

# catena-Poly[[ $(2,2'$ -bipyridine- $2\kappa^2N,N'$ )- $\mu$ -cyanido-1: $2\kappa^2N:C$ -dicopper(I)]- $\mu$ -bromido-[( $2,2'$ -bipyridine- $2\kappa^2N,N'$ )- $\mu$ -cyanido-1: $2\kappa^2N:C$ -dicopper(I)]- $\mu$ -cyanido- $\kappa^2N:C$ ]

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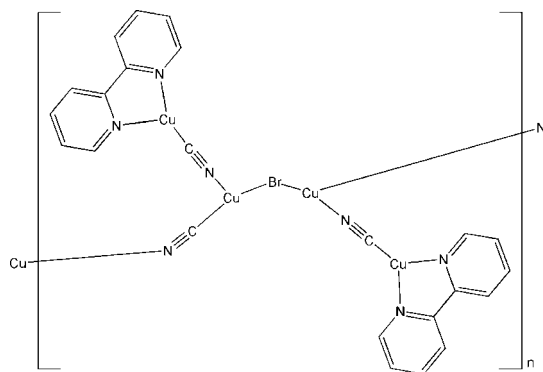
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 Key indicators: single-crystal X-ray study;  $T = 273$  K; mean  $\sigma(C-C) = 0.006$  Å; R factor = 0.035; wR factor = 0.084; data-to-parameter ratio = 19.5.

In the title complex,  $[Cu_4Br(CN)_3(C_{10}H_8N_2)_2]_n$ , the four independent  $Cu^I$  atoms are all in distorted trigonal-planar geometries. One is formed by one N atom and one C atom from two cyanide groups and one Br atom, one is formed by two N atoms from two cyanide groups and one Br atom, and the other two are formed by two N atoms from a chelating  $2,2'$ -bipyridine (bpy) ligand and one C atom from a cyanide group. The structure exhibits a zigzag chain backbone along [101] constructed by bromide and cyanide anions bridging the  $Cu^I$  atoms, with the  $[Cu(bpy)(CN)]$  units pointing laterally.

## Related literature

For copper cyanide coordination polymers, see: Korzeniak *et al.* (2005); Yi *et al.* (2004). For structures containing cyanide groups, see: Zhang *et al.* (2000). For related copper complexes, see: He *et al.* (2006).



## Experimental

### Crystal data

$[Cu_4Br(CN)_3(C_{10}H_8N_2)_2]$   
 $M_r = 724.53$   
 Monoclinic,  $P2_1/n$   
 $a = 10.0074$  (10) Å  
 $b = 17.7556$  (17) Å  
 $c = 14.5125$  (14) Å  
 $\beta = 102.924$  (1)°

$V = 2513.4$  (4) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 4.96$  mm<sup>-1</sup>  
 $T = 273$  K  
 $0.24 \times 0.24 \times 0.22$  mm

### Data collection

Bruker APEXII CCD diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 2001)  
 $T_{min} = 0.383$ ,  $T_{max} = 0.409$

23142 measured reflections  
 6171 independent reflections  
 3491 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.035$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.084$   
 $S = 1.00$   
 6171 reflections

317 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{max} = 0.37$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.41$  e Å<sup>-3</sup>

**Table 1**

Selected bond lengths (Å).

Cu1—N1	2.025 (3)	Cu3—N5	1.876 (3)
Cu1—N2	2.029 (3)	Cu3—Br1	2.5163 (6)
Cu1—C21	1.836 (4)	Cu3—C22	1.842 (3)
Cu2—N3	2.055 (3)	Cu4—N6 <sup>i</sup>	1.906 (3)
Cu2—N4	2.010 (3)	Cu4—N7	1.878 (3)
Cu2—C23	1.836 (3)	Cu4—Br1	2.4650 (6)

 Symmetry code: (i)  $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$ .

Data collection: APEX2 (Bruker, 2007); cell refinement: SAINT (Bruker, 2007); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008) and DIAMOND (Brandenburg, 1999); 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: HY2536).

## References

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 Yi, L., Ding, B., Zhao, B., Cheng, P., Liao, D.-Z., Yan, S.-P. & Jiang, Z.-H. (2004). *Inorg. Chem.* **43**, 33–43.  
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## supplementary materials

*Acta Cryst.* (2012). E68, m693 [doi:10.1107/S1600536812018120]

**catena-Poly[[*(2,2'*-bipyridine-2 $\kappa^2$ N,N')- $\mu$ -cyanido-1:2 $\kappa^2$ N:C-dicopper(I)]- $\mu$ -bromido-[(*2,2'*-bipyridine-2 $\kappa^2$ N,N')- $\mu$ -cyanido-1:2 $\kappa^2$ N:C-dicopper(I)]- $\mu$ -cyanido- $\kappa^2$ N:C]**

**Jia Gu, Xuee Jiang, Zhanhua Su and Baibin Zhou**

### Comment

Considerable attention has been paid to the study of copper cyanide coordination polymers due to their fascinating structural frameworks, physical and chemical properties, and potential applications in many fields (Korzeniak *et al.*, 2005; Yi *et al.*, 2004). Cyanide group is a versatile ligand that can act as a monodentate ligand as well as a  $\mu_2$ -,  $\mu_3$ - or  $\mu_4$ -bridging ligand, exhibiting intriguing topological architectures (Zhang *et al.*, 2000). Copper atom has versatile coordination properties and normally adopts two-, three-, four-, five-, or six-coordination, forming diverse geometries (He *et al.*, 2006). Herein, we report a copper cyanide coordination polymers derived from 2,2'-bipyridine ligand. The title complex contains four unique Cu<sup>I</sup> ions, which are all in distorted trigonal-planar geometries. However, the detailed coordination environments of these Cu<sup>I</sup> atoms are different, as Cu1 and Cu2 are each coordinated by two N atoms of a 2,2'-bipyridine ligand and one  $\mu_2$ -cyanide group. Cu3 and Cu4 are each coordinated by two  $\mu_2$ -cyanide groups and one bromide ion (Fig. 1, Table 1). The structure exhibits by a zigzag chain backbone, [Cu<sub>2</sub>Br(CN)]<sub>n</sub>, along [1 0 1] (Fig. 2). The [Cu(bpy)(CN)] units point lateral of the chain.

### Experimental

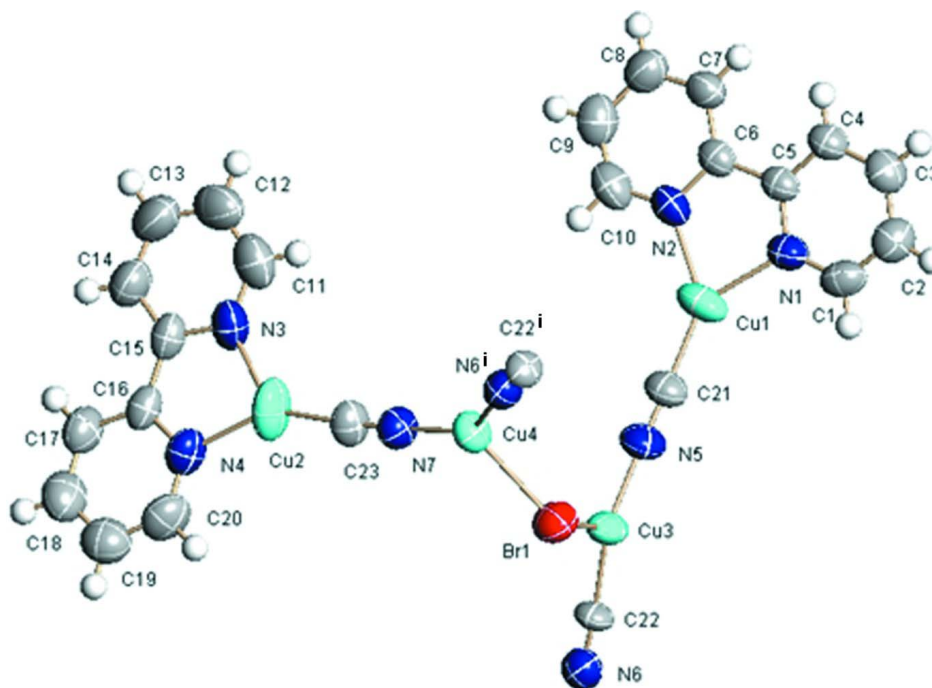
A mixture of CuBr<sub>2</sub> (0.33 g, 1.48 mmol), K<sub>4</sub>Fe(CN)<sub>6</sub>·3H<sub>2</sub>O (0.42 g, 0.99 mmol), 2,2'-bipyridine (0.156 g, 1.00 mmol) and 24 ml H<sub>2</sub>O was stirred for 30 min in air. The resulting gel was then transferred to a 30 ml Teflon-lined autoclave and kept at 160°C for 5 days. After the mixture was slowly cooled to room temperature, yellow block crystals of the title complex were filtered, washed with water and dried at room temperature (yield: 0.17 g, 66%).

### Refinement

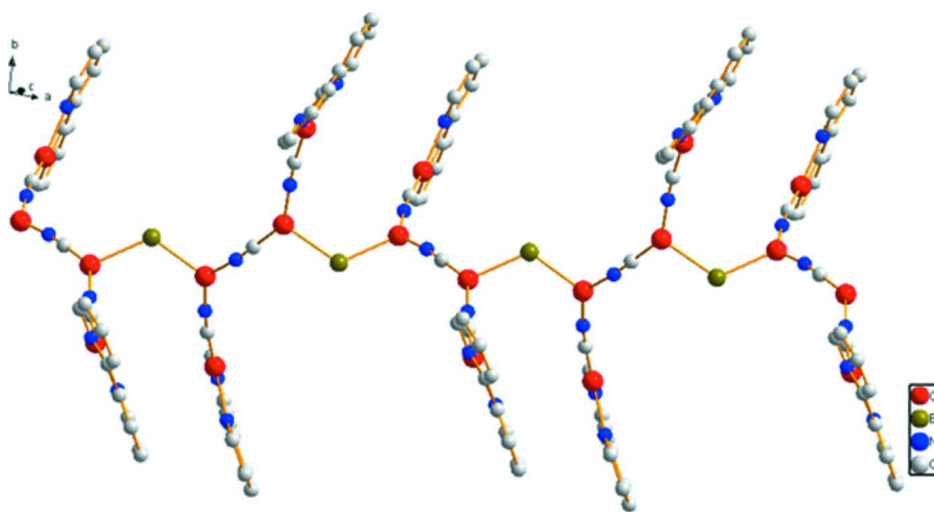
H atoms were positioned geometrically and refined as riding atoms, with C—H = 0.93 Å and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

### Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).


**Figure 1**

The asymmetric unit of the title complex, showing the coordination environments around the Cu<sup>I</sup> atoms. Displacement ellipsoids are drawn at 50% probability level. [Symmetry code: (i)  $x+1/2, -y+1/2, z+1/2$ .]


**Figure 2**

The zigzag chain in the title complex.

*catena*-Poly[[*(2,2'*-bipyridine-2,2'- $\kappa^2N,N'$ )- $\mu$ -cyanido-1:2 $\kappa^2N:C$ -dicopper(I)- $\mu$ -bromido-*(2,2'*-bipyridine-2,2'- $\kappa^2N,N'$ )- $\mu$ -cyanido-1:2 $\kappa^2N:C$ -dicopper(I)- $\mu$ -cyanido- $\kappa^2N:C$ ]

*Crystal data*

$[\text{Cu}_4\text{Br}(\text{CN})_3(\text{C}_{10}\text{H}_8\text{N}_2)_2]$

$M_r = 724.53$

Monoclinic,  $P2_1/n$

Hall symbol:  $-P 2_1n$

$a = 10.0074 (10) \text{ \AA}$

$b = 17.7556 (17) \text{ \AA}$

$c = 14.5125 (14) \text{ \AA}$   
 $\beta = 102.924 (1)^\circ$   
 $V = 2513.4 (4) \text{ \AA}^3$   
 $Z = 4$   
 $F(000) = 1416$   
 $D_x = 1.915 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$

Cell parameters from 4357 reflections

$\theta = 2.3\text{--}22.8^\circ$   
 $\mu = 4.96 \text{ mm}^{-1}$   
 $T = 273 \text{ K}$   
 Block, yellow  
 $0.24 \times 0.24 \times 0.22 \text{ mm}$

*Data collection*

Bruker APEXII CCD  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (SADABS; Bruker, 2001)  
 $T_{\min} = 0.383$ ,  $T_{\max} = 0.409$

23142 measured reflections  
 6171 independent reflections  
 3491 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.035$   
 $\theta_{\max} = 28.3^\circ$ ,  $\theta_{\min} = 2.3^\circ$   
 $h = -13 \rightarrow 13$   
 $k = -21 \rightarrow 23$   
 $l = -19 \rightarrow 19$

*Refinement*

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.084$   
 $S = 1.00$   
 6171 reflections  
 317 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  
 $w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 0.2889P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.37 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.41 \text{ e \AA}^{-3}$   
 Extinction correction: SHELXL97 (Sheldrick,  
 2008),  $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$   
 Extinction coefficient: 0.00042 (11)

*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 ( $\text{\AA}^2$ )*

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	0.35793 (5)	0.01457 (3)	0.84772 (3)	0.08134 (17)
Cu2	1.10313 (5)	0.03539 (3)	0.62780 (4)	0.1015 (2)
Cu3	0.46792 (5)	0.19932 (3)	0.63059 (3)	0.07283 (15)
Cu4	0.87398 (4)	0.19909 (2)	0.81033 (3)	0.06160 (13)
Br1	0.66910 (4)	0.26922 (3)	0.72846 (3)	0.08278 (14)
N1	0.2531 (3)	0.01213 (16)	0.95197 (18)	0.0624 (7)
N2	0.4332 (3)	-0.08313 (16)	0.91135 (18)	0.0633 (7)
N3	1.1656 (3)	-0.07460 (17)	0.6509 (2)	0.0754 (8)
N4	1.2024 (3)	0.02421 (17)	0.5226 (2)	0.0719 (8)

N5	0.4205 (3)	0.12318 (17)	0.70702 (19)	0.0722 (8)
N6	0.4104 (3)	0.26904 (16)	0.4389 (2)	0.0695 (8)
N7	0.9502 (3)	0.13623 (16)	0.73146 (19)	0.0681 (7)
C1	0.1708 (4)	0.0657 (2)	0.9725 (3)	0.0736 (10)
H1	0.1423	0.1037	0.9284	0.088*
C2	0.1261 (4)	0.0676 (2)	1.0554 (3)	0.0766 (10)
H2	0.0695	0.1061	1.0674	0.092*
C3	0.1669 (4)	0.0114 (2)	1.1194 (3)	0.0718 (10)
H3	0.1379	0.0109	1.1760	0.086*
C4	0.2521 (3)	-0.04517 (19)	1.0997 (2)	0.0605 (8)
H4	0.2813	-0.0836	1.1431	0.073*
C5	0.2931 (3)	-0.04371 (18)	1.0149 (2)	0.0535 (8)
C6	0.3839 (3)	-0.10117 (18)	0.9871 (2)	0.0550 (8)
C7	0.4153 (3)	-0.1688 (2)	1.0339 (2)	0.0668 (9)
H7	0.3800	-0.1803	1.0863	0.080*
C8	0.4990 (4)	-0.2189 (2)	1.0022 (3)	0.0851 (12)
H8	0.5201	-0.2650	1.0324	0.102*
C9	0.5519 (4)	-0.2003 (3)	0.9248 (3)	0.0854 (12)
H9	0.6096	-0.2331	0.9022	0.102*
C10	0.5169 (4)	-0.1325 (3)	0.8830 (3)	0.0805 (11)
H10	0.5533	-0.1196	0.8315	0.097*
C11	1.1467 (4)	-0.1211 (3)	0.7194 (3)	0.0967 (14)
H11	1.0891	-0.1057	0.7580	0.116*
C12	1.2070 (5)	-0.1896 (3)	0.7354 (3)	0.1034 (15)
H12	1.1926	-0.2199	0.7845	0.124*
C13	1.2888 (5)	-0.2128 (3)	0.6784 (4)	0.1056 (15)
H13	1.3310	-0.2597	0.6873	0.127*
C14	1.3087 (4)	-0.1667 (2)	0.6077 (3)	0.0893 (12)
H14	1.3652	-0.1821	0.5684	0.107*
C15	1.2458 (3)	-0.0972 (2)	0.5940 (3)	0.0633 (9)
C16	1.2631 (3)	-0.0431 (2)	0.5204 (2)	0.0617 (9)
C17	1.3361 (4)	-0.0580 (2)	0.4522 (3)	0.0811 (11)
H17	1.3769	-0.1049	0.4504	0.097*
C18	1.3487 (4)	-0.0046 (3)	0.3876 (3)	0.0975 (13)
H18	1.3981	-0.0147	0.3418	0.117*
C19	1.2890 (4)	0.0634 (3)	0.3904 (3)	0.0954 (12)
H19	1.2972	0.1009	0.3473	0.114*
C20	1.2164 (4)	0.0755 (2)	0.4580 (3)	0.0903 (12)
H20	1.1742	0.1221	0.4593	0.108*
C21	0.3923 (3)	0.0802 (2)	0.7580 (2)	0.0658 (9)
C22	0.4283 (3)	0.24393 (18)	0.5130 (2)	0.0536 (8)
C23	1.0047 (4)	0.09831 (19)	0.6881 (3)	0.0706 (10)

Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cu1	0.0947 (3)	0.0914 (4)	0.0562 (3)	-0.0338 (3)	0.0130 (2)	0.0137 (2)
Cu2	0.0880 (3)	0.0867 (4)	0.1408 (5)	0.0024 (3)	0.0487 (3)	-0.0510 (3)
Cu3	0.0990 (3)	0.0733 (3)	0.0532 (3)	0.0211 (2)	0.0318 (2)	0.0187 (2)
Cu4	0.0725 (3)	0.0637 (3)	0.0520 (2)	-0.0044 (2)	0.02109 (19)	-0.0135 (2)

Br1	0.0697 (2)	0.0949 (3)	0.0768 (3)	0.0063 (2)	0.00151 (19)	0.0136 (2)
N1	0.0643 (16)	0.0648 (19)	0.0558 (17)	-0.0068 (14)	0.0085 (13)	0.0070 (15)
N2	0.0630 (16)	0.073 (2)	0.0557 (17)	-0.0154 (14)	0.0176 (13)	-0.0033 (15)
N3	0.0662 (17)	0.072 (2)	0.095 (2)	-0.0112 (15)	0.0324 (17)	-0.0206 (18)
N4	0.0713 (18)	0.056 (2)	0.088 (2)	0.0030 (15)	0.0171 (16)	-0.0208 (17)
N5	0.093 (2)	0.075 (2)	0.0492 (17)	-0.0009 (16)	0.0170 (15)	0.0079 (15)
N6	0.0674 (18)	0.069 (2)	0.072 (2)	-0.0068 (14)	0.0151 (15)	-0.0024 (16)
N7	0.0760 (18)	0.0662 (19)	0.0627 (18)	0.0042 (15)	0.0169 (15)	-0.0111 (15)
C1	0.077 (2)	0.058 (2)	0.079 (3)	-0.0036 (19)	0.004 (2)	0.012 (2)
C2	0.078 (2)	0.071 (3)	0.078 (3)	0.001 (2)	0.011 (2)	-0.010 (2)
C3	0.078 (2)	0.080 (3)	0.059 (2)	-0.008 (2)	0.0191 (18)	-0.011 (2)
C4	0.066 (2)	0.063 (2)	0.052 (2)	-0.0099 (17)	0.0114 (16)	0.0017 (17)
C5	0.0533 (17)	0.057 (2)	0.0477 (19)	-0.0139 (15)	0.0061 (14)	0.0019 (16)
C6	0.0524 (17)	0.061 (2)	0.0503 (19)	-0.0149 (15)	0.0090 (14)	-0.0022 (16)
C7	0.066 (2)	0.066 (2)	0.070 (2)	-0.0063 (18)	0.0191 (17)	0.0082 (19)
C8	0.076 (3)	0.073 (3)	0.104 (3)	0.005 (2)	0.017 (2)	0.007 (2)
C9	0.076 (3)	0.088 (3)	0.095 (3)	-0.005 (2)	0.024 (2)	-0.022 (3)
C10	0.079 (3)	0.099 (3)	0.068 (3)	-0.019 (2)	0.027 (2)	-0.011 (2)
C11	0.082 (3)	0.108 (4)	0.108 (4)	-0.022 (3)	0.039 (3)	-0.016 (3)
C12	0.083 (3)	0.108 (4)	0.116 (4)	-0.020 (3)	0.015 (3)	0.026 (3)
C13	0.083 (3)	0.092 (4)	0.138 (4)	0.013 (2)	0.018 (3)	0.022 (3)
C14	0.078 (3)	0.082 (3)	0.108 (3)	0.015 (2)	0.021 (2)	-0.001 (3)
C15	0.0484 (17)	0.061 (2)	0.079 (2)	-0.0021 (16)	0.0100 (16)	-0.0222 (19)
C16	0.0492 (17)	0.061 (2)	0.071 (2)	0.0034 (16)	0.0059 (16)	-0.0193 (19)
C17	0.083 (3)	0.082 (3)	0.079 (3)	0.018 (2)	0.020 (2)	-0.014 (2)
C18	0.100 (3)	0.120 (4)	0.075 (3)	0.011 (3)	0.025 (2)	-0.009 (3)
C19	0.098 (3)	0.099 (4)	0.084 (3)	-0.005 (3)	0.011 (2)	0.005 (3)
C20	0.100 (3)	0.057 (3)	0.112 (4)	0.008 (2)	0.018 (3)	-0.008 (3)
C21	0.073 (2)	0.073 (2)	0.050 (2)	-0.0087 (18)	0.0102 (16)	0.0081 (18)
C22	0.0647 (19)	0.059 (2)	0.0359 (17)	-0.0024 (15)	0.0098 (14)	0.0112 (15)
C23	0.075 (2)	0.059 (2)	0.082 (3)	-0.0009 (18)	0.027 (2)	-0.019 (2)

*Geometric parameters (Å, °)*

Cu1—N1	2.025 (3)	C4—C5	1.383 (4)
Cu1—N2	2.029 (3)	C4—H4	0.9300
Cu1—C21	1.836 (4)	C5—C6	1.480 (4)
Cu2—N3	2.055 (3)	C6—C7	1.381 (4)
Cu2—N4	2.010 (3)	C7—C8	1.370 (5)
Cu2—C23	1.836 (3)	C7—H7	0.9300
Cu3—N5	1.876 (3)	C8—C9	1.385 (5)
Cu3—Br1	2.5163 (6)	C8—H8	0.9300
Cu3—C22	1.842 (3)	C9—C10	1.357 (5)
Cu4—N6 <sup>i</sup>	1.906 (3)	C9—H9	0.9300
Cu4—N7	1.878 (3)	C10—H10	0.9300
Cu4—Br1	2.4650 (6)	C11—C12	1.354 (6)
N1—C1	1.334 (4)	C11—H11	0.9300
N1—C5	1.347 (4)	C12—C13	1.351 (6)
N2—C10	1.339 (4)	C12—H12	0.9300
N2—C6	1.341 (3)	C13—C14	1.362 (5)

N3—C15	1.336 (4)	C13—H13	0.9300
N3—C11	1.338 (5)	C14—C15	1.379 (5)
N4—C20	1.337 (5)	C14—H14	0.9300
N4—C16	1.344 (4)	C15—C16	1.474 (5)
N5—C21	1.141 (4)	C16—C17	1.381 (4)
N6—C22	1.141 (4)	C17—C18	1.360 (5)
N7—C23	1.140 (4)	C17—H17	0.9300
C1—C2	1.374 (5)	C18—C19	1.351 (6)
C1—H1	0.9300	C18—H18	0.9300
C2—C3	1.363 (5)	C19—C20	1.363 (5)
C2—H2	0.9300	C19—H19	0.9300
C3—C4	1.387 (5)	C20—H20	0.9300
C3—H3	0.9300		
C21—Cu1—N1	138.90 (14)	C8—C7—C6	119.2 (3)
C21—Cu1—N2	139.10 (13)	C8—C7—H7	120.4
N1—Cu1—N2	80.99 (11)	C6—C7—H7	120.4
C23—Cu2—N4	146.27 (15)	C7—C8—C9	119.4 (4)
C23—Cu2—N3	132.60 (15)	C7—C8—H8	120.3
N4—Cu2—N3	81.13 (13)	C9—C8—H8	120.3
C22—Cu3—N5	145.80 (13)	C10—C9—C8	117.8 (4)
C22—Cu3—Br1	106.87 (10)	C10—C9—H9	121.1
N5—Cu3—Br1	107.33 (9)	C8—C9—H9	121.1
N7—Cu4—N6 <sup>i</sup>	139.32 (12)	N2—C10—C9	124.0 (4)
N7—Cu4—Br1	114.45 (9)	N2—C10—H10	118.0
N6 <sup>i</sup> —Cu4—Br1	106.16 (8)	C9—C10—H10	118.0
Cu4—Br1—Cu3	119.81 (2)	N3—C11—C12	123.4 (4)
C1—N1—C5	118.5 (3)	N3—C11—H11	118.3
C1—N1—Cu1	126.9 (2)	C12—C11—H11	118.3
C5—N1—Cu1	113.4 (2)	C13—C12—C11	118.4 (5)
C10—N2—C6	117.8 (3)	C13—C12—H12	120.8
C10—N2—Cu1	127.9 (2)	C11—C12—H12	120.8
C6—N2—Cu1	114.2 (2)	C12—C13—C14	119.3 (4)
C15—N3—C11	118.6 (3)	C12—C13—H13	120.4
C15—N3—Cu2	112.8 (3)	C14—C13—H13	120.4
C11—N3—Cu2	128.3 (3)	C13—C14—C15	120.5 (4)
C20—N4—C16	118.1 (3)	C13—C14—H14	119.7
C20—N4—Cu2	127.7 (3)	C15—C14—H14	119.7
C16—N4—Cu2	114.1 (3)	N3—C15—C14	119.8 (4)
C21—N5—Cu3	175.6 (3)	N3—C15—C16	115.9 (3)
C22—N6—Cu4 <sup>ii</sup>	174.1 (3)	C14—C15—C16	124.3 (3)
C23—N7—Cu4	175.3 (3)	N4—C16—C17	120.1 (4)
N1—C1—C2	123.4 (3)	N4—C16—C15	115.8 (3)
N1—C1—H1	118.3	C17—C16—C15	124.1 (3)
C2—C1—H1	118.3	C18—C17—C16	120.4 (4)
C3—C2—C1	118.2 (4)	C18—C17—H17	119.8
C3—C2—H2	120.9	C16—C17—H17	119.8
C1—C2—H2	120.9	C19—C18—C17	119.5 (4)
C2—C3—C4	119.6 (3)	C19—C18—H18	120.3

C2—C3—H3	120.2	C17—C18—H18	120.3
C4—C3—H3	120.2	C18—C19—C20	118.4 (4)
C5—C4—C3	119.2 (3)	C18—C19—H19	120.8
C5—C4—H4	120.4	C20—C19—H19	120.8
C3—C4—H4	120.4	N4—C20—C19	123.5 (4)
N1—C5—C4	121.0 (3)	N4—C20—H20	118.2
N1—C5—C6	115.5 (3)	C19—C20—H20	118.2
C4—C5—C6	123.5 (3)	N5—C21—Cu1	175.3 (3)
N2—C6—C7	121.7 (3)	N6—C22—Cu3	175.7 (3)
N2—C6—C5	114.8 (3)	N7—C23—Cu2	175.0 (3)
C7—C6—C5	123.5 (3)		

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