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Cluster Compounds

Synthesis of Gold–Silver Luminescent Honeycomb Aggregates by Both Solvent-Based and Solvent-Free Methods**

M. Carmen Blanco, Jéssica Cámara, M. Concepción Gimeno, Antonio Laguna, Stuart L. James, M. Cristina Lagunas, and M. Dolores Villacampa*

Group 11 metal alkynyl complexes continue to receive great attention owing in part to their rich emissive properties.[1] Homometallic derivatives are significantly more numerous than the heteronuclear species, which is probably due to the synthetic difficulty in controlling the selective formation of heterometallic arrays.[2] Synthetic strategies to heteronuclear aggregates include self-assembly reactions involving 1) direct combination of metal ions and ligands,[3] and 2) preorganized metallo-ligand fragments, such as reactions between $[\{Ag(C{\equiv}CC_6H_4R\text{-}4)\}_n]$ and $[Au_2(\mu\text{-dppm})_2]^{2+}$ to give gold–silver clusters.[4] Self-assembly reactions have also been used to obtain different types of gold aggregates, such as catenate complexes $[(AuC{\equiv}C)_2(P(CH_2)_nP)]$,[5] or diphosphine–diacetylide derivatives with $R_2P(CH_2)_nPR_2$,[6] including some based on $[Au_xM_y(C{\equiv}CR)_{2x}]^{x-y}$ clusters.[7] Herein, we describe unprecedented polynuclear aggregates based on the latter structural unit. In particular, the metalloligand $[Au(C{\equiv}CPh)PPh_3]$ is reacted with metallic salts to give unusually large, highly ordered heterometallic materials that are only supported by acetylide–metal or metal–metal interactions. Interestingly, the nuclearity of the products is controlled through the addition of different donor ligands, with all the new derivatives exhibiting honeycomb metallic cores and strong luminescence. Apart from conventional solvent-based approaches, solventless mechanochemistry[8] is used for the first time to synthesize this type of gold complex.

The 1:2 reaction of $[Au(C{\equiv}CPh)PPh_3]$ with $[Ag(OTf)]$ leads to the high nuclearity cluster $[Ag_{12}Au_{10}(C{\equiv}CPh)_{17}(OTf)_5(PPh_3)_3]$ (**1**). The X-ray structure shows a central core formed by three hexagonal Ag_6Au_3 prisms, which share the three faces joined by the same central edge (Figure 1). The silver atoms are placed at the ends of longitudinal alternate edges in the hexagonal prisms. The edges that remain free are occupied by bis(acetylide)gold fragments, $\{Au(C{\equiv}CPh)_2\}$, with the gold atoms at the mid-points of the edges. The main core has a metallic composition $Ag_{12}Au_7$, which differs from the previously reported metastable cage $Ag_{13}Au_6$ containing a central silver atom.[9] Defining the main core are $\{Au(C{\equiv}CPh)PPh_3\}$ fragments, which are coordinated to the silver atoms occupying the non-shared edges. Overall this forms an unprecedented $Ag_{12}Au_{10}$ framework, which is very stable and can serve as suitable starting point for further aggregation.

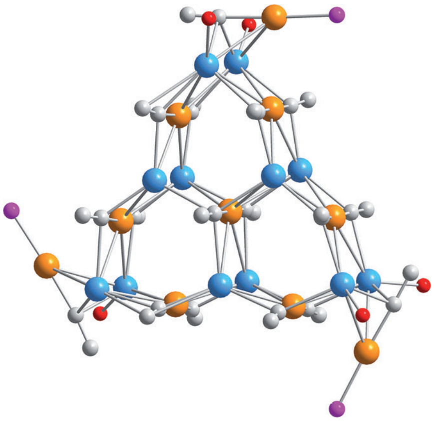

Figure 1. X-ray structure of **1**. Phenyl groups and solvents molecules have been removed for clarity. Ag blue, Au orange, C gray, O red, P purple.

To investigate the influence of additional ligands on the metal coordination environments, the reactivity of $[Au(C{\equiv}CPh)PPh_3]$ was tested with $[Ag(OTf)(tht)]$ (tht = tetrahydrothiophene). Remarkably, the 1:2 reaction led to the formation of an even higher nuclearity complex $[Ag_{26}Au_{20}(C{\equiv}CPh)_{34}(OTf)_{12}(PPh_3)_6(tht)_2]$ (**2**). The X-ray structure (Figure 2) can be described as a dimer of honeycomb units connected by a bridging $Ag(\mu\text{-tht})_2Ag$ group. The central core of three hexagonal prisms remains unchanged, and the new linking group has been added to one of the terminal $\{Au(C{\equiv}CPh)PPh_3\}$ fragments.

The reaction between $[Au(C{\equiv}CPh)PPh_3]$ and $[Ag(OTf)]$ was also carried out in the presence of pyridine, which, unlike tht, does not usually act as bridging ligand. The product of this reaction is the new aggregate, $[Ag_{14}Au_{10}(C{\equiv}CPh)_{17}(OTf)_6$-

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[*] Dr. M. C. Blanco, Dr. J. Cámara, Prof. Dr. M. C. Gimeno,
Prof. Dr. A. Laguna, Dr. M. D. Villacampa
Departamento de Química Inorgánica
Instituto de Síntesis Química y Catálisis Homogénea (ISQCH)
Universidad de Zaragoza-CSIC
50009 Zaragoza (Spain)

Dr. M. C. Blanco
Centro Universitario de la Defensa, Academia General Militar
50090 Zaragoza (Spain)
E-mail: mablanor@unizar.es

Prof. S. L. James, Dr. M. C. Lagunas
School of Chemistry and Chemical Engineering
Queen's University Belfast
Belfast BT9 5AG, Northern Ireland (UK)

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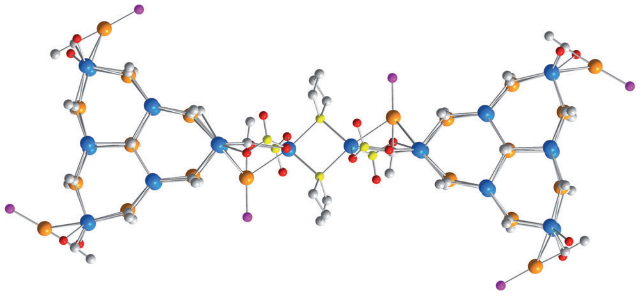


Figure 2. X-ray structure of **2**. Phenyl groups and solvents molecules have been removed for clarity. Ag blue, Au orange, C gray, O red, P purple, S yellow.

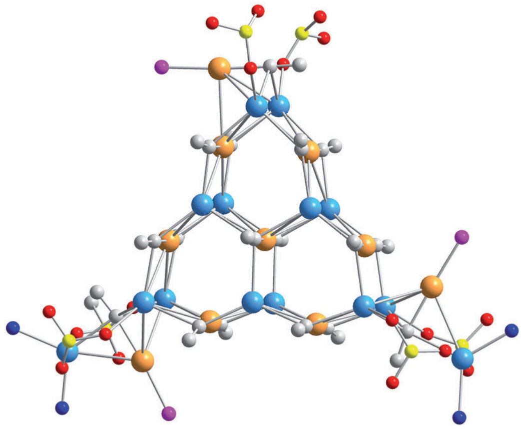


Figure 3. X-ray structure of **3**. Phenyl groups and solvents molecules have been removed for clarity. Ag blue, Au orange, C gray, O red, P purple, S yellow, N dark blue.

$(PPh_3)_3(py)_4]OTf$ (**3**), the X-ray structure shows a central core that again remains unchanged (Figure 3). The new $[Ag(py)_2]$ moieties are coordinated through Au⋯Ag interactions and to the acetylene ligands of the $\{Au(C{\equiv}CPh)PPh_3\}$ fragments located around the heterometallic core.

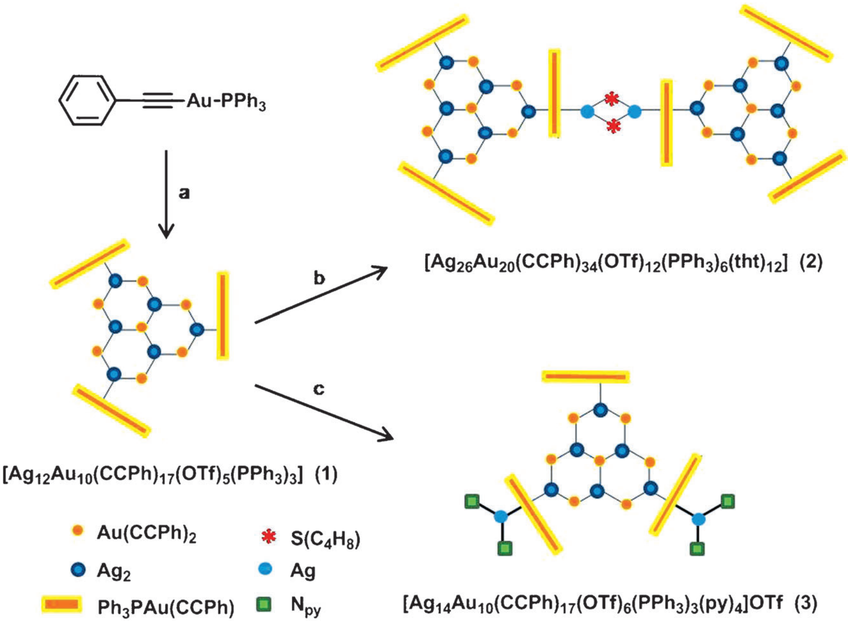
Following structural elucidation of complexes **1**–**3**, their syntheses were optimized, as summarized in Scheme 1 (for full synthetic details and spectroscopic data, see the Supporting Information, Experimental Section and Figures S1–S15).

Interestingly, the hexagonal arrangement of the metal centers for the three derivatives is also reproduced macroscopically, as shown by scanning electron microscopy (Supporting Information, Figures S16–S21).

The electronic absorption spectra for complexes **1**–**3** in dichloromethane show intense absorption bands at about 220–270 and low-energy shoulders tailing to ca. 450 nm (Supporting Information, Table S1). The high-energy bands below 270 nm are typical for phosphine and alkynyl ligands and are assigned as IL ($\pi \rightarrow \pi^*$) transitions.[10] The absorptions centered at about 300 nm can be assigned to electronic transitions from the σ (Au-P) to empty antibonding aryl π^* orbitals. The tails extending down to 450 nm, which are not exhibited by the homonuclear starting complexes $[Au(C{\equiv}CPh)PPh_3]$ or $[Au(C{\equiv}CPh)_2]^-$, and may arise from cluster-centered (Au_xAg_y) transitions or from the Ag-π-(alkynyl) core.[11]

All of the compounds exhibit strong luminescence in the solid state and in solution, at both 298 K and 77 K (Supporting Information, Tables S2, S3 and Figures S22–S24). Upon excitation at $\lambda_{ex} > 300$ nm, the emission spectra of **1**–**3** show a band at about 570 nm that is red-shifted compared to that of the starting material $[Au(C{\equiv}CPh)PPh_3]$. The origin of this emission can be assigned as a mixture of MLCT ($Au_xAg_y \rightarrow C{\equiv}CPh$) transitions and metal-cluster-centered transitions in the heterometallic core.[4a] Although the different nuclearities of the metal cores of **1**–**3** do not affect the emission, similar excited states in solid and in solution indicate the strong coordination of the metallic core to the alkynyl unit. In glass solution, dual emission is observed for compounds **1** and **3**. Apart from the transitions already described, a structured band appears at about 450 nm, which most likely originates from IL ($\pi \rightarrow \pi^*$ C≡CPh and/or phosphine) transitions.

The generally low solubility of metalloligands has been one of the greatest difficulties in self-assembly reactions. Because of this, as well as reasons of reducing environmental contamination,[8] we carried out preliminary studies using solventless ball-milling synthetic techniques. Reactions to obtain **1** and **2** were carried out in a shaker mill where $[Au(C{\equiv}CPh)PPh_3]$ was combined with $[Ag(OTf)]$ or $[Ag(OTf)(tht)]$. The colors of the mixtures changed as the grinding took place, from the pale yellow of the starting materials to the characteristic bright yellow of the reaction products. Furthermore, when the reaction mixtures were placed under UV



Scheme 1. Synthesis of **1**, **2**, and **3**. a) $[Au(C{\equiv}CPh)]_n + [Ag(C{\equiv}CPh)]_n + AgOTf$; b) $[Ag(OTf)(tht)]$; c) AgOTf/py. See the text and Supporting Information for details.

light, the emission changed from blue, which is due to the starting material $[Au(C\equiv CPh)PPh_3]$, to orange owing to **1** and **2** (pictures taken during solvent-less synthesis of **2**, under both visible and UV light, can be seen in the Supporting Information, Figure S25).

Reactions were complete after 70 (**1**) or 45 min (**2**) milling. Spectroscopic characterization of the samples by IR, luminescence and $^{31}P\{^1H\}$ NMR spectroscopies showed similar results to those obtained in the solvent-based synthesis. It is notable that dimer **2** forms more quickly than complex **1**, suggesting a possible role of the tht as a solvent during the reaction. The presence of small amounts of internal solvent in starting materials, such as coordinated or cocrystallized water, has previously been shown to have an accelerating effect of mechanochemical formation of metal complexes.[8f]

In conclusion, unusually large, luminescent, heteronuclear alkynyl clusters with different nuclearities can been prepared through the addition of different donor ligands; the metal cores of the new derivatives adopt a honeycomb structure both at micro- and macroscopic level, and the compounds can be prepared using mechanochemistry as well as solvent-based methods.

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