

Bis(2,2'-bi-1*H*-imidazole)copper(II) bis(1,1,3,3-tetracyano-2-ethoxypropenide)

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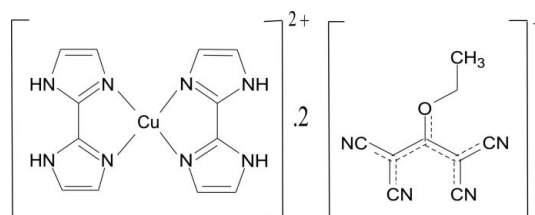
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Key indicators: single-crystal X-ray study; $T = 170$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.034; wR factor = 0.077; data-to-parameter ratio = 13.5.

In the title compound, $[\text{Cu}(\text{C}_6\text{H}_6\text{N}_4)_2](\text{C}_9\text{H}_5\text{N}_4\text{O})_2$, the Cu^{2+} ion (site symmetry $\bar{1}$) is coordinated by two N,N' -bidentate 2,2'-biimidazole (H_2biim) ligands, generating a square-planar CuN_4 geometry. The dihedral angle between the aromatic rings in the ligand is 0.70 (9°). In the polynitrile 1,1,3,3-tetracyano-2-ethoxypropenide (tcnoet) anion, the $\text{C}-\text{N}$, $\text{C}-\text{C}$ and $\text{C}-\text{O}$ bond lengths indicate extensive electronic delocalization. An alternative description for the metal-ion geometry is an extremely distorted CuN_6 octahedron, with two N -bonded tcnoet anions completing the coordination. In the crystal, the components are linked by $\text{N}-\text{H}\cdots\text{N}$ and $\text{C}-\text{H}\cdots\text{N}$ interactions.

Related literature

For the structures and properties of related compounds containing polynitrile anions, see: Atmani *et al.* (2008); Batten & Murray (2003); Bencini & Mani (1988); Benmansour *et al.* (2007); Cancela *et al.* (2001); Cromer *et al.* (1987); Jones *et al.* (2006); Setifi *et al.* (2006, 2007); Thétiot *et al.* (2003); Triki *et al.* (2005); Yuste *et al.* (2007). For the synthesis of the H_2biim and Ktcnoet ligands, see: Bernarducci *et al.* (1983) and Middleton & Engelhardt (1958), respectively.



Experimental

Crystal data

$[\text{Cu}(\text{C}_6\text{H}_6\text{N}_4)_2](\text{C}_9\text{H}_5\text{N}_4\text{O})_2$
 $M_r = 702.18$
Monoclinic, $P2_1/c$
 $a = 8.1001$ (8) Å
 $b = 26.1834$ (11) Å
 $c = 8.2185$ (7) Å
 $\beta = 117.086$ (1°)

$V = 1551.9$ (2) Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.76$ mm⁻¹
 $T = 170$ K
 $0.40 \times 0.30 \times 0.20$ mm

Data collection

Oxford Diffraction Xcalibur CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
 $T_{\min} = 0.750$, $T_{\max} = 0.862$

8646 measured reflections
3002 independent reflections
1854 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.077$
 $S = 0.93$
3002 reflections

223 parameters
H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.38$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

| | | | |
|-----------|-------------|--------|-----------|
| Cu1—N1 | 1.9727 (19) | Cu1—N7 | 2.821 (2) |
| Cu1—N2 | 2.0397 (18) | | |
| N1—Cu1—N2 | 82.04 (8) | | |

Table 2

Hydrogen-bond geometry (Å, °).

| $D-\text{H}\cdots A$ | $D-\text{H}$ | $\text{H}\cdots A$ | $D\cdots A$ | $D-\text{H}\cdots A$ |
|--|--------------|--------------------|-------------|----------------------|
| $\text{N3}-\text{H3}\cdots\text{N9}^i$ | 0.88 | 2.22 | 3.011 (3) | 149 |
| $\text{N4}-\text{H4}\cdots\text{N9}^i$ | 0.88 | 2.17 | 2.967 (3) | 150 |
| $\text{C3}-\text{H3A}\cdots\text{N8}^{ii}$ | 0.95 | 2.42 | 3.187 (3) | 138 |

Symmetry codes: (i) $x - 1, y, z$; (ii) $x, y, z - 1$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

The X-ray data were collected at the University of Bretagne Occidentale (UBO; UMR CNRS 6521). FS thanks Professor S.

Triki for providing diffraction facilities and the Université Ferhat Abbas de Sétif, Algérie, for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HB5555).

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supporting information

Acta Cryst. (2010). E66, m1044–m1045 [https://doi.org/10.1107/S1600536810029752]

Bis(2,2'-bi-1*H*-imidazole)copper(II) bis(1,1,3,3-tetracyano-2-ethoxypropenide)

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S1. Comment

Polynitrile anions are known to be interesting ligands in coordination chemistry because of their high electronic delocalization and their cyano groups juxtaposed in such a way that they cannot all coordinate to the same metal ion. They adopt different bridging or nonbridging coordination modes which afford discrete or extended molecular architectures (Atmani *et al.*, 2008; Benmansour *et al.*, 2007; Triki *et al.*, 2005; Thétiot *et al.*, 2003). Following these structural and electronic characteristics, several series of binary systems "polynitrile/*M*(II)" with only polynitrile bridges or ternary systems "polynitrile/co-ligand/*M*(II)" (*M*(II), transition metal ion) involving an additional bridging or chelate co-ligand have been reported. Most of them display one-dimensional, two-dimensional and three-dimensional polymeric assemblies, in which the polynitrile anions act as μ 2-, μ 3- and/or μ 4- bridging ligands and exhibit unusual magnetic properties (Batten & Murray, 2003; Jones *et al.*, 2006; Yuste *et al.*, 2007; Setifi *et al.*, 2006; Setifi *et al.*, 2007).

In our case we have chosen to investigate the ternary system including 2,2'-biimidazole (H_2bim) selected as co-ligand because it is bifunctional: the imino moieties can be coordinated to a metal ion acting as the first coordination sphere and the amino N—H and C—H groups, as the second coordination sphere, may donate multifold hydrogen bonds to tcnocet anions, extending the structure into a high-dimensional network. In this contribution we report the synthesis and the crystal structure of a new copper(II) compound with neutral 2,2'-biimidazole, $Cu(H_2biim)_2$ (tcnoet)₂, (I).

The crystal of (I) is built of $[Cu(H_2biim)_2]^{2+}$ cations and (tcnoet)⁻ anions interconnected by hydrogen bonds. As shown in Fig. 1, the Cu(II) ion has a square coordination geometry, it locates on a symmetry inversion center and relates four nitrogen atoms of two symmetry-related 2,2'-biimidazole molecules which bind bidentately arranged *trans* to each other in the square plane [Cu1—N1 = 1.973 (2) Å and Cu1—N2 = 2.040 (2) Å] and interacts with two nitrogen atoms belonging to tcnocet ligands occupying the apical coordination sites [Cu1—N7 = 2.821 (3) Å]. Selected interatomic distances and angles are listed in Table 1.

The Cu—N bond distances to H_2biim and inter-ring C1—C2 bond length in (I) present no unusual features and are consistent with the previous report in $[Cu(H_2biim)_2]Cl_2$ [Bencini & Mani, 1988], $[Cu(Me_4biim)ONO_2]Cl$ [Bernarducci *et al.*, 1983] and $[VOCl(H_2Biim)_2]Cl$ [Cancela *et al.*, 2001] complexes. In our case the principal coordination is planar and the Cu atom lies within that plane. Both imidazole rings are planar, with no atoms deviating by more than 0.007 Å° from the least-squares plane. The two rings of H_2biim are nearly coplanar, making an angle of 0.70 (9)°. This value compares well with that found in the mononuclear copper(II) species $[Cu(H_2biim)_2]^{2+}$ which are in a strictly planar environment (Bencini & Mani, 1988) and that observed in the free H_2biim molecule (Cromer *et al.*, 1987), but it is smaller than that found for the mononuclear oxovanadium(IV) species $[VOCl(H_2biim)_2]Cl$ (Cancela *et al.*, 2001).

$[Cu(H_2biim)_2](tcnoet)_2$ units are connected to each other *via* hydrogen bonds N—H...N resulting in a one-dimensional chains as shown in Fig. 2. Furthermore these chains are maintained through van der Waals interactions on the (*ab*) plane

and connect each other *via* C—H···N hydrogen bonds into a two-dimensional network (Fig. 3). Interestingly, each tcnocet anion help to sustain the one-dimensional assembly and at the same time the final two-dimensional array.

In this complex, the three central C atoms (C11, C12 and C13) of the anionic ligand present an sp^2 hybridization as indicated by the sum of the three angles around them (359.98° or 360.0°). Two additional facts support the idea of electron delocalization over the three central C atoms: (i) the six central C—C bond distances (1.389 \AA - 1.428 \AA) are longer than a normal C=C double bond (1.340 \AA) and close to those of benzene and (ii) the C11—O1 bond distance 1.352 \AA is much shorter than the normal C—O single bond, suggesting that the two central and the C11—O1 bond present a partial double character.

S2. Experimental

H₂biim and Ktcnoet ligands were synthesized with the published procedures respectively (Bernarducci *et al.*, 1983; Middleton *et al.*, 1958). To a methanolic suspension of H₂biim (0.025 g, 5 ml) was added dropwise a solution of CuCl₂·2H₂O (0.032 g, 5 ml) resulting in a green solution. Ktcnoet was dissolved in water (0.084 g, 10 ml) and was added quickly to the former solution. The final solution was filtered and allowed to evaporate for a week, giving green blocks of (I). X band EPR spectrum from a polycrystalline powdered sample of (I) recorded at room temperature exhibits a well defined axial signal with $g_{\text{parallel}} = 2.27 > g_{\text{perpendicular}} = 2.07$ consistent with a Cu(II) monomer.

S3. Refinement

All H atoms were placed in geometrical positions and refined using a riding model, with C—H distances in the range 0.95–0.99 Å and their displacement parameters were set to $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl group and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for all others, while N—H bond lengths were fixed to 0.88 Å with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier N atom})$.

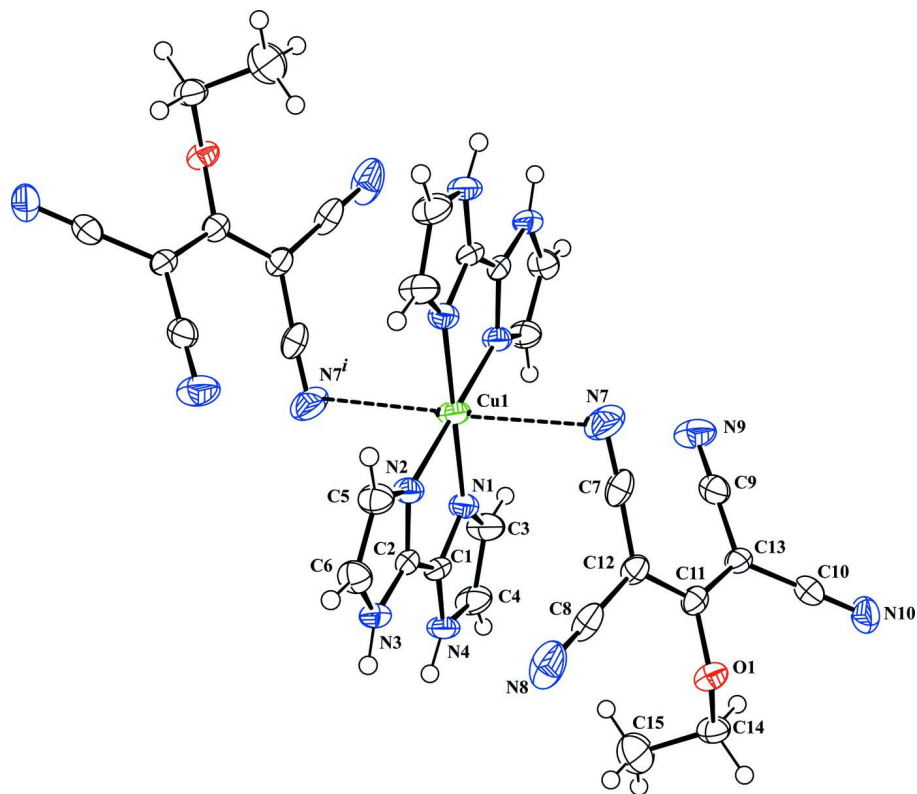


Figure 1

The metal environment in (I), with displacement ellipsoids drawn at the 50% probability level. Unlabelled atoms are related to labelled atoms by the symmetry operation $1 - x, 1 - y, 1 - z$.

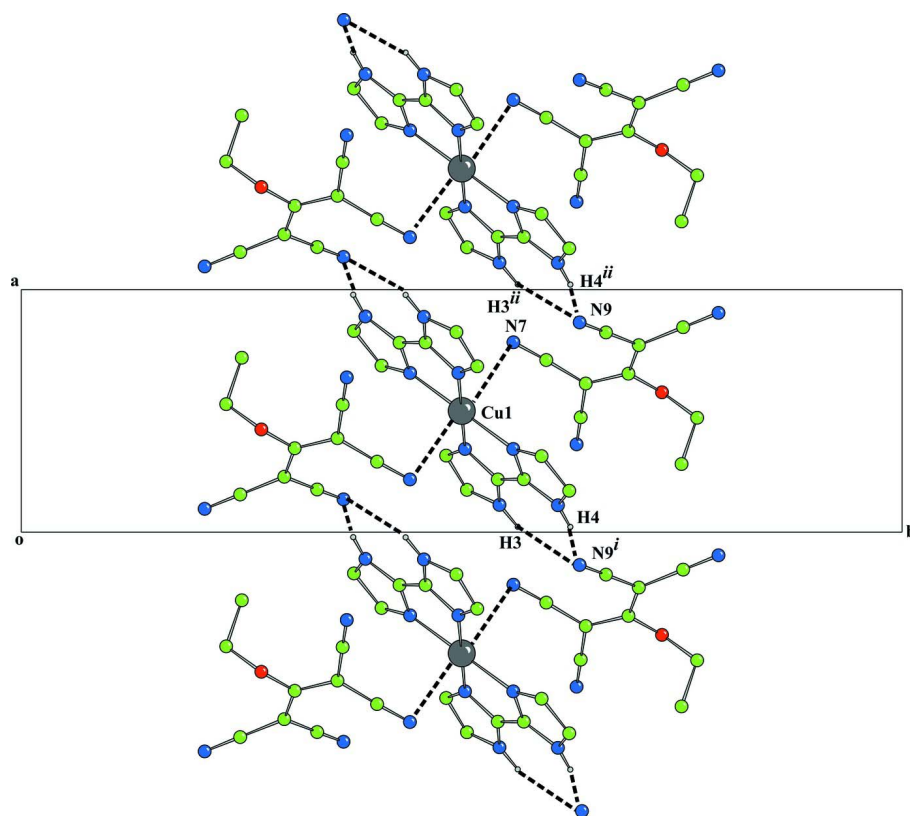


Figure 2

View of the one one-dimensional hydrogen bonded chain on the *ab* plane. Symmetry codes: $i(-1 + x,y,z)$, $ii(1 + x,y,z)$

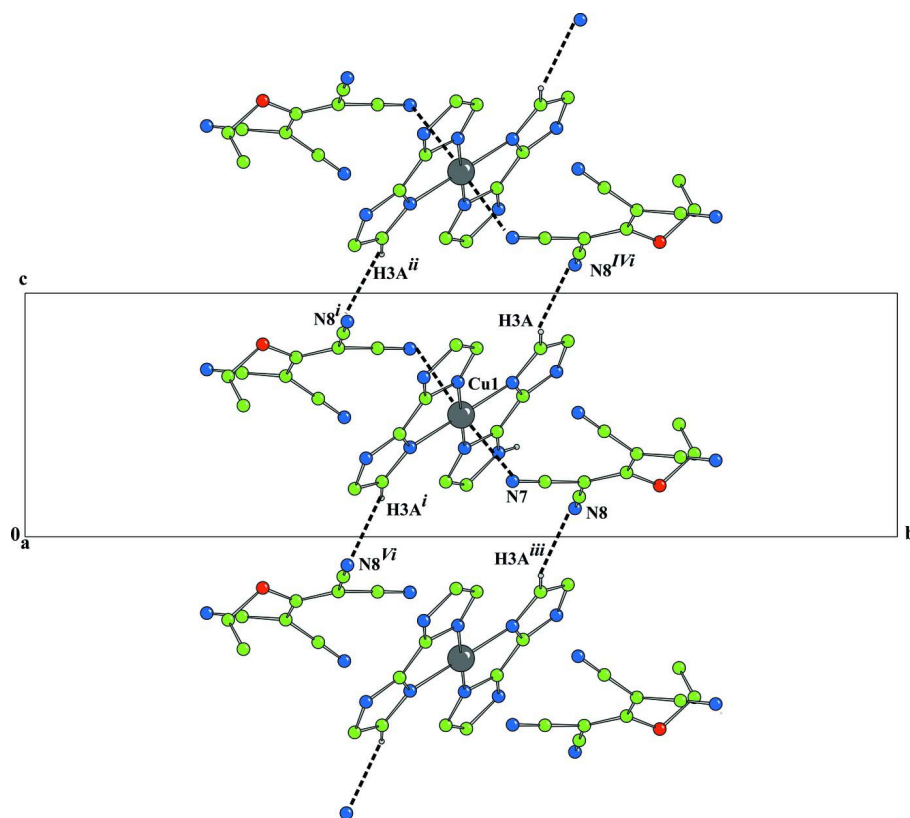


Figure 3

View of the hydrogen bonded maintaining the chains along the *c* axis. Symmetry codes *i*(1 - *x*, 1 - *y*, 1 - *z*), *ii*(1 - *x*, 1 - *y*, -*z*), *iii*(*x*, *y*, 1 + *z*), *Vi*(*x*, *y*, -1 + *z*), *Vii*(1 - *x*, 1 - *y*, 2 - *z*).

Bis(2,2'-bi-1*H*-imidazole)copper(II) bis(1,1,3,3-tetracyano-2-ethoxypropenide)

Crystal data

[Cu(C₆H₆N₄)₂](C₉H₅N₄O)₂

M_r = 702.18

Monoclinic, *P*2₁/*c*

Hall symbol: -*P* 2₁/*c*

a = 8.1001 (8) Å

b = 26.1834 (11) Å

c = 8.2185 (7) Å

β = 117.086 (11)°

V = 1551.9 (2) Å³

Z = 2

F(000) = 718

D_x = 1.503 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 3092 reflections

θ = 2.8–31.5°

μ = 0.76 mm⁻¹

T = 170 K

Block, green

0.40 × 0.30 × 0.20 mm

Data collection

Oxford Diffraction Xcalibur CCD
diffractometer

Radiation source: Enhance (Mo) X-ray Source

Graphite monochromator

Detector resolution: 8.3622 pixels mm⁻¹

ω and φ scans

Absorption correction: multi-scan

(*CrysAlis RED*; Oxford Diffraction, 2007)

T_{min} = 0.750, *T_{max}* = 0.862

8646 measured reflections

3002 independent reflections

1854 reflections with *I* > 2σ(*I*)

R_{int} = 0.037

θ_{max} = 26.0°, θ_{min} = 2.8°

h = -9→9

k = -30→32

l = -10→9

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.077$
 $S = 0.93$
 3002 reflections
 223 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
 $w = 1/[\sigma^2(F_o^2) + (0.0371P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$

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 | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|------------|--------------|------------|----------------------------------|
| Cu1 | 0.5000 | 0.5000 | 0.5000 | 0.02739 (14) |
| O1 | 0.5765 (2) | 0.72753 (6) | 0.7896 (2) | 0.0279 (4) |
| N1 | 0.3433 (3) | 0.55852 (7) | 0.3669 (3) | 0.0270 (5) |
| N2 | 0.3432 (3) | 0.50383 (7) | 0.6359 (2) | 0.0250 (4) |
| N3 | 0.1123 (3) | 0.54298 (7) | 0.6550 (3) | 0.0276 (5) |
| H3 | 0.0198 | 0.5642 | 0.6311 | 0.033* |
| N4 | 0.1107 (3) | 0.60926 (7) | 0.3218 (3) | 0.0301 (5) |
| H4 | 0.0189 | 0.6235 | 0.3346 | 0.036* |
| N7 | 0.7829 (4) | 0.55883 (8) | 0.7720 (3) | 0.0473 (7) |
| N8 | 0.3624 (4) | 0.63047 (9) | 0.8836 (3) | 0.0523 (7) |
| N9 | 0.8650 (3) | 0.63404 (8) | 0.4902 (3) | 0.0431 (6) |
| N10 | 0.9040 (3) | 0.79164 (8) | 0.6867 (3) | 0.0388 (6) |
| C1 | 0.2179 (3) | 0.57061 (8) | 0.4219 (3) | 0.0240 (6) |
| C2 | 0.2177 (3) | 0.54105 (8) | 0.5686 (3) | 0.0235 (6) |
| C3 | 0.3131 (4) | 0.59086 (9) | 0.2255 (4) | 0.0362 (7) |
| H3A | 0.3820 | 0.5912 | 0.1579 | 0.043* |
| C4 | 0.1704 (4) | 0.62228 (9) | 0.1967 (4) | 0.0365 (7) |
| H4A | 0.1211 | 0.6484 | 0.1069 | 0.044* |
| C5 | 0.3157 (4) | 0.48229 (9) | 0.7740 (3) | 0.0306 (6) |
| H5 | 0.3858 | 0.4548 | 0.8490 | 0.037* |
| C6 | 0.1746 (3) | 0.50594 (9) | 0.7877 (3) | 0.0306 (6) |
| H6 | 0.1278 | 0.4985 | 0.8721 | 0.037* |
| C7 | 0.7098 (4) | 0.59593 (10) | 0.7744 (3) | 0.0312 (7) |
| C8 | 0.4741 (4) | 0.63526 (9) | 0.8363 (3) | 0.0335 (7) |
| C9 | 0.8243 (4) | 0.66396 (10) | 0.5669 (4) | 0.0297 (6) |

| | | | | |
|------|------------|--------------|------------|------------|
| C10 | 0.8449 (3) | 0.75144 (10) | 0.6727 (3) | 0.0286 (6) |
| C11 | 0.6541 (3) | 0.68945 (8) | 0.7366 (3) | 0.0234 (6) |
| C12 | 0.6126 (3) | 0.64089 (8) | 0.7755 (3) | 0.0255 (6) |
| C13 | 0.7714 (3) | 0.70132 (8) | 0.6596 (3) | 0.0241 (6) |
| C14 | 0.4716 (3) | 0.76732 (9) | 0.6587 (3) | 0.0303 (6) |
| H14A | 0.5344 | 0.7762 | 0.5836 | 0.036* |
| H14B | 0.4669 | 0.7984 | 0.7252 | 0.036* |
| C15 | 0.2811 (4) | 0.74960 (11) | 0.5388 (4) | 0.0507 (8) |
| H15A | 0.2125 | 0.7766 | 0.4517 | 0.076* |
| H15B | 0.2185 | 0.7413 | 0.6132 | 0.076* |
| H15C | 0.2860 | 0.7191 | 0.4720 | 0.076* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| Cu1 | 0.0314 (3) | 0.0214 (2) | 0.0359 (3) | 0.0069 (2) | 0.0209 (2) | 0.0044 (2) |
| O1 | 0.0385 (11) | 0.0222 (8) | 0.0283 (9) | 0.0026 (8) | 0.0200 (9) | 0.0005 (8) |
| N1 | 0.0270 (13) | 0.0232 (11) | 0.0362 (13) | 0.0033 (10) | 0.0191 (11) | 0.0019 (10) |
| N2 | 0.0249 (12) | 0.0226 (10) | 0.0291 (11) | 0.0045 (10) | 0.0137 (9) | 0.0026 (10) |
| N3 | 0.0281 (13) | 0.0241 (11) | 0.0352 (12) | 0.0040 (10) | 0.0183 (11) | -0.0030 (10) |
| N4 | 0.0303 (13) | 0.0236 (11) | 0.0426 (14) | 0.0087 (10) | 0.0221 (11) | 0.0039 (10) |
| N7 | 0.0602 (18) | 0.0228 (12) | 0.0658 (17) | 0.0040 (12) | 0.0348 (14) | 0.0053 (12) |
| N8 | 0.078 (2) | 0.0439 (15) | 0.0591 (17) | -0.0250 (14) | 0.0521 (16) | -0.0141 (13) |
| N9 | 0.0543 (17) | 0.0358 (13) | 0.0539 (15) | 0.0115 (12) | 0.0376 (14) | 0.0048 (12) |
| N10 | 0.0317 (14) | 0.0336 (13) | 0.0491 (15) | -0.0085 (12) | 0.0165 (12) | 0.0003 (12) |
| C1 | 0.0268 (16) | 0.0156 (12) | 0.0318 (15) | 0.0018 (11) | 0.0154 (13) | -0.0030 (11) |
| C2 | 0.0231 (15) | 0.0173 (12) | 0.0320 (15) | -0.0031 (11) | 0.0141 (12) | -0.0067 (11) |
| C3 | 0.0447 (19) | 0.0298 (15) | 0.0478 (18) | 0.0104 (14) | 0.0330 (16) | 0.0119 (14) |
| C4 | 0.0472 (19) | 0.0245 (14) | 0.0442 (18) | 0.0081 (14) | 0.0263 (15) | 0.0093 (13) |
| C5 | 0.0335 (17) | 0.0273 (14) | 0.0319 (15) | 0.0063 (12) | 0.0156 (13) | 0.0069 (11) |
| C6 | 0.0330 (16) | 0.0345 (15) | 0.0304 (14) | 0.0003 (13) | 0.0198 (12) | 0.0007 (13) |
| C7 | 0.0423 (19) | 0.0214 (14) | 0.0312 (16) | -0.0089 (14) | 0.0180 (14) | 0.0014 (12) |
| C8 | 0.053 (2) | 0.0215 (13) | 0.0309 (15) | -0.0099 (13) | 0.0231 (15) | -0.0060 (11) |
| C9 | 0.0281 (17) | 0.0274 (14) | 0.0380 (16) | 0.0020 (12) | 0.0187 (13) | 0.0087 (13) |
| C10 | 0.0212 (16) | 0.0343 (15) | 0.0291 (15) | 0.0023 (13) | 0.0105 (12) | 0.0035 (12) |
| C11 | 0.0257 (16) | 0.0216 (13) | 0.0184 (12) | -0.0003 (11) | 0.0062 (11) | -0.0009 (10) |
| C12 | 0.0315 (16) | 0.0198 (13) | 0.0280 (14) | -0.0024 (12) | 0.0160 (12) | -0.0011 (11) |
| C13 | 0.0257 (15) | 0.0178 (12) | 0.0309 (14) | 0.0012 (11) | 0.0147 (12) | 0.0008 (11) |
| C14 | 0.0320 (17) | 0.0243 (13) | 0.0353 (16) | 0.0066 (12) | 0.0158 (13) | 0.0033 (12) |
| C15 | 0.039 (2) | 0.0549 (19) | 0.048 (2) | -0.0006 (16) | 0.0106 (16) | -0.0014 (16) |

Geometric parameters (Å, °)

| | | | |
|---------------------|-------------|---------|-----------|
| Cu1—N1 | 1.9727 (19) | N10—C10 | 1.140 (3) |
| Cu1—N1 ⁱ | 1.9727 (19) | C1—C2 | 1.433 (3) |
| Cu1—N2 ⁱ | 2.0397 (18) | C3—C4 | 1.349 (3) |
| Cu1—N2 | 2.0397 (18) | C3—H3A | 0.9500 |
| Cu1—N7 | 2.821 (2) | C4—H4A | 0.9500 |

| | | | |
|--------------------------------------|-------------|---------------|-------------|
| O1—C11 | 1.352 (3) | C5—C6 | 1.349 (3) |
| O1—C14 | 1.460 (3) | C5—H5 | 0.9500 |
| N1—C1 | 1.324 (3) | C6—H6 | 0.9500 |
| N1—C3 | 1.367 (3) | C7—C12 | 1.419 (3) |
| N2—C2 | 1.333 (3) | C8—C12 | 1.428 (4) |
| N2—C5 | 1.374 (3) | C9—C13 | 1.421 (3) |
| N3—C2 | 1.337 (3) | C10—C13 | 1.425 (3) |
| N3—C6 | 1.372 (3) | C11—C12 | 1.389 (3) |
| N3—H3 | 0.8800 | C11—C13 | 1.395 (3) |
| N4—C1 | 1.343 (3) | C14—C15 | 1.477 (3) |
| N4—C4 | 1.364 (3) | C14—H14A | 0.9900 |
| N4—H4 | 0.8800 | C14—H14B | 0.9900 |
| N7—C7 | 1.143 (3) | C15—H15A | 0.9800 |
| N8—C8 | 1.143 (3) | C15—H15B | 0.9800 |
| N9—C9 | 1.144 (3) | C15—H15C | 0.9800 |
| | | | |
| N1—Cu1—N1 ⁱ | 180.00 | C3—C4—H4A | 126.7 |
| N1—Cu1—N2 ⁱ | 97.96 (8) | N4—C4—H4A | 126.7 |
| N1 ⁱ —Cu1—N2 ⁱ | 82.04 (8) | C6—C5—N2 | 110.0 (2) |
| N1—Cu1—N2 | 82.04 (8) | C6—C5—H5 | 125.0 |
| N1 ⁱ —Cu1—N2 | 97.96 (8) | N2—C5—H5 | 125.0 |
| N2 ⁱ —Cu1—N2 | 180.0 | C5—C6—N3 | 106.1 (2) |
| N1—Cu1—N7 | 95.79 (7) | C5—C6—H6 | 126.9 |
| N1 ⁱ —Cu1—N7 | 84.21 (7) | N3—C6—H6 | 126.9 |
| N2 ⁱ —Cu1—N7 | 88.69 (7) | N7—C7—C12 | 177.8 (3) |
| N2—Cu1—N7 | 91.31 (7) | N8—C8—C12 | 179.4 (3) |
| C11—O1—C14 | 119.25 (18) | N9—C9—C13 | 179.1 (3) |
| C1—N1—C3 | 105.9 (2) | N10—C10—C13 | 178.6 (3) |
| C1—N1—Cu1 | 113.35 (16) | O1—C11—C12 | 113.8 (2) |
| C3—N1—Cu1 | 140.66 (17) | O1—C11—C13 | 119.61 (19) |
| C2—N2—C5 | 105.23 (19) | C12—C11—C13 | 126.5 (2) |
| C2—N2—Cu1 | 110.87 (15) | C11—C12—C7 | 124.4 (2) |
| C5—N2—Cu1 | 143.89 (17) | C11—C12—C8 | 119.1 (2) |
| C2—N3—C6 | 107.6 (2) | C7—C12—C8 | 116.3 (2) |
| C2—N3—H3 | 126.2 | C11—C13—C9 | 121.6 (2) |
| C6—N3—H3 | 126.2 | C11—C13—C10 | 121.2 (2) |
| C1—N4—C4 | 107.3 (2) | C9—C13—C10 | 117.2 (2) |
| C1—N4—H4 | 126.3 | O1—C14—C15 | 110.4 (2) |
| C4—N4—H4 | 126.3 | O1—C14—H14A | 109.6 |
| C7—N7—Cu1 | 103.7 (2) | C15—C14—H14A | 109.6 |
| N1—C1—N4 | 110.7 (2) | O1—C14—H14B | 109.6 |
| N1—C1—C2 | 116.9 (2) | C15—C14—H14B | 109.6 |
| N4—C1—C2 | 132.4 (2) | H14A—C14—H14B | 108.1 |
| N2—C2—N3 | 111.0 (2) | C14—C15—H15A | 109.5 |
| N2—C2—C1 | 116.8 (2) | C14—C15—H15B | 109.5 |
| N3—C2—C1 | 132.2 (2) | H15A—C15—H15B | 109.5 |
| C4—C3—N1 | 109.5 (2) | C14—C15—H15C | 109.5 |
| C4—C3—H3A | 125.2 | H15A—C15—H15C | 109.5 |

| | | | |
|----------------------------|--------------|-----------------|------------|
| N1—C3—H3A | 125.2 | H15B—C15—H15C | 109.5 |
| C3—C4—N4 | 106.6 (2) | | |
| N2 ⁱ —Cu1—N1—C1 | 178.54 (16) | C6—N3—C2—N2 | 1.3 (3) |
| N2—Cu1—N1—C1 | -1.46 (16) | C6—N3—C2—C1 | -179.2 (2) |
| N7—Cu1—N1—C1 | -91.98 (17) | N1—C1—C2—N2 | -0.4 (3) |
| N2 ⁱ —Cu1—N1—C3 | 2.7 (3) | N4—C1—C2—N2 | 178.3 (2) |
| N2—Cu1—N1—C3 | -177.3 (3) | N1—C1—C2—N3 | -179.9 (2) |
| N7—Cu1—N1—C3 | 92.2 (3) | N4—C1—C2—N3 | -1.2 (4) |
| N1 ⁱ —Cu1—N2—C2 | -178.76 (15) | C1—N1—C3—C4 | 0.2 (3) |
| N7—Cu1—N2—C2 | 96.90 (16) | Cu1—N1—C3—C4 | 176.3 (2) |
| N1—Cu1—N2—C5 | -178.8 (3) | N1—C3—C4—N4 | -0.1 (3) |
| N1 ⁱ —Cu1—N2—C5 | 1.2 (3) | C1—N4—C4—C3 | -0.1 (3) |
| N7—Cu1—N2—C5 | -83.1 (3) | C2—N2—C5—C6 | 0.7 (3) |
| N1—Cu1—N7—C7 | 24.02 (19) | Cu1—N2—C5—C6 | -179.3 (2) |
| N1 ⁱ —Cu1—N7—C7 | -155.98 (19) | N2—C5—C6—N3 | 0.1 (3) |
| N2 ⁱ —Cu1—N7—C7 | 121.89 (19) | C2—N3—C6—C5 | -0.9 (3) |
| N2—Cu1—N7—C7 | -58.11 (19) | C14—O1—C11—C12 | -129.2 (2) |
| C3—N1—C1—N4 | -0.2 (3) | C14—O1—C11—C13 | 54.0 (3) |
| Cu1—N1—C1—N4 | -177.52 (15) | O1—C11—C12—C7 | -164.3 (2) |
| C3—N1—C1—C2 | 178.7 (2) | C13—C11—C12—C7 | 12.3 (4) |
| Cu1—N1—C1—C2 | 1.4 (3) | O1—C11—C12—C8 | 10.1 (3) |
| C4—N4—C1—N1 | 0.2 (3) | C13—C11—C12—C8 | -173.3 (2) |
| C4—N4—C1—C2 | -178.6 (2) | O1—C11—C13—C9 | -166.3 (2) |
| C5—N2—C2—N3 | -1.2 (3) | C12—C11—C13—C9 | 17.2 (4) |
| Cu1—N2—C2—N3 | 178.75 (15) | O1—C11—C13—C10 | 14.4 (4) |
| C5—N2—C2—C1 | 179.2 (2) | C12—C11—C13—C10 | -162.0 (2) |
| Cu1—N2—C2—C1 | -0.8 (2) | C11—O1—C14—C15 | 81.6 (3) |

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------------------|-------|-------------|-------------|---------------|
| N3—H3 \cdots N9 ⁱⁱ | 0.88 | 2.22 | 3.011 (3) | 149 |
| N4—H4 \cdots N9 ⁱⁱ | 0.88 | 2.17 | 2.967 (3) | 150 |
| C3—H3A \cdots N8 ⁱⁱⁱ | 0.95 | 2.42 | 3.187 (3) | 138 |

Symmetry codes: (ii) $x-1, y, z$; (iii) $x, y, z-1$.