Molecular Aggregates

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Halide-Directed Assembly of Multicomponent Systems: Highly Ordered Au^I–Ag^I Molecular Aggregates**

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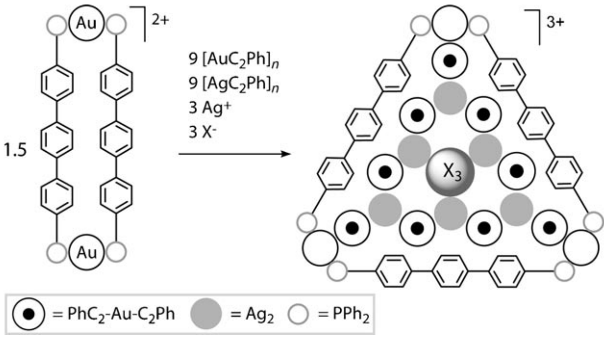
A great deal of research in inorganic and organometallic chemistry is devoted to investigation of self-assembly processes, which spontaneously lead to formation of complex multimetallic supramolecular entities from relatively simple building blocks under mild conditions. The resulting well-ordered species are of significant interest due to their fascinating structural characteristics and promising optical, electronic, or catalytic properties.[1,2] In most cases these species are prepared by a metal–ligand coordination-based strategy. However, group 11 metal ions tend to exhibit effective noncovalent metal–metal interactions, which often complicate the assembly processes and may result in formation of polymers or networks, catenanes, and polymetallic clusters.[2,3] Hence, it is difficult to predict the structural topology of coinage metal aggregates, and controlling the system organization at the molecular or nanoscale level is a major synthetic challenge.

One of the approaches to high-nuclearity coinage metal clusters is an elegant anion-templated synthesis of homometallic silver alkynyl cage compounds, which were shown to incorporate halides,[4] carbonate,[5] chromate,[6] and even polyoxometalates.[7] However, this approach is very little studied and the assembly processes of the d^{10} heterometallic compounds in the presence of coordinating anions have never been investigated.

In the course of our studies on coinage metal clusters[8–10] we isolated the novel complex $[Au_{12}Ag_{12}(C_2Ph)_{18}Cl_3(P^3P)_3]^{3+}$ (**1**, $P^3P = 4,4''\text{-}PPh_2(C_6H_4)_3PPh_2$) after prolonged (ca. two weeks) exposure to daylight of a mixture of $[AuC_2Ph]_n$, $[AgC_2Ph]_n$, and $[Au_2(P^3P)_2]^{2+}$ in CH_2Cl_2—a reported reaction which initially gives the structurally different cluster $[Au_{12}Ag_{10}(C_2Ph)_{16}(P^3P)_2]^{2+}$.[9] This preparative route, which eventually involves cleavage of C−Cl bonds of CH_2Cl_2 molecules as a source of chloride, was quite ineffective (yield of < 20 %). Alternatively, it was found that treatment of a stoichiometric reaction mixture with Ag^+ and Cl^- ions results in rather fast and nearly quantitative formation of **1** (Scheme 1).



Scheme 1. Assembly of the clusters $[Au_{12}Ag_{12}(C_2Ph)_{18}X_3(P^3P)_3]^{3+}$ (CH_2Cl_2/acetone, 12 h); X = Cl (**1**, 92 %), Br (**2**, 89 %), I (**3**, 88 %).

The bromide- and iodide-containing congeners (**2** and **3**) were obtained analogously, though some addition of $CHBr_3$ and MeI, respectively, was necessary to decrease possible halide exchange with solvent (CH_2Cl_2). Complexes **1**–**3** were characterized by ^1H and ^{31}P NMR spectroscopy. An X-ray diffraction study on **3** revealed its structure in the solid state (Figure 1).[11] The molecule consists of the heterometallic cluster $[Au_9Ag_{12}(C_2Ph)_{18}I_3]$ surrounded by a cationic "belt" $[Au_3(P^3P)_3]^{3+}$. Even though the general structural motif—a bimetallic cluster $[Au_xM_y(C_2Ph)_z]$ inside a $[Au_3(P^nP)_3]^{3+}$ triangle—has been described before,[12,13] the peculiarity of **3** resides in the central "axis" of three I^- ions, which effectively directed the framework aggregation process and stabilized the resulting metal core. The I−Ag distances of 2.8330(14)–3.0173(13) Å suggest a significant contribution of a conventional bonding between the halide and metal ions. The Au−Ag contacts vary significantly from 2.7844(11) to 3.3472(11) Å, the longest of which involve silver ions bound to iodide ions. The average Au-Ag distance (3.02 Å) and the Au−Au bonds between the central cluster and the external "belt" (2.8813(6)–2.9055(6) Å) are not exceptional and agree with the previously reported values.[9,10,13]

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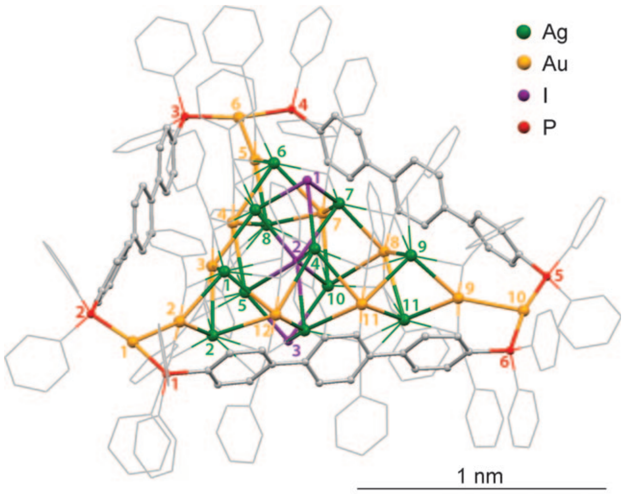
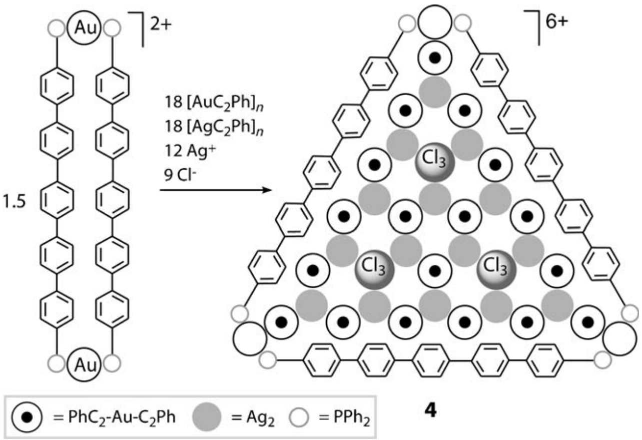


Figure 1. Molecular structure of trication **3**, as determined by X-ray analysis.

The NMR characteristics of **1**–**3** are very similar to each other and completely consistent with the solid-state structure of **3**. According to the idealized D_{3h} symmetry group ^{31}P NMR spectra of **1**–**3** show single resonances at 43.3, 43.2, and 43.2 ppm, respectively.

The low-field parts of the proton spectra show the signals of the phosphine ligand protons (Figure S1–S3, Supporting Information), while the high-field resonances correspond to the "*ortho–meta–para*" protons of the alkynyl ligands and match exactly the 3:6 ratio of two inequivalent groups of gold dialkynyl "rods" (Scheme 1).

The effectiveness of this halide-directed assembly reaction prompted us to investigate possible extension of the preparative route. According to a geometrical assumption, a diphosphine with five phenylene spacers would be able to form a related halide-stabilized cluster. Indeed, the use of this ligand allowed isolation of the novel aggregate $[Au_{21}Ag_{30}(C_2Ph)_{36}Cl_9(P^5P)_3]^{6+}$ (**4**, $P^5P = 4,4''''$-$PPh_2(C_6H_4)_5PPh_2$) in good yield (Scheme 2).



Scheme 2. Assembly of the cluster $[Au_{21}Ag_{30}(C_2Ph)_{36}Cl_9(P^5P)_3]^{6+}$ (CH_2Cl_2/THF, 12 h, 71%).

While in the case of the P^3P ligand the assembly reaction in the absence of halides leads to formation of other heterometallic clusters characterized previously,[9,13] the reaction mixtures based on diphosphine P^5P did not allow for isolation of any molecular species until the chloride ions were added.

Cluster **4** was characterized by ^{1}H and ^{31}P NMR spectroscopy. An X-ray diffraction study on **4** proved to be difficult due to the poor diffraction of the crystals in general and a sharp drop of the intensity of the reflections after $2\theta \approx 30$–$40°$—a problem already mentioned for high-nuclearity clusters.[14] Therefore, we were only able to get a dataset that did not allow for high-quality refinement, but confirmed the proposed structural motif (Figure S4, Supporting Information). Cluster **4** consists of a central metal alkynyl halide cluster $[Au_{18}Ag_{30}(C_2Ph)_{36}Cl_9]^{3+}$ placed inside a $[Au_3(P^5P)_3]^{3+}$ "belt". The nearly 2D heterometallic framework contains three equivalent trichloride "axes", which were found to be in a similar metal environment as in **1**–**3**. To the best of our knowledge, this is the largest Au^I–Ag^I aggregate of unprecedented well-ordered structural arrangement.

The NMR spectra of **4** are completely compatible with the proposed structure. In accord with D_{3h} symmetry, **4** displays a singlet resonance in the ^{31}P NMR spectrum at 45.1 ppm. Similar to **1**–**3**, in the ^{1}H NMR spectrum of **4** (Figure S5, Supporting Information) the phosphine ligand resonances are well separated and shifted to low field compared to the signals of the alkynyl ligands. Relative intensities of the signals in the both groups as well as their multiplicity fit well the structural motif of a $[Au_3(P^5P)_3]^{3+}$ "belt" with eighteen gold dialkynyl "rods" inside it. The latter are divided into four groups to give four sets of "*ortho–meta–para*" resonances with relative intensities of 3:3:6:6, which match exactly the arrangement of the central cluster core (Scheme 2 and Figure S6, Supporting Information).

The structural characteristics and electronic properties of **1**–**4** were also investigated by means of density functional calculations (see Supporting information). The geometries of the complexes were optimized at the BP86 DFT level of theory and, in line with the experimentally observed structural characteristics, the central heterometallic cores were found to fit well inside the triangular belts for all complexes. A DFT-optimized structure of hexacation **4** is shown in Figure 2.

Photophysical data for **1**–**4** in CH_2Cl_2 solution are summarized in Table S2 of the Supporting Information. The complexes display moderately strong green (**1**–**3**) and orange (**4**) luminescence with maximum quantum yield of 13% (Table S2, Supporting Information), and lifetimes in microsecond domain indicate its triplet origin. Maxima of emission bands of **1**–**3** are very similar to each other (535, 528, 530 nm, respectively), but in the case of **3** a weak long-wavelength emission (670 nm) appears in the spectrum, the origin of which is not clear. Cluster **4** shows substantial red shift in the emission maximum down to 664 nm. Accordingly, the theoretical results showed the emission energy gap for the T_1 state to be significantly smaller for cluster **4** in comparison to **1**–**3**. For all the complexes the emission is free of oxygen quenching effect: **1**–**3** show intensity drops of less than a

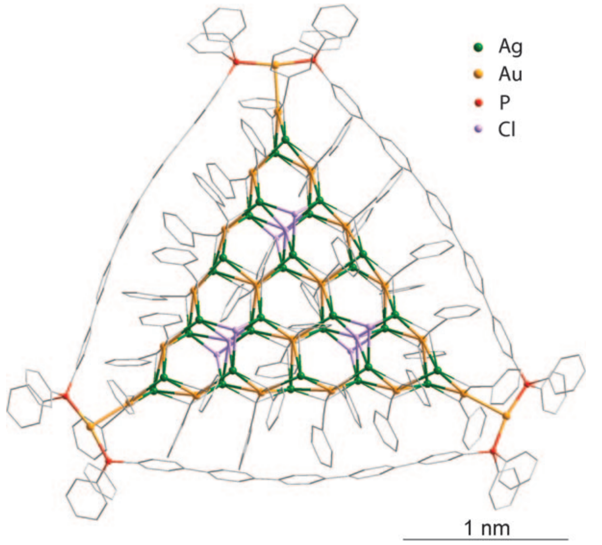


Figure 2. DFT-optimized structure of hexacation **4**.

factor of two in aerated solutions, and quenching is completely absent for **4**. This is presumably due to efficient isolation of the chromophore center from dipole–dipole interaction with O_2 by the organic groups. Additionally, complexes **1** and **2** display reasonable nonlinear properties. The two-photon absorption (TPA) cross sections were measured to be 45 and 57 GM (800 nm) for **1** and **2**, respectively, which are comparable with that of Rhodamine 6G (65 GM).[15]

In conclusion, we have demonstrated an effective and unusual halide-directed self-assembly of luminescent nanoscale Au^I–Ag^I clusters, which show unprecedented nuclearity and high structural ordering. This rational synthetic methodology may open new possibilities for future design and precise anion-controlled preparation of polymetallic coinage metal aggregates on the borderline of molecular, materials, and nanochemistry.

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[11] Crystal data for **3**: $C_{286}H_{223}Ag_{12}Au_{12}F_{18}I_3O_5P_9$, $M = 8399.11$, yellow plate, $0.17 \times 0.15 \times 0.08$ mm, monoclinic, space group $P2_1/c$, $a = 16.19050(10)$, $b = 41.8183(3)$, $c = 40.2024(3)$ Å, $\alpha = 90$, $\beta = 98.83$, $\gamma = 90°$, $V = 26896.9(3)$ Å^3, $Z = 4$, $\rho_{\text{cald}} = 2.074$ g cm^{-3}, $F(000) = 15788$, Nonius KappaCCD, $Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å, $T = 100(2)$ K, $2\theta_{\max} = 50.04°$, 215756 reflections collected, 46788 unique ($R_{\text{int}} = 0.0543$). Final GoF = 1.015, $R1 = 0.0516$, $wR2 = 0.1166$, with $I > 2\sigma(I)$ (refinement on F^2), 2879 parameters, 338 restraints. Lp and absorption corrections applied, $\mu = 7.830$ mm^{-1}. The structure was solved by direct methods. Some of the diethyl ether, acetone, and methanol solvent molecules in **3** were partially lost and slightly disordered. Therefore, two diethyl ether molecules, one acetone molecule, and the methanol molecule were refined with occupancies of 0.5. No disorder models were used for final refinement. Several geometric and displacement restraints were applied to solvent molecules and to aromatic rings of some phenylacetylide ligands. The MeOH hydrogen atom was located from the difference Fourier map but constrained to ride on its parent oxygen atom. Other hydrogen atoms were positioned geometrically and were also constrained to ride on their parent atoms. CCDC 784361 and 784362 contain 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.

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