Supporting Information:

A highly stable face-extended diamondoid cluster-organic framework incorporating infinite inorganic guests

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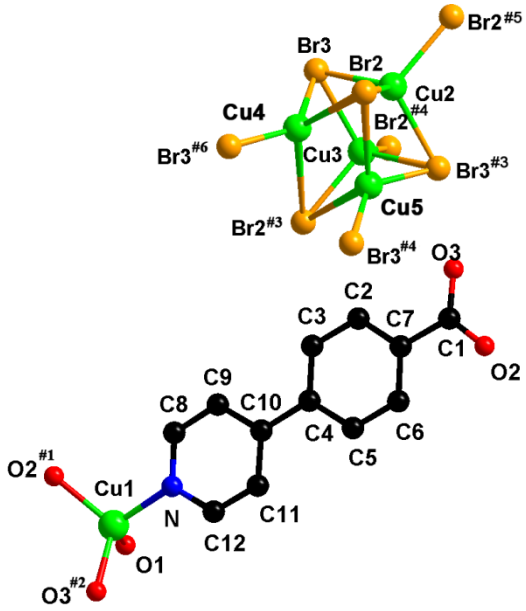
Content

Experimental Section:

Materials and physical measurements. All chemicals and solvents were commercially purchased and used without further purification. Elemental analysis was measured on a Vario MICRO Elemental Analyzer instrument. IR spectra (KBr pellets) were recorded on an ABB Bomem MB102 spectrometer over a range 400-4000 cm^{-1}. The thermogravimetric analyses (TGA) were performed on a Mettler Toledo TGA/SDTA 851^e analyzer in air atmosphere with a heating rate of 10 ºC/min from 30 ºC to 1000 ºC. Powder X-ray diffraction (PXRD) data were collected on a Rigaku Mini Flex II diffractometer using CuKα radiation (λ = 1.54056Å) under ambient conditions. The UV diffuse reflection data were recorded at room temperature using a powder sample with $BaSO_4$ as a standard (100% reflectance) on a PerkinElmer Lamda-950 UV spectrophotometer and scanned at 200-800 nm. The absorption data are calculated from the Kubelka-Munk function, (F(R)=(1-R)^2/2R),[1] where R representing the reflectance, K the absorption, and S the scattering. Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy (HRTEM) images were obtained on a Tecnai G2 F20 field emission transmission electron microscope at an accelerating voltage of 200 kV. The powder sample was dispersed in ethanol and a drop of the slurry was placed onto a TEM grid.

X-Ray Crystallography. Crystallographic data of complexes **1** were collected on a Supernova single crystal diffractometer equipped with graphite-monochromatic CuKα radiation (λ = 1.54178 Å) at 100 K and 298 K. The test temperature was controlled by dry N_2 flow using a Cryo Stream 700 system (Agilent Technologies, USA), and corrected by a thermal couple at the crystal position. The variable temperature unit-cell parameters were obtained by indexing the diffraction spots that were obtained with diffraction images. The structure was solved with direct methods using SHELXS-97[2] and refined with the full-matrix least-squares technique based on F^2 using the SHELXL-97.[3] Non-hydrogen atoms were refined anisotropically, and all hydrogen atoms bond C were generated geometrically. Crystallographic diagrams were drawn using the DIAMOND software package.[4]

Supporting Fig.s:



a)

Fig. S1 a) The asymmetric unit of complex **1**. All H atoms are omitted for clarity. Symmetry codes: #1 *x*-3/4, *y*-1/4, -*z*+1/2; #2 *x*-3/4, -*y*+1, *z*+1/4; #3 -*x*+9/4, *y*, -*z*+1/4; #4 *x*+1/2, -*y*+3/4, -*z*+1/4; #5 -*x*+11/4, -*y*+3/4, *z*; #6 *x*-1/2, -*y*+3/4, -*z*+1/4. b) The 1-D chain-like guest based on the Cu_4Br_4 clusters shared by Cu_2Br_2 ring, in which four Cu atoms of the Cu_4Br_4 cluster possess tetrahedral geometry.

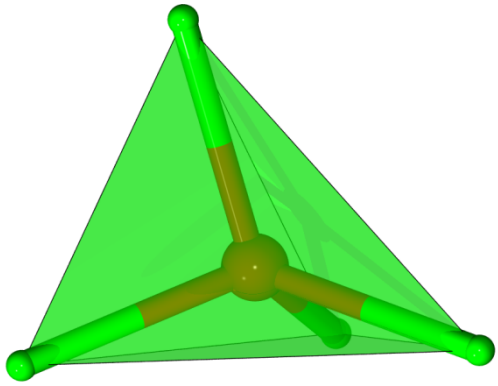


Fig. S2 The perspective view of the Cu_4O motif in the structure.

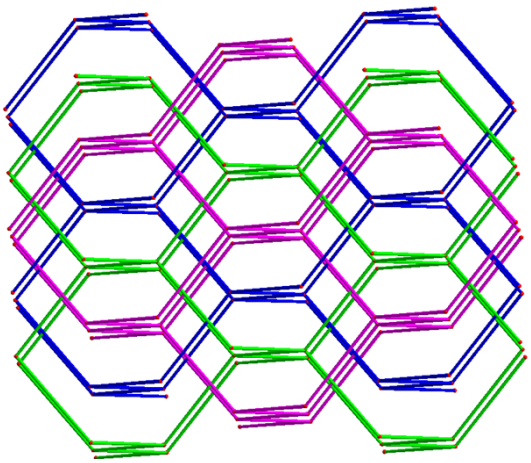


Fig. S3 The topological representation of the three-fold interpenetrating *dia* net of complex **1**.

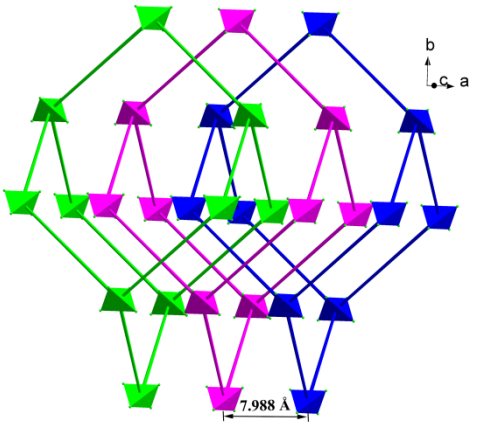


Fig. S4 The interlocked adamantane units of three independent diamond-like nets.

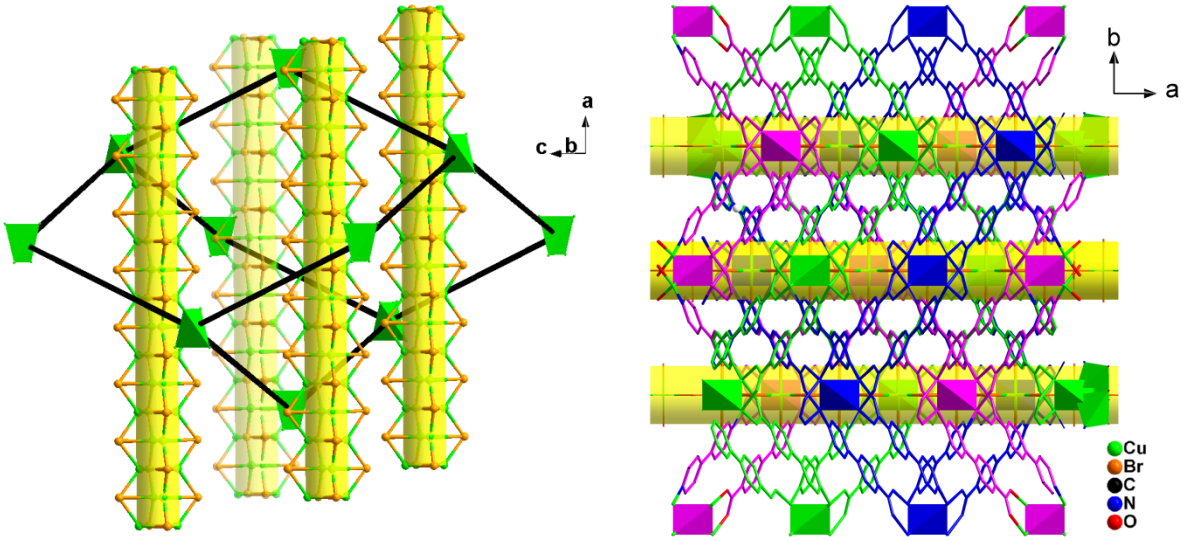


Fig. S5 The scheme representation of the 1D copper halide chains inset in an adamantane unit (left) and the overall side view of the host-guest compound (right).

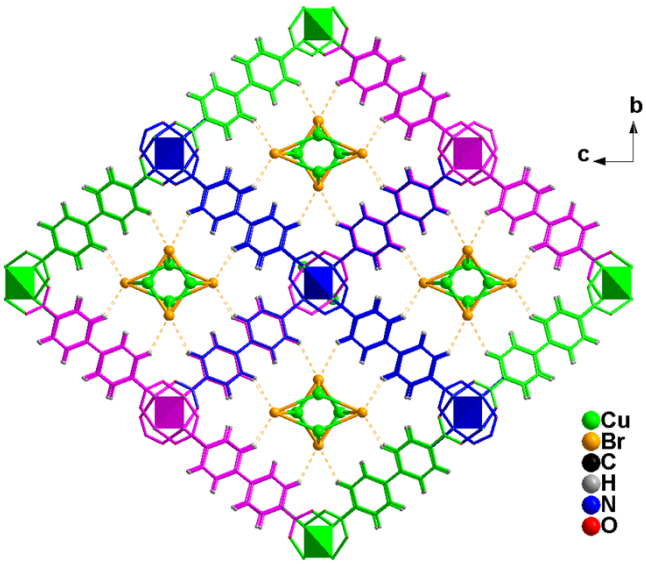


Fig. S6 The H-bonding interactions between host framework and guest chains.

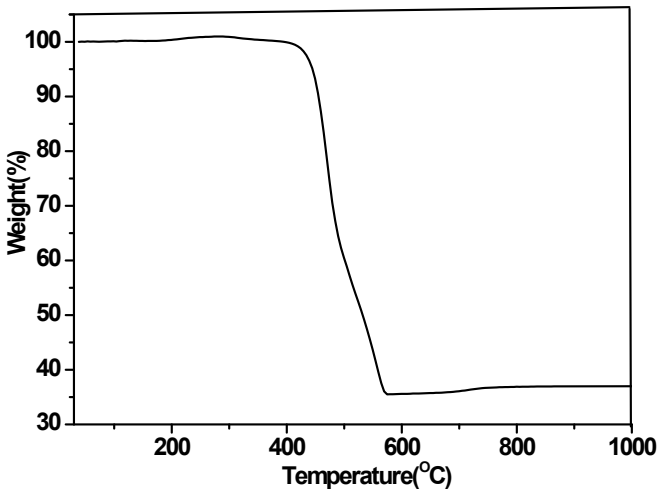


Fig. S7 The TGA curves of the compound **1**.

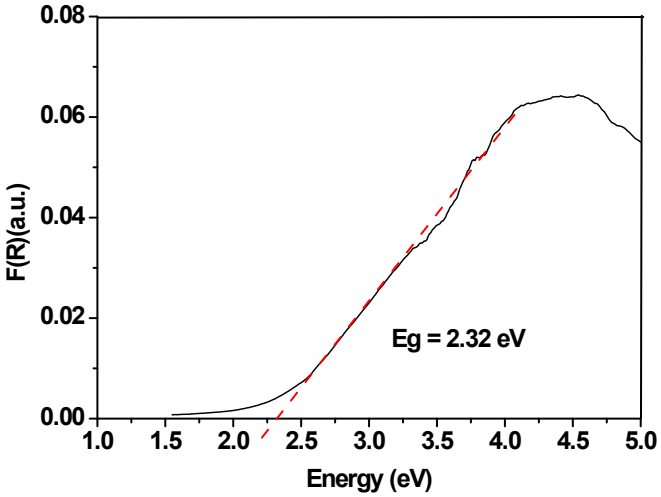


Fig. S8 The bands gap of the compound **1.**

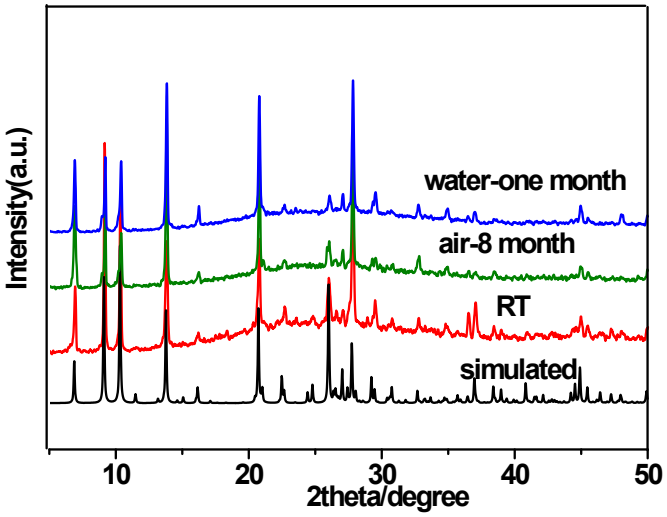


Fig. S9 PXRD patterns of **1** after being soaked in water and exposed in air for months.

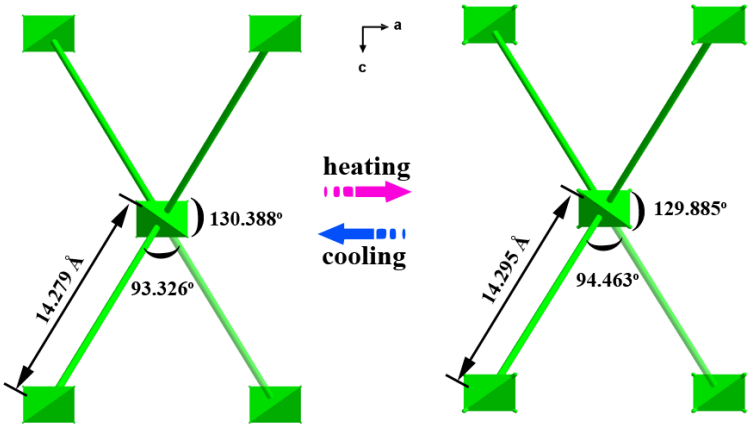


Fig. S10 Illustration of the "rhombus grid" showing the crystal structure transformation.

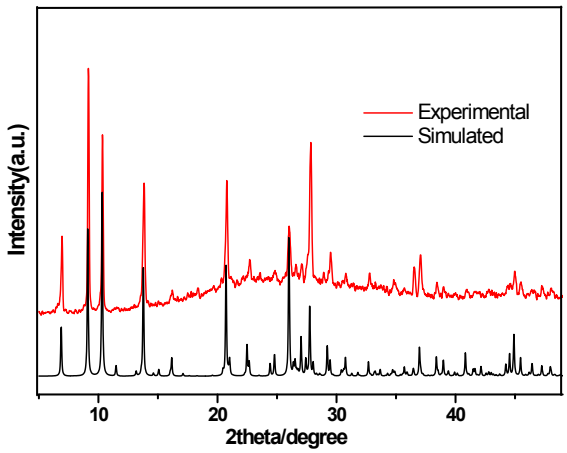


Fig. S11 The simulated and experimental PXRD patterns of compound **1**.

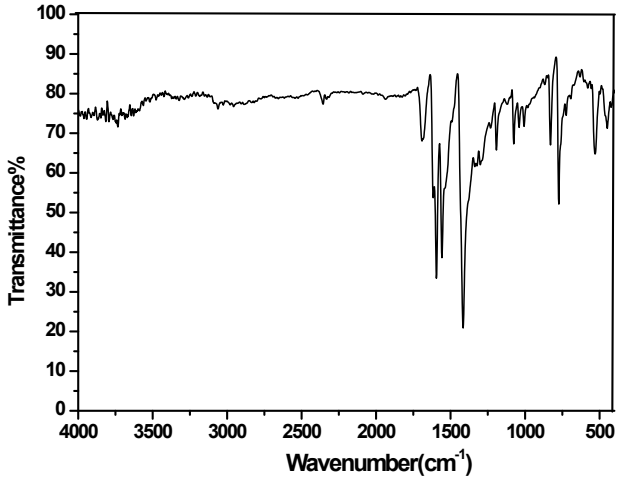


Fig. S12 The IR spectra of the complex **1**.

Supporting Tables:

Table S1 A summary of interpenetrating *dia* nets assembled by L ligands

Formula	interpenetrating degree	Ref.
$Cd^{II}Cu^{I}_2L_4$	25	5
$CdL_2·H_2O$	7	6
$CuL·2H_2O$	6	7
$[Zn_2(\mu\text{-}OH)L_3]·EtOH$	5	6
$[Cd(L_2)_2](DMF)(H_2O)_{0.25}$	4	8
$[CoL_2]·(MeOH)_{2.5}·(H_2O)$	4	9
$[CoL_2]·2DMF$	4	10
$Co(L_2)_2$	4	11
$[Cu^{II}_4(\mu_4\text{-}O)L_4][Cu^{I}_6Br_8]$	3	this work

Table S2. Bond valence sum (BVS) analysis[a]

bond	r_0	r_{ij}	B	$S_{ij} = \exp[(r_0\text{-}r_{ij})/B]$
Cu(1)-O(1)	1.679	1.968	0.37	0.458
Cu(1)-O(2)#1	1.679	1.943	0.37	0.490
Cu(1)-O(3)#2	1.679	1.948	0.37	0.483
Cu(1)-N	1.61	1.972	0.37	0.376
				V_{Cu1} = 1.81
Cu(2)-Br(2)	1.99	2.478	0.37	0.267
Cu(2)-Br(2)#3	1.99	2.478	0.37	0.267
Cu(2)-Br(3)#4	1.99	2.567	0.37	0.210
Cu(2)-Br(3)#5	1.99	2.567	0.37	0.210
				V_{Cu2} = 0.95
Cu(3)-Br(2)	1.99	2.494	0.37	0.256
Cu(3)-Br(2)#6	1.99	2.494	0.37	0.256
Cu(3)-Br(3)	1.99	2.542	0.37	0.225
Cu(3)-Br(3)#6	1.99	2.542	0.37	0.225
				V_{Cu3} = 0.96
Cu(4)-Br(2)(av)	1.99	3.1605	0.37	0.430
Cu(4)-Br(2)#6(av)	1.99	3.1605	0.37	0.430
Cu(4)-Br(3)(av)	1.99	2.302	0.37	0.042
Cu(4)-Br(3)#7(av)	1.99	2.302	0.37	0.042
				V_{Cu4} = 0.94

Cu(5)-Br(2)(av)	1.99	3.1339	0.37	0.045
Cu(5)-Br(2)#3(av)	1.99	3.1339	0.37	0.045
Cu(5)-Br(3)(av)	1.99	2.2923	0.37	0.442
Cu(5)-Br(3)#3(av)	1.99	2.2923	0.37	0.442
				V_{Cu5} = 0.97

Symmetry codes: #1 *x*-3/4, *y*-1/4, -*z*+1/2; #2 *x*-3/4, -*y*+1, *z*+1/4; #3 -*x*+9/4, *y*, -*z*+1/4; #4 *x*+1/2, -*y*+3/4, -*z*+1/4; #5 -*x*+11/4, -*y*+3/4, *z*; #6 *x*-1/2, -*y*+3/4, -*z*+1/4; #7 -*x*+5/4, *y*, -*z*+1/4.

[a] $V_i = \Sigma S_{ij} = \Sigma \exp[(r_0 - r_{ij})/B]$, where r_0 is the length of a single bond, r_{ij} is the bond length between atoms *i* and *j*; B is a constant, the "universal parameter" ~0.37 Å; S_{ij} is the valence of a bond between atoms *i* and *j*; V_i is the sum of all bond valences of the bonds formed by a given atom *i*.

Table S3 Hydrogen bond lengths (Å) and bond angles (°) for compound **1**

Hydrogen bonds				
D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
C(5)-H(5A)···Br(2)#1	0.93	3.111(7)	3.826(8)	134.92
C(2)-H(2A)···Br(3)·	0.93	3.247(2)	3.968(8)	136.07
Symmetry codes: #1 -3/4+*x*, 1-*y*, 1/4+*z*.				

Table S4 Temperature dependence of the unit-cell parameters of compound **1**.

T/K	a/ Å	b/Å	c/Å	V/ Å^3
100	7.990(2)	33.891(12)	39.171(10)	10606(7)
150	8.016(4)	34.031(15)	39.104(12)	10667(7)
200	8.029(3)	34.156(15)	39.004(11)	10697(7)
250	8.048(3)	34.246(15)	38.862(10)	10712(7)
300	8.081(5)	34.383(2)	38.714(17)	10757(10)
350	8.108(6)	34.426(3)	38.659(3)	10791(15)
400	8.122(5)	34.494(15)	38.558(10)	10803(11)
450	8.133(3)	34.586(11)	38.477(10)	10824(10)
500	8.147(5)	34.774(10)	38.424(12)	10877(12)

Table S5 Crystal data and structural refinement results

Complex	**1**	**2**
formula	$[Cu^{II}_4(\mu_4\text{-}O)L_4][Cu^{I}_6Br_8]$	$[Cu^{II}_4(\mu_4\text{-}O)L_4][Cu^{I}_6Br_8]$
formula weight	2083.46	2083.46
Temperature (K)	100(2)	298(2)
crystal system	orthorhombic	orthorhombic
Space group	*Fddd*	*Fddd*
a (Å)	7.98780(10)	8.072(2)
b (Å)	33.9352(6)	34.284(10)
c (Å)	39.1992(7)	38.825(11)

V (Å^3)	10625.6(3)	10745(5)
Z	8	8
Dc (g cm^{-3})	2.605	2.576
μ (mm^{-1})	11.810	9.883
reflns collected	9896	19873
unique reflns	2692	3073
R_{int}	0.0227	0.0545
completeness	99.1%	99.1%
GOF on F^2	1.166	1.091
R_1[a]/wR_2[b][$I>2\sigma(I)$]	0.0606/0.1881	0.0616/0.1963
R_1[a]/wR_2[b](all data)	0.0616/0.1884	0.0685/0.2043

[a]$R_1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$. [b]$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$.

Table S6 Coordination bond lengths and angles of **1**

Bond lengths	100 K	298 K	Bond angles	100 K	298 K
Cu(1)-O(1)	1.9684(10)	1.9735(8)	O(2)#1-Cu(1)-O(3)#2	113.5(2)	114.8(3)
Cu(1)-O(2)#1	1.943(5)	1.942(5)	O(2)#1-Cu(1)-O(1)	102.84(15)	102.37(16)
Cu(1)-O(3)#2	1.948(6)	1.951(5)	O(3)#2-Cu(1)-O(1)	105.88(15)	105.97(16)
Cu(1)-N	1.972(6)	1.973(5)	O(2)#1-Cu(1)-N	106.2(2)	105.0(3)
Cu(2)-Br(2)	2.4776(16)	2.4755(19)	O(3)#2-Cu(1)-N	112.0(2)	112.1(2)
Cu(2)-Br(2)#3	2.4776(16)	2.4755(19)	N-Cu(1)-O(1)	116.27(17)	116.59(19)
Cu(2)-Br(3)#4	2.5666(16)	2.5914(18)	Br(2)-Cu(2)-Br(2)#3	110.95(12)	108.99(10)
Cu(2)-Br(3)#5	2.5666(16)	2.5914(18)	Br(2)-Cu(2)-Br(3)#4	108.75(3)	109.12(3)
Cu(3)-Br(2)	2.4935(17)	2.4872(19)	Br(2)-Cu(3)-Br(3)	108.74(3)	108.98(3)
Cu(3)-Br(2)#6	2.4935(17)	2.4872(19)	Br(2)#6-Cu(3)-Br(3)	109.33(3)	109.62(3)
Cu(3)-Br(3)	2.5421(16)	2.5672(18)	Br(3)#6-Cu(3)-Br(3)	113.69(11)	114.30(10)
Cu(3)-Br(3)#6	2.5421(16)	2.5672(18)	Br(3)-Cu(4)-Br(3)#7	121.6(2)	123.2(2)
Cu(4)-Br(2)(av)	3.1605(1)	3.1575(5)	Br(3)#5-Cu(4)-Br(2)	117.89(18)	116.9(2)
Cu(4)-Br(2)#6(av)	3.1605(1)	3.1575(5)	Br(3)-Cu(5)-Br(2)#4	116.9(2)	117.0(2)
Cu(4)-Br(3)(av)	2.302(1)	2.3072(5)	Br(3)#4-Cu(5)-Br(2)#4	117.1(2)	115.6(2)
Cu(4)-Br(3)#7(av)	2.302(1)	2.3072(5)			
Cu(5)-Br(2)(av)	3.1339(5)	3.1331(5)			
Cu(5)-Br(2)#3(av)	3.1339(5)	3.1331(5)			
Cu(5)-Br(3)(av)	2.2923(5)	2.3016(5)			
Cu(5)-Br(3)#3(av)	2.2923(5)	2.3016(5)			

Symmetry codes: #1 x-3/4, y-1/4, -z+1/2; #2 x-3/4, -y+1, z+1/4; #3 -x+9/4, y, -z+1/4; #4 x+1/2, -y+3/4, -z+1/4; #5 -x+11/4, -y+3/4, z; #6 x-1/2, -y+3/4, -z+1/4; #7 -x+5/4, y, -z+1/4.

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