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Poly[di-μ_3-azido-μ_2-4,4′-bipyridine-dicopper(I)]

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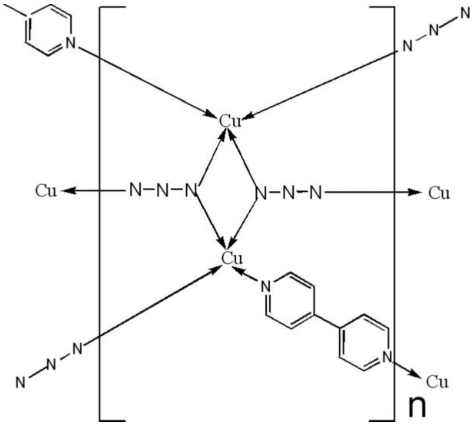
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.004 Å; R factor = 0.035; wR factor = 0.073; data-to-parameter ratio = 15.3.

In the crystal structure of the title compound, $[Cu_2(N_3)_2(C_{10}H_8N_2)]_n$, each Cu^I atom is coordinated by two symmetry-related azide anions and 4,4′-bipyridine (bipy) ligands in a strongly distorted tetrahedral geometry. The Cu atom and the azide anion occupy general positions while the bipy molecule is located on a centre of inversion. Each two symmetry-related copper(I) cations and two symmetry-related azide anions form dimers, which are additionally connected by the anions into layers. These layers are linked by the 4,4′-bipyridine ligands into a three-dimensional coordination network.

Related literature

For related literature, see: Han *et al.* (2000); Liu *et al.* (1999).



Experimental

Crystal data

$[Cu_2(N_3)_2(C_{10}H_8N_2)]$
M_r = 367.32
Monoclinic, $P2_1/n$
a = 8.8107 (18) Å
b = 8.0616 (16) Å
c = 9.2636 (19) Å
β = 112.53 (3)°
V = 607.7 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.50 mm^{-1}
T = 293 (2) K
0.24 × 0.22 × 0.20 mm

Data collection

Bruker SMART diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 1998)
T_{min} = 0.456, T_{max} = 0.501
6162 measured reflections
1391 independent reflections
1163 reflections with $I > 2\sigma(I)$
R_{int} = 0.034

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.074
S = 1.14
1391 reflections
91 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.31 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N2	1.920 (2)	Cu1—N4^{ii}	2.381 (2)
Cu1—N1	1.986 (2)	Cu1—Cu1^{iii}	3.0061 (9)
Cu1—N4^{i}	2.077 (2)		
N2—Cu1—N1	133.23 (10)	N2—Cu1—N4^{ii}	104.35 (10)
N2—Cu1—N4^{i}	114.75 (10)	N1—Cu1—N4^{ii}	91.66 (9)
N1—Cu1—N4^{i}	106.83 (9)	N4^{i}—Cu1—N4^{ii}	95.50 (8)

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); 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: NC2073).

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supporting information

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Poly[di-μ_3-azido-μ_2-4,4′-bipyridine-dicopper(I)]

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S1. Comment

Because of its versatile coordination modes the azide ligand is a good candidate for the design of coordination polymers with novel structures. To extend the structural diversity, in most cases additional ligands like for example 4,4′-bipyridine were used for the preparation of metal-azido complexes (Han *et al.*, 2000 and Liu *et al.*, 1999). As a part of our ongoing investigations in this field we have investigated the title compound (I) which is a new copper(I)azido complex.

The asymmetric unit of the title compound consists of one copper(I) cation, one azide anion which occupy general positions and and half a 4,4′-bipyridine ligands which is located on a centre of inversion. Each two symmetry related copper(I) cations are connected by two symmetry related azide anions *via* $\mu_{1,1}$ coordination into $[(Cu^IN_3)_2$ dimers, which are located on centres of inversion. These dimers are additionally connected by the azide anions *via* $\mu_{1,3}$ coordination into layers, which are perpendicular to the b-/c-plane. These layers are linked by the 4,4′-bipyridine ligands into a three dimensional coordination network.

S2. Experimental

A mixture of CuI(0.19 g, *ca* 1 mmol), NaN_3 (0.065 g, *ca* 1 mmol), 4,4′-bpy (0.08 g, *ca* 1 mmol) and H_2O (18 g, *ca* 1 mol) was sealed in a Teflon-lined autoclave and heated to 403 K for 2 days. On cooling to room temperature red crystals of the title compound are obtained in about 30% yield based on copper.

S3. Refinement

H atoms were included in calculated positions and treated in the subsequent refinement as riding atoms, with C···H = 0.93 Å and $U_{iso}(H) = 1.2 U_{eq}(C)$.

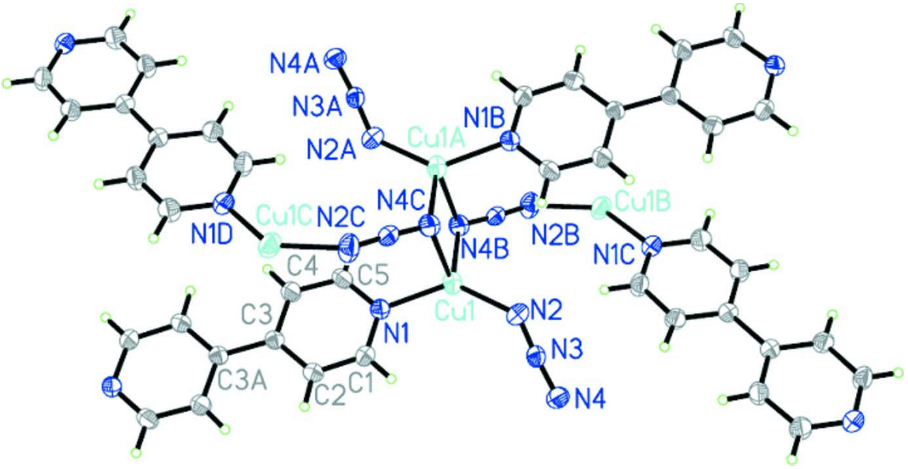

Figure 1

Crystal structure of compound (I) with labeling and displacement ellipsoids drawn at the 40% probability level. Symmetry codes: A = -*x* + 1,-*y*,-*z* + 1, B = -*x* + 1/2,*y* - 1/2,-*z* + 1/2, C = *x* + 1/2,-*y* + 1/2,*z* + 1/2 and D = -*x* + 2,-*y* + 1,-*z* + 1.

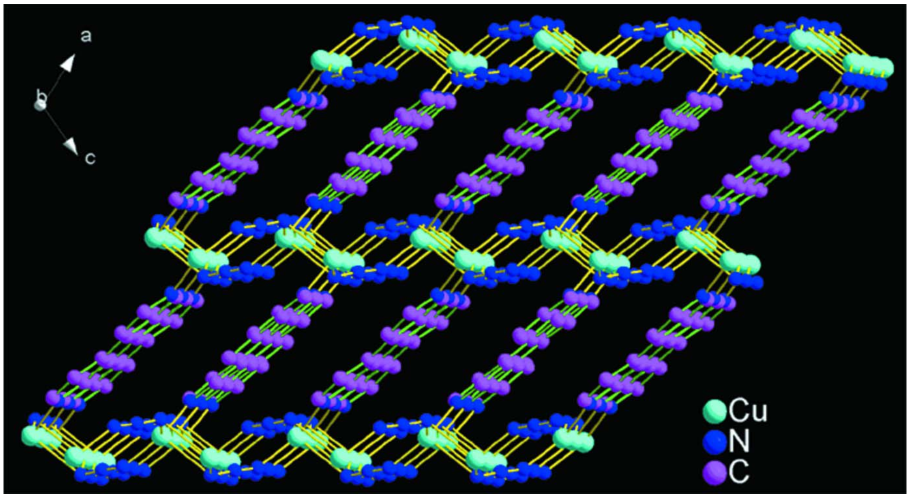

Figure 2

Crystal structure of the title compound with view along the *b* axis. H atoms are omitted for clarity.

Poly[di-μ_3-azido-μ_2-4,4′-bipyridine-dicopper(I)]

Crystal data

$[Cu_2(N_3)_2(C_{10}H_8N_2)]$
M_r = 367.32
Monoclinic, $P2_1/n$
a = 8.8107 (18) Å
b = 8.0616 (16) Å
c = 9.2636 (19) Å
β = 112.53 (3)°
V = 607.7 (2) Å^3
Z = 2

F(000) = 364
D_x = 2.007 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 5570 reflections
θ = 3.5–27.5°
μ = 3.50 mm^{-1}
T = 293 K
Prism, red
0.24 × 0.22 × 0.20 mm

Data collection

Bruker P4
diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 0 pixels mm^{-1}
ω scans
Absorption correction: multi-scan
(*SADABS*; Bruker, 1998)
$T_{\min} = 0.456$, $T_{\max} = 0.501$

6162 measured reflections
1391 independent reflections
1163 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.034$
$\theta_{\max} = 27.5°$, $\theta_{\min} = 3.5°$
$h = -11 \rightarrow 11$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.074$
$S = 1.14$
1391 reflections
91 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
$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2 + 0.2141P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.28$ e Å^{-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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Cu1	0.43386 (4)	0.13310 (4)	0.37825 (4)	0.04726 (15)
N1	0.6334 (2)	0.2628 (3)	0.4012 (2)	0.0364 (5)
N2	0.2044 (3)	0.1876 (3)	0.3036 (3)	0.0514 (6)
N3	0.1145 (2)	0.2903 (3)	0.2295 (2)	0.0342 (5)
N4	0.0161 (3)	0.3872 (3)	0.1542 (3)	0.0412 (5)
C1	0.6300 (3)	0.4272 (4)	0.3839 (3)	0.0441 (7)
H1A	0.5282	0.4796	0.3449	0.053*
C2	0.7694 (3)	0.5243 (3)	0.4207 (3)	0.0406 (6)
H2A	0.7598	0.6386	0.4069	0.049*
C3	0.9233 (3)	0.4506 (3)	0.4784 (3)	0.0300 (5)
C4	0.9264 (3)	0.2788 (3)	0.4954 (3)	0.0411 (6)
H4A	1.0263	0.2229	0.5336	0.049*
C5	0.7814 (3)	0.1914 (4)	0.4556 (3)	0.0428 (6)
H5A	0.7871	0.0768	0.4674	0.051*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0334 (2)	0.0455 (2)	0.0562 (3)	−0.00674 (14)	0.00983 (16)	0.00118 (16)
N1	0.0340 (11)	0.0380 (13)	0.0349 (11)	−0.0035 (9)	0.0106 (9)	0.0023 (9)
N2	0.0373 (14)	0.0513 (15)	0.0563 (15)	0.0053 (11)	0.0076 (11)	0.0137 (12)
N3	0.0310 (11)	0.0382 (12)	0.0320 (11)	−0.0059 (10)	0.0105 (9)	−0.0034 (10)
N4	0.0400 (12)	0.0387 (13)	0.0411 (13)	0.0048 (10)	0.0113 (10)	0.0017 (10)
C1	0.0300 (14)	0.0388 (15)	0.0554 (17)	0.0020 (12)	0.0073 (12)	0.0065 (13)
C2	0.0376 (14)	0.0280 (14)	0.0511 (16)	−0.0010 (11)	0.0115 (12)	0.0034 (11)
C3	0.0332 (13)	0.0335 (14)	0.0256 (12)	−0.0019 (10)	0.0139 (10)	0.0015 (10)
C4	0.0334 (14)	0.0361 (15)	0.0547 (17)	0.0020 (11)	0.0179 (12)	0.0050 (12)
C5	0.0408 (15)	0.0316 (14)	0.0577 (18)	−0.0031 (12)	0.0209 (13)	0.0060 (12)

Geometric parameters (Å, º)

Cu1—N2	1.920 (2)	N4—Cu1^{v}	2.381 (2)
Cu1—N1	1.986 (2)	C1—C2	1.384 (4)
Cu1—N4^{i}	2.077 (2)	C1—H1A	0.9300
Cu1—N4^{ii}	2.381 (2)	C2—C3	1.387 (4)
Cu1—Cu1^{iii}	3.0061 (9)	C2—H2A	0.9300
N1—C1	1.334 (4)	C3—C4	1.393 (4)
N1—C5	1.335 (3)	C3—C3^{vi}	1.485 (5)
N2—N3	1.170 (3)	C4—C5	1.379 (4)
N3—N4	1.177 (3)	C4—H4A	0.9300
N4—Cu1^{iv}	2.077 (2)	C5—H5A	0.9300

N2—Cu1—N1	133.23 (10)	Cu1^{iv}—N4—Cu1^{v}	84.50 (8)
N2—Cu1—N4^{i}	114.75 (10)	N1—C1—C2	123.7 (2)
N1—Cu1—N4^{i}	106.83 (9)	N1—C1—H1A	118.1
N2—Cu1—N4^{ii}	104.35 (10)	C2—C1—H1A	118.1
N1—Cu1—N4^{ii}	91.66 (9)	C1—C2—C3	119.8 (2)
N4^{i}—Cu1—N4^{ii}	95.50 (8)	C1—C2—H2A	120.1
N2—Cu1—Cu1^{iii}	119.05 (8)	C3—C2—H2A	120.1
N1—Cu1—Cu1^{iii}	102.88 (7)	C2—C3—C4	116.3 (2)
N4^{i}—Cu1—Cu1^{iii}	52.04 (6)	C2—C3—C3^{vi}	121.9 (3)
N4^{ii}—Cu1—Cu1^{iii}	43.46 (6)	C4—C3—C3^{vi}	121.8 (3)
C1—N1—C5	116.6 (2)	C5—C4—C3	120.1 (2)
C1—N1—Cu1	122.16 (17)	C5—C4—H4A	119.9
C5—N1—Cu1	120.66 (18)	C3—C4—H4A	119.9
N3—N2—Cu1	139.1 (2)	N1—C5—C4	123.5 (3)
N2—N3—N4	175.8 (3)	N1—C5—H5A	118.3
N3—N4—Cu1^{iv}	124.77 (19)	C4—C5—H5A	118.3
N3—N4—Cu1^{v}	116.26 (18)		

N2—Cu1—N1—C1	10.3 (3)	N2—N3—N4—Cu1^{iv}	169 (4)
N4^{i}—Cu1—N1—C1	162.5 (2)	N2—N3—N4—Cu1^{v}	−89 (4)
N4^{ii}—Cu1—N1—C1	−101.3 (2)	C5—N1—C1—C2	−0.8 (4)

Cu1$^{\mathrm{iii}}$—Cu1—N1—C1	−143.69 (19)	Cu1—N1—C1—C2	170.3 (2)
N2—Cu1—N1—C5	−179.0 (2)	N1—C1—C2—C3	0.4 (4)
N4$^{\mathrm{i}}$—Cu1—N1—C5	−26.8 (2)	C1—C2—C3—C4	0.0 (4)
N4$^{\mathrm{ii}}$—Cu1—N1—C5	69.5 (2)	C1—C2—C3—C3$^{\mathrm{vi}}$	−179.2 (3)
Cu1$^{\mathrm{iii}}$—Cu1—N1—C5	27.1 (2)	C2—C3—C4—C5	0.0 (4)
N1—Cu1—N2—N3	17.2 (4)	C3$^{\mathrm{vi}}$—C3—C4—C5	179.3 (3)
N4$^{\mathrm{i}}$—Cu1—N2—N3	−133.4 (3)	C1—N1—C5—C4	0.9 (4)
N4$^{\mathrm{ii}}$—Cu1—N2—N3	123.5 (3)	Cu1—N1—C5—C4	−170.4 (2)
Cu1$^{\mathrm{iii}}$—Cu1—N2—N3	167.9 (3)	C3—C4—C5—N1	−0.5 (4)
Cu1—N2—N3—N4	165 (4)		

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