# A Rock-Salt-Like Lattice Structure Consisting of Monocationic and Monoanionic $Au^{I}Ag^{I}Cu^{II}$ Supramolecular Cages of D-Penicillaminate[**]

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Over the past decade, considerable interest has been devoted to the controlled synthesis of metallosupramolecular species, such as finite coordination rings and cages and infinite coordination polymers, not only because of their intriguing structural diversity but also because of their potential as new functional materials.[1] While the most common approach to obtain metallosupramolecules is based on the self-assembly of multidentate organic ligands and metal ions, our synthetic strategy has been directed toward the use of metal complexes with sulfur-containing aminocarboxylates such as L-cysteinate (L-cys) and D-penicillaminate (D-pen) as building blocks, which are aggregated by forming S-bridged structures with transition metal ions.[2] Recently, we have found that the six-coordinate complexes $[Co(\text{L-cys-}N,S)(en)_2]^+$ (en = ethylenediamine) and $[Re^{V}O(\text{D-pen-}N,S)(\text{D-pen-}N,O,S)]^-$ can bind to $Ag^{I}$ ions not only through thiolato groups but also through pendant carboxylate groups to produce a variety of supramolecular structures, including 1D helix and 2D sheet.[2b–d] This result showed the suitability of L-cys and D-pen metal complexes as favorable building blocks that adopt various binding modes toward transition metal ions.

To expand the range of mixed-metal supramolecular architectures constructed from simple sulfur-containing aminocarboxylates, we investigated the binding ability of the two-coordinate $Au^{I}$ complex $[Au(\text{D-pen-}S)_2]^{3-}$,[3] which was prepared as a model of gold-based antiarthritis drugs. In this complex, two D-pen ligands coordinate to a linear $Au^{I}$ center only through thiolato groups, thus leaving two amino and two carboxylate groups as potential binding sites for additional metal ions, besides two coordinated thiolato groups. Here we report that the stepwise reaction of $[Au(\text{D-pen-}S)_2]^{3-}$ with $Ag^{I}$ and $Cu^{II}$ in the presence of $Cl^-$ (Scheme 1) creates a

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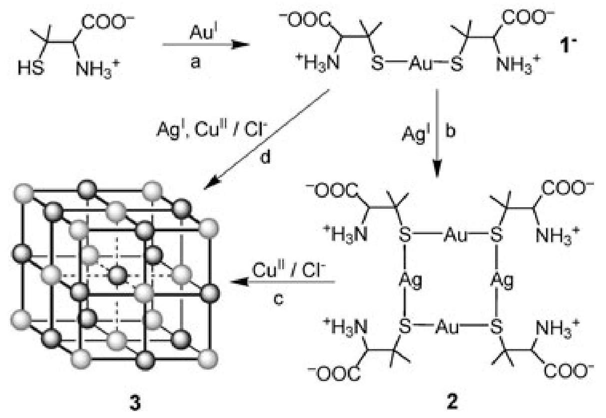
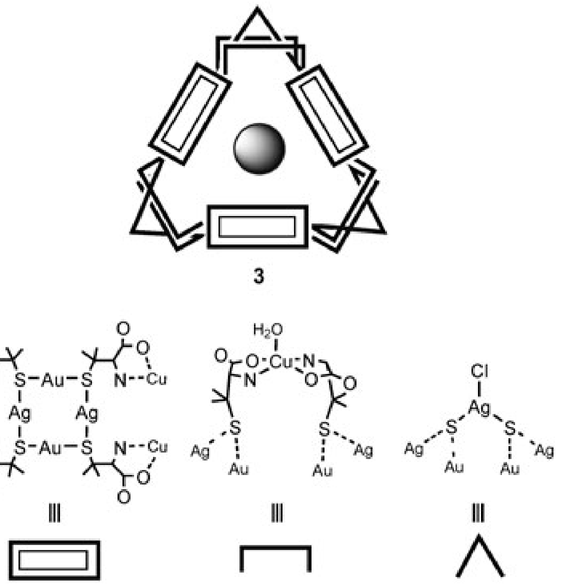


*Scheme 1.* Synthetic routes to **3** by way of **1** and **2**. a) $[AuCl\{S(CH_2CH_2OH)_2\}]$ in methanol; b) $AgNO_3$ in water; c) $CuCl_2$ in aqueous acetate buffer; d) $AgNO_3$, $Cu(NO_3)_2{\cdot}3\,H_2O$, and $NH_4Cl$ in aqueous acetate buffer.

metallosupramolecular architecture containing all three coinage metals, gold(I), silver(I), and copper(II). While several metal compounds with two of the three coinage metals have been prepared,[4] to our knowledge, incorporation of $Au^I$, $Ag^I$, and $Cu^{II}$ in one supramolecular structure is unprecedented. Remarkably, this product was found to be composed of monocationic 20-nuclear $Au^I_6Ag^I_8Cu^{II}_6$ and monoanionic 21-nuclear $Au^I_6Ag^I_9Cu^{II}_6$ supramolecular cages encapsulating a $Cl^-$ ion, which are regularly coupled to each other to construct a unique rock-salt-like lattice structure comprising huge monocationic and monoanionic metallosupramolecules.

Treatment of $(NH_4)[Au(\text{D-Hpen})_2]$ (**1**)[5] with $AgNO_3$ in a 1:1 ratio rapidly gave a photoluminescent white powder (**2**).[6] Compound **1** is sparingly soluble in water at neutral pH, but shows good solubility in acidic or basic aqueous solution. X-ray fluorescence spectrometry confirmed the presence of Au and Ag in **2**, and its elemental analytical data were in good agreement with the 1:1 stoichiometry of $Ag[Au(\text{D-Hpen})_2]$. The $^1H$ and $^{13}C$ NMR spectra of **2** in $D_2O$ (1 M $Na_2CO_3$), each of which exhibits only a single set of signals, are very similar to those of **1**. However, the $^{13}C$ NMR signal ($\delta = 54.33$ ppm) due to the tertiary C atom adjacent to the S atom is strongly shifted downfield relative to the corresponding signal for **1** ($\delta = 51.02$ ppm). This suggests that in solution $Ag^I$ ions are connected to $[Au(\text{D-Hpen-}S)_2]^-$ through S atoms, compatible with the tendency of soft $Ag^I$ ions to coordinate to soft thiolato groups. Accordingly, **2** is assumed to be the neutral $Au^I_2Ag^I_2$ complex $[Au_2Ag_2(\text{D-Hpen-}S)_4]$ in which two $[Au(\text{D-Hpen-}S)_2]^-$ molecules are linked by two $Ag^I$ atoms through S atoms to form a $Au^I_2Ag^I_2S_4$ square (Scheme 1). Consistent with this assumption, the electrospray mass spectrum (ES-MS) of **2** in methanol:water (1:1/$Na_2CO_3$) gave a main signal at $m/z = 1201$, the calculated molecular mass and the isotopic distribution of which match well with those for $[Au_2Ag_2(\text{D-pen-}S)(\text{D-Hpen-}S)_3]^-$. If this proposed structure is correct, **2** is expected to bind with a third metal ion by using the four free N,O arms to form a metalloaggregate composed of $[Au_2Ag_2(\text{D-pen-}S)_4]^{4-}$ square units. Indeed, when **2** was treated with an excess of $CuCl_2$ in an aqueous buffer solution (pH 6.2), blue cubelike crystals of **3** were isolated from the blue reaction solution. While the quite poor solubility of **3** precluded its characterization in solution, the presence of Au, Ag, and Cu atoms and D-pen ligands was revealed by the X-ray fluorescence, IR ($\tilde{\nu}_{CO} = 1600\ \text{cm}^{-1}$), UV/Vis (broad band at ca. 615 nm), and CD (broad positive band at ca. 595 nm) spectroscopy in the solid state, together with the elemental analysis. The structure of **3**, which crystallizes in the cubic space group $P2_13$, was established by single-crystal X-ray crystallography.[7]

The asymmetric unit of **3** contains one-third of two crystallographically independent $Au^IAg^ICu^{II}$ clusters with D-pen ligands (**3a** and **3b**), besides lattice water molecules (see Supporting Information). As shown in Scheme 2 and Figure 1, the entire cluster **3a** consists of three distorted square units of $[Au_2Ag_2(\text{D-pen-}S)_4]^{4-}$, in which two $Au^I$ and two $Ag^I$ atoms are alternately bridged by four S atoms from four $\text{D-pen}^{2-}$ ligands (av Au–S 2.301(5), Ag–S 2.485(4) Å, S-Au-S 171.8(2), S-Ag-S 152.7(2)°). The three $[Au_2Ag_2(\text{D-pen-}S)_4]^{4-}$ units are linked by six $Cu^{II}$ atoms through $NH_2$ and $COO^-$ groups to form a cyclic cage structure (av Cu–N 1.99(2), Cu–O 1.90(2) Å). In this structure, six $Cu^{II}$ and six $Ag^I$ ions are arranged to form an outer and an inner twisted trigonal prism, respectively, and six $Au^I$ atoms are located between them. Each $Cu^{II}$ atom is chelated in a planar fashion by two N,O arms from two different $[Au_2Ag_2(\text{D-pen-}S)_4]^{4-}$ units in a *trans* geometry, while its apical site is occupied by a water molecule (av Cu–O 2.44(2) Å). This $Au^I_6Ag^I_6Cu^{II}_6$ cage structure is sustained by three additional $Ag^I$ atoms, each of which is trigonally coordinated by two S atoms from two different $[Au_2Ag_2(\text{D-pen-}S)_4]^{4-}$ units and a $Cl^-$ atom (av Ag–S 2.558(5), Ag–Cl 2.406(5) Å). In addition, one $Cl^-$ ion is encapsulated in the center of the cage and has short contacts with the six inner $Ag^I$ atoms (av Ag···Cl 3.072(4) Å). Thus, **3a** is a 21-nuclear monoanionic cage cluster with a diameter of about 16 Å and a height of about 12 Å, which is composed of 6 $Au^I$, 9 $Ag^I$, and



*Scheme 2.* Representation of the anionic cluster **3a**.

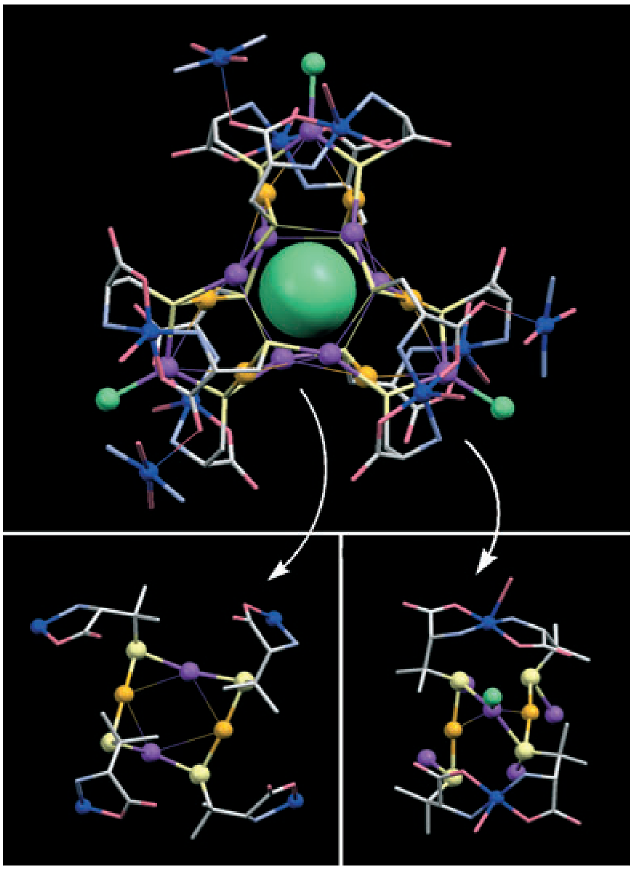


*Figure 1.* Top: stereoview of the anionic cluster **3a** bound by three $Cu^{II}$ ions from the three adjacent cationic clusters **3b**: Au orange, Ag purple, Cu blue, Cl green, S yellow, O pink, N light blue, C light gray. Lower: structural details.

6 $Cu^{II}$ ions in combination with 12 D-$pen^{2-}$ ligands, 4 $Cl^-$ atoms, and 6 $H_2O$ molecules. Of note is the presence of 18 metallophilic Au···Ag interactions with distances of 2.880(2)–3.249(2) Å in **3a**,[4b–d] together with six Ag···S interactions (2.875(5)–2.936(5) Å), which complete the rigid $Au^I_6Ag^I_9S_{12}$ core structure. The structure of cluster **3b**, which also encapsulates a $Cl^-$ atom at the center of the cage (av Ag···Cl 3.140(5) Å), appears to be virtually the same as that of cluster **3a** (Figure 2). However, in **3b** the cage consisting of three $[Au_2Ag_2(\text{D-pen-}S)_4]^{4-}$ units (av Au–S 2.298(5), Ag–S 2.472(5) Å, S-Au-S 173.5(2), S-Ag-S 157.2(2)°) and six $Cu^{II}$ ions is bound by two $[Ag(H_2O)]^+$ moieties (av Ag–S 2.534(6), Ag–O 2.34(2) Å), which are disordered in two of three positions, in place of three $[AgCl]^0$ moieties in **3a**. Thus, **3b** is composed of 6 $Au^I$, 8 $Ag^I$, and 6 $Cu^{II}$ ions in combination with 12 D-$pen^{2-}$ ligands, one $Cl^-$ atom, and two $H_2O$ molecules, which construct a 20-nuclear monocationic cage structure. In **3b** only three of six *trans*-$CuN_2O_2$ planes are coordinated by apical water molecules (Cu–O 2.30(1) Å), each of which forms a hydrogen bond to the carboxylato O atom of the adjacent monoanionic cluster of **3a** (O···O 2.85(2) Å).[8] The apical positions of the remaining three *trans*-$CuN_2O_2$ planes are bound by three $COO^-$ groups from three different monoanionic clusters with a Cu–O distance of 2.38(1) Å. As a result, the monoanionic and monocationic cage clusters are connected to each other such that each anionic/cationic cage is octahedrally surrounded by six cationic/anionic cages to form a rock-salt-like lattice structure with a volume that is about 200 times larger than that of NaCl (Figure 3).[8,9]

The EPR spectrum of a solid sample of **3** at 77 K displays a simple isotropic signal with $g = 2.12$, consistent with the presence of $Cu^{II}$ ions. Furthermore, a very weak half-field transition band is observed, which is indicative of the presence of a weak magnetic exchange interaction between two adjacent $Cu^{II}$ centers.[10] The weak antiferromagnetic character of the interaction between $Cu^{II}$ centers was revealed by the magnetic measurements for **3** in the temperature range of 2 to 300 K. The plot of $\chi_m T$ versus $T$ is almost constant in

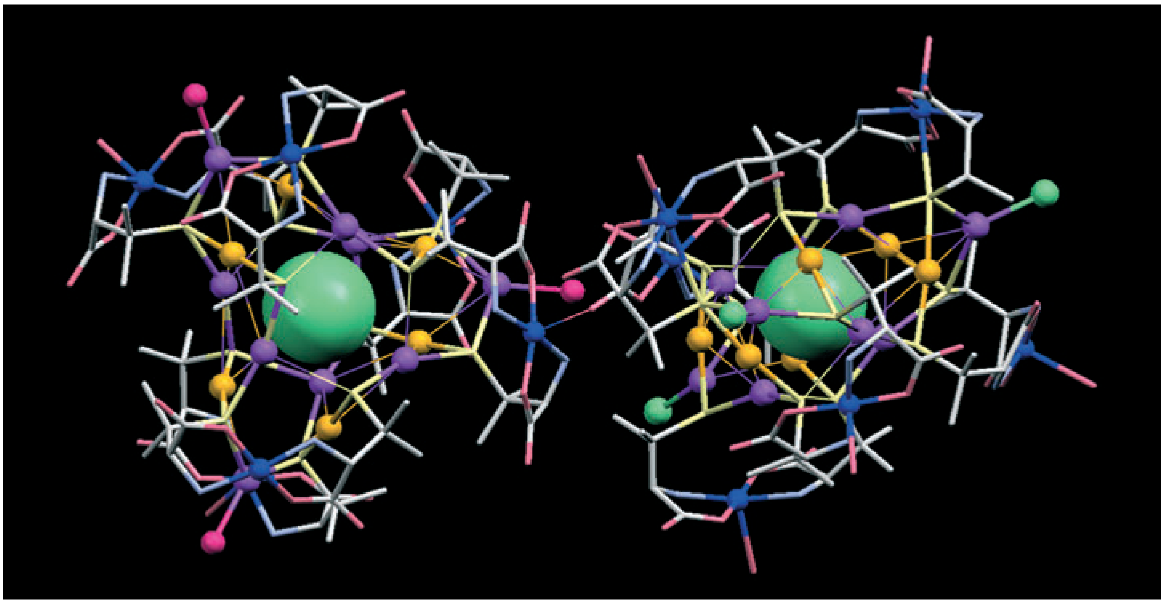


*Figure 2.* Stereoview of the cationic cluster **3b** (left) linked with the anionic cluster **3a** (right): Au orange, Ag purple, Cu blue, Cl green, S yellow, O pink, N light blue, C light gray.

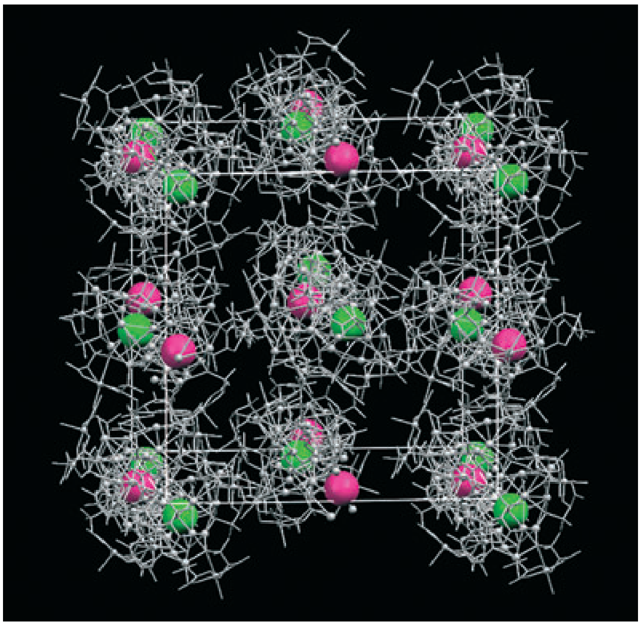


*Figure 3.* Rock-salt-like lattice structure of **3**. Green balls: central $Cl^-$ ions in anionic clusters **3a**, pink balls: central $Cl^-$ ions in cationic clusters **3b**.

the range of 300 to 40 K with a $\chi_m T$ value of about 4.72 $cm^3 K mol^{-1}$, which is slightly smaller than the spin-only value of 5.05 $cm^3 K mol^{-1}$ for the magnetically dilute 12 $Cu^{II}$ centers, and then decreases sharply to 4.10 $cm^3 K mol^{-1}$ at 2 K on lowering the temperature.

When one equivalent of $AgNO_3$ was added to the reaction mixture of **2** and $CuCl_2$, **3** was obtained in higher yield, as expected from the presence of additional $Ag^I$ atoms that support the cage structure in **3**. On the other hand, the use of $CuNO_3 \cdot 3H_2O$ instead of $CuCl_2$ did not afford **3**, and a green–blue powder was obtained instead. Thus, the $Cl^-$ ion incorporated in the center of each cage is essential for the formation of **3**. Interestingly, **3** was also produced by the one-pot reaction of **1** with a mixture of $AgNO_3$ and $Cu(NO_3)_2 \cdot 3H_2O$ in the presence of $NH_4Cl$ (Scheme 1).[11,12]

In summary, $(NH_4)[Au(D\text{-}Hpen)_2]$ (**1**) readily reacts with $Ag^I$ to afford $[Au_2Ag_2(D\text{-}Hpen\text{-}S)_4]$ (**2**) as a white solid, which further reacts with $Cu^{II}$ in the presence of $Cl^-$ ions to produce blue crystals of $Au^IAg^ICu^{II}$ complex **3**. Thus, $[Au(D\text{-}pen\text{-}S)_2]^{3-}$ can bind to both soft and hard metal ions using two amino and two carboxylate groups, besides two coordinated thiolato groups. Compound **3** was found to be a remarkable heterometallic aggregate comprising two kinds of supramolecular cages, $[Au_6Ag_8Cu_6Cl(H_2O)_5(D\text{-}pen)_{12}]^+$ and $[Au_6Ag_9Cu_6Cl_4(H_2O)_6(D\text{-}pen)_{12}]^-$, each of which accommodates a $Cl^-$ ion. Although several metallocages templated by a $Cl^-$ ion have been reported,[13] **3** is the first example of a supramolecular cage involving three coinage metal ions, $Ag^I$, $Au^I$, and $Cu^{II}$. The overall charge of each cage in **3** is ingeniously regulated by the attachment of $[AgCl]^0$ or $[Ag(H_2O)]^+$ fragments, such that the 20-nuclear monocationic and the 21-nuclear monoanionic cage clusters combine to generate an unprecedented 1:1 supramolecular salt with a rock-salt-like lattice structure. Finally, the results demonstrate that heterometallic supramolecular species exhibiting unique structures and multiple supramolecular interactions can be created exclusively from simple sulfur-containing aminocarboxylates by stepwise combination with appropriate transition metal ions. Work is in progress to construct other supramolecular structures based on **1** and **2** in combination with other transition metal ions.

## Experimental Section

**3**: A solution of $CuCl_2$ (23 mg, 0.17 mmol) in an acetate buffer solution (pH 6.2, 150 mL) was added to a colorless solution containing **2** (50 mg, 0.04 mmol) and $Na_2CO_3$ (25 mg) in water (10 mL). The green mixture was stirred at RT overnight, during which time the solution turned blue. The blue solution was concentrated to ca. 10 mL and allowed to stand at RT for several days. The resulting blue cubelike crystals were collected by filtration. Yield: 24 mg (42 % based on Au); elemental analysis (%) calcd for $[Au_6Ag_8Cu_6Cl(H_2O)_5(D\text{-}pen)_{12}][Au_6Ag_9Cu_6Cl_4(H_2O)_6(D\text{-}pen)_{12}] \cdot 13.5\,H_2O$ ($C_{120}H_{265}Ag_{17}Au_{12}Cl_5Cu_{12}N_{24}O_{72.5}S_{24}$): C 15.82, H 2.93, N 3.69; found: C 15.54, H 2.88, N 3.65. The addition of 1 equiv of $AgNO_3$ (7 mg, 0.04 mmol) to the above green mixture led to the formation of blue crystals in higher yield (72 % based on Au).

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**Keywords:** aggregation · cage compounds · S ligands · supramolecular chemistry · transition metals

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[5] A white crystalline sample of **1** was prepared in 84 % yield from $Au^I$ and $D\text{-}H_2pen$ according to a modified literature method[3b] using chloro(thiodiethanol)gold(I) instead of chloro(tetrahydrothiophene)gold(I). Elemental analysis (%) calcd for $NH_4[Au(D\text{-}Hpen)_2] \cdot 11/3\,H_2O$ ($C_{10}H_{31.3}AuN_3O_{7.67}S_2$): C 20.80, H 5.47, N 7.28; found: C 20.84, H 5.14, N 7.23; $^1H$ NMR (270 MHz, $D_2O$/1 M

$Na_2CO_3$): $\delta = 1.30$ and 1.61 ($CH_3$), 3.47 ppm (CH); $^{13}C$ NMR (68 MHz, $D_2O$/1 M $Na_2CO_3$): $\delta = 31.06$ and 37.99 ($CH_3$), 51.02 (SC), 70.71 (CH), 177.22 ppm (COO).

[6] A solution of $AgNO_3$ (0.23 g, 1.36 mmol) in water (24 mL) was added to a stirred solution of **1** (0.80 g, 1.39 mmol) in water (12 mL), which gave a white precipitate immediately. After stirring at RT for 90 min, followed by cooling in an ice bath for 30 min, the resulting white powder of **2** was collected by filtration and washed with water and methanol. Yield: 0.83 g (95%); elemental analysis (%) calcd for $[Au_2Ag_2(D\text{-}Hpen)_4]\cdot 4H_2O$ ($C_{20}H_{48}Ag_2Au_2N_4O_{12}S_4$): C 18.85, H 3.80, N 4.40; found: C 18.75, H 3.62, N 4.50; $^1H$ NMR (270 MHz, $D_2O$/1 M $Na_2CO_3$): $\delta = 1.40$ and 1.64 ($CH_3$), 3.36 ppm (CH); $^{13}C$ NMR (68 MHz, $D_2O$/1 M $Na_2CO_3$): $\delta = 31.22$ and 38.11 ($CH_3$), 54.33 (SC), 71.00 (CH), 180.52 ppm (COO). Excitation of a solid sample of **2** at 308 nm at RT and 77 K gave a strong emission band at 709 and 672 nm, respectively.

[7] Crystal structure analysis for **3**: Bruker SMART-1000 CCD-based diffractometer, $T = 213$ K, $Mo_{K\alpha}$ radiation ($\lambda = 0.71069$ Å). The structure was solved by the Patterson method with DIRDIF92 (PATTY) and refined by full-matrix least-squares techniques on $F^2$ using SHELXL-93. Hydrogen atoms were not included in the calculations. $C_{120}H_{265}Ag_{17}Au_{12}Cl_5Cu_{12}N_{24}O_{72.5}S_{24}$, $M_r = 9111.12$ crystal size $0.2 \times 0.2 \times 0.1$ mm$^3$, cubic, space group $P2_13$, $a = 32.749(2)$ Å, $V = 35124(3)$ Å$^3$, $Z = 4$, $\rho_{calcd} = 1.723$ g cm$^{-3}$, $\mu = 6.851$ mm$^{-1}$, $\omega$–$2\theta$ scan mode, $2\theta_{max} = 50.0$, 221649 reflections collected, 20699 independent reflections, 15791 observed reflections ($I > 2\sigma(I)$), 880 parameters, semiempirical absorption corrections with SADABS, max./min. transmission 0.478/0.345, $R1$ ($I > 2\sigma(I)$) = 0.055, $wR2$ (all data) = 0.174, Flack parameter 0.010(6), residual electron density 3.34/−1.55 e Å$^{-3}$ (the peaks larger than 1.5 e Å$^{-3}$ were found in the vicinity of heavy atoms). The disordered Ag and O atoms in cluster **3b** were refined with a site occupancy factor of $^2/_3$, which gave satisfactory thermal parameters. CCDC 247589 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[8] Each *trans*-$[CuN_2O_2(H_2O)]$ moiety of **3b** is triply hydrogen bonded to the adjacent *trans*-$[CuN_2O_2(H_2O)]$ moiety of **3a** through $COO_{(3b)}\cdots H_2O_{(3a)}$ (2.82(2) Å) and $COO_{(3a)}\cdots H_2N_{(3b)}$ (2.86(2) Å), besides $COO_{(3a)}\cdots H_2O_{(3b)}$ (2.85(2) Å). The distance between the encapsulated $Cl^-$ ions in **3a** and **3b** connected by hydrogen bonds ($Cl_{(3a)}\cdots Cl_{(3b)}$ 17.015(6) Å) is comparable with that for connection by a $Cu{-}O_{COO}$ coordination bond ($Cl_{(3a)}\cdots Cl_{(3b)}$ 16.145(6) Å). Furthermore, the *cis* angles among the encapsulated $Cl^-$ ions in **3a** and **3b** are roughly close to the octahedral angle of 90° ($Cl_{(3a)}$-$Cl_{(3b)}$-$Cl_{(3a)}$ = 80.13(2)–100.75(3)°, $Cl_{(3b)}$-$Cl_{(3a)}$-$Cl_{(3b)}$ = 79.73(3)–100.33(3)°).

[9] Once isolated from the mother liquor, a crystalline sample of **3** loses water molecules of solvation, as revealed by the loss of surface luster. The powder X-ray diffraction pattern of a dried sample of **3** shows small peaks, indicative of the collapse of the lattice structure after the removal of solvating water molecules. Thermogravimetric (TGA) analysis shows a gradual weight loss of 16.5% up to 85 °C, followed by a quick weight loss of 20.1% at around 145 °C (see Supporting Information). The remaining weight at 150 °C is 62.5%, which corresponds well with that of the Au, Ag, Cu, and S atoms in **3** (62.9% calcd). This implies that the pyrolysis of organic groups and dehydration are complete in a relatively low temperature range.

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[11] A solution of $AgNO_3$ (0.15 g, 0.87 mmol) in an acetate buffer solution (pH 6.2, 150 mL) was added to a solution of **1** (0.50 g, 0.87 mmol) in an acetate buffer solution (150 mL). After stirring at RT for 30 min, a solution containing $Cu(NO_3)_2\cdot 3H_2O$ (0.42 g, 1.7 mmol) and $NH_4Cl$ (0.05 g) in an acetate buffer (150 mL) was added. The mixture was stirred at RT overnight, concentrated to ca. 110 mL, and then allowed to stand at RT for several days to give blue crystals of **3** (0.42 g, 67% based on Au).

[12] All crystalline samples of **3** obtained from different synthetic routes showed identical IR spectra. Furthermore, eight crystals selected from independent synthetic crops had identical unit-cell parameters, and four of them gave the same X-ray analytical data.

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