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Poly[(2,2′-bipyridine-κ^2N,N')[μ_4-2,2′-(1,3-phenylene)bis(imidazol-1-yl)-$\kappa^4N:N':N'':N'''$]dicopper(I)]

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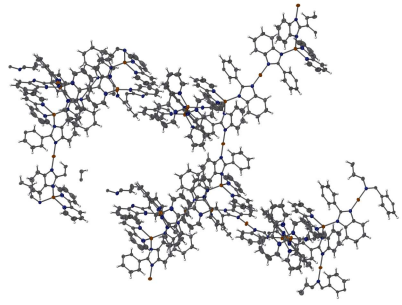
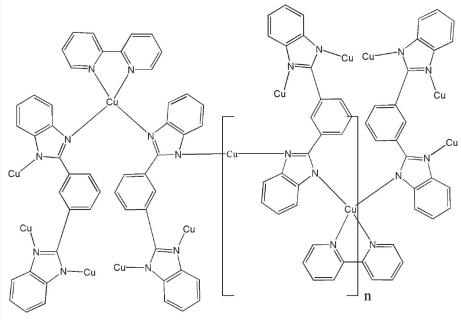
Two Cu^I atoms are present in the asymmetric unit of the polymeric title complex, $[Cu_2(C_{20}H_{12}N_4)(C_{10}H_8N_2)]_n$. One of the cations is located on an inversion centre and is linearly coordinated by the N atoms of benzimidazolyl moieties of the 1,2-bis(2-benzimidazolium)benzene ligand, whereas the second cation is located on a twofold rotation axis and is tetrahedrally coordinated by two N atoms of a chelating 2,2′-bipyridine ligand and two other N atoms of the benzimidazolyl moieties. The bridging character of the 1,2-bis(2-benzimidazolyl)benzene leads to the formation of a three-dimensional framework structure.

3D view



Chemical scheme



Structure description

Copper complexes have attracted significant attention because of their biological activities. Apart from a low toxicity, copper complexes can potentially inhibit cellular proteasomal activity, enhance apoptosis and DNA binding activities (Gopalakrishnan *et al.*, 2014). Benzimidazole and its derivatives exhibit anticancer (Rodríguez-Solano *et al.*, 2011), antifungal (Coyle *et al.*, 2004), anti-inflammatory (Sączewski *et al.*, 2006), anti-rheumatism (Rowan *et al.*, 2009) or insect-repellent activities (Rowan *et al.*, 2009), and are widely used in metal-organic chemistry. In the current project we have combined copper and a benzimidazole derivative together with 2,2′-bipyridine as a co-ligand to yield the title complex, $[Cu_2(C_{20}H_{12}N_4)(C_{10}H_8N_2)]_n$.

As shown in Fig. 1, the asymmetric unit contains two Cu^I ions. The Cu1 site is linearly coordinated by the N1 atoms from symmetry-related benzimidazolium moieties at a distance of 1.887 (2) Å. The Cu2 site shows a tetrahedral coordination by the other two N atoms of the benzimidazolyl moieties and the N atoms of the 2,2′-bipyridine ligand. The small bite angle of the latter [N—Cu—N 79.01 (13)°] causes a considerable distortion of the coordination sphere [angular range 79.01 (13) − 117.21 (8)°]. The dihedral angle between two benzimidazolyl rings is 37.00 (9)°, in good agreement with those of other Cu

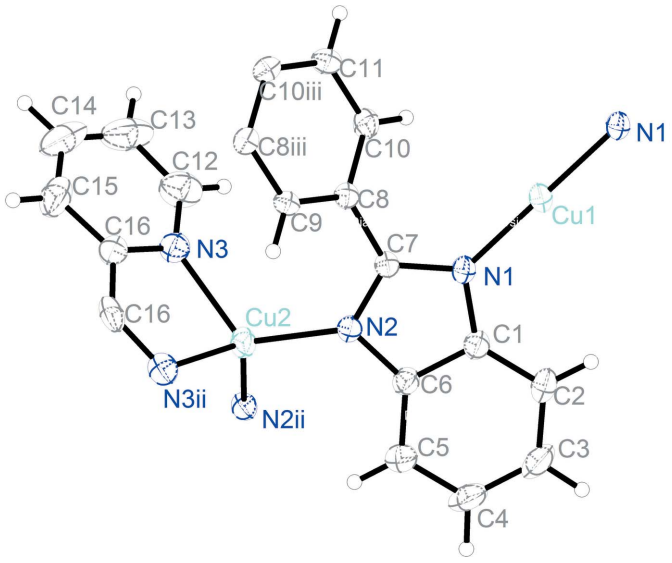


Figure 1
The coordination environments around the two different Cu^{I} atoms. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $-x+\frac{5}{4}, -y+\frac{5}{4}, z$; (iii) $-x+7/4, y, -z+\frac{3}{4}$.]

complexes containing benzimidazolyl ligands (Lin *et al.*, 2015). The dihedral angle of 15.07 (15)° between the two pyridinyl rings in the 2,2′-bipyridine ligand indicates considerable twisting. The bridging character of the organic anion leads to the formation of a three-dimensional polymeric structure (Fig. 2).

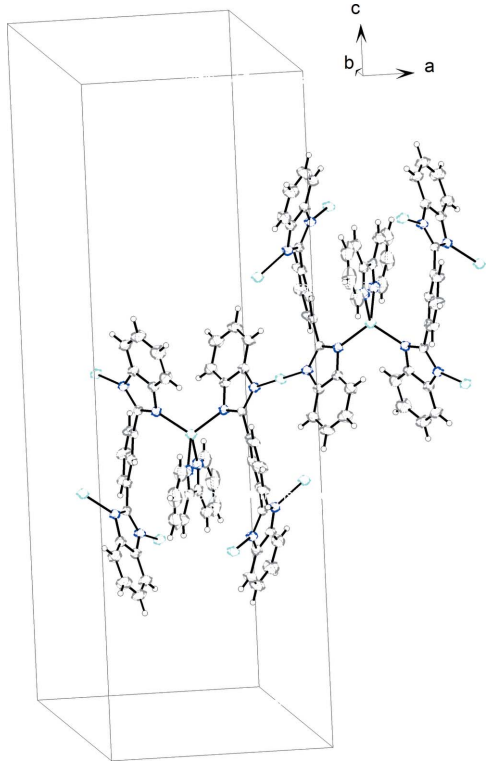


Figure 2
Part of the crystal packing in the title structure.

Table 1
Experimental details.

Crystal data	
Chemical formula	$[Cu_2(C_{20}H_{12}N_4)(C_{10}H_8N_2)]$
M_r	591.60
Crystal system, space group	Orthorhombic, *Fddd*
Temperature (K)	298
a, *b*, *c* (Å)	10.857 (3), 26.523 (8), 33.064 (10)
V (Å^3)	9521 (5)
Z	16
Radiation type	Mo *Kα*
μ (mm^{-1})	1.82
Crystal size (mm)	0.3 × 0.2 × 0.1
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2013)
T_{min}, T_{max}	0.752, 0.940
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	17682, 2438, 1969
R_{int}	0.042
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.625
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.035, 0.084, 1.09
No. of reflections	2438
No. of parameters	175
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.43, −0.24

Computer programs: *APEX2* and *SAINT* (Bruker, 2013), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*) and *OLEX2* (Dolomanov *et al.*, 2009).

Synthesis and crystallization

1,2-Bis(2-benzimidazolyl)benzene was synthesized according to a reported procedure (Deng *et al.*, 2012). 1,2-bis(2-benzimidazolyl)benzene (0.1 mmol, 0.0312 g), 2,2′-bipyridine (0.1 mmol, 0.0156 g) and $CuCl_2$ (0.1 mmol, 0.0170 g) were added to 15 ml aqueous NH_3 and stirred for 30 s. Then the solution was placed in a 23 ml Teflon-lined stainless-steel vessel and heated at 466 K for 3 d, then cooled to room temperature at 5 K h^{-1}. Dark-red block-like crystals were obtained directly from the reaction mixture. IR (KBr, cm^{-1}): 3444.6 (*s*), 1605.7 (*m*), 1439.3 (*m*), 1372.6 (*s*), 1283.0 (*s*), 860.5 (*w*), 747.0 (*w*), 699.0 (*w*).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Acknowledgements

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full crystallographic data

IUCrData (2016). **1**, x161007 [doi:10.1107/S2414314616010075]

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Crystal data

$[Cu_2(C_{20}H_{12}N_4)(C_{10}H_8N_2)]$
M_r = 591.60
Orthorhombic, *Fddd*
a = 10.857 (3) Å
b = 26.523 (8) Å
c = 33.064 (10) Å
V = 9521 (5) Å^3
Z = 16
$F(000)$ = 4800
D_x = 1.651 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 4559 reflections
θ = 3.0–26.7°
μ = 1.82 mm^{-1}
T = 298 K
Block, dark red
0.3 × 0.2 × 0.1 mm

Data collection

Bruker APEXII CCD diffractometer
Graphite monochromator
phi and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2013)
T_{min} = 0.752, T_{max} = 0.940
17682 measured reflections
2438 independent reflections
1969 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 26.4°, θ_{min} = 2.7°
h = −13→13
k = −33→32
l = −40→41

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.084
S = 1.09
2438 reflections
175 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0421P)^2 + 18.4382P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.43 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cu1	1.0000	0.5000	0.5000	0.02680 (14)
Cu2	0.6250	0.6250	0.41384 (2)	0.02941 (14)
N1	0.89614 (18)	0.55364 (8)	0.48437 (6)	0.0240 (4)
N2	0.77124 (18)	0.60678 (8)	0.44890 (6)	0.0238 (5)
N3	0.5862 (2)	0.57785 (8)	0.36543 (6)	0.0313 (5)
C8	0.8571 (2)	0.53486 (9)	0.41133 (7)	0.0207 (5)
C9	0.8750	0.56041 (12)	0.3750	0.0202 (7)
H9	0.8750	0.5955	0.3750	0.024*
C1	0.8628 (2)	0.59333 (10)	0.50958 (7)	0.0255 (5)
C7	0.8393 (2)	0.56451 (9)	0.44871 (7)	0.0203 (5)
C10	0.8574 (2)	0.48240 (9)	0.41092 (7)	0.0287 (6)
H10	0.8456	0.4646	0.4349	0.034*
C6	0.7865 (2)	0.62607 (10)	0.48737 (7)	0.0250 (5)
C11	0.8750	0.45660 (14)	0.3750	0.0348 (9)
H11	0.8750	0.4215	0.3750	0.042*
C2	0.8954 (3)	0.60438 (11)	0.54960 (8)	0.0364 (7)
H2	0.9454	0.5828	0.5645	0.044*
C5	0.7417 (3)	0.67038 (11)	0.50444 (8)	0.0366 (7)
H5	0.6910	0.6920	0.4899	0.044*
C16	0.5963 (2)	0.59969 (11)	0.32881 (8)	0.0319 (6)
C3	0.8506 (3)	0.64837 (13)	0.56591 (9)	0.0454 (8)
H3	0.8709	0.6567	0.5924	0.054*
C4	0.7754 (3)	0.68100 (12)	0.54375 (10)	0.0470 (8)
H4	0.7474	0.7105	0.5558	0.056*
C15	0.5544 (3)	0.57578 (15)	0.29392 (10)	0.0520 (9)
H15	0.5602	0.5917	0.2689	0.062*
C12	0.5399 (3)	0.53138 (12)	0.36714 (11)	0.0497 (8)
H12	0.5348	0.5157	0.3923	0.060*
C13	0.4992 (3)	0.50542 (15)	0.33384 (15)	0.0662 (12)
H13	0.4687	0.4728	0.3364	0.079*
C14	0.5042 (3)	0.52832 (17)	0.29698 (14)	0.0680 (13)
H14	0.4741	0.5120	0.2741	0.082*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0312 (2)	0.0276 (2)	0.0215 (2)	0.00712 (19)	−0.00507 (18)	0.00262 (18)
Cu2	0.0312 (3)	0.0374 (3)	0.0196 (2)	0.0108 (2)	0.000	0.000
N1	0.0285 (11)	0.0256 (11)	0.0179 (10)	0.0025 (9)	−0.0015 (8)	0.0018 (9)
N2	0.0250 (10)	0.0262 (11)	0.0203 (10)	0.0049 (9)	−0.0026 (8)	−0.0021 (8)
N3	0.0301 (12)	0.0331 (13)	0.0308 (13)	0.0032 (10)	−0.0018 (9)	−0.0034 (10)
C8	0.0187 (11)	0.0241 (12)	0.0193 (12)	0.0022 (9)	0.0008 (9)	0.0001 (10)
C9	0.0180 (15)	0.0186 (17)	0.0239 (17)	0.000	0.0011 (13)	0.000
C1	0.0264 (13)	0.0288 (14)	0.0213 (12)	0.0005 (11)	−0.0016 (10)	−0.0006 (10)
C7	0.0190 (11)	0.0227 (12)	0.0192 (12)	0.0012 (9)	0.0004 (9)	0.0016 (10)

C10	0.0386 (15)	0.0254 (13)	0.0221 (13)	−0.0029 (11)	−0.0034 (11)	0.0059 (11)
C6	0.0251 (12)	0.0283 (13)	0.0217 (12)	0.0014 (10)	0.0000 (10)	−0.0024 (11)
C11	0.054 (2)	0.0175 (18)	0.033 (2)	0.000	−0.0078 (19)	0.000
C2	0.0425 (16)	0.0435 (17)	0.0232 (14)	0.0038 (13)	−0.0090 (12)	−0.0015 (12)
C5	0.0401 (16)	0.0344 (16)	0.0354 (16)	0.0091 (13)	−0.0052 (12)	−0.0094 (13)
C16	0.0248 (13)	0.0427 (16)	0.0283 (14)	0.0151 (11)	−0.0018 (10)	−0.0096 (12)
C3	0.0531 (19)	0.055 (2)	0.0283 (15)	0.0016 (16)	−0.0095 (14)	−0.0177 (14)
C4	0.0559 (19)	0.0441 (19)	0.0410 (18)	0.0075 (15)	−0.0032 (15)	−0.0238 (15)
C15	0.0415 (17)	0.080 (3)	0.0345 (17)	0.0216 (18)	−0.0073 (14)	−0.0187 (18)
C12	0.0423 (17)	0.0397 (18)	0.067 (2)	−0.0047 (14)	0.0005 (16)	−0.0031 (17)
C13	0.045 (2)	0.049 (2)	0.105 (4)	−0.0020 (17)	−0.008 (2)	−0.035 (2)
C14	0.0407 (19)	0.081 (3)	0.082 (3)	0.015 (2)	−0.0173 (19)	−0.056 (3)

Geometric parameters (Å, º)

Cu1—N1	1.887 (2)	C10—C11	1.384 (3)
Cu1—N1^{i}	1.887 (2)	C6—C5	1.391 (4)
Cu2—N2^{ii}	2.024 (2)	C11—C10^{iii}	1.384 (3)
Cu2—N2	2.024 (2)	C11—H11	0.9300
Cu2—N3^{ii}	2.075 (2)	C2—H2	0.9300
Cu2—N3	2.075 (2)	C2—C3	1.374 (4)
N1—C1	1.391 (3)	C5—H5	0.9300
N1—C7	1.362 (3)	C5—C4	1.379 (4)
N2—C7	1.343 (3)	C16—C16^{ii}	1.480 (6)
N2—C6	1.381 (3)	C16—C15	1.393 (4)
N3—C16	1.347 (3)	C3—H3	0.9300
N3—C12	1.332 (4)	C3—C4	1.397 (4)
C8—C9	1.393 (3)	C4—H4	0.9300
C8—C7	1.477 (3)	C15—H15	0.9300
C8—C10	1.391 (3)	C15—C14	1.375 (5)
C9—C8^{iii}	1.393 (3)	C12—H12	0.9300
C9—H9	0.9300	C12—C13	1.372 (5)
C1—C6	1.407 (3)	C13—H13	0.9300
C1—C2	1.401 (4)	C13—C14	1.363 (6)
C10—H10	0.9300	C14—H14	0.9300
N1—Cu1—N1^{i}	180.00 (8)	N2—C6—C5	130.1 (2)
N2^{ii}—Cu2—N2	110.13 (11)	C5—C6—C1	121.0 (2)
N2^{ii}—Cu2—N3^{ii}	117.21 (8)	C10^{iii}—C11—C10	120.7 (3)
N2—Cu2—N3	117.21 (8)	C10—C11—H11	119.6
N2^{ii}—Cu2—N3	115.24 (9)	C10^{iii}—C11—H11	119.6
N2—Cu2—N3^{ii}	115.25 (9)	C1—C2—H2	121.3
N3^{ii}—Cu2—N3	79.01 (13)	C3—C2—C1	117.3 (3)
C1—N1—Cu1	124.19 (16)	C3—C2—H2	121.3
C7—N1—Cu1	131.87 (17)	C6—C5—H5	121.2
C7—N1—C1	103.9 (2)	C4—C5—C6	117.5 (3)
C7—N2—Cu2	128.91 (16)	C4—C5—H5	121.2
C7—N2—C6	104.3 (2)	N3—C16—C16^{ii}	115.12 (16)

C6—N2—Cu2	122.24 (16)	N3—C16—C15	121.5 (3)
C16—N3—Cu2	114.70 (18)	C15—C16—C16^{ii}	123.4 (2)
C12—N3—Cu2	127.0 (2)	C2—C3—H3	119.1
C12—N3—C16	117.8 (3)	C2—C3—C4	121.8 (3)
C9—C8—C7	118.7 (2)	C4—C3—H3	119.1
C10—C8—C9	118.5 (2)	C5—C4—C3	121.5 (3)
C10—C8—C7	122.7 (2)	C5—C4—H4	119.3
C8—C9—C8^{iii}	121.8 (3)	C3—C4—H4	119.3
C8^{iii}—C9—H9	119.1	C16—C15—H15	120.5
C8—C9—H9	119.1	C14—C15—C16	119.0 (3)
N1—C1—C6	107.9 (2)	C14—C15—H15	120.5
N1—C1—C2	131.2 (2)	N3—C12—H12	118.3
C2—C1—C6	120.8 (2)	N3—C12—C13	123.5 (4)
N1—C7—C8	123.5 (2)	C13—C12—H12	118.3
N2—C7—N1	115.0 (2)	C12—C13—H13	120.6
N2—C7—C8	121.4 (2)	C14—C13—C12	118.8 (4)
C8—C10—H10	119.9	C14—C13—H13	120.6
C11—C10—C8	120.2 (2)	C15—C14—H14	120.3
C11—C10—H10	119.9	C13—C14—C15	119.3 (3)
N2—C6—C1	108.9 (2)	C13—C14—H14	120.3

Cu1—N1—C1—C6	179.22 (16)	C1—C2—C3—C4	0.1 (5)
Cu1—N1—C1—C2	1.3 (4)	C7—N1—C1—C6	0.2 (3)
Cu1—N1—C7—N2	−179.99 (16)	C7—N1—C1—C2	−177.7 (3)
Cu1—N1—C7—C8	−4.5 (4)	C7—N2—C6—C1	−1.3 (3)
Cu2—N2—C7—N1	−154.51 (17)	C7—N2—C6—C5	177.2 (3)
Cu2—N2—C7—C8	29.9 (3)	C7—C8—C9—C8^{iii}	179.7 (2)
Cu2—N2—C6—C1	156.77 (17)	C7—C8—C10—C11	−179.75 (19)
Cu2—N2—C6—C5	−24.8 (4)	C10—C8—C9—C8^{iii}	0.01 (16)
Cu2—N3—C16—C16^{ii}	10.2 (3)	C10—C8—C7—N1	44.2 (3)
Cu2—N3—C16—C15	−169.4 (2)	C10—C8—C7—N2	−140.5 (2)
Cu2—N3—C12—C13	169.7 (2)	C6—N2—C7—N1	1.5 (3)
N1—C1—C6—N2	0.7 (3)	C6—N2—C7—C8	−174.1 (2)
N1—C1—C6—C5	−177.9 (2)	C6—C1—C2—C3	−0.4 (4)
N1—C1—C2—C3	177.3 (3)	C6—C5—C4—C3	−0.7 (5)
N2—C6—C5—C4	−177.9 (3)	C2—C1—C6—N2	178.8 (2)
N3—C16—C15—C14	−1.5 (4)	C2—C1—C6—C5	0.2 (4)
N3—C12—C13—C14	−1.1 (5)	C2—C3—C4—C5	0.5 (5)
C8—C10—C11—C10^{iii}	0.01 (17)	C16—N3—C12—C13	−1.8 (4)
C9—C8—C7—N1	−135.5 (2)	C16^{ii}—C16—C15—C14	178.9 (3)
C9—C8—C7—N2	39.7 (3)	C16—C15—C14—C13	−1.4 (5)
C9—C8—C10—C11	0.0 (3)	C12—N3—C16—C16^{ii}	−177.3 (3)
C1—N1—C7—N2	−1.1 (3)	C12—N3—C16—C15	3.1 (4)
C1—N1—C7—C8	174.4 (2)	C12—C13—C14—C15	2.7 (5)
C1—C6—C5—C4	0.3 (4)		

Symmetry codes: (i) −*x*+2, −*y*+1, −*z*+1; (ii) −*x*+5/4, −*y*+5/4, *z*; (iii) −*x*+7/4, *y*, −*z*+3/4.