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catena-Poly[copper(II)-di- μ -dicyan-amido- μ -1,3-di-4-pyridylpropane]

Jin Fang Zhang

Institute of Science and Technology, Jiangsu University, 301 Xuefu Road, Zhenjiang 212013, People's Republic of China

Correspondence e-mail: zjf260@ujs.edu.cn

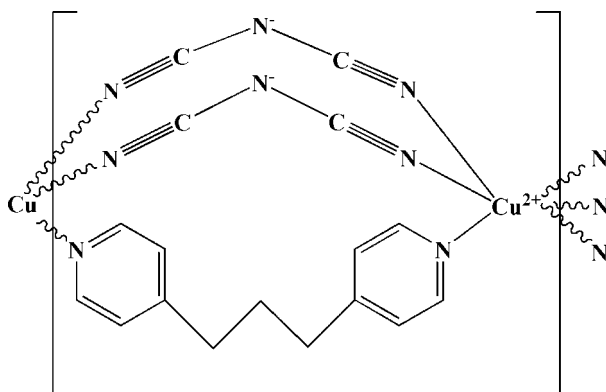
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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.059; wR factor = 0.154; data-to-parameter ratio = 14.2.

In the title compound, $[\text{Cu}(\text{C}_2\text{N}_3)_2(\text{C}_{13}\text{H}_{14}\text{N}_2)]_n$, the Cu^{II} atom, located on an inversion centre, adopts a distorted octahedral coordination by six N atoms, two from 1,3-di-4-pyridylpropane and four from dicyanamide ligands, with significantly different Cu–N distances. The metal centres are linked in an unusual triple-bridged mode into chains parallel to [101].

Related literature

For the architectures and topologies of metal-organic compounds, see: Eddaoudi *et al.* (2001). For their potential applications, see: Zhang *et al.* (2007); Banerjee *et al.* (2008). For compounds constructed in single or double-bridged modes, see: Zhang *et al.* (2008); Lang *et al.* (2004).



Experimental

Crystal data

$[\text{Cu}(\text{C}_2\text{N}_3)_2(\text{C}_{13}\text{H}_{14}\text{N}_2)]$
 $M_r = 393.91$
 Monoclinic, $C2/c$
 $a = 16.097$ (3) Å
 $b = 10.163$ (2) Å
 $c = 12.920$ (3) Å
 $\beta = 123.10$ (3)°

$V = 1770.6$ (6) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 1.25$ mm⁻¹
 $T = 293$ K
 $0.20 \times 0.15 \times 0.10$ mm

Data collection

Rigaku Saturn724+ diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.798$, $T_{\text{max}} = 0.882$

4144 measured reflections
 1713 independent reflections
 1490 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$
 $wR(F^2) = 0.154$
 $S = 1.09$
 1713 reflections

121 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.42$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.32$ e Å⁻³

Table 1

Selected bond lengths (Å).

Cu1–N1	2.027 (3)	Cu1–N2	2.388 (5)
Cu1–N4	2.031 (4)		

Data collection: *CrystalClear* (Rigaku, 2008); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); 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: PV2188).

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supplementary materials

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catena-Poly[copper(II)-di- μ -dicyanamido- μ -1,3-di-4-pyridylpropane]

J. Zhang

Comment

The design and syntheses of metal-organic compounds have attracted great attention in recent years because of not only their intriguing architectures and topologies (Eddaoudi *et al.*, 2001) but also due to their potential applications (Banerjee *et al.*, 2008; Zhang *et al.*, 2007). The flexible bridging ligands can construct metal-organic frameworks with various structures. The title compound, (I), was constructed by two kinds of flexible bridging ligands through diffusion reactions of copper(II) nitrate trihydrate, sodium dicyanamide and 1,3-di-4-pyridylpropane which were self-assembled to form a one-dimensional neutral metal-organic compound. In this paper, the crystal structure of (I) is presented.

As illustrated in Fig. 1, Cu²⁺ adopts a distorted octahedral geometry, generated by six nitrogen atoms two from 1,3-di-4-pyridylpropane (bpp) and four from dicyanamide (dca) ligands. Interestingly, the distance Cu1—N2 ([2.388 (5) Å] is significantly longer than those of Cu1—N1 (2.027 (3) Å) and Cu1—N4 (2.031 (4) Å).

Two neighboring Cu atoms are linked by one bpp and two dca ligands forming a one-dimensional neutral chain in a triple-bridged mode. Compared to single or double-bridged modes (Zhang *et al.*, 2008; Lang *et al.*, 2004), this triple-bridged mode is unfamiliar in coordination compounds.

Experimental

Cu(NO₃)₂·3H₂O (96.6 mg, 0.4 mmol) was added to 2 ml H₂O with thorough stirring for 5 minutes and filtered. The blue filtrate was carefully laid on the surface of a solution of bpp (99.1 mg, 0.5 mmol) and NaN(CN)₂ (89.1 mg, 1 mmol) in 4 ml *i*-PrOH and 2 ml H₂O. Blue block crystals were obtained after five days.

Refinement

H atoms were positioned geometrically and refined with riding model, with $U_{\text{iso}} = 1.2U_{\text{eq}}$ for methylene and pyridyl H atoms, the C—H bonds are 0.97 Å and 0.93 Å in methylene and pyridyl groups, respectively.

Figures



Fig. 1. The molecular structure of the title compound, with atomic labels and 30% probability displacement ellipsoids; H atoms have been omitted for clarity.

catena-Poly[copper(II)-di- μ -dicyanamido- μ -1,3-di-4-pyridylpropane]

Crystal data

[Cu(C ₂ N ₃) ₂ (C ₁₃ H ₁₄ N ₂)]	$F_{000} = 804$
$M_r = 393.91$	$D_x = 1.478 \text{ Mg m}^{-3}$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: $-C 2yc$	Cell parameters from 3458 reflections
$a = 16.097 (3) \text{ \AA}$	$\theta = 2.6\text{--}29.1^\circ$
$b = 10.163 (2) \text{ \AA}$	$\mu = 1.25 \text{ mm}^{-1}$
$c = 12.920 (3) \text{ \AA}$	$T = 293 \text{ K}$
$\beta = 123.10 (3)^\circ$	Block, blue
$V = 1770.6 (6) \text{ \AA}^3$	$0.20 \times 0.15 \times 0.10 \text{ mm}$
$Z = 4$	

Data collection

Rigaku Saturn724+ diffractometer	1713 independent reflections
Radiation source: fine-focus sealed tube	1490 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.027$
$T = 293 \text{ K}$	$\theta_{\text{max}} = 26.0^\circ$
dtprofit.ref scans	$\theta_{\text{min}} = 2.6^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -19 \rightarrow 15$
$T_{\text{min}} = 0.798$, $T_{\text{max}} = 0.882$	$k = -12 \rightarrow 12$
4144 measured reflections	$l = -12 \rightarrow 15$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.059$	$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 4.1353P]$
$wR(F^2) = 0.154$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.09$	$(\Delta/\sigma)_{\text{max}} < 0.001$
1713 reflections	$\Delta\rho_{\text{max}} = 0.42 \text{ e \AA}^{-3}$
121 parameters	$\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Extinction correction: SHELXTL (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.0025 (8)

Special details

Experimental. Yield: 82.1 mg in pure form, 52.1% based on Cu. Analysis calculated for C₁₇H₁₄CuN₈: C 51.83, H 3.58, N 28.45%; found: C 51.72, H 3.45, N 28.61%. IR: ν , cm⁻¹, 2182 s, 1606 s, 1424 s, 809 s.

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)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Cu1	0.2500	0.2500	0.0000	0.0533 (3)	
N1	0.3080 (2)	0.4314 (3)	0.0637 (3)	0.0568 (8)	
N2	0.1117 (3)	0.3051 (5)	0.0129 (5)	0.0969 (16)	
N3	-0.0582 (3)	0.3715 (6)	-0.1106 (4)	0.1082 (19)	
N4	0.3218 (3)	0.1822 (4)	0.1764 (4)	0.0835 (13)	
C1	0.5000	0.8653 (7)	0.2500	0.166 (6)	
H1A	0.5117	0.9240	0.2001	0.199*	0.50
H1B	0.4883	0.9240	0.2999	0.199*	0.50
C2	0.0327 (3)	0.3341 (4)	-0.0500 (4)	0.0614 (11)	
C4	0.3810 (3)	0.1618 (4)	0.2776 (4)	0.0635 (11)	
C5	0.3299 (4)	0.6216 (5)	0.1826 (5)	0.0795 (14)	
H5	0.3203	0.6624	0.2398	0.095*	
C6	0.2971 (3)	0.4963 (5)	0.1450 (4)	0.0680 (12)	
H6	0.2653	0.4539	0.1778	0.082*	
C7	0.3545 (3)	0.4953 (5)	0.0197 (4)	0.0681 (12)	
H7	0.3639	0.4520	-0.0365	0.082*	
C8	0.3770 (3)	0.6876 (5)	0.1364 (5)	0.0771 (15)	
C9	0.4068 (4)	0.8298 (5)	0.1660 (6)	0.101 (2)	
H9A	0.3884	0.8723	0.0891	0.121*	
H9B	0.3655	0.8681	0.1915	0.121*	
C3	0.3891 (4)	0.6210 (5)	0.0527 (5)	0.0757 (13)	
H3	0.4207	0.6615	0.0187	0.091*	

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.0436 (4)	0.0493 (5)	0.0453 (5)	-0.0036 (3)	0.0103 (3)	-0.0012 (3)
N1	0.0464 (17)	0.0520 (18)	0.0527 (19)	-0.0028 (15)	0.0146 (16)	-0.0036 (16)
N2	0.056 (2)	0.078 (3)	0.097 (3)	0.005 (2)	0.004 (2)	-0.013 (3)
N3	0.068 (3)	0.161 (5)	0.068 (3)	0.028 (3)	0.019 (2)	-0.032 (3)

supplementary materials

N4	0.060 (2)	0.071 (3)	0.068 (3)	0.002 (2)	0.002 (2)	-0.004 (2)
C1	0.074 (5)	0.040 (4)	0.226 (12)	0.000	-0.019 (7)	0.000
C2	0.058 (3)	0.058 (2)	0.049 (2)	0.001 (2)	0.017 (2)	-0.001 (2)
C4	0.050 (2)	0.061 (3)	0.060 (3)	-0.004 (2)	0.018 (2)	-0.001 (2)
C5	0.062 (3)	0.071 (3)	0.080 (3)	-0.002 (2)	0.023 (3)	-0.026 (3)
C6	0.061 (2)	0.069 (3)	0.065 (3)	-0.007 (2)	0.028 (2)	-0.013 (2)
C7	0.070 (3)	0.063 (3)	0.064 (3)	-0.006 (2)	0.031 (2)	-0.005 (2)
C8	0.047 (2)	0.049 (3)	0.087 (3)	0.000 (2)	0.006 (2)	-0.005 (3)
C9	0.071 (3)	0.049 (3)	0.120 (5)	0.003 (2)	0.011 (3)	-0.014 (3)
C3	0.068 (3)	0.058 (3)	0.086 (3)	-0.015 (2)	0.033 (3)	0.001 (3)

Geometric parameters (Å, °)

Cu1—N1 ⁱ	2.027 (3)	C1—H1A	0.9700
Cu1—N1	2.027 (3)	C1—H1B	0.9700
Cu1—N4	2.031 (4)	C4—N3 ^{iv}	1.270 (6)
Cu1—N4 ⁱ	2.031 (4)	C5—C6	1.363 (7)
Cu1—N2	2.388 (5)	C5—C8	1.370 (8)
Cu1—N2 ⁱ	2.388 (5)	C5—H5	0.9300
N1—C7	1.330 (6)	C6—H6	0.9300
N1—C6	1.331 (5)	C7—C3	1.366 (7)
N2—C2	1.112 (6)	C7—H7	0.9300
N3—C4 ⁱⁱ	1.270 (6)	C8—C3	1.376 (8)
N3—C2	1.283 (6)	C8—C9	1.505 (7)
N4—C4	1.141 (6)	C9—H9A	0.9700
C1—C9 ⁱⁱⁱ	1.335 (6)	C9—H9B	0.9700
C1—C9	1.335 (6)	C3—H3	0.9300
N1 ⁱ —Cu1—N1	180.00 (8)	C9—C1—H1B	99.6
N1 ⁱ —Cu1—N4	90.06 (16)	H1A—C1—H1B	104.1
N1—Cu1—N4	89.94 (16)	N2—C2—N3	172.9 (6)
N1 ⁱ —Cu1—N4 ⁱ	89.94 (16)	N4—C4—N3 ^{iv}	174.1 (6)
N1—Cu1—N4 ⁱ	90.06 (16)	C6—C5—C8	120.0 (5)
N4—Cu1—N4 ⁱ	180.0 (2)	C6—C5—H5	120.0
N1 ⁱ —Cu1—N2	90.08 (16)	C8—C5—H5	120.0
N1—Cu1—N2	89.92 (16)	N1—C6—C5	123.6 (5)
N4—Cu1—N2	88.97 (19)	N1—C6—H6	118.2
N4 ⁱ —Cu1—N2	91.03 (19)	C5—C6—H6	118.2
N1 ⁱ —Cu1—N2 ⁱ	89.92 (16)	N1—C7—C3	123.5 (5)
N1—Cu1—N2 ⁱ	90.08 (16)	N1—C7—H7	118.2
N4—Cu1—N2 ⁱ	91.03 (19)	C3—C7—H7	118.2
N4 ⁱ —Cu1—N2 ⁱ	88.97 (19)	C5—C8—C3	116.9 (4)
N2—Cu1—N2 ⁱ	180.0 (2)	C5—C8—C9	122.3 (5)
C7—N1—C6	116.3 (4)	C3—C8—C9	120.7 (6)
C7—N1—Cu1	120.8 (3)	C1—C9—C8	121.8 (5)
C6—N1—Cu1	122.8 (3)	C1—C9—H9A	106.9

C2—N2—Cu1	138.5 (5)	C8—C9—H9A	106.9
C4 ⁱⁱ —N3—C2	121.9 (5)	C1—C9—H9B	106.9
C4—N4—Cu1	162.8 (4)	C8—C9—H9B	106.9
C9 ⁱⁱⁱ —C1—C9	148.6 (8)	H9A—C9—H9B	106.7
C9 ⁱⁱⁱ —C1—H1A	99.6	C7—C3—C8	119.8 (5)
C9—C1—H1A	99.6	C7—C3—H3	120.1
C9 ⁱⁱⁱ —C1—H1B	99.6	C8—C3—H3	120.1

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

Fig. 1

