metal-organic compounds

catena-Poly[[[2-(2-methyl-1*H*-benzimidazol-1-yl)acetonitrile-κN^3]-copper(I)]-μ-cyanido]

Tian Hang, Da-Wei Fu and Qiong Ye*

Ordered Matter Science Research Center, Southeast University, Nanjing 210096, People's Republic of China
Correspondence e-mail: yeqiong@seu.edu.cn

The title compound, $[Cu(CN)(C_{10}H_9N_3)]_n$, was prepared by the solvothermal treatment of CuCN with 2-[2-methyl(1*H*-benzo[*d*]imidazol-1-yl)]acetonitrile. The X-ray crystal structure shows that the title compound is a new cyano-bridged homometallic Cu^I coordination polymer in which the Cu^I atoms are linked by equally disordered CN groups, and are bonded to the N atom of the 2-[2-methyl(1*H*-benzo[*d*]-imidazol-1-yl)]acetonitrile ligand. This ligand is alternately distributed along the zigzag chain. A three-dimensional structure is formed through a weak Cu—H interaction and π–π stacking between neighbouring benzimidazole ring systems.

Related literature

For solvothermal synthesis, see: Qu *et al.* (2004). For related structures, see: Mühle & Sheldrick (2003); Colacio *et al.* (2005).
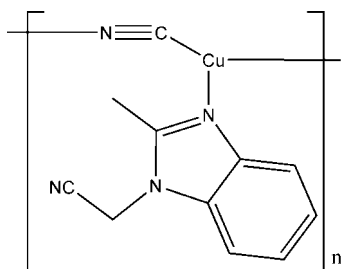
Experimental

Crystal data

$[Cu(CN)(C_{10}H_9N_3)]$
$M_r = 260.76$
Monoclinic, $P2_1/c$
$a = 13.267 (3)$ Å
$b = 9.2456 (18)$ Å
$c = 9.1109 (18)$ Å
$\beta = 109.11 (3)°$
$V = 1056.0 (4)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 2.04$ mm^{-1}
$T = 293 (2)$ K
$0.22 \times 0.18 \times 0.12$ mm

Data collection

Rigaku Mercury2 diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2005)
$T_{min} = 0.645$, $T_{max} = 0.796$
10564 measured reflections
2411 independent reflections
1523 reflections with $I > 2\sigma(I)$
$R_{int} = 0.114$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.121$
$S = 1.03$
2411 reflections
146 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C3—H3$A\cdots$Cu1^i	0.97	3.08	3.830 (4)	135

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

Table 2
π–π interaction in the title compound. α is the dihedral angle between the planes, DCC is the length of the CC vector (centroid to centroid), τ is the angle(s) subtended by the plane normal(s) to CC. $Cg1$ is the centroid of ring N3, C7, N4, C11, C8; $Cg2$ of ring C1, C2, C4, C6, C8, C11.

Group 1	Group 2	α /°	DCC /Å	τ /°
$Cg1$	$Cg2^i$	1.48	3.639 (3)	14.9

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

Data collection: *CrystalClear* (Rigaku, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *XP* in *SHELXTL/PC* (Sheldrick, 1998); software used to prepare material for publication: *SHELXTL/PC*.

References

Colacio, E., Debdoubi, A., Kivekäs, R. & Rodríguez, A. (2005). *Eur. J. Inorg. Chem.* pp. 2860–2868.
Mühle, J. & Sheldrick, W. S. (2003). *Z. Anorg. Allg. Chem.* **629**, 2097–2102.
Qu, Z.-R., Zhao, H., Wang, Y.-P., Wang, X.-S., Ye, Q., Li, Y.-H., Xiong, R.-G., Abrahams, B. H., Liu, Z.-G., Xue, Z.-L. & You, X.-Z. (2004). *Chem. Eur. J.* **10**, 54–60.
Rigaku (2005). *CrystalClear*. Version 1.4.0. Rigaku Corporation, Tokyo, Japan.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Sheldrick, G. M. (1998). *SHELXTL/PC*. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

supplementary materials

catena-Poly[[[2-(2-methyl-1*H*-benzimidazol-1-yl)acetonitrile-*κN*³]copper(I)]-*μ*-cyanido]

T. Hang, D.-W. Fu and Q. Ye

Comment

Under hydrothermal or solvothermal conditions, some interesting reactions and compounds can be obtained, while It is worth noting that these products could not be synthesized using conventional solution techniques. (Qu *et al.*(2004)). In sealed tube, unstable copper (I) salt can exist under vacuums, and then interesting copper (I) coordination compound can be obtained. The title compound is obtained through solvothermal treatment of 2-(2-methyl(1*H*-benzol*[d]* imidazol-1-yl) acetonitrile and CuCN in methanol solvent at 80°C, colorless block crystals suitable for X-ray diffractions have been isolated.

The copper(I) is coordinated to two disordered cyano group and one nitrogen atom from benzolimidazole ligand in a trigonal environment (Fig 1). The cyano bridges link the molecules to form an homometallic CuI coordination polymer developping along the *c* axis. The 2-(2-methyl(1*H*- benzol*[d]* imidazol-1-yl) acetonitrile ligands are alternatively distributed along the polymeric zigzag chain (Fig. 1).

It is important to note that the bridging CN groups are statistically disoredered. This means that discrimination between the N and C atoms of the CN group linking the Cu (I) centre is impossible, and they are assumed to have 50% probability for each of the C and N designated as NC, in the structure refinement.

Two neighboring chains are interconnected through weak Cu—H interactions forming a two-dimensionnal layer (Table 1, Fig. 2). Futhermore, there are weak π-π stacking interactions between symetry related benzolimidazole rings (Table 2) resulting in a three dimensionnal ABAB sequence.

Experimental

A mixture of 2-(2-methyl(1*H*-benzol*[d]* imidazol-1-yl) acetonitrile (20 mg, 0.2 mmol), CuCN (17.9 mg,0.2 mmol), and methanol (2 ml) sealed in a glass tube were maintained at 80 °C. Crystals suitable for X-ray analysis were obtained after 5 days

Refinement

All H atoms were fixed geometrically and treated as riding with C—H = 0.93 Å (aromatic), 0.97 Å (methylene) or 0.96Å (methyl) with $U_{iso}(H) = 1.2U_{eq}$(Caromatic, Cmethylene) or $U_{iso}(H) = 1.5U_{eq}$(Cmethyl).

The large difference in the isotropic thermal parameters within the cyano bridge indicates the occurrence of a statistical distribution C—N or N—C for the cyano bridge. This disorder was treated with the tools available in *SHELXL97* (Sheldrick, 1997).
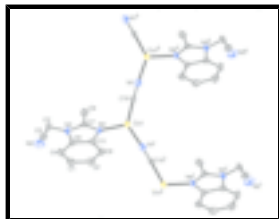
supplementary materials

Figures

Fig. 1. A view of the asymmetric unit of the title compoud with atomic numbering scheme. Displacement ellipsoids were drawn at the 30% probability level. [Symmetry codes: (i) x, $3/2 - y$, $-1/2 + z$; (ii) x, $3/2 - y$, $1/2 + z$].
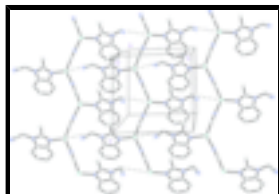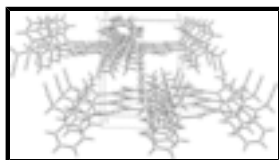
Fig. 2. the two-dimensionnal layer structure of the title compound formed by weak C—H···Cu hydrogen bonding interaction. Hydrogen bonds are shown as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

Fig. 3. The crystal packing of the title compound viewed along the c axis.

(µ$_2$-Cyano)-2-[2-methyl(1*H*-benzo[*d*]imidazol-1-yl)acetonitrile]copper(I)

Crystal data

[Cu(CN)(C$_{10}$H$_9$N$_3$)]	$F_{000} = 528$
$M_r = 260.76$	$D_x = 1.640$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 8475 reflections
$a = 13.267$ (3) Å	$\theta = 3.3–27.5°$
$b = 9.2456$ (18) Å	$\mu = 2.04$ mm^{-1}
$c = 9.1109$ (18) Å	$T = 293$ (2) K
$\beta = 109.11$ (3)°	Block, colorless
$V = 1056.0$ (4) Å^3	$0.22 \times 0.18 \times 0.12$ mm
$Z = 4$	

Data collection

Mercury2 (2x2 bin mode) diffractometer	2411 independent reflections
Radiation source: fine-focus sealed tube	1523 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.114$
Detector resolution: 13.6612 pixels mm^{-1}	$\theta_{max} = 27.5°$
$T = 293(2)$ K	$\theta_{min} = 3.2°$

CCD_Profile_fitting scans	$h = -17 \rightarrow 17$
Absorption correction: multi-scan (CrystalClear; Rigaku, 2005)	$k = -11 \rightarrow 12$
$T_{min} = 0.645$, $T_{max} = 0.796$	$l = -11 \rightarrow 11$
10564 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.059$	H-atom parameters constrained
$wR(F^2) = 0.121$	$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.03$	$(\Delta/\sigma)_{max} < 0.001$
2411 reflections	$\Delta\rho_{max} = 0.40$ e Å^{-3}
146 parameters	$\Delta\rho_{min} = -0.38$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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	$U_{iso}*/U_{eq}$	Occ. (<1)
C1	0.0444 (4)	0.1630 (5)	−0.1163 (5)	0.0452 (12)	
H1	−0.0019	0.1011	−0.1875	0.054*	
C2	0.0320 (4)	0.3111 (5)	−0.1390 (5)	0.0424 (12)	
H2	−0.0220	0.3459	−0.2252	0.051*	
C3	0.3109 (4)	0.0462 (4)	0.3248 (5)	0.0391 (11)	
H3A	0.2589	−0.0280	0.2768	0.047*	
H3B	0.3170	0.0516	0.4337	0.047*	
C4	0.1235 (4)	0.1043 (5)	0.0093 (5)	0.0421 (12)	
H4	0.1325	0.0049	0.0234	0.051*	
C5	0.4145 (4)	0.0051 (5)	0.3121 (5)	0.0414 (12)	
C6	0.0980 (3)	0.4083 (5)	−0.0364 (5)	0.0352 (11)	
H6	0.0900	0.5075	−0.0523	0.042*	
C7	0.3085 (3)	0.3196 (4)	0.3065 (5)	0.0281 (10)	

C8	0.1884 (3)	0.2021 (4)	0.1124 (5)	0.0287 (10)	
C9	0.3986 (4)	0.3413 (5)	0.4509 (5)	0.0405 (12)	
H9A	0.4642	0.3200	0.4326	0.061*	
H9B	0.3908	0.2782	0.5302	0.061*	
H9C	0.3994	0.4400	0.4842	0.061*	
N1B	0.2695 (4)	0.7159 (4)	0.4355 (5)	0.0471 (12)	0.50
C10A	0.2695 (4)	0.7159 (4)	0.4355 (5)	0.0471 (12)	0.50
C11	0.1765 (3)	0.3518 (4)	0.0908 (4)	0.0268 (9)	
Cu1	0.26730 (5)	0.64111 (6)	0.23978 (6)	0.0411 (2)	
N1A	0.2663 (4)	0.7661 (4)	0.5510 (5)	0.0431 (11)	0.50
C10B	0.2663 (4)	0.7661 (4)	0.5510 (5)	0.0431 (11)	0.50
N2	0.4948 (4)	−0.0270 (5)	0.3056 (5)	0.0694 (14)	
N3	0.2733 (3)	0.1842 (3)	0.2514 (4)	0.0295 (8)	
N4	0.2535 (3)	0.4221 (4)	0.2148 (3)	0.0286 (8)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.046 (3)	0.045 (3)	0.041 (3)	−0.010 (2)	0.010 (2)	−0.012 (2)
C2	0.037 (3)	0.056 (3)	0.030 (2)	0.000 (2)	0.005 (2)	−0.002 (2)
C3	0.049 (3)	0.023 (2)	0.049 (3)	0.005 (2)	0.021 (3)	0.010 (2)
C4	0.048 (3)	0.028 (3)	0.053 (3)	−0.006 (2)	0.019 (3)	−0.012 (2)
C5	0.052 (3)	0.044 (3)	0.027 (2)	0.016 (3)	0.011 (3)	0.004 (2)
C6	0.034 (3)	0.036 (2)	0.033 (2)	0.005 (2)	0.009 (2)	0.003 (2)
C7	0.029 (2)	0.030 (2)	0.027 (2)	−0.0079 (19)	0.012 (2)	−0.0002 (18)
C8	0.029 (2)	0.024 (2)	0.035 (2)	0.0012 (19)	0.012 (2)	−0.0028 (18)
C9	0.039 (3)	0.047 (3)	0.030 (2)	−0.008 (2)	0.004 (2)	0.003 (2)
N1B	0.078 (4)	0.025 (2)	0.036 (2)	−0.002 (2)	0.014 (2)	0.0061 (19)
C10A	0.078 (4)	0.025 (2)	0.036 (2)	−0.002 (2)	0.014 (2)	0.0061 (19)
C11	0.030 (2)	0.025 (2)	0.028 (2)	−0.0035 (19)	0.0136 (19)	−0.0041 (18)
Cu1	0.0608 (4)	0.0280 (3)	0.0326 (3)	−0.0038 (3)	0.0126 (3)	−0.0023 (2)
N1A	0.074 (3)	0.025 (2)	0.030 (2)	−0.003 (2)	0.017 (2)	−0.0009 (17)
C10B	0.074 (3)	0.025 (2)	0.030 (2)	−0.003 (2)	0.017 (2)	−0.0009 (17)
N2	0.064 (3)	0.094 (4)	0.047 (3)	0.035 (3)	0.015 (3)	0.002 (2)
N3	0.033 (2)	0.0245 (18)	0.0291 (19)	0.0012 (16)	0.0081 (17)	0.0043 (14)
N4	0.035 (2)	0.0226 (18)	0.0268 (19)	−0.0010 (16)	0.0083 (17)	0.0016 (14)

Geometric parameters (Å, °)

C1—C4	1.385 (6)	C7—N3	1.372 (5)
C1—C2	1.387 (6)	C7—C9	1.473 (6)
C1—H1	0.9300	C8—C11	1.400 (5)
C2—C6	1.382 (6)	C8—N3	1.401 (5)
C2—H2	0.9300	C9—H9A	0.9600
C3—N3	1.451 (5)	C9—H9B	0.9600
C3—C5	1.467 (7)	C9—H9C	0.9600
C3—H3A	0.9700	N1B—N1A	1.164 (5)
C3—H3B	0.9700	N1B—Cu1	1.904 (4)
C4—C8	1.383 (6)	C11—N4	1.409 (5)

C4—H4	0.9300	Cu1—C10B[i]	1.918 (4)
C5—N2	1.126 (6)	Cu1—N1A[i]	1.918 (4)
C6—C11	1.381 (5)	Cu1—N4	2.039 (3)
C6—H6	0.9300	N1A—Cu1[ii]	1.918 (4)
C7—N4	1.315 (5)		
C4—C1—C2	122.1 (4)	C11—C8—N3	105.3 (3)
C4—C1—H1	119.0	C7—C9—H9A	109.5
C2—C1—H1	119.0	C7—C9—H9B	109.5
C6—C2—C1	121.5 (4)	H9A—C9—H9B	109.5
C6—C2—H2	119.3	C7—C9—H9C	109.5
C1—C2—H2	119.2	H9A—C9—H9C	109.5
N3—C3—C5	112.4 (4)	H9B—C9—H9C	109.5
N3—C3—H3A	109.1	N1A—N1B—Cu1	176.4 (4)
C5—C3—H3A	109.1	C6—C11—C8	120.7 (4)
N3—C3—H3B	109.1	C6—C11—N4	130.4 (4)
C5—C3—H3B	109.1	C8—C11—N4	108.9 (3)
H3A—C3—H3B	107.9	N1B—Cu1—C10B[i]	132.14 (17)
C8—C4—C1	116.1 (4)	N1B—Cu1—N1A[i]	132.14 (17)
C8—C4—H4	121.9	C10B[i]—Cu1—N1A[i]	0.0 (2)
C1—C4—H4	121.9	N1B—Cu1—N4	116.01 (14)
N2—C5—C3	178.5 (5)	C10B[i]—Cu1—N4	111.72 (14)
C11—C6—C2	117.3 (4)	N1A[i]—Cu1—N4	111.72 (14)
C11—C6—H6	121.4	N1B—N1A—Cu1[ii]	176.2 (4)
C2—C6—H6	121.4	C7—N3—C8	107.4 (3)
N4—C7—N3	111.9 (4)	C7—N3—C3	127.5 (4)
N4—C7—C9	126.1 (4)	C8—N3—C3	125.0 (3)
N3—C7—C9	122.0 (4)	C7—N4—C11	106.5 (3)
C4—C8—C11	122.3 (4)	C7—N4—Cu1	129.3 (3)
C4—C8—N3	132.4 (4)	C11—N4—Cu1	124.2 (3)

Symmetry codes: (i) x, $-y+3/2$, $z-1/2$; (ii) x, $-y+3/2$, $z+1/2$.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C3—H3A···Cu1[iii]	0.97	3.08	3.830 (4)	135

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

Table 2

π-π interaction in (I).

α is dihedral angle between the planes, DCC is the length of the CC vector (centroid to centroid), τ is the angle(s) subtended by the plane normal(s) to CC. Cg1 is the centroid of ring N3, C7, N4, C11, C8, Cg2 of ring C1 C2 C4 C6 C8 C11.

Group 1	Group 2	α /°	DCC /Å	τ /°
*Cg*1	*Cg*2[i]	1.48	3.639 (3)	14.9

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

Fig. 1

Fig. 2

Fig. 3

Fig. 4