Gold Clusters

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Ionically Cross-Linked Gold Clusters and Gold Nanoparticles

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Gold cluster compounds have a tradition going back more than forty years. If the comparatively large and stoichiometrically no longer exactly defined nanoparticles are included, it even goes back to the 19th century, when Michael Faraday investigated the mysterious red gold nanoparticles (colloids).[1] There is no clear differentiation between clusters and nanoparticles in the literature, though it would be helpful to have one. Herein, only species which are clearly defined stoichiometrically and of uniform structure are called gold clusters. By comparison, nanoparticles shall be understood as particles on the nanoscale which are no longer uniform in size and structure.

The first gold clusters can be traced back to Malatesta et al.[2,3] However, their structures could not be fully elucidated at that time. The first gold cluster for which the structure was clearly defined by single crystal X-ray analysis was $[Au_{11}(PPh_3)_7](SCN)_3$.[4] Subsequently, a series of smaller and larger gold clusters were synthesized and structurally characterized: $[Au_6(PPh_3)_4][Co(CO)_4]_2$,[5] $[Au_8(PPh_3)_8](NO_3)_2$,[5] $[Au_8(PPh_3)_7](NO_3)_2$,[6] $[Au_9\{P(C_6H_4\text{-}p\text{Me})_3\}_8](PF_6)_3$,[7,8] and $[Au_{10}Cl_3](PCy_2Ph)_6NO_3$ (Cy = cyclohexyl).[9] An almost continuous series of gold clusters was, for the time being, completed with the full-shell cluster $[Au_{13}(dppm)_6](NO_3)_2$[10] (dppm = $Ph_2PCH_2PPh_2$), although the discoveries did not happen in a chronological order. Apart from some minor details, these cluster compounds structurally document the stepwise development up to the perfect icosahedral Au_{13} cluster.

The jump to the next, but cuboctahedrally structured, gold full-shell cluster occurred in 1981 with $Au_{55}(PPh_3)_{12}Cl_6$,[11] and was recently followed by the synthesis and characterization of the largest stoichiometrically and structurally uniform gold cluster to date, $[Au_{102}(mba)_{44}]$ (mba = *p*-mercaptobenzoic acid).[12] In between, the synthesis of $[Au_{39}(PPh_3)_{14}Cl_6]Cl_2$ was achieved.[13] A long line of gold nanoparticles with diameters between 2 and 100 nm shall only be referred to briefly. They do not fulfill the criteria for the clusters mentioned above; nevertheless they attained an increasing importance in nanosciences owing to their special electronic and optical properties. Dense packed structures are usually formed for the frequently observed self-organization of nanoparticles in two or three dimensions. Gold nanoparticles that are three- and two-dimensionally cross-linked by spacer molecules are numerous, but shall not be discussed herein. This Highlight will concentrate on some current discoveries involving ionically cross-linked gold clusters and gold nanoparticles.

If the mutual attraction is based on electrostatic interactions between particles of same size with opposite charges, then novel structures may be formed. For example, 5.1 nm gold nanoparticles were modified with $HS(CH_2)_{11}COO^-M^+$ and $HS(CH_2)_{11}NMe_3^+Cl^-$, respectively. Whereas the two species are monodisperse and stable in separated aqueous solutions, micrometer-sized salt-like crystals of oppositely charged particles are formed if equivalent amounts are mixed. X-ray diffraction analyses and scanning tunneling microscopy surprisingly showed that the crystals have a diamond structure, with nanoparticles tetrahedrally coordinated by oppositely charged neighbors.[14] Au_{55} clusters can also be cross-linked by electrostatic forces if the acid-modified derivative $Au_{55}(Ph_2PC_6H_4SO_3H)_{12}Cl_6$ is reacted with diamines, resulting in NH_3^+–SO_3^- interactions.[15]

However, the interaction of cationic small molecular gold clusters by different complex anions shall be in the focus of this Highlight. These novel ionic crystals, arising from investigations by Jansen and Schulz-Dobrick, have brought about a renaissance in the chemistry of these long-known gold clusters. The work by Jansen and Schulz-Dobrick began in 2006 with the synthesis of $[Au_9(PPh_3)_8]PW_{12}O_{40}$, which can be obtained from $[Au_9(PPh_3)_8](NO_3)_3$ and the polytungstate α-$(n\text{Bu}_4N)_3PW_{12}O_{40}$.[16] Depending on the crystallization conditions, either orange–red needles or black–green platelets and prisms are formed, which differ structurally in the Au_9 skeleton and in the crystal packing. Figure 1 shows the crystal structure of the orange–red form, which can be derived from the CsCl structure. In contrast, the dark green isomer (not shown) shows similarity to the NaCl structure. Further examples are $[Au_9(dpph)_4]Mo_8O_{26}$ (dpph = 1,6-bis(diphenylphosphino)hexane) and $[Au_{11}(PPh_3)_8Cl_2]W_6O_{19}$.[17] A decavanadate serves as the anion in $[Au_9(PPh_3)_8]_2(V_{10}O_{28}H_3)_2$.[18] Decavanadate dimers formed by hydrogen bridges and two

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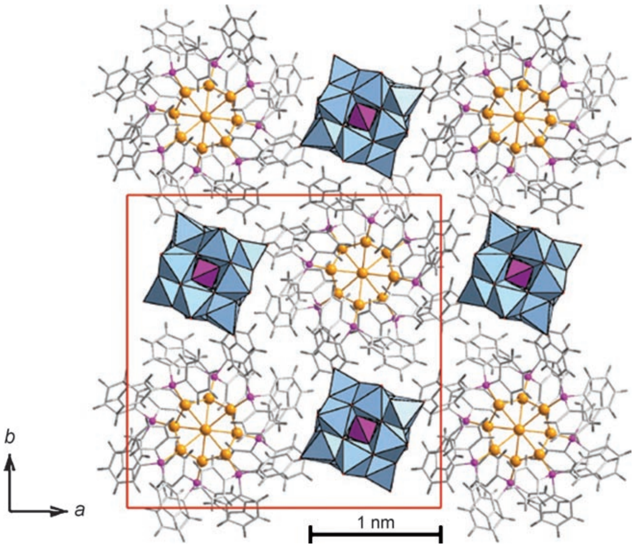

Figure 1. Crystal structure of $[Au_9(PPh_3)_8][PW_{12}O_{40}]$ in the [001] direction. Cation: C gray, Au yellow, P pink; anion: P pink, WO_6 octahedra gray.

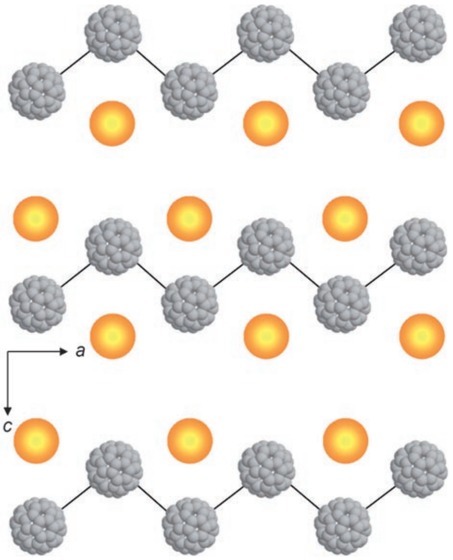

Figure 2. Simplified presentation of the crystal structure of $[Au_7(PPh_3)_7]C_{60}\cdot$THF in the [010] direction. C gray, Au yellow.

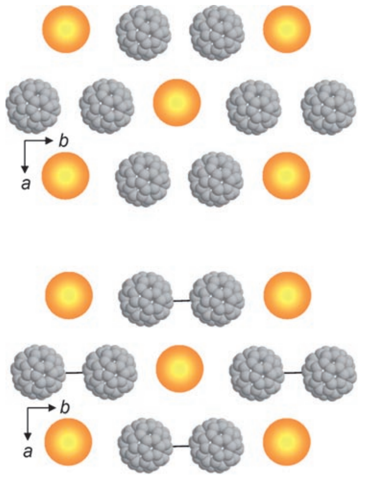

Figure 3. Simplified sketch of the crystal structures of $[Au_8(PPh_3)_8](C_{60})_2$ in the [001] direction at 230 K (above) and at 100 K (below). C gray, Au yellow.

crystallographic independent Au_9 clusters are the building blocks of the crystal structure that is derived from that of Cs_2S.

A current high point in the short story of intercluster compounds is without doubt the first combinations of Au_7 and Au_8 clusters with fullerides, which was also reported by Jansen and Schulz-Dobrick.[19] Fullerides, anionic derivatives of the fullerenes, have been known for a considerable time. Singly- and doubly-charged C_{60} anions and anionic dimeric species are known, along with the (on first appearance) simple salts KC_{60} and RbC_{60}, which are of more complex nature in that both salts contain C_{60} chains formed by [2+2]-cycloadditions between C_{60} units.[20]

The reaction of KC_{60} with $[Au_8(PPh_3)_8](NO_3)_2$ in acetonitrile/THF lead Jansen and Schulz-Dobrick to the novel black intercluster compounds $[Au_8(PPh_3)_8](C_{60})_2$ and $[Au_7(PPh_3)_7]C_{60}\cdot$ THF. The latter compound is formed by a transformation reaction of the Au_8 cluster, which is not described in more detail. As is shown by the X-ray structure analysis of $[Au_7(PPh_3)_7](C_{60})_2$, the crystals consist of zigzag chains of isolated C_{60} monoanions in the [100] direction, with the cluster cations arranged in double rows in between. Jansen and Schulz-Dobrick state that a CsCl or a NaCl structure was expected. The reason for the formation of the observed structure is seen in the fact that, in spite of like charges, structure-determining intermolecular interactions between the cations and between the anions exist, causing the cluster double rows and the C_{60} zigzag chains, respectively, as can be seen in Figure 2. C–H/π interactions between the ligand spheres of the gold clusters and π–π interactions between the fullerides thus overcompensate the electrostatic repulsion forces.

Crystal structure analyses of $[Au_8(PPh_3)_8](C_{60})_2$ at 230 K and at 100 K show considerable disorder. Unlike the structure determined at 230 K, at 100 K a dimerization of the fullerides is observed. In both cases, the Au_8 clusters form hexagonal layers and the fulleride ions are found in the trigonal prismatic cavities. Figure 3 shows both structure variants along the [001] directions. Cations and anions are arranged in such a way that anion–anion and cation–cation interactions can result, as was found in the case of $[Au_7(PPh_3)_7](C_{60})_2$. In the structure obtained at 100 K, C_{60} dimers are formed, as has already been observed in the simpler salts.

The use of molecular cationic gold clusters for the generation of intercluster systems is a new approach in gold cluster chemistry. Not only do novel structures result, but the as yet only sparsely investigated properties promise that possible applications may follow.

[1] M. Faraday, *Philos. Trans. R. Soc. London* **1861**, *151*, 183.

[2] L. Malatesta, L. Naldini, G. Simonetta, F. Cariati, *Coord. Chem. Rev.* **1966**, 1255.

[3] L. Naldini, F. Cariati, G. Simonetta, L. Malatesta, *J. Chem. Soc. Chem. Commun.* **1966**, 647.

[4] M. McPartlin, R. Mason, *J. Chem. Soc. Chem. Commun.* **1969**, 334.

[5] J. W. A. van der Velden, J. J. Bour, W. P. Bosman, J. H. Hoordik, *Inorg. Chem.* **1983**, *22*, 1913.

[6] J. W. A. van der Velden, J. J. Bour, W. P. Bosmann, J. H. Hoordik, *J. Chem. Soc. Chem. Commun.* **1981**, 1218.

[7] P. L. Bellon, F. Cariati, M. Manassero, L. Naldini, M. Sansoni, *J. Chem. Soc. Chem. Commun.* **1971**, 1423.

[8] K. P. Hall, B. R. C. Theobald, D. I. Gilmour, D. M. P. Mingos, A. J. Welch, *J. Chem. Soc. Chem. Commun.* **1982**, 528.

[9] C. E. Briant, K. P. Hall, A. C. Wheeler, D. M. P. Mingos, *J. Chem. Soc. Chem. Commun.* **1984**, 248.

[10] J. W. A. van der Velden, F. A. Vollenbroek, J. J. Bour, P. I. Beurskens, J. M. M. Smits, W. P. Bosman, *J. R. Neth. Chem. Soc.* **1981**, *47*, 1121.

[11] G. Schmid, R. Boese, R. Pfeil, F. Bandermann, S. Mayer, G. H. M. Calis, J. W. A. van der Velden, *Chem. Ber.* **1981**, *114*, 3634.

[12] P. D. Jadzinsky, G. Calero, C. J. Ackerson, D. A. Bushnell, R. D. Kornberg, *Science* **2007**, *318*, 430.

[13] B. K. Teo, X. Shi, H. Zhang, *J. Am. Chem. Soc.* **1992**, *114*, 2743.

[14] A. M. Kalsin, M. Fialkowski, M. Paszewski, S. K. Smoukov, K. J. M. Bishop, B. A. Grzybowski, *Science* **2006**, *312*, 420.

[15] G. Schmid, U. Simon, *Chem. Commun.* **2005**, 697.

[16] M. Schulz-Dobrick, M. Jansen, *Eur. J. Inorg. Chem.* **2006**, 4498.

[17] M. Schulz-Dobrick, M. Jansen, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2326.

[18] M. Schulz-Dobrick, M. Jansen, *Inorg. Chem.* **2007**, *46*, 4380.

[19] M. Schulz-Dobrick, M. Jansen, *Angew. Chem.* **2008**, *120*, 2288; *Angew. Chem. Int. Ed.* **2008**, *47*, 2266.

[20] P. W. Stephens, G. Bortel, G. Faigel, M. Tegze, A. Janossy, S. Pekker, G. Oszlanyi, L. Forro, *Nature*, **1994**, *370*, 636.