Molecular Gold—Multinuclear Gold(I) Complexes

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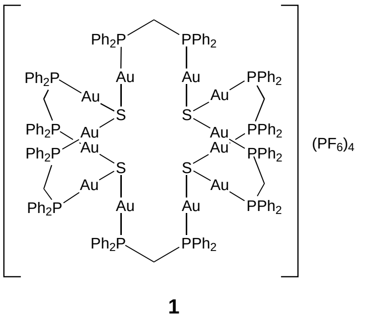
Gold, being an emblem of wealth, has been deeply involved in our daily lives for thousands of years. Its chemistry, however, has developed fairly slowly, until the last few decades, which may to a certain extent be attributed to its high elemental stability. The recent growth of interest in the study of polynuclear gold(I) compounds has stemmed from the findings that gold(I) atoms with a closed-shell electronic configuration show a strong tendency to form aggregates through aurophilic interaction. These compounds usually possess interesting structural properties and may serve as model systems for the understanding of structure and bonding in solid-state nano-materials.[1]

Gold(I) chalcogenide clusters represent one such class of compounds that has amused chemists and offers a synthetic challenge. High-nuclearity gold(I) chalcogenide clusters are rare despite the numerous examples of clusters of the lighter congeners, that is, copper(I) and silver(I).[2] For copper(I) and silver(I), an usual coordination number of four can be easily achieved, whereas for gold(I), a coordination number of two is usually observed. The more restricted coordination chemistry of monovalent gold is in part responsible for the less prevailing nature of these clusters. The difficulty is further complicated by the tendency of monovalent gold to form insoluble binary chalcogenides or polymeric materials, a tendency which has to be circumvented or avoided by stabilization with phosphane ligands. This poses further limitations on the availability of coordination sites for chalcogenides. In spite of all these problems and difficulties examples of gold(I) chalcogenide clusters are known, such as the cubane-type clusters $[Au_{12}S_8]^{4-}$ and $[Au_{12}Se_8Na]^{3-}$, and the phosphane-containing aggregates $[(AuPR_3)_3(\mu_3\text{-}S)]^+$ and $[(AuPR_3)_4(\mu_4\text{-}S)]^{2+}$.[3, 4] However, examples involving the use of bridging phosphane ligands, which may open up new avenues for the construction of high-nuclearity clusters, are extremely rare.[5] Recently, two sulfido-based gold(I) clusters, $[Au_{12}S_4(dppm)_6](PF_6)_4$ (**1**) and $[Au_{10}S_4\{Ph_2PN(n\text{Pr})PPh_2\}_4](PF_6)_4$ (**2**), were reported with the diphosphane ligands, bis(diphenylphosphanyl)methane (dppm) and bis(diphenylphosphanyl)-*n*-propylamine ($Ph_2PN(n\text{Pr})PPh_2$).[6]



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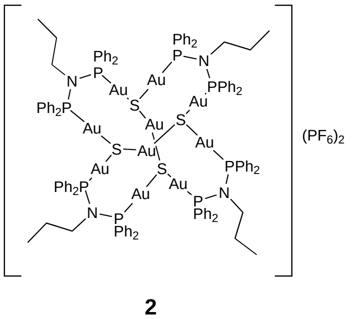

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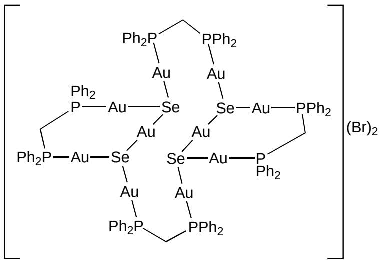
Cluster **1** has a "cross-road" sign structure whereas **2** is propeller-shaped. These complexes have also been shown to exhibit rich luminescence properties.[6] Fenske et al. added to the scanty list of high-nuclearity gold(I) clusters with the isolation of the gold(I) selenido clusters, $[Au_{10}Se_4(dppm)_4]Br_2$ (**3**) and $[Au_{18}Se_8(dppe)_6]^{2+}$ (**4**, Figure 1; dppe = bis(diphenylphosphanyl)ethane).[7]



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Although clusters **2** and **3** share a similar molecular formula, they have completely different structures in the solid-state. While in **2** the four sulfur atoms are oriented in an alternating up-and-down fashion forming a tetrahedron, the four selenium atoms in **3** are coplanar. The delicate balance between the nuclearity of the metal atoms and the nature of diphosphane ligands is revealed in the dramatic difference in the molecularity and the structure of the clusters **3** and **4**, with just a change of the diphosphane ligand from dppm to dppe. Cluster **4** shows an interesting structure in which the gold atoms are arranged in two major layers (Figure 1), with a Au_6Se_2 distorted cubane core at the center and the remaining twelve Au atoms, which are attached to the dppe ligands, in the outer shell. The inner core and outer shell are interconnected by six Se atoms. A gold-sulfide cluster, $[Au_{18}S_8(dppe)_6]\cdot H_2O$ (**5**), isostructural to **4**, was reported in 1987 by the Waters group and also mentioned in a review by Pyykkö.[8] However, in the X-ray crystal structure determination, the anion could not be located, a similar problem was encountered in the structural solution of **4**. From the published Au^I–Au^I bond lengths (2.909(5)–3.330(6) Å), it would be reasonable to suggest that **5**, like **4**, is a multinuclear gold(I) cluster, rather than a Au^I–Au^0 mixed-valent species. In **5** the anions could not be identified and located, whereas in **4** the cocrystallized CH_2Cl_2 molecules are disordered. Such problematic issues and difficulties are commonly encountered in large clusters of this sort. Further complications and difficulties come from the loss of solvent of crystallization from these clusters; solvents have been found to play an important role in the crystallization of closed-shell d^{10} systems.

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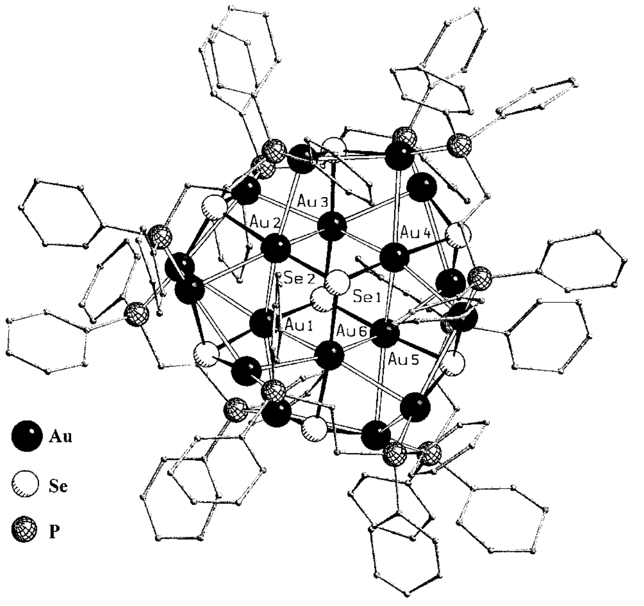
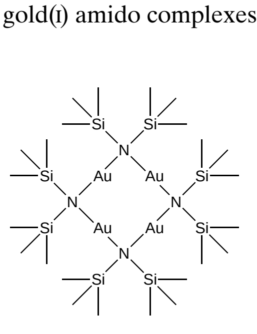


Figure 1. Molecular structure of **4**. The H atoms are omitted for clarity. (Reprinted from ref. [7].)

Electrospray ionization (ESI), a "soft" ionization source for mass spectrometry, has proved to be an extremely powerful and versatile method for the characterization not only of multinuclear metal clusters but also in the identification of coordination compounds and organometallic complexes. It provides a convenient and effective way to produce intact ions from thermally labile complexes and from multiply charged metal clusters.[9] Clusters **1**–**4** have been characterized by ESI mass spectrometry and shown to be intact in solution. Details on the fragmentation pattern, dissociation behavior, as well as bond energies can be readily estimated using collision-induced-dissociation studies.[9]

Apart from the soft chalcogenide ligand, hard nitrogen donor ligands have been shown to bridge gold(I) centers in a limited number of complexes. The best-known example is $[(AuPPh_3)_3(\mu_3\text{-}NR)]^+$ with a μ_3-bridged imido ligand;[10] base-stabilized gold(I) amido complexes such as $[Au(PMe_3)\{N(SiMe_3)_2\}]$ and $[Au_2(PEt_3)_2\{N(SiMe_3)_2\}]^+$ are also known.[11] However, it was only very recently that the first base-free gold(I) amido complex $[\{Au[\mu\text{-}N(SiMe_3)_2]\}_4]$ (**6**) was isolated by Rees, Jr and co-workers.[12]

Gold(I) is widely accepted as a soft Lewis acid, and will form stable compounds with soft Lewis bases. However, amides are hard Lewis bases and this may account for the scarcity of gold(I) amido complexes. The cluster **6** is tetrameric in nature, forming a molecular square with N-Au-N edges. Aurophilic contacts of 3.0100(3)–3.0355(3) Å have been observed. Analogous copper(I) and silver(I) complexes have been synthesized, by Miele et al. and Hitchcock et al., respectively.[13] The copper analogue did show some metal–metal interaction but not the silver analogue. $[\{Cu[\mu\text{-}N(SiMe_3)_2]\}_4]$ was reported to phosphoresce at 512 nm with a long radiative lifetime of 30 μs.[14] A related tetrameric complex of nitrogen donor ligand, $[Au_4Cl_4(pip)_4]$ (pip = piperidine), has also been shown to show intense phosphorescence.[15]



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The extension of gold(I) chemistry to mixed-metal clusters has attracted much attention in the last decade. The incorporation of other metal centers can increase the structural diversity and variety of the final complexes formed. The employment of the metalloligand approach brings structural chemistry into a new era. Laguna et al. reported the syntheses and characterization of a series of novel polynuclear gold(I)–copper(I) and gold(I)–silver(I) mixed-metal organometallic clusters with unsupported gold–metal bonds.[16] The isolation of $[M\{Au(mes)\}_5]X$; (M = Cu, X = PF_6 **7**; M = Ag, X = ClO_4 **8**; mes = 2,4,6-trimethylphenyl (mesityl)) was accomplished by the reaction of the electron-rich $[Au(mes)]_5$ complex with the corresponding metal ion precursors in an appropriate mole ratio. When the 2,4,6-triisopropylphenyl group (trip) was employed in place of the mesityl group, a "cart-wheel" like cluster, $[Ag\{Au(trip)\}_6]CF_3SO_3$ (**9**) was isolated.[16] Figure 2 shows the X-ray crystal structure of the cation of **9**. The silver(I) atom is situated at the center of a regular hexagon of gold(I) atoms to form an almost planar $AgAu_6$ core, with the six gold(I) atoms disposed to donate electron density to the central silver atom. Short intermetallic interactions have been demonstrated which might account for the stability of the heptanuclear heterometallic clusters. This may open up a new generalized synthetic route for the synthesis of other mixed-metal clusters.

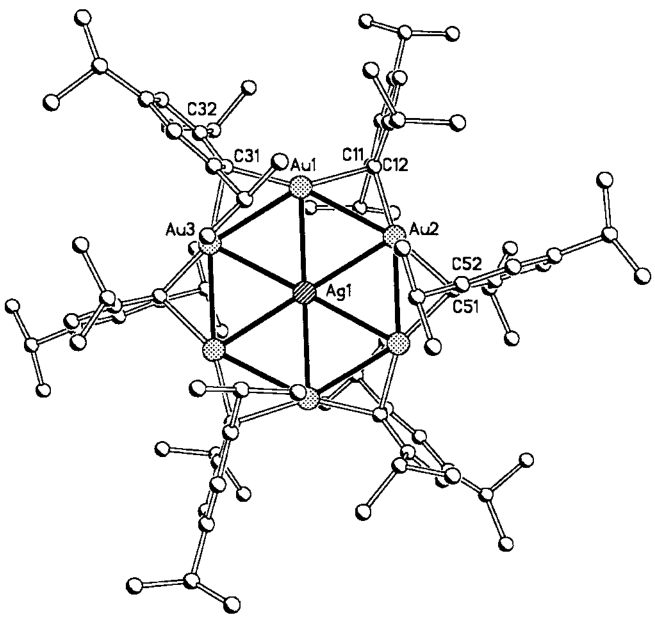

Figure 2. Molecular structure of the cation of complex **9**. The H atoms are omitted for clarity. (Reprinted from ref. [16].)

Gold, because of its inherent and unique features, has made a significant contribution to the study and design of new classes of polynuclear metal complexes and metal clusters. A more thorough and insightful understanding of binary or ternary solids such as the recently reported alkali metal auride aurates(I) $[MAu_4][M_3AuO_2]$ (M = Rb, Cs), formed by the disproportionation of gold into Au^+ and Au^-,[17] requires the synthetic cluster chemists to extend their work to the construction of nanoscale high-nuclearity homo- and heterometallic clusters. Through the strategy of employing bridging ligands, whether soft such as sulfide or selenide or hard such as amides, the nuclearity of the gold clusters can be increased easily, in a uniform, systematic, and controllable fashion. The versatility of the synthetic design strategies can be further elaborated by using the metalloligand approach. With such an ability and the potential to assemble new multinuclear supramolecular arrays, gold has important implications for the future design and development of advanced nanomaterials.

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[1] a) *Gold: Progress in Chemistry, Biochemistry, and Technology* (Ed.: H. Schmidbaur), Wiley, Chichester, **1999**; b) H. Schmidbaur, *Gold Bull.* **1990**, *23*, 11; c) H. Schmidbaur, *Chem. Soc. Rev.* **1995**, 391.

[2] See, for example: a) A. Deveson, S. Dehnen, D. Fenske, *J. Chem. Soc. Dalton Trans.* **1997**, 4491; b) J. F. Corrigan, D. Fenske, *Angew. Chem.* **1997**, *109*, 2070; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1981; c) J. F. Corrigan, D. Fenske, W. P. Power, *Angew. Chem.* **1997**, *109*, 1224; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1176; d) V. W.-W. Yam, K. K.-W. Lo, *Comments Inorg. Chem.* **1997**, *19*, 209.

[3] a) G. Marbach, J. Strähle, *Angew. Chem.* **1984**, *96*, 695; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 715; b) S.-P. Huang, M. G. Kanatzidis, *Angew. Chem.* **1992**, *104*, 799; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 787.

[4] a) C. Kowala, J. M. Swan, *Aust. J. Chem.* **1966**, *19*, 547; b) P. G. Jones, G. M. Sheldrick, E. Hädicke, *Acta Crystallogr. Sect. B* **1980**, *36*, 2777; c) K. Angermaier, H. Schmidbaur, *Chem. Ber.* **1994**, *127*, 2387; d) F. Canales, M. C. Gimeno, P. G. Jones, A. Laguna, *Angew. Chem.* **1994**, *106*, 811; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 769.

[5] F. Canales, M. C. Gimeno, A. Laguna, P. G. Jones, *J. Am. Chem. Soc.* **1996**, *118*, 4839.

[6] a) V. W.-W. Yam, E. C.-C. Cheng, K.-K. Cheung, *Angew. Chem.* **1999**, *111*, 193; *Angew. Chem. Int. Ed.* **1999**, *38*, 197; b) V. W.-W. Yam, E. C.-C. Cheng, Z.-Y. Zhou, *Angew. Chem.* **2000**, *112*, 1749; *Angew. Chem. Int. Ed.* **2000**, *39*, 1683.

[7] D. Fenske, T. Langetepe, M. M. Kappes, O. Hampe, P. Weis, *Angew. Chem.* **2000**, *112*, 1925; *Angew. Chem. Int. Ed.* **2000**, *39*, 1857.

[8] a) P. A. Bates, J. M. Waters, *Acta Crystallogr. Sect. A* **1987**, *43*, C194; b) P. Pyykkö, *Chem. Rev.* **1997**, *97*, 597.

[9] C. E. C. A. Hop, R. Bakhtiar, *J. Chem. Educ.* **1996**, *73*, A162, and references therein.

[10] a) V. Ramamoorthy, P. R. Sharp, *Inorg. Chem.* **1990**, *29*, 3336; b) A. Grohmann, J. Riede, H. Schmidbaur, *J. Chem. Soc. Dalton Trans.* **1991**, 783.

[11] a) K. Angermaier, H. Schmidbaur, *Chem. Ber.* **1995**, *128*, 817; b) A. Shiotani, H. Schmidbaur, *J. Am. Chem. Soc.* **1970**, *92*, 7003.

[12] S. D. Bunge, O. Just, W. S. Rees, Jr., *Angew. Chem.* **2000**, *112*, 3199; *Angew. Chem. Int. Ed.* **2000**, *39*, 3082.

[13] a) P. Miele, J. D. Foulon, N. Hovnanian, J. Durand, L. Cot, *Eur. J. Solid State Inorg. Chem.* **1992**, *29*, 573; b) P. B. Hitchcock, M. F. Lappert, L. J.-M. Pierssens, *Chem. Commun.* **1996**, 1189.

[14] A. M. James, R. K. Laxman, F. R. Fronczek, A. W. Maverick, *Inorg. Chem.* **1998**, *37*, 3785.

[15] A. Vogler, H. Kunkely, *Chem. Phys. Lett.* **1988**, *150*, 135.

[16] E. Cerraga, M. Contel, A. D. Valencia, M. Laguna, T. Gelbrich, M. B. Hursthouse, *Angew. Chem.* **2000**, *112*, 2443; *Angew. Chem. Int. Ed.* **2000**, *39*, 2353.

[17] A.-V. Mudring, M. Jansen, *Angew. Chem.* **2000**, *112*, 3194; *Angew. Chem. Int. Ed.* **2000**, *39*, 3066.

Single Fullerene Molecules and the Wave – Particle Dualism

K. O. Greulich

In the past, new developments in physics often have fostered progress in applied chemistry. Now it is applied chemistry which boosts physics in one of its central questions: wave – particle dualism. C_{60} and C_{70} molecules, fullerenes, help solve two of the most important questions of physics: "Is the wave – particle dualism also valid for large objects?" and "Can particles interfere with themselves?"

C_{60} molecules have a molecular weight of approximately 1000 Dalton. This corresponds to a peptide of 8 – 9 amino acids or an oligonucleotide of 3 – 4 monomers. The linear dimension of such a fullerene is equivalent to four carbon atoms (since $4^3 = 64$), namely, three C–C bonds or five Ångströms. Objects of this size can be visualized with good scanning – tunneling or atomic force microscopes. Most readers would probably agree that these are true particles.

If it were possible to show that fullerenes of this size also have wave properties, this would represent a major breakthrough in one of the most basic questions of physics. Exactly this is reported by the group of Anton Zeilinger, Vienna.[1]

Recall that when a (plane) wave encounters a double slit, part of it will move through slit A, the other one through slit B. When the slit width as well as the distance between the slits are of the order of the wavelength, both slits are the origin of spherical waves which interfere with each other, that is, they generate regions of amplification and regions of extinction. A screen in the path of such interfering waves will register an intensity pattern with maxima and minima. One

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