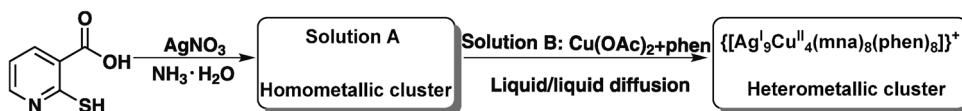


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Stepwise Construction of a $\text{Ag}^{\text{I}}_9\text{-Cu}^{\text{II}}_4$ Heterometallic Cluster Incorporating Two Unusual Vertex-Shared Trigonal-Bipyramidal Silver Polyhedra

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The chemistry of heterometallic clusters is of great interest because of their structural diversities and distinctive functionalities, such as optical,^[1] magnetic,^[2] and electrical^[3] properties. In contrast to homometallic clusters, heterometallic clusters remain relatively rare, given that their assembly is usually more intricate because it requires hierarchical donors to bind different metal ions. To date, a number of 3d–4f polynuclear clusters, such as $\text{Pr}_{20}\text{Ni}_{21}$, $\text{La}_{20}\text{Ni}_{30}$, $\text{Gd}_{54}\text{Ni}_{54}$, and $\text{La}_{60}\text{Ni}_{76}$, have been synthesized in one-pot procedures by simultaneous combination of inorganic metal salts and organic ligands;^[4] however, stepwise assembly of heterometallic clusters based on presynthesized metal-containing precursors with vacant donors is still a great challenge.^[5] Although simple mono- and binuclear species have been extensively employed in the preparation of heterometallic compounds,^[6] polynuclear silver(I) clusters as precursors have received much less attention. We have synthesized a series of polymeric and discrete $\text{Ag}^{\text{I}}\text{-M}^{\text{II}}$ ($\text{M} = \text{Cu}, \text{Zn}$) heterometallic complexes^[7] through the use of carboxy-containing hexanuclear $[\text{Ag}_6(\text{mna})_6]^{6-}$, $\text{H}_2\text{mna} = 2\text{-mercaptopyridonic acid}$ ^[8] or nonanuclear $[\text{Ag}_9(\text{mba})_9]^{9-}$, $\text{H}_2\text{mba} = 2\text{-mercaptobenzoic acid}$ ^[7b] silver cluster as metalloligand. As an extension of our work on heterometallic complexes and under consideration of the fact that greater diversity translates to a loss of structural predictability, as slight variations in synthetic procedures and reactants can yield novel structures, when replacing previous Cu^{II} 2,2'-bipyridine or Cu^{II} ethylenediamine component by Cu^{II} phen, we surprisingly obtained a homometallic $[\text{Ag}_9(\text{mna})_8]^{7-}$ cluster built from two vertex-shared trigonal-bipyramidal silver polyhedra, which is an important precursor in the formation of the heterometallic $\text{Ag}^{\text{I}}_9\text{-Cu}^{\text{II}}$



Scheme 1. Schematic presentation of stepwise synthesis of **1**.

cluster, namely $\{[\text{Ag}^{\text{I}}_9\text{Cu}^{\text{II}}_4(\text{mna})_8(\text{phen})_8](\text{OAc})\cdot 16\text{H}_2\text{O}\}$ (**1**, phen = 1,10-phenanthroline).

In a typical synthesis, green crystals of **1** were obtained using a stepwise approach (Scheme 1): 1) synthesis of the anionic silver cluster precursor; 2) synthesis of cationic component containing the Cu^{II} center; 3) assembly of the two presynthesized components through liquid/liquid diffusion

method. It is noteworthy that the liquid/liquid diffusion method in the last step is very important for forming the heterometallic cluster. Both directly mixing the two presynthesized solutions and a one-pot synthetic route resulted in the formation of a precipitate. The composition of **1** was further deduced from X-ray single crystal diffraction, elemental analysis, energy-dispersive X-ray spectroscopy (EDS), and IR spectroscopy. The IR spectrum (Figure S1 in the Supporting Information) of complex **1** shows 1) an intense broad band around 3450 cm^{-1} attributed to the existence of water molecules, 2) disappearance of the S–H stretching band around 2560 cm^{-1} due to the SH group in the “free” H_2mba , suggesting the formation of Ag–S bond in **1**, and 3) the absence of band in the region of $1690\text{--}1730\text{ cm}^{-1}$, indicating complete deprotonation of the carboxy groups.^[9] Phase purity of **1** is ascertained by its powder X-ray diffraction pattern, which is consistent with that simulated on the basis of the single-crystal X-ray diffraction data (Figure S2 in the Supporting Information). EDS confirms the nature of the elements in **1** (Figure S3 in the Supporting Information). These results are in good agreement with solid-state crystal structures.

In spite of the long-known light-sensitive behavior of silver complexes,^[10] this heterometallic cluster is stable under ambient conditions without shade for several weeks to months. The molecular structure of **1** is determined from single-crystal X-ray diffraction data (Table S1 in the Supporting Information), and selected bond lengths and angles are presented in Table S2 in the Supporting Information. Cluster **1** crystallizes in the tetragonal space group $P4_2/n$ with a C_4i symmetry. On the basis of bond valence sum cal-

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culations (BVS) for Ag and Cu centers,^[11] uniform valence states of +1 and +2 can be assigned to all Ag and Cu positions, respectively. Analysis of the local symmetry of the cationic $[\text{Ag}^{\text{I}}_9\text{Cu}^{\text{II}}_4(\text{mna})_8(\text{phen})_8]^+$ part showed that a four-fold axis passes through Ag3 (site occupancy factor=0.25), which is also located on a crystallographic inversion center. As shown in Figure 1, cluster **1** consists of a homometallic $[\text{Ag}_9(\text{mna})_8]^{7-}$ cluster in the interior and four $[\text{Cu}(\text{phen})_2]^{2+}$ units on the periphery. The Ag_9 cluster structure can be un-

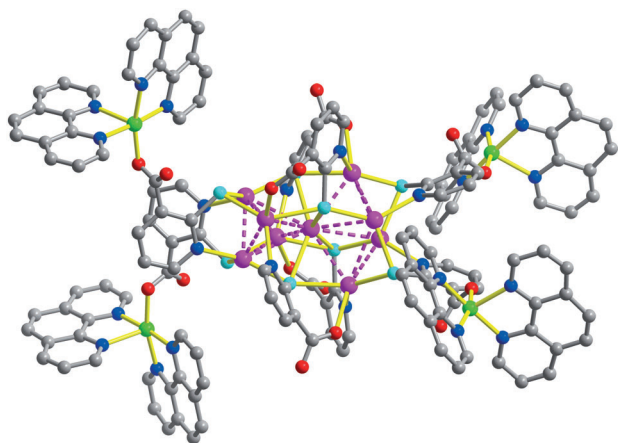


Figure 1. Centrosymmetric structure of the cationic part of **1**. Hydrogen atoms, OH^- , and water molecules are omitted for clarity. Ag violet, Cu green, S cyan, N blue, O red, C gray.

derstood as two symmetry-related trigonal-bipyramidal silver polyhedra (Figure 2) that share one vertex, forming a Ag_9 polyhedron surrounded by a hydrophilic sheath of eight mna ligands. Viewed along the a axis (Figure 3), four of eight mna ligands are located in equatorial positions with $\mu_4\text{-}\kappa^3\text{S}$, $\kappa^1\text{N}$, $\kappa^1\text{O}$ coordination mode, and the remaining four $\mu_3\text{-}\kappa^2\text{S}$, $\kappa^1\text{N}$ mna ligands are divided into two groups lying on the north and south poles. Furthermore, four pole mna ligands use free carboxylate groups to bind four $[\text{Cu}(\text{phen})_2]^{2+}$ units, completing the whole tridecanuclear $\text{Ag}^{\text{I}}_9\text{-Cu}^{\text{II}}_4$ heterometallic cluster. The Ag–O, Ag–N, and Ag–S distances are comparable to those in related complexes.^[12]

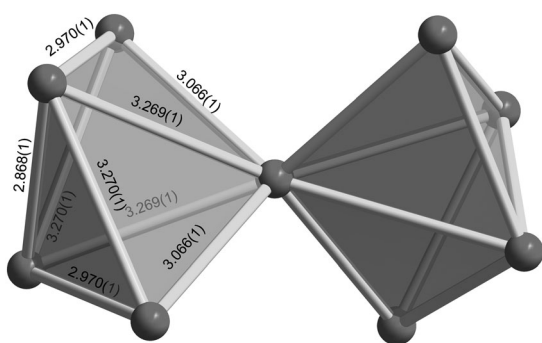


Figure 2. Double cage generated from two vertex-shared trigonal-bipyramidal Ag polyhedra.

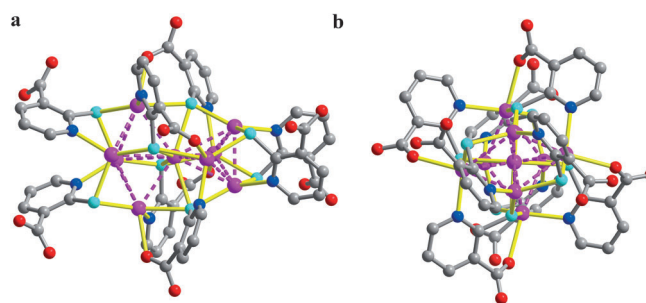


Figure 3. The ball-and-stick view of the anionic silver core with ligands along a) the a axis and b) the c axis. Ag violet, Cu green, S cyan, N blue, O red, C gray.

The shortest Ag \cdots Ag contact in the Ag_9 polyhedron is 2.8679(10) Å, which is slightly shorter than the Ag \cdots Ag distance (2.886 Å) in silver metal^[13] and hence suggests the existence of Ag \cdots Ag interactions of the same order of magnitude. The average Ag \cdots Ag distance of 3.0886(7) Å is still below the sum of the van der Waals radii of two Ag^{I} atoms (3.44 Å).^[14] The Cu^{II} center was coordinated by two phen ligands and one oxygen atom of mna (Cu1–N3 2.053(5), Cu1–N4 1.996(5), Cu1–N5 2.246(6), Cu1–N6 1.994(6), Cu1–O1 1.976(4) Å), resulting in a distorted square-pyramidal geometry with the τ_5 parameter of 0.155 (for an ideal square-pyramidal geometry, $\tau_5=0$).^[15] We also found the Jahn–Teller effect^[16] of this Cu^{II} center, which forms one longer and four shorter coordination bonds, similar to the reported $[\text{Cu}(2,2'\text{-bipyridine})_2\text{Cl}][\text{OH}]$.^[17]

Although silver polyhedra with various geometries, including tetrahedron,^[18] cube,^[19] tetracapped octahedron,^[20] bicapped square antiprism,^[21] triangulated dodecahedron,^[22] pentacapped trigonal prism,^[23] and hexacapped trigonal bipyramidal,^[24] have been documented, to date only one example of a nonanuclear silver(I) polyhedron with distorted monocapped square antiprismatic geometry was presented in the literature.^[22] To our knowledge, both the nuclearity and the structural motif of an interior vertex-shared nonanuclear silver(I) polyhedron in **1** is unprecedented.

The packing of this heterometallic cluster in the crystal is also very interesting. The mna ligands in two poles are clamped by phen ligands through intercluster $\pi_{\text{phen}}\cdots\pi_{\text{mna}}$ interactions (3.878(5) Å), as a consequence, adjacent clusters are assembled to a 1D cylinder along the c axis (Figure S4 in the Supporting Information). Furthermore, the 1D cylinders are extended into 2D sheet through the intercylinder $\pi_{\text{phen}}\cdots\pi_{\text{mna}}$ (3.712(4) Å) and $\pi_{\text{phen}}\cdots\pi_{\text{phen}}$ interactions (3.604(4), 3.669(3), 3.693(4), 3.833(4), and 3.878(5) Å). Owing to the size of the cluster, PLATON/VOID routine^[25] calculation suggests that there is a significant interstitial space of 25.2% (2138.0 Å³ out of the 8482.0 Å³ unit cell volume) accommodating the OAc^- counteranion and the additional water molecules in a severely disordered fashion.

It is noteworthy that the formation of the interior homometallic nonanuclear silver cluster in **1** is a great surprise to us. In our previous reports,^[7a,26] no matter what kinds of 3d

components (such as Cu^{II} 2,2'-bipyridine, Cu^{II} ethylenediamine, and Zn^{II} ethylenediamine) were employed, the hexanuclear silver metalloligand $[\text{Ag}_6(\text{mna})_6]^{6-}$ could keep its nuclearity and the Ag_6 octahedral geometry. However, under the same synthetic conditions, using Cu^{II} phen as the 3d component, we surprisingly obtained a Ag_9 instead of a Ag_6 polyhedron, which was at variance with our previous observation. A plausible explanation is that the bulkier Cu^{II} phen component influences the formation of the Ag_6 polyhedron, which is not stable enough in solution, as we expected. In a word, these kinds of hydrophilic Ag_n polyhedra are rather labile, and their structures can be influenced by many complicated factors. Comparison of the present work with our previous study of the silver-cluster-based heterometallic system shows that a slight change of 3d component can expand the scope of generating novel heterometallic structures.

To estimate the stability of cluster **1**, thermogravimetric analyses (TGA) were carried out under a N_2 stream with a heating rate of 5°Cmin^{-1} (Figure S5 in the Supporting Information). The TGA curve indicated that cluster **1** has a gradual weight loss between 30 and 121°C , corresponding to the release of uncoordinated water molecules (observed, 7.12%; calculated, 6.80%), and then the cluster started to decompose from 175°C along with the loss of phen and mna ligands.

The absorption spectrum of a green powder sample **1** was measured in the solid state at room temperature (Figure 4). The intense broad absorption band for **1** in the range 260–400 nm should be the ligand-based transition involving π orbitals of the aromatic ring of the mna moiety. Moreover, the broad low-energy peak of **1** at approximately 635 nm is

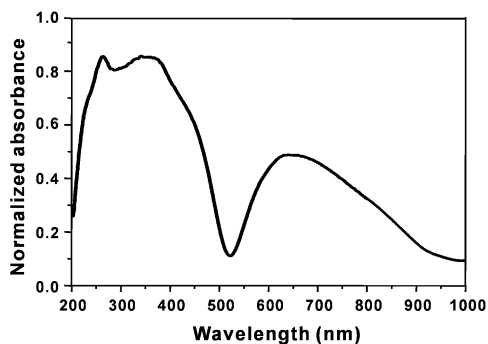


Figure 4. The UV/Vis spectrum of complex **1** in the solid state.

mainly assigned to a metal-centered (MC) transition, which can deactivate via ultrafast nonradiative pathways and is typical for other Cu^{II} complexes.^[27] The luminescent properties of **1** were also considered; however, the emission of cluster **1** is very weak, which suggests that Cu^{II} possessing low-lying MC levels quenches the luminescence by energy transfer or thermal equilibration.^[28]

In conclusion, we have used a stepwise route to assemble and have characterized a heterometallic $\text{Ag}_9^{\text{I}}\text{-Cu}^{\text{II}}_4$ cluster

based on a novel nonanuclear silver cluster precursor that comprises two unusual vertex-shared trigonal-bipyramidal silver polyhedra. The formation of this unexpected heterometallic cluster as well as its UV/Vis absorption and emission behaviors were discussed.

Experimental Section

Materials and General Measurements

IR spectra were recorded on a Nicolet AVATAT FT-IR360 spectrometer as KBr pellets in the frequency range of $4000\text{--}400\text{ cm}^{-1}$. The elemental analyses (C, H, N content) were determined on a CE instruments EA 1110 analyzer. UV/Vis measurements (diffuse-reflectance mode) were carried out at 298 K on a Varian Cary5000 UV/Vis/NIR spectrophotometer equipped with an integrating sphere. Powder X-ray diffraction (PXRD) data were collected on a Philips X'Pert Pro MPD X-ray diffractometer with $\text{Cu}_{\text{K}\alpha}$ radiation equipped with an X'Celerator detector. TG curves were measured from 25 to 800°C on an SDT Q600 instrument at a heating rate of 5°Cmin^{-1} in N_2 atmosphere (100 mL min^{-1}). Energy-dispersive X-ray spectra were obtained on a HITACHI S-4800 scanning electron microscope, which is equipped with an HORIBA EDS unit.

Synthesis and Characterization of Complex **1**

In the first step, a solution of silver cluster precursor was prepared. For this solution A, a mixture of AgNO_3 (167 mg, 1 mmol) and H_2mna (155 mg, 1 mmol) was added to water (6 mL) in a conical flask and exposed to ultrasonic treatment (160 W, 40 KHz) for 20 min at room temperature. The precipitate was dissolved by dropwise addition of aqueous NH_3 (25%, 8 drops, ca. 0.4 mL) to give a clear yellow solution. In the second step a solution of cationic metalloligand containing Cu^{II} ion was prepared. For this solution B, a mixture of $\text{Cu}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (218 mg, 1 mmol) and phen (180 mg, 1 mmol) was added to water/ethanol (8 mL, v:v=2:1) in conical flask and exposed to ultrasonic treatment (160 W, 40 KHz) for 20 min at room temperature to give a clear blue solution. In the third step, solution B was carefully layered on the top of solution A in a tube (length 15 cm, diameter 1 cm). After the solution was allowed to stand for about four days, green crystals of **1** had formed. The crystals were filtered off and washed with ethanol and dried in air. Yield ca. 66% based on Ag. Elemental analysis (%) calcd for $\text{Ag}_9\text{Cu}_4\text{S}_8\text{C}_{146}\text{H}_{123}\text{N}_{24}\text{O}_{34}$: C 41.37, H 2.94, N 7.93; found: C 41.01, H 3.18, N 7.63. Selected IR peaks: $\bar{\nu} = 3430$ (s), 2972 (w), 2927 (w), 1582 (s), 1518 (w), 1424 (w), 1381 (s), 1076 (w), 850 (m), 722 cm^{-1} (w).

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Keywords: cluster compounds • heterometallic compounds • luminescence • silver • stepwise synthesis

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