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An Unprecedented Luminescent Polynuclear Gold(I) μ_3-Sulfido Cluster With a Thiacrown-like Architecture

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Abstract: An unprecedented Au_{18} thiacrown directed by Au(I)···Au(I) interactions and supported by tridentate phosphine (dpepp) and μ_3-sulfido ligands that highly resembles the 18-membered thiacrown ether [18]aneS_6 in appearance has been synthesized. The sulfides of the $Au_3(\mu_3\text{-}S)$ units in the central cavity point toward each other and are located on the same plane, allowing them to bind the soft Ag^+ ion with immediate and pronounced spectroscopic changes. Reversible binding and spectroscopic changes can be readily achieved upon addition of CH_3CN without disruption of the Au_{18} macrocycle.

Because gold(I) complexes show strong tendencies to form self-assembled supramolecular assemblies via Au(I)···Au(I) interactions, polynuclear gold(I) systems have attracted increasing attention in the past few decades.[1−7] The aurophilic interactions offer the complexes the possibility of forming astonishing frameworks and displaying intriguing photophysical properties. Among the gold family, polynuclear gold(I) chalcogenido complexes are one of the promising and important classes,[1h−n,6,7] and sulfido complexes are the most representative systems because of their high stability and rich photophysical properties.[7] The nuclearity and shape of the gold core can be varied dramatically with different μ_n-sulfido ($n = 2-6$) ligands and various monodentate and bidentate auxiliary ligands. Numerous fascinating shapes and structures, including V-shaped structures,[7b,c] pyramids,[7a−c] aggregated or ligand-bridged dimeric pyramids,[7c,d,j] trigonal bipyramids,[7b,c] square pyramids,[7d] square bipyramids,[7b] distorted heterocubanes,[7h] and interesting structures such as propeller[7g] and crossroad-sign shapes[7f] have been observed in polynuclear gold(I) sulfido complexes.[1i] The majority of the clusters are made up of pyramidal $[Au_3(\mu_3\text{-}S)]^+$ units[7f−h] or prepared by further auration of these units.[7a−d] The $[Au_3(\mu_3\text{-}S)]^+$ unit is also capable of binding Ag(I) or Cu(I) ion, forming heteronuclear μ_4-sulfido complexes.[1i,7e,i]

This communication decribes an extraordinary macrocyclic polynuclear gold(I) μ_3-sulfido complex, $[Au_{18}(\mu\text{-dpepp})_6(\mu_3\text{-}S)_6]^{6+}$ (**1**) [dpepp = bis(2-diphenylphosphinoethyl)phenylphosphine], that is directed by Au(I)···Au(I) interactions and supported by covalent bonds. To the best of our knowledge, crown-shaped macrocycles, which are of particular interest in supramolecular chemistry because of their ability to bind the corresponding "guests", are unprecedented in gold(I) sulfido chemistry, not even to mention the gold(I) chalcogenido systems. Although several remarkable gold(I) macrocycles containing dithiocarbamate ligands and exhibiting rich spectroscopic properties, including Au_{12},[5h] Au_{16},[5g] and Au_{36},[5i] have recently been reported, the interiors of their rings are free of potential binding atoms. This absence of binding atoms and the less versatile binding capability of the dithiocarbamate ligands in bridging various metal centers have limited the use of the gold(I) thiocarbamate macrocycles as metallamacrocyclic hosts. We have found that in the present Au_{18} μ_3-sulfido ring, the six sulfur atoms point toward each other and are located on the same plane, rendering the complex a luminescent "gold thiacrown". The potential of the complex to serve as a metallamacrocyclic host or luminescent sensor for Ag^+ was also examined. The six $Au_3(\mu_3\text{-}S)$ units in the central cavity were found to be capable of binding the soft Ag^+ ion reversibly, accompanied by a significant alteration of the spectroscopic properties. While the conventional designs of macrocyclic hosts or sensors rely mainly on the incorporation of signal-generating units such as fluorophores[8] and luminescent transition-metal complexes[5c,j,9] into the organic crown-shaped molecules, the present work demonstrates the development of a new generation of macrocyclic hosts based on polynuclear gold(I) μ_3-sulfido complexes and constructed via metal-directed self-assembly. This may also open up new avenues for applications of polynuclear gold(I) chalcogenido complexes in supramolecular host−guest chemistry.

The reaction of H_2S with a suspension of $[Au_3(\mu\text{-dpepp})Cl_3]$[10] in a dichloromethane-ethanol-pyridine mixture at ∼50 °C followed by removal of the solvent and a metathesis reaction with NH_4PF_6 in methanol-water afforded $[Au_{18}(\mu\text{-dpepp})_6(\mu_3\text{-}S)_6](PF_6)_6$ [**1**$(PF_6)_6$] in moderate yield as a greenish-yellow solid. Recrystallization by slow evaporation of acetonitrile from an acetonitrile−water solution of the product gave **1**$(PF_6)_6$ as greenish-yellow crystals suitable for X-ray structural determination. **1**(OTf)$_6$ was obtained similarly, but ^{n}Bu$_4$N(OTf) was used instead of NH_4PF_6, and the product was obtained by recrystallization from slow evaporation of a methanol-water solution of the product. The structure of **1**$(PF_6)_6$ was confirmed by X-ray crystallography, elemental analysis, electrospray ionization mass spectrometry (ESI-MS), and ^{1}H and ^{31}P NMR spectroscopy. The perspective drawing of the octadecanuclear gold(I) cation **1** with atomic numbering is shown in Figure 1.

The positive-ion ESI-MS spectrum of **1**$(PF_6)_6$ is dominated by the ion cluster at *m*/*z* 1158, which is attributed to $[M]^{6+}$. The $^{31}P\{^1H\}$ NMR spectrum of **1**$(PF_6)_6$ in CD_3CN at 298 K showed a pair of broad signals at 27−35 ppm (Figure S1a in the Supporting Information) that became well-resolved into two sharp singlets at *ca.* 31 and 33 ppm in a ratio of *ca.* 2:1 at 318 K (Figure S1b), corresponding to the two types of phosphorus atoms in dpepp. In the ^{1}H NMR spectra, the multiplets due to the protons of the phenyl rings and the methylene protons were broad at 298 K but became sharp at 318 K. These results suggest that the complex is fluxional in solution at ambient temperature, probably by means of ring flipping, which is commonly observed in other related ring-like systems.[7f,11] The characterization data for **1**(OTf)$_6$ (see the Supporting Information) were similar to those for **1**$(PF_6)_6$, suggesting that their structures strongly resemble each other.

Under the direction of Au(I)···Au(I) interactions, a Au_{18} metallamacrocycle is formed via the interconnection of six trinuclear monomeric units $[Au_3(\mu\text{-dpepp})]$ by six bridging sulfide atoms (Figure 1). The crystallographic determination data and the bond lengths and distances are given in Tables S1 and S2 in the Supporting Information.

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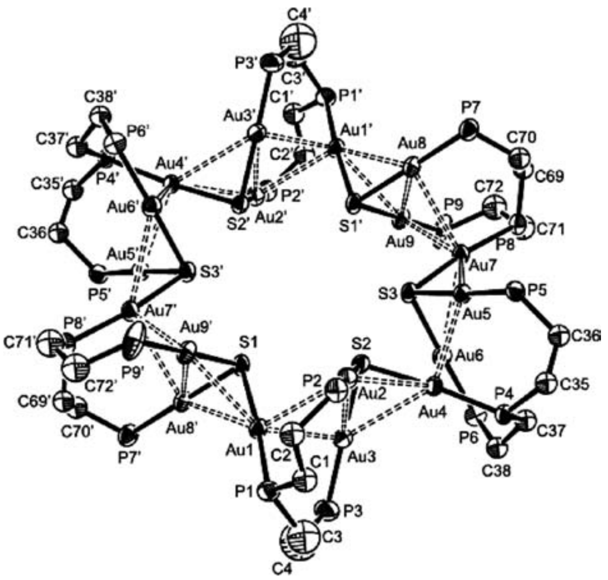
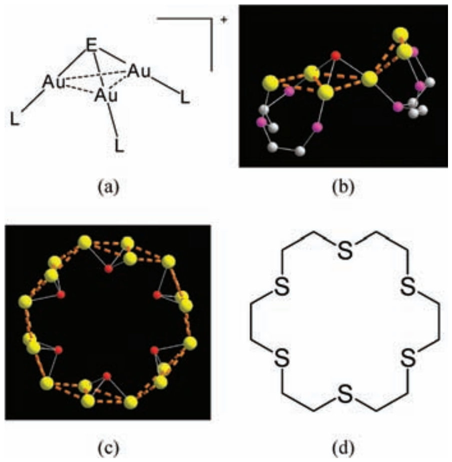


Figure 1. Perspective drawing of the complex cation of **1** with atomic numbering. Phenyl rings, hydrogen atoms, and a water molecule inside the cavity have been omitted for clarity. Thermal ellipsoids are shown at the 30% probability level.

In the typical trinuclear gold(I) chalcogenide complexes containing monodentate phosphines, the $Au_3(\mu_3\text{-}E)$ core commonly adopts a pyramidal structure with the μ_3-bridging E capping the three gold atoms (Figure 2a).[1i] The P−Au and Au−E bonds are nearly collinear, causing the three PPh_3 units to be farther apart. In complex **1**, as shown in Figures 1 and 2b, the three sulfur-bridged gold(I) centers also self-aggregate to form a triangular base, but the three gold(I) atoms are from two separate $Au_3(\mu\text{-dpepp})$ units, probably as a result of the steric constraints imposed by the dpepp ligand, the nearly linear coordination geometry of gold(I) centers (P−Au−S = 170.05−178.34°), and the typical angles of Au_3S triangular pyramids (Au−S−Au = 81.20−91.64°) (Table S2). These values, together with the P−Au (2.254−2.268 Å) and S−Au (2.314−2.342 Å) bond lengths as well as the Au(I)···Au(I) distances (3.0145−3.3295 Å), are typical of those found in other gold(I) μ_3-sulfido systems (Table S2).[1i,7c,e−g] The six sulfur atoms of **1** point toward each other and are located in the same plane, forming a thiacrown cavity (Figure 2c) with diameters (distances between opposite S atoms) of 6.99−7.27 Å that strongly resembles that of the 18-membered thiacrown ether [18]aneS_6 (Figure 2d). The gold core is surrounded by the six dpepp ligands, and the phenyl rings are located on the periphery; the anions are localized around the clusters to balance the high charge of the cluster instead of occupying the central cavity, leaving the thiacrown "open" (Figure S2), though a water molecule is weakly embedded inside the cavity. The "openness" of the cavity is also retained within the coordination ensemble (Figure S2).



(a) (b) (c) (d)

Figure 2. (a) Typical structure of trinuclear gold(I) chalcogenide complexes. (b) Partial view of the crystal structure of **1** showing the μ_3-S binding mode. Color scheme: gold, yellow; sulfur, red; carbon, gray; phosphorus, purple. Phenyl rings and hydrogen atoms have been omitted. (c) **1** as a gold thiacrown. Carbon, phosphorus, and hydrogen atoms have been omitted. (d) Chemical structure of [18]aneS_6.

Unlike [18]aneS_6, the macrocyclic Au_{18} complex is slightly colored [with absorption bands at λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1}) = 318 (82 460) and 346 (82 760)] and highly emissive ($\lambda_{em} \approx 500$ nm) in aerated CH_3CN at ambient temperature upon photoexcitation. The low-energy absorption bands are tentatively assigned as ligand-to-metal charge-transfer (LMCT) transitions modified by Au(I)···Au(I) interactions, while the emission likely originates from metal-perturbed intraligand (IL) phosphorescence on the basis of its occurrence at high energy.[7f]

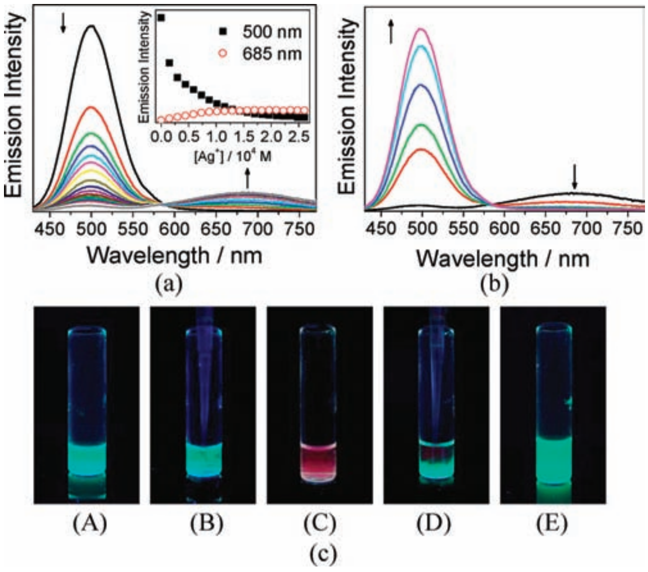


Figure 3. (a) Emission spectral changes of **1**$(OTf)_6$ (1.5×10^{-5} M) in MeOH [with 1 mM $^n Bu_4N(OTf)$] upon addition of Ag(OTf) (0−0.26 mM). Inset: Plots of emission intensity at 500 nm (■) and 685 nm (○) as functions of Ag^+ concentration. (b) Emission spectral changes of **1**$(OTf)_6$ (1.5×10^{-5} M) and Ag(OTf) (0.26 mM) in MeOH [with 1 mM $^n Bu_4N(OTf)$] upon addition of CH_3CN (0−100 μL). (c) Photographs of **1**$(OTf)_6$ (5×10^{-5} M) in MeOH [with 1 mM $^n Bu_4N(OTf)$] under UV irradiation upon addition of (A) 0 M Ag(OTf); (B) <0.75 mM Ag(OTf); (C) 0.75 mM Ag(OTf); (D) 0.75 mM Ag(OTf) and <200 μL of CH_3CN; (E) 0.75 mM Ag(OTf) and 200 μL of CH_3CN.

In view of the similarity of the Au_{18} macrocycle to [18]aneS_6, the complexation behavior of **1** with a "soft" metal cation, Ag^+, which is known to bind to [18]aneS_6, was examined spectroscopically. Upon addition of Ag(OTf) to the solution of **1**$(PF_6)_6$ in CH_3CN, no noticeable spectroscopic changes were observed. Interestingly, remarkable changes in both the electronic absorption and emission properties were observed when **1**$(OTf)_6$ in MeOH was used instead (Figure 3 and Figure S3). Such a difference in the complexation behavior may suggest that **1** is able to bind free Ag^+ ion but not CH_3CN-solvated Ag^+. Figure S3 shows the electronic absorption spectra of **1**$(OTf)_6$ in MeOH [with $^n Bu_4N(OTf)$ as a supporting electrolyte] upon addition of different concentrations of Ag(OTf) at 298 K. The absorbance of the two absorption bands was found to decrease gradually upon addition of Ag(OTf), with a small blue shift of ≤3 nm for the lower-energy absorption band. Upon photoexcitation at 300 nm, the green emission of **1** was found to be quenched, with a low-energy band growing in at *ca.* 685 nm and an isoemissive point appearing at *ca.* 585 nm (Figure 3a), giving rise to the emergence of a red-colored emission (Figure 3c). It is likely that the sulfur atoms of the $Au_3(\mu_3\text{-}S)$ units are susceptible to coordination with the Ag^+ ion to form $Au_3(\mu_4\text{-}S)Ag$ adducts, which abruptly alters the spectroscopic properties. The Ag^+ ion is probably attached not to an apical position at the sulfur atom but instead binds closer to one of the gold atoms, as in the dications $[(AuL)_4(\mu_4\text{-}S)]^{2+}$ [1i,7c,d] and $[\{(AuL)_3(\mu_4\text{-}S)\}_2Ag]^{3+}$,[1i,7e] and is supported by metallophilic bonding. The formation of the low-energy band in the emission spectrum is tentatively ascribed to Au−Ag adduct formation that leads to emission that has metal-centered (ds/dp) Au(I)···Ag(I) and/or ^{3}LMCT [S → Au(I)···Ag(I)] origin. The supramolecular framework of the complex is believed to be essentially retained upon binding, as evidenced by the fact that the ^{31}P NMR spectra of **1** in the absence and in the presence of Ag(OTf) are similar, although the broad multiplet at 7.82−8.10 ppm in the ^{1}H NMR spectrum is resolved into two multiplets at 7.79−7.92 and 7.92−8.11 ppm (Figure S4a,b). It is interesting to note that the emission properties can be promptly restored upon further addition of CH_3CN (Figure 3b,c) or LiCl, suggesting that the Ag^+ binding is reversible. The reversibility was also revealed by the ^{1}H NMR spectral changes (Figure S4c). This can probably be rationalized by the fact that the sulfur atoms of the cationic $[Au_3(\mu_3\text{-}S)]^+$ units are poor donors. However, as shown by ESI-MS, it is possible that various adducts are present, including $[\mathbf{1}-(Ag(OTf))_3]^{6+}$ (*m/z* 1286) and $[\mathbf{1}-(Ag(OTf))_6]^{6+}$ (*m/z* 1415) (Figure S5), making the binding mode and stoichiometry too complicated to be determined. The binding can be even more complex, as the Au(I) centers are also capable of interacting with Ag^+ ions. Attempts to isolate the crystal structure of the Ag^+ ion-bound adduct were not successful.

An unprecedented Au_{18} thiacrown directed by Au(I)···Au(I) interactions and supported by covalent bonds that highly resembles the 18-membered thiacrown ether [18]aneS_6 in appearance has been synthesized. The Au thiacrown displays intense emission upon photoexcitation at ambient temperature. The central thiacrown cavity is wide open and capable of binding Ag^+ ions with immediate and pronounced spectroscopic changes. Reversible binding and spectroscopic changes can be readily achieved upon addition of CH_3CN without disruption of the Au_{18} macrocycle, which is rather unusual for this class of metallasupramolecules. This work has demonstrated the potential of using polynuclear gold(I) sulfido complexes as a new generation of luminescent macrocyclic hosts. Exploration of the possible development of sensors for other guests and the design of various metallamacrocyclic hosts based on Au(I)···Au(I) interactions is in progress.

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Supporting Information Available: Characterization, experimental details of crystal structure determination, Tables S1 and S2, Figures S1−S5, and crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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