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WHAT'S HOT IN CHEMISTRY, March/April 2009

Amid Glut of Superconductivity, Gold Shines Through

by John Emsley



Superconductivity continues to dominate the Hot Ten of chemistry, occupying five positions in the list at #1, #2, #3, #9 and #10. Of those remaining, only #7 and #8 are new to the list. The former reports the structure of a nanoparticle of gold, while the latter reports a way of computing and predicting large polypeptide structures.

Paper #7, from the departments of Structural Biology and Applied Physics at Stanford University, reports the structure of a nano-sized agglomerate of 102 gold atoms sheathed in an outer layer of 44 *p*-mercaptobenzoic acid molecules. Its structure was determined by X-ray crystallography. Large thiolate-protected gold monolayers have been produced by the decomposition of gold(I) benzenethiolate, but paper #7 is the first time that the structure of such a nanoparticle of gold has been determined.

The **crystals** were grown from a solution in which the gold thiolate had to be soluble, and this was achieved with 40% methanol, plus small amounts of sodium chloride and sodium acetate. Fifteen crystals were prepared by this method and, surprisingly, all were found to have the same arrangement of 120 gold atoms. According to the authors of #7, it is electronic forces within the cluster which explains why Au₁₀₂ forms and they suggest that such an arrangement completes a particularly stable 58-electron shell.

The nature of the outer layer of thiolates poses interesting questions also, and these are addressed by **Robert Whetten** and Ryan Price of the Georgia Institute of

Chemistry Top Ten Papers

Rank	Papers	Cites Sep- Oct 08	Rank Jul- Aug 08
1	Y. Kamihara, <i>et al.</i> , "Iron-based layered superconductor La[O _{1-x} F _x]FeAs (x = 0.05-0.12) with T _c = 26 K," <i>J. Am. Chem. Soc.</i> , 130 (11): 3296-7, 19 March 2008. [Tokyo Inst. Technol., Yokohama, Japan] *273SL 92	92	1
2	C. de la Cruz, <i>et al.</i> , "Magnetic order close to superconductivity in the iron-based layered LaO _{1-x} F _x FeAs systems," <i>Nature</i> , 453 (7197): 899-902, 12 June 2008. [6 U.S. and China institutions] *311WV	34	†
3	H. Takahashi, <i>et al.</i> , "Superconductivity at 43 K in an iron-based layered compound LaO _{1-x} F _x FeAs," <i>Nature</i> , 453 (7193): 376-8, 15 May 2008. [Nihon U., Tokyo, Japan; Tokyo Inst. Technol., Japan] *301AI	30	†
4	J.E. Green, <i>et al.</i> , "A 160-kilobit molecular electronic memory patterned at 1011 bits per square centimetre," <i>Nature</i> , 445 (7126): 414-7, 25 January 2007. [Caltech, Pasadena; U. Calif., Los Angeles; Ohio St. U., Columbus] *128WD	16	9
5	M. Dinca, <i>et al.</i> , "Hydrogen storage in a microporous metal-organic framework with exposed Mn ²⁺ coordination sites," <i>J. Am. Chem. Soc.</i> , 128 (51): 16876-83, 27 December 2007. [6 U.S. institutions] *118KQ	16	6

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Technology in the same issue of *Science* (318[5849]: 407-8, 19 October 2007). While there are various ways in which thiolate ligands could bind to gold(I), the most

likely one involves the formation of covalent bonds to two thiolates and these then arrange themselves like a shell around the positively charged core of gold atoms.

Gold also features in a paper which only just failed to make the current list and is at position #12. This reports oxidative rearrangements catalyzed by gold and is the work of a group led by Dean Toste of the University of California at Berkeley. It was published in the *Journal of the American Chemical Society* (C.A. Witham, *et al.*, 129[18]: 5838, 2007; 13 citations this period).

The Berkeley group have demonstrated that oxidative rearrangement reactions of alkynes with sulfoxides as the oxidizing agents can be successfully catalyzed by gold(I) compounds to give yields as high as 94%. The products from such rearrangement reactions contain carbonyl groups and as such offer routes to other molecules. A typical catalyst was triphenylphosphinegold(I) (Ph_3PAuCl) and it was used in conjunction with silver antimony hexafluoride (AgSbF_6).

So how do gold(I) catalysts effect their magic? In their early investigations the group focused on intercepting cyclopropane-gold intermediates which should be present in the formation of ring compounds from alkynes. These intermediates then reacted further with dimethylsulfoxide, but yields were disappointing. However, by a judicious change of reagent to diphenylsulfoxide, and by varying the ligands on the gold catalyst, the yields of desired products were boosted to more than 90%. Further research provided further support for the team's belief that the intermediates which the catalyst was forming were carbenoid in nature.

Subsequent research by the Berkeley group has focussed on a wider range of reactions providing additional support for the carbenoid nature of the gold(I) species in the formation of pyrrolone from an azide. Toste has also studied the effect of ligands in homogeneous gold catalysis (D.J. Gorin, *et al.*, *Chem. Rev.*, 108[8]: 3351, 2008).

In 2008 Toste also showed just how versatile these new catalysts were. They performed well in a ring-expanding cyclo-isomerization that was part of the total synthesis of ventricosene (S.G. Sethofer, *et al.*, *Org. Lett.*, 10[19]: 4315, 2008). They were used in an intermolecular ring formation in the synthesis of azepines (N.D. Shapiro, *et al.*, *J. Am. Chem. Soc.*, 130[29]: 9244, 2008), and in the cyclo-isomerization of 1.5-allenynes (P.H.Y. Cheong, *et al.*, *J. Am. Chem. Soc.*, 130[13]: 4517, 2008). Fluorenes and styrenes were produced by a gold(I)-catalyzed annulation of enynes and alkynes (D.J. Gorin, *et al.*, *J. Am. Chem. Soc.*, 130[12]: 3736, 2008).

Gold, once the Cinderella of metals as far as chemical reactivity was concerned, is now finding itself being wooed and won for all kinds of synthetic and nanotech applications. For example see *Science Watch* January/February 2008 (19[1]: 7), in which other gold catalyst papers made the Hot Ten, reporting equally impressive yields. ■


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6	J. Peet, <i>et al.</i> , "Efficiency enhancement in low-bandgap polymer solar cells by processing with alkane dithiols," <i>Nature Mater.</i> , 6(7): 497-500, July 2007. [U. Calif., Santa Barbara] *184NH	15	2
7	P.D. Jadzinsky, <i>et al.</i> , "Structure of a thiol monolayer-protected gold nanoparticle at 1.1 Å resolution," <i>Science</i> , 318(5849): 430-3, 19 October 2007. [Stanford U., CA] *221LW	15	†
8	H. Lin, Q.Z. Li, "Using pseudo amino acid composition to predict protein structural class: Approached by incorporating 400 dipeptide components," <i>J. Comput. Chem.</i> , 28(9): 1463-6, 15 July 2007. [Inner Mongolia U., China] *169EM	15	†
9	T. Watanabe, <i>et al.</i> , "Nickel-based oxyphosphide superconductor with a layered crystal structure, LaNiOP," <i>Inorganic Chem.</i> , 46(19): 7719-21, 17 September 2007. [Tokyo Inst. Technol., Yokohama, Japan] *209EJ	14	5
10	X.L. Li, <i>et al.</i> , "Chemically derived, ultrasmooth graphene nanoribbon semiconductors," <i>Science</i> , 319(5867): 1229-32, 29 February 2008. [Stanford U., CA] *267SX	14	4

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KEYWORDS: GOLD, GOLD NANOPARTICLES, GOLD(I), GOLD CATALYSIS, DEAN TOSTE, ROBERT WHETTEN, RYAN PRICE.

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