radiation<br>$\lambda = 0.71073$ Å |
| $a = 7.6881$ (12) Å | Cell parameters from 999 reflections |
| $b = 9.0059$ (14) Å | $\theta = 2.4$–$20.1$º |
| $c = 17.737$ (3) Å | $\mu = 1.16$ mm$^{-1}$ |
| $\alpha = 79.953$ (4)º | $T = 293$ (2) K |
| $\beta = 78.131$ (3)º | Block, blue |
| $\gamma = 67.468$ (3)º | 0.16 × 0.15 × 0.10 mm |
| $V = 1103.9$ (3) Å$^3$ | |

*Data collection*

| | |
|---|---|
| Bruker 1K CCD area-detector diffractometer | 3839 independent reflections |
| Radiation source: fine-focus sealed tube | 2781 reflections with $I > 2\sigma(I)$ |
| Monochromator: graphite | $R_{int} = 0.065$ |
| $T = 293$(2) K | $\theta_{max} = 25.0$º |
| φ and ω scans | $\theta_{min} = 2.4$º |
| Absorption correction: multi-scan SADABS (Bruker, 2000) | $h = -9 \rightarrow 9$ |
| $T_{min} = 0.837$, $T_{max} = 0.893$ | $k = -9 \rightarrow 10$ |
| 5551 measured reflections | $l = -21 \rightarrow 16$ |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Secondary atom site location: difference Fourier map |
| Least-squares matrix: full | Hydrogen site location: inferred from neighbouring sites |
| $R[F^2 > 2\sigma(F^2)] = 0.069$ | H-atom parameters constrained |
| $wR(F^2) = 0.168$ | $w = 1/[\sigma^2(F_o^2) + (0.0664P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 1.03$ | $(\Delta/\sigma)_{max} < 0.001$ |
| 3839 reflections | $\Delta\rho_{max} = 0.65$ e Å$^{-3}$ |
| 317 parameters | $\Delta\rho_{min} = -0.38$ e Å$^{-3}$ |
| 12 restraints | Extinction correction: none |
| Primary atom site location: structure-invariant direct methods | |

*Special details*

**Experimental**. The structure was solved by direct methods (Bruker, 2000) and successive difference Fourier syntheses.

**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 | 0.19003 (9) | 0.56335 (8) | 0.25165 (4) | 0.0435 (3) |
| C1 | 0.3784 (8) | 0.6567 (7) | 0.3548 (3) | 0.0448 (14) |
| C2 | 0.4336 (10) | 0.7407 (9) | 0.3973 (3) | 0.0578 (17) |
| H2 | 0.5328 | 0.6874 | 0.4260 | 0.069* |
| C3 | 0.3381 (11) | 0.9058 (10) | 0.3964 (4) | 0.071 (2) |
| H3 | 0.3694 | 0.9651 | 0.4259 | 0.085* |
| C4 | 0.1994 (11) | 0.9799 (9) | 0.3522 (4) | 0.070 (2) |
| H4 | 0.1364 | 1.0913 | 0.3503 | 0.084* |
| C5 | 0.1504 (9) | 0.8919 (8) | 0.3100 (4) | 0.0582 (17) |
| H5 | 0.0536 | 0.9448 | 0.2801 | 0.070* |
| C6 | 0.4731 (7) | 0.4797 (7) | 0.3503 (3) | 0.0439 (14) |
| C7 | 0.6032 (8) | 0.3794 (9) | 0.3970 (3) | 0.0582 (17) |
| H7 | 0.6396 | 0.4219 | 0.4327 | 0.070* |
| C8 | 0.6785 (9) | 0.2178 (9) | 0.3909 (4) | 0.0660 (19) |
| H8 | 0.7659 | 0.1494 | 0.4227 | 0.079* |
| C9 | 0.6260 (8) | 0.1568 (8) | 0.3387 (4) | 0.0591 (17) |

| | | | | |
|---|---|---|---|---|
| H9 | 0.6778 | 0.0467 | 0.3335 | 0.071* |
| C10 | 0.4953 (9) | 0.2600 (7) | 0.2937 (3) | 0.0553 (16) |
| H10 | 0.4581 | 0.2182 | 0.2580 | 0.066* |
| C11 | 0.2155 (8) | 0.6974 (6) | 0.0944 (3) | 0.0424 (13) |
| C12 | 0.2918 (9) | 0.7448 (7) | 0.0211 (3) | 0.0547 (16) |
| H12 | 0.2116 | 0.8091 | −0.0141 | 0.066* |
| C13 | 0.4845 (10) | 0.6975 (8) | 0.0002 (4) | 0.0653 (19) |
| H13 | 0.5366 | 0.7294 | −0.0492 | 0.078* |
| C14 | 0.5998 (9) | 0.6028 (8) | 0.0526 (4) | 0.0612 (17) |
| H14 | 0.7316 | 0.5699 | 0.0396 | 0.073* |
| C15 | 0.5196 (8) | 0.5572 (8) | 0.1239 (3) | 0.0534 (16) |
| H15 | 0.5991 | 0.4919 | 0.1592 | 0.064* |
| C16 | 0.0109 (8) | 0.7505 (7) | 0.1246 (3) | 0.0437 (14) |
| C17 | −0.1305 (9) | 0.8438 (7) | 0.0818 (3) | 0.0550 (16) |
| H17 | −0.1008 | 0.8732 | 0.0292 | 0.066* |
| C18 | −0.3177 (10) | 0.8934 (8) | 0.1180 (4) | 0.0618 (18) |
| H18 | −0.4157 | 0.9558 | 0.0899 | 0.074* |
| C19 | −0.3571 (9) | 0.8500 (8) | 0.1951 (4) | 0.0613 (18) |
| H19 | −0.4820 | 0.8847 | 0.2206 | 0.074* |
| C20 | −0.2115 (9) | 0.7551 (8) | 0.2341 (4) | 0.0599 (17) |
| H20 | −0.2389 | 0.7246 | 0.2867 | 0.072* |
| C21 | 0.0205 (8) | 0.4107 (8) | 0.3986 (4) | 0.0504 (14) |
| C22 | 0.1100 (10) | 0.2596 (9) | 0.5108 (4) | 0.0620 (14) |
| Cl1 | 0.0782 (2) | 0.2387 (2) | 0.14516 (10) | 0.0672 (5) |
| N1 | 0.2396 (6) | 0.7306 (6) | 0.3109 (3) | 0.0447 (11) |
| N2 | 0.4187 (6) | 0.4198 (6) | 0.2993 (3) | 0.0446 (11) |
| N3 | 0.3321 (7) | 0.6019 (6) | 0.1455 (3) | 0.0457 (11) |
| N4 | −0.0303 (6) | 0.7041 (5) | 0.1998 (2) | 0.0435 (11) |
| N5 | 0.0378 (7) | 0.4750 (6) | 0.3393 (3) | 0.0571 (14) |
| N6 | −0.0215 (8) | 0.3402 (7) | 0.4665 (3) | 0.0688 (13) |
| N7 | 0.2105 (9) | 0.1878 (8) | 0.5522 (3) | 0.0827 (19) |
| O1 | 0.140 (2) | 0.0985 (10) | 0.1153 (5) | 0.238 (6) |
| O2 | 0.0414 (9) | 0.3627 (8) | 0.0838 (3) | 0.127 (2) |
| O3 | −0.0722 (9) | 0.2517 (12) | 0.1995 (5) | 0.202 (5) |
| O4 | 0.2253 (10) | 0.2385 (12) | 0.1770 (4) | 0.167 (3) |

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

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Cu1 | 0.0401 (4) | 0.0505 (5) | 0.0348 (4) | −0.0128 (3) | −0.0072 (3) | 0.0025 (3) |
| C1 | 0.043 (3) | 0.058 (4) | 0.036 (3) | −0.027 (3) | 0.003 (3) | −0.001 (3) |
| C2 | 0.067 (4) | 0.076 (5) | 0.039 (4) | −0.041 (4) | 0.002 (3) | −0.005 (3) |
| C3 | 0.089 (6) | 0.085 (6) | 0.053 (4) | −0.051 (5) | 0.007 (4) | −0.021 (4) |
| C4 | 0.074 (5) | 0.063 (5) | 0.071 (5) | −0.033 (4) | 0.022 (4) | −0.023 (4) |
| C5 | 0.050 (4) | 0.053 (4) | 0.064 (4) | −0.017 (3) | 0.005 (3) | −0.006 (3) |
| C6 | 0.037 (3) | 0.059 (4) | 0.034 (3) | −0.022 (3) | −0.002 (2) | 0.009 (3) |
| C7 | 0.047 (4) | 0.080 (5) | 0.044 (4) | −0.024 (4) | −0.009 (3) | 0.005 (3) |
| C8 | 0.047 (4) | 0.074 (5) | 0.061 (5) | −0.009 (4) | −0.017 (3) | 0.018 (4) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C9 | 0.044 (4) | 0.056 (4) | 0.065 (4) | −0.011 (3) | −0.007 (3) | 0.006 (3) |
| C10 | 0.052 (4) | 0.053 (4) | 0.054 (4) | −0.013 (3) | −0.008 (3) | −0.003 (3) |
| C11 | 0.048 (3) | 0.038 (3) | 0.036 (3) | −0.011 (3) | −0.001 (3) | −0.004 (2) |
| C12 | 0.063 (4) | 0.047 (4) | 0.044 (4) | −0.016 (3) | 0.000 (3) | 0.004 (3) |
| C13 | 0.066 (5) | 0.066 (4) | 0.048 (4) | −0.023 (4) | 0.018 (3) | −0.003 (3) |
| C14 | 0.051 (4) | 0.061 (4) | 0.069 (5) | −0.023 (3) | 0.007 (3) | −0.013 (3) |
| C15 | 0.046 (4) | 0.065 (4) | 0.046 (4) | −0.018 (3) | 0.002 (3) | −0.012 (3) |
| C16 | 0.048 (3) | 0.046 (3) | 0.035 (3) | −0.014 (3) | −0.010 (3) | −0.002 (2) |
| C17 | 0.065 (4) | 0.048 (4) | 0.045 (4) | −0.014 (3) | −0.014 (3) | 0.006 (3) |
| C18 | 0.060 (4) | 0.056 (4) | 0.064 (5) | −0.012 (3) | −0.026 (4) | 0.003 (3) |
| C19 | 0.041 (4) | 0.060 (4) | 0.069 (5) | −0.006 (3) | −0.008 (3) | −0.001 (3) |
| C20 | 0.045 (4) | 0.076 (5) | 0.046 (4) | −0.015 (3) | −0.001 (3) | 0.001 (3) |
| C21 | 0.048 (3) | 0.063 (4) | 0.045 (3) | −0.026 (3) | −0.010 (3) | 0.001 (3) |
| C22 | 0.062 (3) | 0.078 (3) | 0.048 (3) | −0.032 (3) | −0.011 (2) | 0.009 (2) |
| Cl1 | 0.0588 (11) | 0.0839 (13) | 0.0510 (10) | −0.0225 (9) | −0.0081 (8) | 0.0050 (9) |
| N1 | 0.037 (3) | 0.048 (3) | 0.046 (3) | −0.016 (2) | −0.001 (2) | −0.002 (2) |
| N2 | 0.043 (3) | 0.047 (3) | 0.042 (3) | −0.016 (2) | −0.010 (2) | 0.005 (2) |
| N3 | 0.045 (3) | 0.049 (3) | 0.039 (3) | −0.014 (2) | −0.004 (2) | −0.003 (2) |
| N4 | 0.038 (3) | 0.046 (3) | 0.037 (3) | −0.008 (2) | −0.006 (2) | 0.003 (2) |
| N5 | 0.060 (3) | 0.070 (4) | 0.042 (3) | −0.031 (3) | −0.009 (2) | 0.013 (3) |
| N6 | 0.065 (3) | 0.085 (3) | 0.053 (3) | −0.031 (3) | −0.009 (2) | 0.015 (2) |
| N7 | 0.084 (4) | 0.084 (5) | 0.073 (4) | −0.022 (4) | −0.031 (4) | 0.016 (3) |
| O1 | 0.482 (19) | 0.125 (7) | 0.126 (7) | −0.112 (9) | −0.082 (9) | −0.011 (5) |
| O2 | 0.107 (5) | 0.128 (5) | 0.098 (5) | −0.015 (4) | −0.013 (4) | 0.046 (4) |
| O3 | 0.076 (5) | 0.266 (11) | 0.160 (7) | −0.019 (5) | 0.032 (5) | 0.086 (7) |
| O4 | 0.119 (6) | 0.284 (11) | 0.118 (6) | −0.092 (7) | −0.058 (5) | 0.023 (6) |

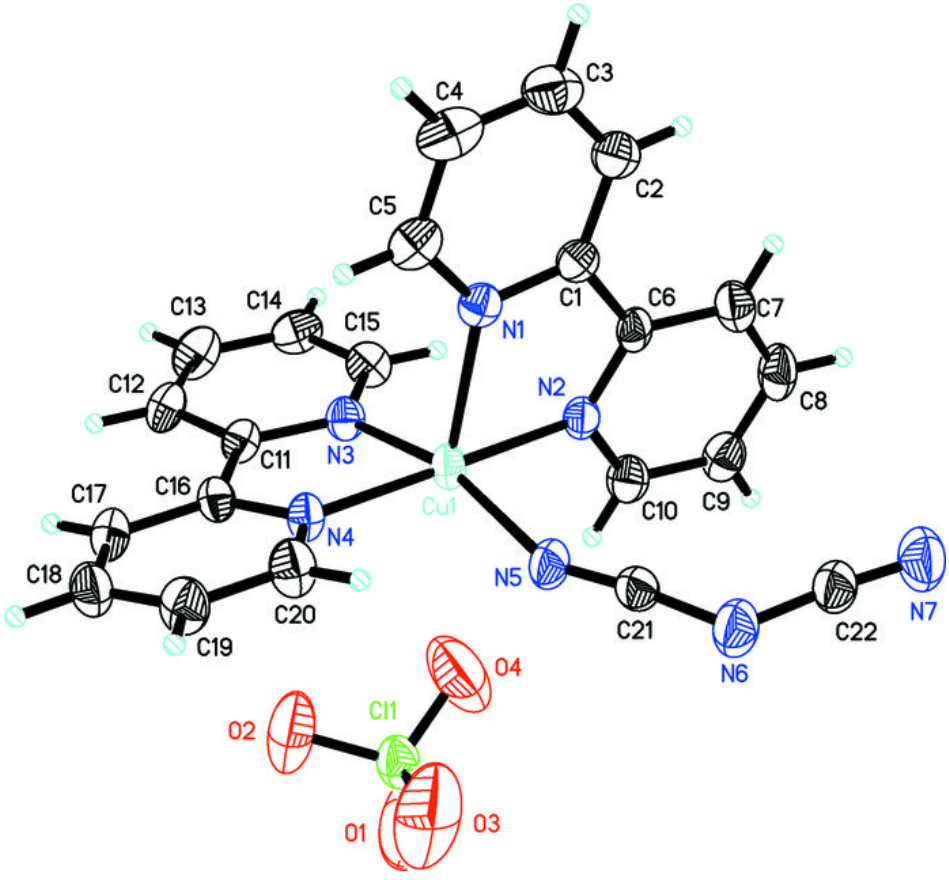
*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| Cu1—N4 | 1.978 (4) | C11—C16 | 1.469 (7) |
| Cu1—N5 | 1.988 (5) | C12—C13 | 1.364 (8) |
| Cu1—N2 | 1.991 (4) | C12—H12 | 0.9300 |
| Cu1—N3 | 2.019 (5) | C13—C14 | 1.364 (9) |
| Cu1—N1 | 2.163 (5) | C13—H13 | 0.9300 |
| C1—N1 | 1.343 (7) | C14—C15 | 1.357 (8) |
| C1—C2 | 1.377 (8) | C14—H14 | 0.9300 |
| C1—C6 | 1.486 (8) | C15—N3 | 1.329 (7) |
| C2—C3 | 1.383 (9) | C15—H15 | 0.9300 |
| C2—H2 | 0.9300 | C16—N4 | 1.336 (6) |
| C3—C4 | 1.346 (9) | C16—C17 | 1.372 (7) |
| C3—H3 | 0.9300 | C17—C18 | 1.382 (9) |
| C4—C5 | 1.372 (9) | C17—H17 | 0.9300 |
| C4—H4 | 0.9300 | C18—C19 | 1.359 (8) |
| C5—N1 | 1.346 (7) | C18—H18 | 0.9300 |
| C5—H5 | 0.9300 | C19—C20 | 1.358 (8) |
| C6—N2 | 1.336 (7) | C19—H19 | 0.9300 |
| C6—C7 | 1.375 (7) | C20—N4 | 1.334 (7) |
| C7—C8 | 1.359 (9) | C20—H20 | 0.9300 |
| C7—H7 | 0.9300 | C21—N5 | 1.117 (7) |

| | | | |
|---|---|---|---|
| C8—C9 | 1.350 (9) | C21—N6 | 1.299 (7) |
| C8—H8 | 0.9300 | C22—N7 | 1.112 (7) |
| C9—C10 | 1.366 (8) | C22—N6 | 1.317 (8) |
| C9—H9 | 0.9300 | Cl1—O3 | 1.325 (6) |
| C10—N2 | 1.343 (7) | Cl1—O1 | 1.331 (8) |
| C10—H10 | 0.9300 | Cl1—O4 | 1.364 (6) |
| C11—N3 | 1.355 (7) | Cl1—O2 | 1.405 (6) |
| C11—C12 | 1.378 (7) | | |
| N4—Cu1—N5 | 95.2 (2) | C12—C13—C14 | 119.1 (6) |
| N4—Cu1—N2 | 177.48 (18) | C12—C13—H13 | 120.5 |
| N5—Cu1—N2 | 86.8 (2) | C14—C13—H13 | 120.5 |
| N4—Cu1—N3 | 81.29 (18) | C15—C14—C13 | 119.1 (6) |
| N5—Cu1—N3 | 161.8 (2) | C15—C14—H14 | 120.5 |
| N2—Cu1—N3 | 96.32 (19) | C13—C14—H14 | 120.5 |
| N4—Cu1—N1 | 102.75 (18) | N3—C15—C14 | 122.8 (6) |
| N5—Cu1—N1 | 98.96 (19) | N3—C15—H15 | 118.6 |
| N2—Cu1—N1 | 78.38 (18) | C14—C15—H15 | 118.6 |
| N3—Cu1—N1 | 99.24 (18) | N4—C16—C17 | 121.0 (5) |
| N1—C1—C2 | 122.2 (6) | N4—C16—C11 | 114.5 (5) |
| N1—C1—C6 | 114.6 (5) | C17—C16—C11 | 124.4 (5) |
| C2—C1—C6 | 123.1 (6) | C16—C17—C18 | 119.0 (6) |
| C1—C2—C3 | 118.5 (6) | C16—C17—H17 | 120.5 |
| C1—C2—H2 | 120.8 | C18—C17—H17 | 120.5 |
| C3—C2—H2 | 120.8 | C19—C18—C17 | 119.3 (6) |
| C4—C3—C2 | 119.2 (6) | C19—C18—H18 | 120.3 |
| C4—C3—H3 | 120.4 | C17—C18—H18 | 120.3 |
| C2—C3—H3 | 120.4 | C20—C19—C18 | 119.0 (6) |
| C3—C4—C5 | 120.4 (7) | C20—C19—H19 | 120.5 |
| C3—C4—H4 | 119.8 | C18—C19—H19 | 120.5 |
| C5—C4—H4 | 119.8 | N4—C20—C19 | 122.4 (6) |
| N1—C5—C4 | 121.4 (6) | N4—C20—H20 | 118.8 |
| N1—C5—H5 | 119.3 | C19—C20—H20 | 118.8 |
| C4—C5—H5 | 119.3 | N5—C21—N6 | 172.9 (7) |
| N2—C6—C7 | 120.6 (6) | N7—C22—N6 | 174.5 (8) |
| N2—C6—C1 | 115.8 (5) | O3—Cl1—O1 | 110.9 (7) |
| C7—C6—C1 | 123.6 (5) | O3—Cl1—O4 | 109.8 (6) |
| C8—C7—C6 | 119.8 (6) | O1—Cl1—O4 | 106.1 (7) |
| C8—C7—H7 | 120.1 | O3—Cl1—O2 | 113.1 (4) |
| C6—C7—H7 | 120.1 | O1—Cl1—O2 | 107.6 (5) |
| C9—C8—C7 | 119.8 (6) | O4—Cl1—O2 | 109.1 (5) |
| C9—C8—H8 | 120.1 | C1—N1—C5 | 118.3 (5) |
| C7—C8—H8 | 120.1 | C1—N1—Cu1 | 112.6 (4) |
| C8—C9—C10 | 118.7 (6) | C5—N1—Cu1 | 129.1 (4) |
| C8—C9—H9 | 120.6 | C6—N2—C10 | 118.8 (5) |
| C10—C9—H9 | 120.6 | C6—N2—Cu1 | 117.6 (4) |
| N2—C10—C9 | 122.3 (6) | C10—N2—Cu1 | 122.3 (4) |
| N2—C10—H10 | 118.9 | C15—N3—C11 | 118.9 (5) |
| C9—C10—H10 | 118.9 | C15—N3—Cu1 | 127.7 (4) |
| N3—C11—C12 | 120.0 (5) | C11—N3—Cu1 | 113.1 (4) |

| | | | |
|---|---|---|---|
| N3—C11—C16 | 115.3 (5) | C20—N4—C16 | 119.2 (5) |
| C12—C11—C16 | 124.6 (5) | C20—N4—Cu1 | 125.1 (4) |
| C13—C12—C11 | 120.2 (6) | C16—N4—Cu1 | 115.7 (4) |
| C13—C12—H12 | 119.9 | C21—N5—Cu1 | 151.6 (5) |
| C11—C12—H12 | 119.9 | C21—N6—C22 | 121.1 (6) |

**Fig. 1**


C4
C3
C2
C5
C1
C6
C7
C13
C14
C15
N1
C12
N2
C8
N3
C11
Cu1
C17
C16
C10
C9
N4
N5
C18
C20
C21
N7
C19
N6
C22
O4
Cl1
O2
O1
O3