Electronic Supplementary Information

$Ag_{10}Cu_{16}$ Nanocluster with Triple-Ligand Protection: Total Structure and Electronic Structure Analysis

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EXPERIMENTAL SECTION

Reagents: Copper (II) trifluoroacetate ($Cu(CF_3CO_2)_2$, 98%) was purchased from Adamas. (Shanghai, China). Silver trifluoroacetate ($AgCF_3CO_2$, 98%) and triphenylphosphine (PPh_3, 99%) was purchased from EnergyChemical. (Shanghai, China). Sodium borohydride ($NaBH_4$, 99%) and 2-phenylethylmercaptan ($C_8H_{10}S$, 99.5%) was purchased from Bide Pharmatech Ltd. (Beijing, China). Dichloromethane (CH_2Cl_2, A.R.), methanol (CH_3OH, A.R.) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). All other reagents were used as received without further purification.

Synthesis of $[Ag_{10}Cu_{16}(C_8H_9S)_{16}(PPh_3)_4(CF_3CO_2)_8]$: $Cu(CF_3CO_2)_2$ (22 mg, 0.076 mmol), $AgCF_3CO_2$ (5.5 mg, 0.025 mmol), $C_8H_{10}S$ (8 uL, 0.060 mmol) and PPh_3 (10 mg, 0.038 mmol) were dissolved in 4 ml of a mixed solvents of CH_2Cl_2 and MeOH (CH_2Cl_2:MeOH = 3:1). The reducing agent, 40 mg $NaBH_4$ in 1 mL ethanol, was then added dropwise, followed by stirring for 24 hours. The supernatant was harvested by centrifugation. After that, the solution was subjected to diffusion of hexane. Red block crystals were obtained after two weeks in the yield of ~34.5% (based on Ag). Elemental Anal. Theoretical: C, 41.55%; H, 3.29%; S, 8.22%; Found: C, 42.34%; H, 3.68%; S, 8.62%.

Characterizations

UV/Vis spectra of $Ag_{10}Cu_{16}$ cluster were collected by JascoV-650 Spectrophotometer using a quartz cuvette of 1 mm path length. The spectra were recorded in diluted solutions of dichloromethane and the signal of the blank solvent was subtracted.

Electrospray ionization mass spectra (ESI-MS) of $Ag_{10}Cu_{16}$ cluster were recorded using an Agilent 6224 time-of-flight mass spectrometer in both positive and negative modes. The samples dissolved in dichloromethane were directly infused at a flow rate of 1.2 mL/h by a syringe pump. Typical parameters used for the measurements were as follows: capillary voltage: 4.0 kV; drying gas temp: 150℃; drying gas flow: 4 L/min; nebulizer pressure: 20 psi.

^1H and ^{13}C NMR spectra of $Ag_{10}Cu_{16}$ cluster were recorded at room temperature on a Bruker AV-600 spectrometer with TMS and solvent residual signal as an internal reference. All NMR data were processed on MestReNova software.

X-ray single-crystal analysis: The diffraction data of the single crystals of $Ag_{10}Cu_{16}$ cluster was collected on a Rigaku Oxford Diffraction system X-ray single-crystal diffractometer using Cu Kα (λ= 1.54184 Å) at 100 K. The data was processed using CrysAlis^{Pro}. The structure was solved and refined using Full-matrix least-squares based on F^2 using ShelXT,[1] ShelXL[2] in Olex2,[3] and Shelxle.[4] The thermal ellipsoids of the ORTEP diagram were done at 50% probability. Detailed crystal data and structure refinements for the compound is given in Table S1. CCDC 2257991 contains the

supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

Computational Details

Density functional theory (DFT) calculations were performed by using Gaussian 16 package.[5] The generalized gradient approximation (GGA) Perdew−Burke−Ernzerhof (PBE) exchange-correlation functional,[6,7] together with an all-electron triple-z-polarized Def2_TZVP[8] basis set were used. Dispersion forces were considered via the empirical pairwise corrections of Grimme (DFT-D3).[9] The plots of the molecular orbitals were generated by using Multiwfn software[10] with an isovalue of 0.02 (e/bohr3) 1/2.

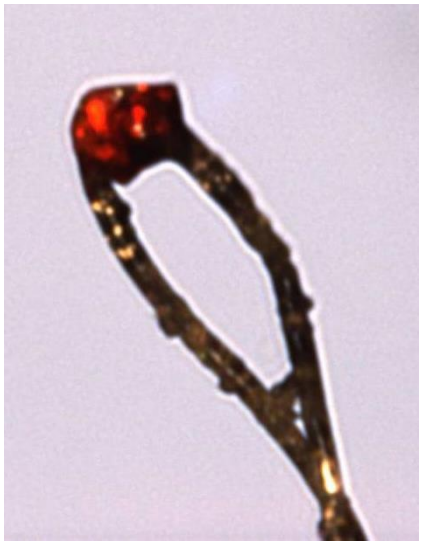

Figure S1. Digital photographs of single crystals of $Ag_{10}Cu_{16}$ cluster.

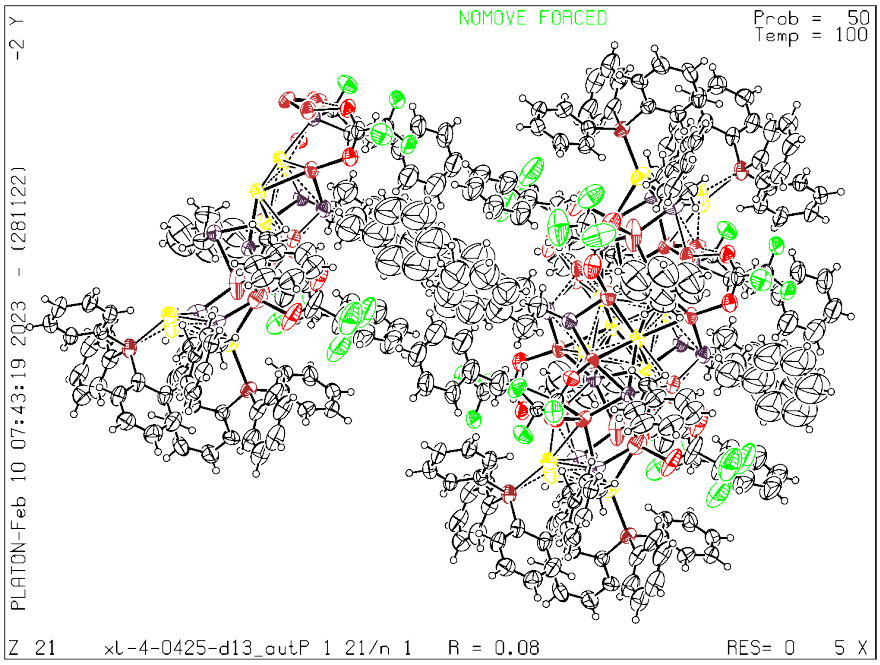

Figure S2. The thermal ellipsoids of the ORTEP diagram of $Ag_{10}Cu_{16}$ cluster.

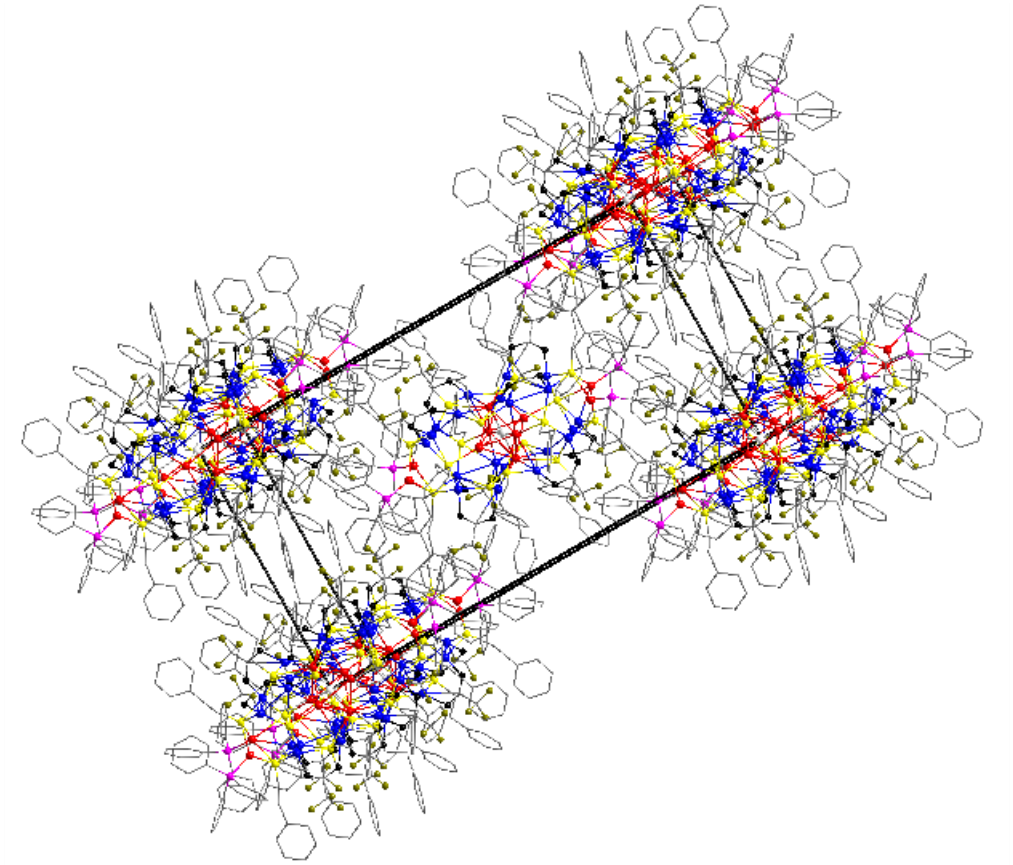

Figure S3. The packing structure of $Ag_{10}Cu_{16}$ clusters in their single crystals. Color legend: red spheres, Ag; blue spheres, Cu; pink spheres, P; yellow spheres, S; brown spheres, F; black spheres, O; gray spheres, C. All hydrogen atoms are omitted for clarity.

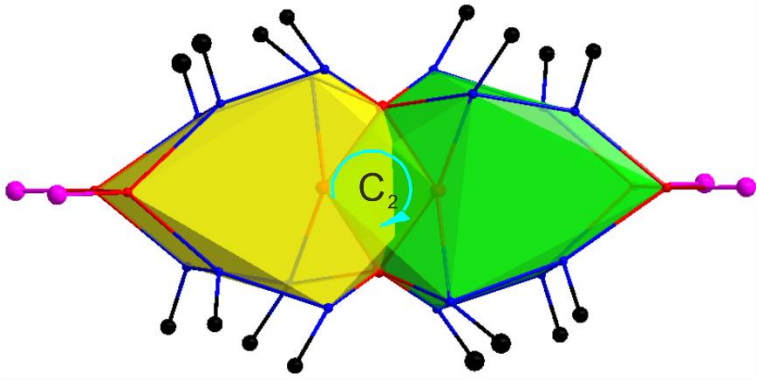

Figure S4. Structure of $Ag_{10}Cu_{16}$ showing the crystallographic C_2 symmetry axis. Color legend: red spheres, Ag; blue spheres, Cu; pink spheres, P; black spheres, O; gray spheres, C. All other atoms are omitted for clarity.

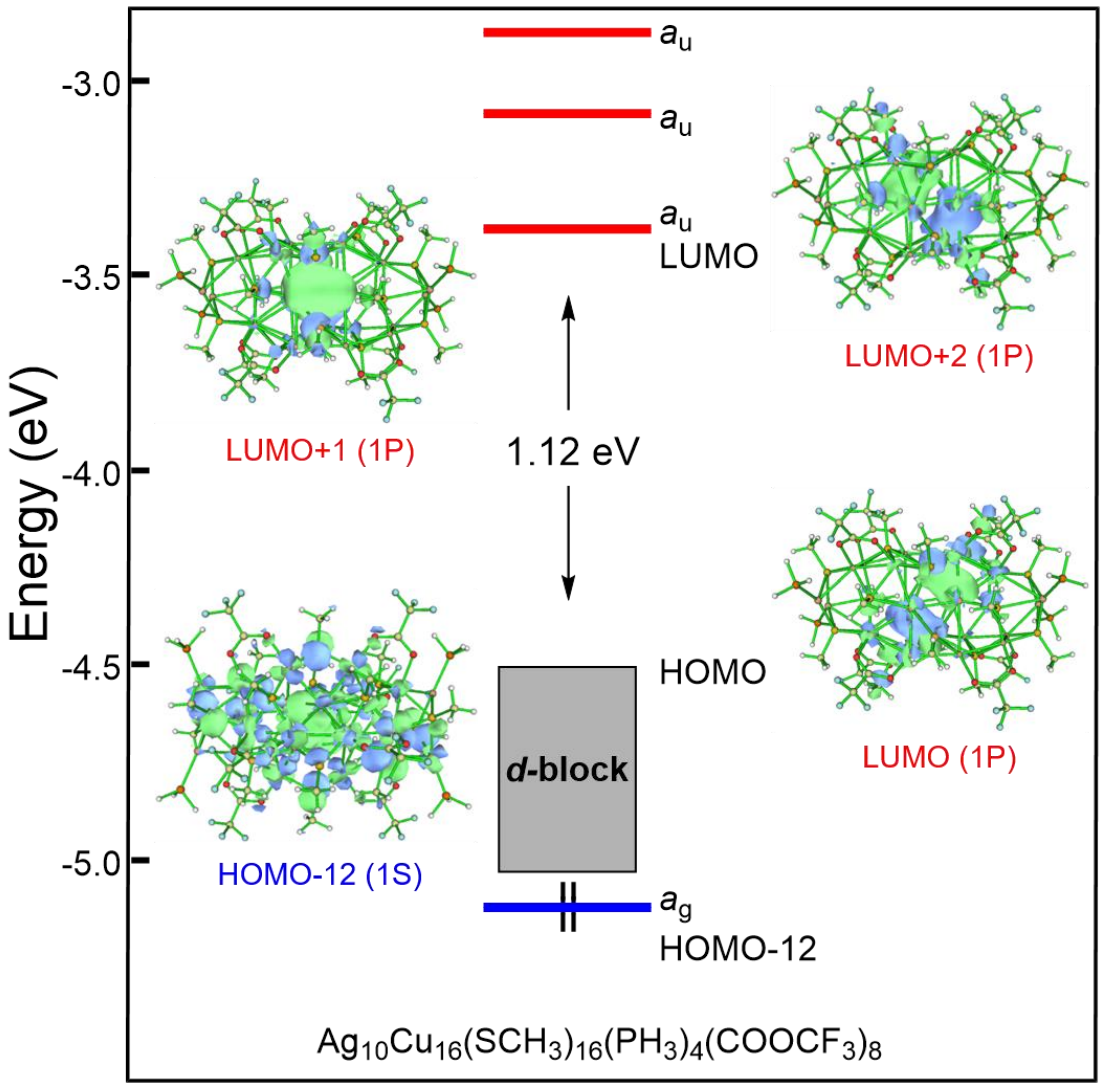

Figure S5. Kohn-Sham MO diagram of $Ag_{10}Cu_{16}(SCH_3)_{16}(PH_3)_4(CF_3CO_2)_8$ with the plots of the occupied *superatomic* 1S orbital (blue stick) and three vacant *superatomic* 1P orbitals (red sticks). The isovalue is 0.02 (e/bohr3) 1/2.

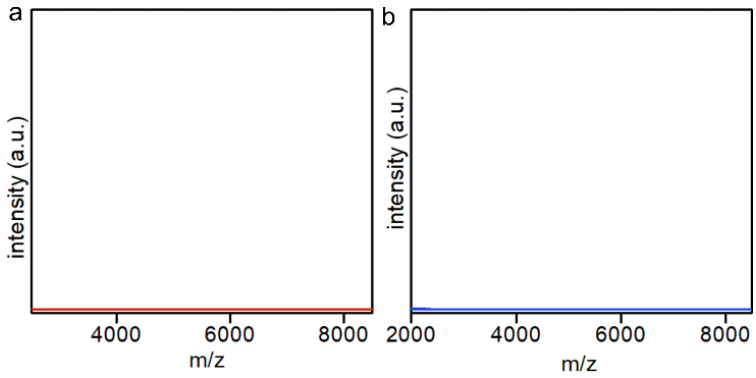

Figure S6. ESI-MS of $Ag_{10}Cu_{16}$ clusters in the positive and negative mode. The absence of molecular peaks suggests the neutral state of the cluster.

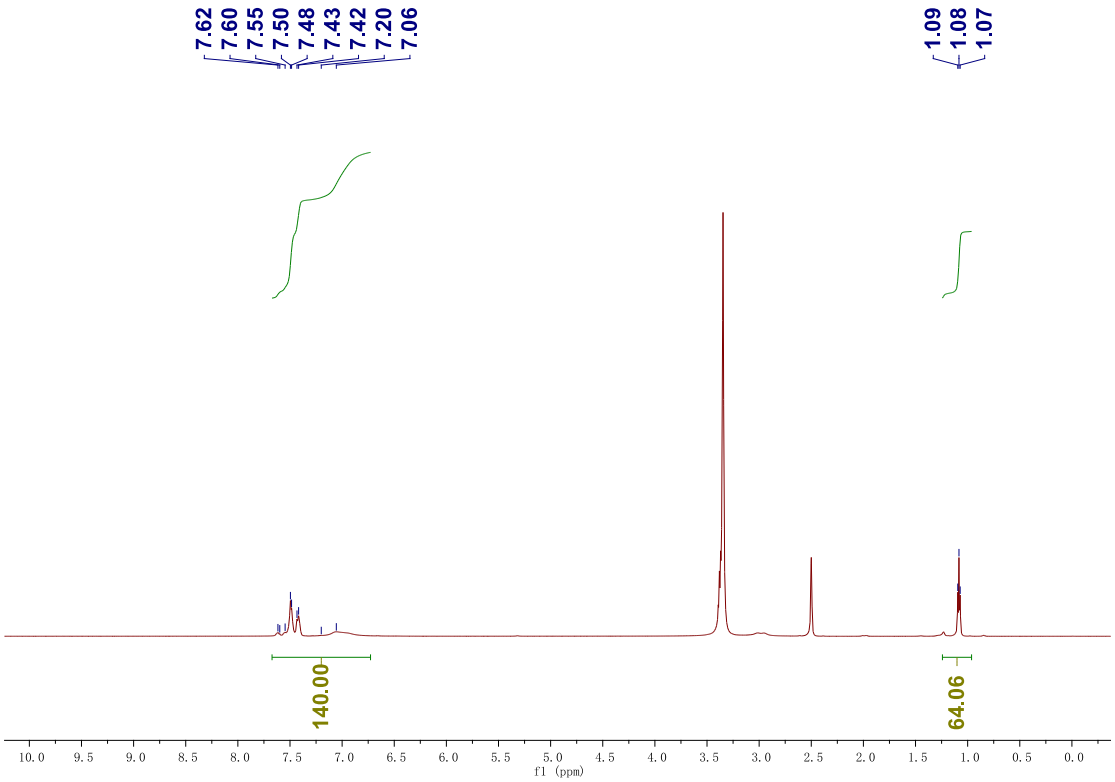

Figure S7. ^{1}H NMR of $Ag_{10}Cu_{16}$ clusters in d_6-DMSO.

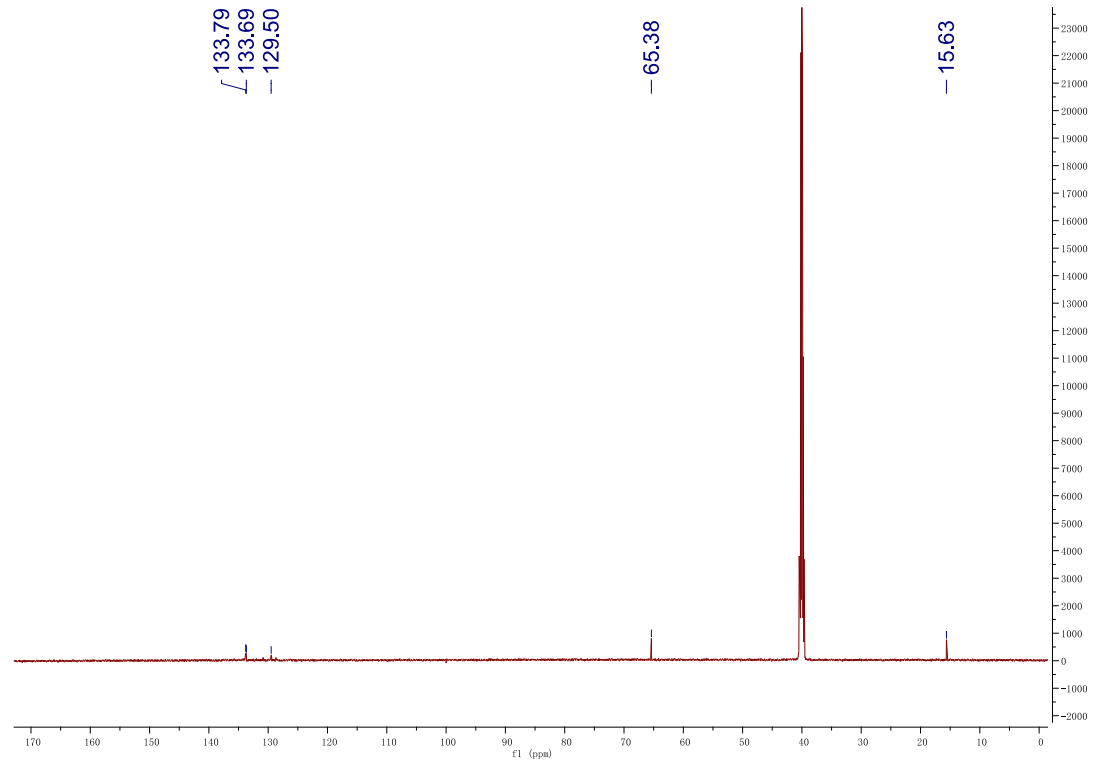

Figure S8. ^{13}C NMR of $Ag_{10}Cu_{16}$ clusters in d_6-DMSO.

Table S1. Crystal data and structure refinement for $Ag_{10}Cu_{16}(C_8H_9S)_{16}(PPh_3)_4(CF_3CO_2)_8$.

Identification code	cif-revised
Empirical formula	$C_{216}H_{204}Ag_{10}Cu_{16}F_{24}O_{16}P_4S_{16}$
Formula weight	6243.96
Temperature/K	100(1)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	18.3848(2)
b/Å	34.2944(4)
c/Å	18.6956(2)
α/°	90
β/°	96.2820(10)
γ/°	90
Volume/Å^3	11716.7(2)
Z	2
ρ_{calc}g/cm^3	1.770
μ/mm^{-1}	10.258
F(000)	6188.0
Radiation	CuK\a (λ = 1.54184)
2Θ range for data collection/°	5.154 to 128
Index ranges	$-21 \le h \le 21$, $-39 \le k \le 33$, $-21 \le l \le 18$
Reflections collected	121130
Independent reflections	19432 [R_{int} = 0.0479 R_{sigma} = 0.0296]
Data/restraints/parameters	19432 /921/1492
Goodness-of-fit on F^2	1.097
Final R indexes [I>=2σ (I)]	R_1 = 0.0778, wR_2 = 0.2393
Final R indexes [all data]	R_1 = 0.0932, wR_2 = 0.2525
Largest diff. peak/hole / e Å^{-3}	1.97/-2.07

Table S2. Selected bond lengths (Å) for cluster $Ag_{10}Cu_{16}$.

Parameter	value	Parameter	value
Ag01-Ag02	2.8090(12)	Ag05-Cu0C	3.204(3)
Ag01-Ag03	2.8733(11)	Ag05-S00G	2.840(3)
Ag01-Ag03	2.8235(11)	Ag05-S00I	2.477(3)
Ag01-Cu06	2.6962(16)	Ag05-S00K	2.589(3)
Ag01-Cu08	2.6731(17)	Ag05-P00L	2.341(3)
Ag01-Cu09	2.721(2)	Cu06-Ag01	2.6963(16)
Ag01-Cu0B	2.687(2)	Cu06-Cu07	2.885(2)
Ag01-S00E	2.762(3)	Cu06-Cu09	3.037(2)
Ag01-S00F	2.842(3)	Cu06-S00E	2.250(3)
Ag02-Ag01	2.8050(12)	Cu06-S00N	2.183(4)
Ag02-Ag03	2.8013(14)	Cu06-O00O	2.059(7)
Ag02-Ag03	2.7850(14)	Cu07-Ag05	3.145(2)
Ag02-Cu09	2.8259(18)	Cu07-Cu0A	2.828(3)
Ag02-Cu0B	2.888(2)	Cu07-S00E	2.411(3)
Ag02-S00H	2.471(3)	Cu07-S00G	2.270(3)
Ag02-S00N	2.774(4)	Cu07-S00I	2.357(3)
Ag03-Ag01	2.8734(11)	Cu07-O00Q	2.116(7)
Ag03-Ag02	2.8013(14)	Cu08-Cu0C	2.858(3)
Ag03-Cu06	3.0910(16)	Cu08-S00F	2.242(3)
Ag03-Cu08	2.9898(17)	Cu08-S00M	2.193(4)
Ag03-S00G	2.453(3)	Cu08-O00W	2.063(8)
Ag04-Ag05	3.1044(15)	Cu09-Ag01	2.7211(19)
Ag04-Cu0A	2.983(3)	Cu09-S00F	2.235(3)
Ag04-Cu00	3.175(4)	Cu09-S00N	2.203(4)
Ag04-S00I	2.524(3)	Cu09-O010	2.074(10)
Ag04-P00J	2.315(3)	Cu0A-Cu07	2.828(3)
Ag04-S00K	2.436(3)	Cu0A-S00H	2.218(3)
Ag05-Cu07	3.146(2)	Cu0A-S00I	2.203(4)
Cu0A-O00Z	2.039(9)	Cu0C-S00K	2.306(4)
Cu0B-S00E	2.259(3)	Cu0C-O00V	2.049(8)

Cu0B-S00M	2.173(4)	Cu00-Cu0C	2.749(3)
Cu0B-O019	2.112(13)	Cu00-S00F	2.691(4)
Cu0C-Ag05	3.204(3)	Cu00-S00H	2.230(4)
Cu0C-Cu00	2.749(3)	Cu00-S00K	2.283(5)
Cu0C-S00F	2.560(4)	Cu00-O00Y	2.064(9)
Cu0C-S00G	2.256(4)		

Table S3. Optimized Fractional Atomic Coordinates of $Ag_{10}Cu_{16}$.

Ag	-0.264559	0.2635	-1.969589	C	-0.17597	6.58254	3.288486
Ag	-1.578947	1.166386	0.341092	H	0.725856	6.304802	3.846886
Ag	-1.663288	6.564344	-0.126737	H	-0.20318	7.668632	3.146748
Cu	-1.829484	-1.613665	2.987925	C	-4.25816	4.307407	4.92573
Cu	-1.371942	-4.162981	2.34541	H	-1.07709	6.249661	3.816502
Cu	-2.15874	-1.464149	-2.779215	C	-4.131847	-3.283702	0.232404
Cu	-1.808429	1.224274	3.044265	H	-4.661392	-3.863851	0.997346
Cu	-1.364672	-3.820596	-1.758897	H	-4.243897	-2.209693	0.422197
Cu	-1.190648	3.577905	1.838875	H	0.463726	2.433298	5.709853
Cu	-1.164295	4.580237	-2.022178	H	-4.126624	4.505573	0.836283
Ag	0.264559	-0.2635	1.969589	C	-3.984789	3.746127	0.058978
Ag	1.578947	-1.166386	-0.341092	H	-4.468141	4.038691	-0.879667
Cu	1.829484	1.613665	-2.987925	H	-4.389922	2.783963	0.393359
Cu	1.371942	4.162981	-2.34541	C	-4.788525	5.040125	-4.342757
Cu	2.15874	1.464149	2.779215	H	-4.509902	-3.528505	-0.76651
Cu	1.808429	-1.224274	-3.044265	H	-4.346167	0.582219	-4.236578
Cu	1.364672	3.820596	1.758897	C	-4.792899	0.213302	-3.308707
Cu	1.190648	-3.577905	-1.838875	H	-5.2307	-0.777201	-3.47076
Cu	1.164295	-4.580237	2.022178	H	-5.554359	0.926735	-2.973052
Ag	1.663288	-6.564344	0.126737	S	0.21441	-2.593927	3.19392
Cu	-2.344369	2.029442	-2.190368	S	-0.151336	-2.334363	-3.317052
Ag	-1.175646	-1.607086	-0.09443	S	-0.400223	-6.269318	1.800341
Ag	1.993971	6.396138	0.212826	S	0.117185	-5.763801	-1.655712
Cu	2.344369	-2.029442	2.190368	S	-3.174412	-0.185365	1.947861
Ag	1.175646	1.607086	0.09443	S	2.362302	3.736019	-0.316235
Ag	-1.993971	-6.396138	-0.212826	S	2.189608	-3.53735	0.242616
S	-0.21441	2.593927	-3.19392	S	3.532091	-0.083067	1.971722
S	0.151336	2.334363	3.317052	P	3.636702	-7.540661	0.979105
S	-2.362302	-3.736019	0.316235	F	3.314561	3.838757	-6.994888
S	-2.189608	3.53735	-0.242616	F	5.674455	4.908746	3.703738

S	0.400223	6.269318	-1.800341	F	5.152378	3.930926	5.590925
S	-0.117185	5.763801	1.655712	F	5.158518	3.50578	-5.854703
S	-3.532091	0.083067	-1.971722	F	4.206087	5.470585	-5.844757
P	-3.636702	7.540661	-0.979105	F	4.209261	5.825071	5.054473
F	-3.314561	-3.838757	6.994888	F	5.384436	-4.194537	5.204278
F	-5.674455	-4.908746	-3.703738	F	5.006283	-3.491481	-5.691467
F	-5.152378	-3.930926	-5.590925	F	4.479609	-6.170874	5.01442
F	-5.158518	-3.50578	5.854703	F	5.713991	-5.376628	3.387602
F	-4.206087	-5.470585	5.844757	F	5.101904	-5.084911	-4.203122
F	-4.209261	-5.825071	-5.054473	F	3.554479	-5.12832	-5.757282
F	-5.384436	4.194537	-5.204278	O	2.984853	2.443706	-4.505918
F	-5.006283	3.491481	5.691467	O	2.622524	4.611839	-3.907038
F	-4.479609	6.170874	-5.01442	O	2.820334	4.622354	3.051206
F	-5.713991	5.376628	-3.387602	O	3.465356	2.641775	3.973696
F	-5.101904	5.084911	4.203122	O	2.739139	-4.2496	-3.107666
F	-3.554479	5.12832	5.757282	O	2.645744	-5.22319	3.31376
O	-2.984853	-2.443706	4.505918	O	3.0875	-2.320844	-4.270087
O	-2.622524	-4.611839	3.907038	O	3.638795	-3.17259	3.418847
O	-2.820334	-4.622354	-3.051206	C	3.105289	3.692064	-4.616999
O	-3.465356	-2.641775	-3.973696	C	3.521224	3.880088	3.795281
O	-2.739139	4.2496	3.107666	C	3.962592	4.14335	-5.838347
O	-2.645744	5.22319	-3.31376	H	4.745104	-6.68276	1.194132
O	-3.0875	2.320844	4.270087	C	0.492131	-2.765261	4.995406
O	-3.638795	3.17259	-3.418847	H	1.166289	-3.614686	5.152658
C	-3.105289	-3.692064	4.616999	H	-0.468776	-2.938321	5.49105
C	-3.521224	-3.880088	-3.795281	H	0.952158	-1.843617	5.368043
C	-3.962592	-4.14335	5.838347	C	-0.451057	-7.265199	3.338006
H	-4.745104	6.68276	-1.194132	H	0.474699	-7.085946	3.896867
C	-0.492131	2.765261	-4.995406	H	-0.532345	-8.325647	3.073276
H	-1.166289	3.614686	-5.152658	H	-1.318104	-6.949401	3.929419
H	0.468776	2.938321	-5.49105	H	4.342446	-8.609092	0.360864
H	-0.952158	1.843617	-5.368043	C	4.647516	4.637073	4.565448
C	0.451057	7.265199	-3.338006	C	-0.205595	-3.172961	-4.944853
H	-0.474699	7.085946	-3.896867	H	-0.965171	-3.960143	-4.903731
H	0.532345	8.325647	-3.073276	H	0.780649	-3.601581	-5.148954
H	1.318104	6.949401	-3.929419	H	3.567083	-8.083376	2.287544
H	-4.342446	8.609092	-0.360864	C	3.552596	-4.40479	3.633713
C	-4.647516	-4.637073	-4.565448	C	3.266576	-3.536499	-4.000237
C	0.205595	3.172961	4.944853	C	0.17597	-6.58254	-3.288486
H	0.965171	3.960143	4.903731	H	-0.725856	-6.304802	-3.846886
H	-0.780649	3.601581	5.148954	H	0.20318	-7.668632	-3.146748
H	-3.567083	8.083376	-2.287544	C	4.25816	-4.307407	-4.92573
C	-3.552596	4.40479	-3.633713	H	1.07709	-6.249661	-3.816502

C	-3.266576	3.536499	4.000237	C	4.131847	3.283702	-0.232404
H	4.243897	2.209693	-0.422197				
H	-0.463726	-2.433298	-5.709853				
H	4.126624	-4.505573	-0.836283				
C	3.984789	-3.746127	-0.058978				
H	4.468141	-4.038691	0.879667				
H	4.389922	-2.783963	-0.393359				
C	4.788525	-5.040125	4.342757				
H	4.509902	3.528505	0.76651				
H	4.346167	-0.582219	4.236578				
C	4.792899	-0.213302	3.308707				
H	5.2307	0.777201	3.47076				
H	5.554359	-0.926735	2.973052				
S	3.174412	0.185365	-1.947861				
P	3.890035	7.265588	1.321028				
H	4.997944	6.392346	1.466481				
H	3.739797	7.595515	2.691984				
H	4.617426	8.422287	0.92473				
P	-3.890035	-7.265588	-1.321028				
H	-4.997944	-6.392346	-1.466481				
H	-3.739797	-7.595515	-2.691984				
H	-4.617426	-8.422287	-0.92473				
C	-4.808058	-0.018172	2.780921				
C	4.808058	0.018172	-2.780921				
H	-4.859613	0.940512	3.305954				
H	-5.582778	-0.083765	2.007571				
H	-4.904736	-0.841631	3.497401				
H	4.859613	-0.940512	-3.305954				
H	5.582778	0.083765	-2.007571				
H	4.904736	0.841631	-3.497401				

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