Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

For

An unusual anionic copper(I) cyanide 3D framework encapsulating cationic copper(II) complex as a guest

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Experimental

Physical measurements

The IR spectrum was recorded on a VERTEX 80v FT-IR spectrometer with KBr pellet in the range 4000 ~ 400 cm^{-1}. Elemental analysis was carried out on a CHNS-932 elemental analyser. Thermogravimetric analysis (TGA) was performed under nitrogen on a SDT Q600 thermogravimetric analyser. The sample was heated using a 10^{o}C/min heating rate from 25 to 900^{o}C.The solid-state excitation and emission spectra were performed on a RF-5301 spectrophotometer.

Crystallographic Structure Determinations

All data were collected on a Bruker Smart diffractometer equipped with a graphitemonochromated Mo *Kα* (λ = 0.71073 Å) radiation source and a CCD detector. The 45frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. A total of 1271 frames of two-dimensional diffraction images were collected, each of which was measured for 5 sec. Decay was monitored by 50 standard data frames measured at the beginning and end of data collection. The crystal showed no significant decay. The frame data were processed to give structure factors using the SAINT-plus.[Sref1] Semi-empirical absorption corrections were applied to the data sets using the SADABS.[Sref2] The structure was solved by direct methods and refined by full matrix least squares methods on F^2 for all data using SHELXTL software.[Sref3] For all atoms of the CN groups, a 50% probability of C and N was used at the preliminary stage of the structure refinement. Judging from the difference in the displacement parameters and the site occupancies, discrimination was possible for the three CN groups (C1≡N1, C2≡N2, and C3≡N3), but impossible for remaining two μ_2-CN groups, although the C and N are crystallographically independent of each other. Therefore, the orientations of two μ_2-CN groups were named X and treated as disordered. The site occupancies of each disordered CN group were then refined with the constraint that the total occupancy for each site was 1.00 and the thermal parameters of C and N on the same site constrained to be equal. The occupancies for all atoms of the disordered CN groups are listed in Table S2. The non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms for coordinated and guest water molecules were located from the difference electron density

maps while all others were placed in calculated positions, and refined with a riding model with U_{iso} constrained to be 1.2 times U_{eq} of the parent atom. Crystallographic data and structural refinement data for **1** is summarized in Table S1.

References

Sref1. Bruker, SMART (*ver. 5.625*) and SAINT-plus (*ver. 6.22*): *Area Detector Control and Integration Software*; Bruker AXS Inc.: Madison, Wisconsin, 2000.

Sref2. Bruker, SADABS (*ver. 2.03*): *Empirical absorption and correction software*; Bruker AXS Inc.: Madison, Wisconsin, 1999.

Sref3. Bruker, SHELXTL (*ver. 6.10*): *Program for Solution and Refinement of Crystal Structures*; Bruker AXS Inc.: Madison, Wisconsin, 2000.

Table S1. Crystallographic data and structural refinement data for **1**.

Empirical formula	$C_5H_{16}Cu_4N_9O_2$
Formula weight	488.43
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 7.8845(3) Å
	b = 10.4605(4) Å
	c = 18.8317(7) Å
	α = 90°
	β = 90°
	γ = 90°
Volume	1553.16(10) Å^3
Z	4
Density (calculated)	2.089 Mg/m^3
Absorption coefficient	5.416 mm^{-1}
F(000)	964
Crystal size	0.40 x 0.25 x 0.20 mm^3
Theta range for data collection	2.23 to 27.00°.
Index ranges	-10<=h<=9, -12<=k<=13, -23<=l<=17
Reflections collected	9263
Independent reflections	3364 [R(int) = 0.0303]
Completeness to theta = 27.00°	99.8 %
Absorption correction	Empirical
Max. and min. transmission	0.3446 and 0.2206
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3364 / 0 / 183
Goodness-of-fit on F^2	1.082
Final R indices [I>2sigma(I)]	$R1$ = 0.0291, $wR2$ = 0.0625
R indices (all data)	$R1$ = 0.0372, $wR2$ = 0.0656
Absolute structure parameter	0.00(2)
Largest diff. peak and hole	0.425 and -0.794 e.Å^{-3}

Table S2. Fractional coordinates, isotropic thermal parameters ($Å^2$) and occupancies of disordered CN groups for **1**.

Atom	*x*	*y*	*z*	*U*(eq)	C/N Occ*
Cu(1)	0.6857(1)	0.3972(1)	0.4916(1)	0.017(1)	1.0
Cu(2)	0.8171(1)	0.4003(1)	0.3715(1)	0.020(1)	1.0
Cu(3)	0.6834(1)	0.2072(1)	0.1346(1)	0.019(1)	1.0
Cu(4)	0.2555(1)	0.4050(1)	0.1384(1)	0.018(1)	1.0
C(1)	0.6000(6)	0.5108(4)	0.4075(2)	0.015(1)	1.0
N(1)	0.5099(5)	0.5890(4)	0.3888(2)	0.020(1)	1.0
C(2)	0.8854(6)	0.2826(4)	0.4658(2)	0.017(1)	1.0
N(2)	0.9932(5)	0.2113(3)	0.4763(2)	0.016(1)	1.0
C(3)	0.7452(6)	0.2995(4)	0.2919(2)	0.018(1)	1.0
N(3)	0.6985(5)	0.2506(3)	0.2406(2)	0.022(1)	1.0
X(4)/X(4')	1.0080(6)	0.5165(4)	0.3714(2)	0.023(1)	0.66(4)/0.34(4)
X(5)/X(5')	1.1204(5)	0.5866(4)	0.3746(2)	0.026(1)	0.66(4)/0.34(4)
X(6)/X(6')	0.7896(5)	0.6308(4)	0.5856(2)	0.016(1)	0.74(4)/0.26(4)
X(7)/X(7')	0.7580(5)	0.5351(3)	0.5585(2)	0.018(1)	0.74(4)/0.26(4)
N(8)	0.4284(5)	0.4771(4)	0.2087(2)	0.028(1)	1.0
N(9)	0.2155(6)	0.2535(4)	0.2038(2)	0.033(1)	1.0
N(10)	0.1309(5)	0.3068(4)	0.0600(2)	0.027(1)	1.0
N(11)	0.3417(5)	0.5283(4)	0.0628(2)	0.031(1)	1.0
O(1)	0.0351(5)	0.5198(4)	0.1790(2)	0.043(1)	1.0
O(2)	0.3340(7)	0.2709(5)	0.3539(2)	0.086(2)	1.0

* X is either C or N of a disordered CN group.

Table S3. Hydrogen bond, and N-H···π and O-H···π interactions (Å and °) for **1**. Cg denotes the centeroid of the CN group given in parenthesis.

D-H···A	d(D-H)	d(H···A)	d(D···A)	<(D-H···A)
N9-H9A···O2	0.91	2.09	2.982(5)	166.7
N8-H8B···Cg1 (C3≡N3)	0.91	2.43	3.32	163.7
N9-H9B···Cg2^{i} (C1≡N1)	0.91	2.53	3.39	158.4
N10-H10B···Cg3^{i} (X4≡X5)	0.91	2.77	3.33	121.1
N10-H10B···Cg4^{ii} (X6≡X7)	0.91	2.69	3.40	135.2
N10-H10C···Cg4^{i} (X6≡X7)	0.91	2.81	3.50	133.0
N11-H11A···Cg5^{iii} (C2≡N2)	0.91	2.39	3.25	157.3
N11-H11C···Cg4^{iv} (X6≡X7)	0.91	2.56	3.25	133.6
O1-H1A···Cg3^{v} (X4≡X5)	0.90	2.80	3.68	166.4
O2-H2A···Cg2 (C1≡N1)	1.01	2.75	3.50	130.7
O2-H2B···Cg5^{vi} (C2≡N2)	1.01	2.80	3.40	118.9

Symmetry operations: i) 1-*x*, -0.5+*y*, 0.5-*z*; ii) 0.5-*x*, 1-*y*, -0.5+*z*; iii) 1-*x*, 0.5+*y*, 0.5-*z*; iv) 1.5-*x*, 1-*y*, -0.5+*z*; v) -1+*x*, *y*, *z*; vi) -0.5+*x*, 0.5-*y*, 1-*z*.

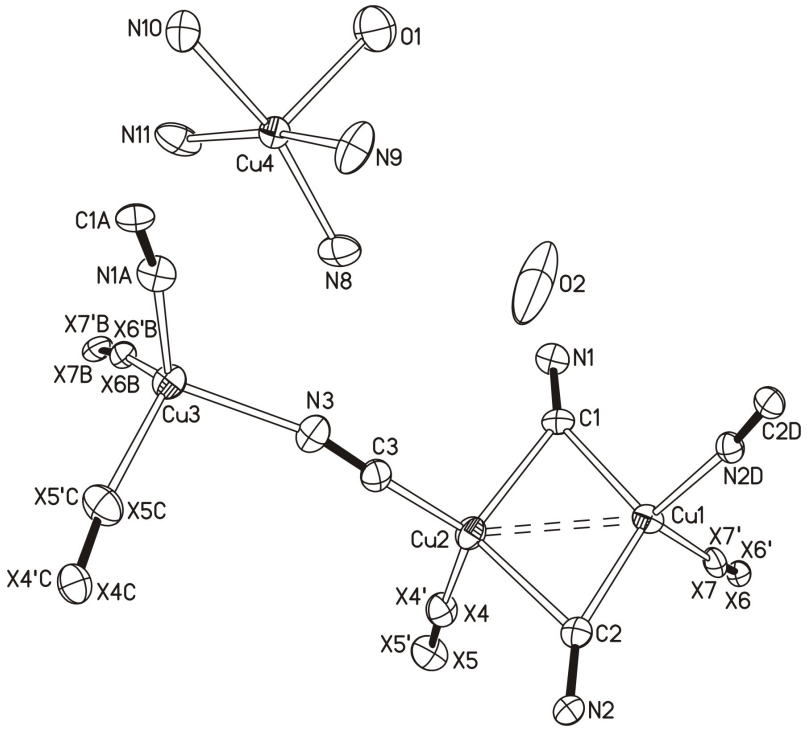


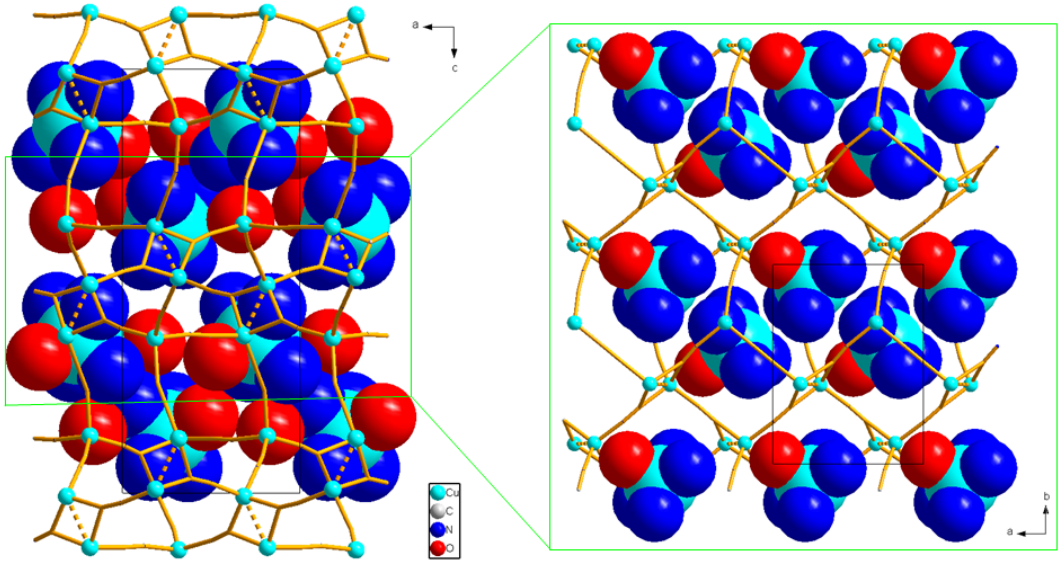
Figure S1. ORTEP representation showing the coordination geometries about metal centers in $\{[Cu(NH_3)_4(H_2O)][Cu_3(CN)_5]\cdot H_2O\}_n$ (**1**). Ellipsoids are drawn at the 50 % probability level. Hydrogen atoms are omitted for clarity. Disordered CN groups are denoted by X.

Selected bond lengths (Å) and angles (°):

Cu1-C1	2.093(4)	Cu1-C2	2.038(5)	Cu1-N2D	1.988(4)	Cu1-X7	1.998(4)
Cu2-C1	2.173(4)	Cu2-C2	2.228(4)	Cu2-C3	1.918(4)	Cu2-X4	1.934(4)
Cu3-N3	2.051(4)	Cu3-N1A	2.011(4)	Cu3-X6B	1.942(4)	Cu3-X5C	2.004(4)
Cu4-N8	2.044(4)	Cu4-N9	2.032(4)	Cu4-N10	2.049(4)	Cu4-N11	2.038(4)
Cu4-O1	2.246(4)	C1-N1	1.139(6)	C2-N2	1.148(5)	C3-N3	1.153(5)
X4-X5	1.152(6)	X6-X7	1.150(5)	Cu1…Cu2	2.4885(7).		

C1-Cu1-C2	113.76(17)	C1-Cu1-N2D	107.91(16)	C1-Cu1-X7	99.14(15)
C2-Cu1-N2D	109.06(16)	C2-Cu1-X7	110.74(16)	N2D-Cu1-X7	116.04(15)
C1-Cu2-C2	103.63(16)	C1-Cu2-C3	107.64(18)	C1-Cu2-X4	106.21(17)
C2-Cu2-C3	112.99(16)	C2-Cu2-X4	99.18(17)	C3-Cu2-X4	125.10(19)
N3-Cu3-N1A	113.14(15)	N3-Cu3-X5C	100.26(16)	N3-Cu3-X6B	105.25(15)
N1A-Cu3-X6B	121.06(16)	N1A-Cu3-X5C	100.33(15)	X5C-Cu3-X6B	115.09(17)
N8-Cu4-N9	89.92(17)	N8-Cu4-N10	166.17(16)	N8-Cu4-N11	89.79(18)
N8-Cu4-O1	95.66(15)	N9-Cu4-N10	88.35(16)	N9-Cu4-N11	165.67(17)
N9-Cu4-O1	95.21(17)	N10-Cu4-N11	88.51(17)	N10-Cu4-O1	98.17(15)
N11-Cu4-O1	99.07(16)	Cu1-C1-N1	147.5(4)	Cu1-C2-N2	156.0(4)
Cu1-N2D-C2D	171.1(3)	Cu1-X7-X6	165.8(3)	Cu2-C1-N1	140.9(4)
Cu2-C2-N2	132.5(4)	Cu2-C3-N3	173.0(4)	Cu2-X4-X5	177.0(4)
Cu3-N3-C3	158.8(4)	Cu3-N1A-C1A	168.9(4)	Cu3-X5C-X4C	172.1(4)
Cu3-X6B-X7B	173.6(4)	Cu1-C1-Cu2	71.34(14)	Cu1-C2-Cu2	71.22(14)

[Symmetry codes: (A) –*x*+1, *y*-0.5, -*z*+0.5; (B) –*x*+1.5, -*y*+1, *z*-0.5; (C) –*x*+2, *y*-0.5, -*z*+0.5; (D) *x*-0.5, -*y*+0.5, -*z*+1.]



(a) (b)

Figure S2. (a) Packing structure of **1**, $\{[Cu^{II}(NH_3)_4(H_2O)](H_2O)@[Cu^{I}_3(CN)_5]\}_n$ and (b) an embossing 2-D layer with encapsulated $[Cu^{II}(NH_3)_4(H_2O)]^{2+}$ cationic guests: Guest water molecules are omitted for clarity.

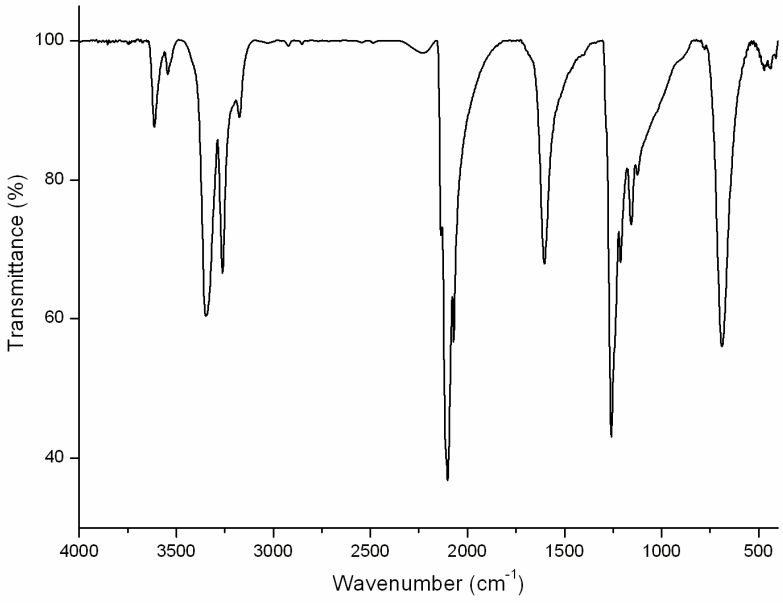


Figure S3. IR spectrum of **1**