J|A|C|S
COMMUNICATIONS

All-Aromatic, Nanometer-Scale, Gold-Cluster Thiolate Complexes

Ryan C. Price and Robert L. Whetten*

Department of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400

Received June 15, 2005; E-mail: whetten@chemistry.gatech.edu

Hereby disclosed is a method for the preparation and isolation of a class of previously elusive giant gold-cluster thiolates, specifically all-aromatic monolayer-protected clusters (MPCs). Their characterization and salient properties are also briefly described. Thiolate-passivated MPCs are robust, nanometer-scale, metal-core entities tending toward molecular precision. Their exceptional electronic and chemical properties have attracted great interest in both fundamental and applied chemical research. A recent comprehensive review by Daniel and Astruc and other reviews cited therein provide an overview.[1]

All-aromatic MPC variants are of potential value for enhanced rates of electron and excitation transfer, and benzenethiolates ($-SC_6H_5$) are prototypical for this class of material. Complete conjugation gives a maximally coupled electronic structure. The structural rigidity and compactness of these materials leads to improved crystallinity, conducive to total structure determination. We believe these substances show promise as a crystalline material for complete elucidation of the gold−thiolate bonding interaction.

Adequate substances of this type have not been previously isolated.[2] The lack of a suitable preparation method has precluded investigation of Au−benzenethiolate MPCs and might be erroneously attributed to an intrinsic lack of stability or hyper-reactivity. The unusual solubility and oxidation-state properties of the all-aromatic complexes are likely responsible, as the method we now describe uses their varying solubility properties to separate the dominant core types formed by this reaction. The materials are similar in size and composition to gold:arenethiolate compounds reported by Murray et al.[3]

Our preparation method, in brief, involves differential extraction of the poly-anionic products, $Au_N(SC_6H_5)_M^{(z-)}$, generated by the usual phase-transfer tetraoctylammonium (TOA^+)-catalyzed reduction of $Au^ISC_6H_5$ polymers by excess sodium borohydride in an organic solvent. The method is similar to the reaction first reported by Brust et al., but dichloromethane is the reaction medium, rather than toluene.[4] The products can be further oxidatively etched to obtain smaller clusters of near-molecular purity.[5] (See details in the Supporting Information.)

The materials possess several salient characteristics in addition to s*ize quantization* analogous to that found for non-aromatic Au−thiolate MPCs. Gold MPCs in this size range are typically redox active, with effective capacitances approaching 1 aF, implying electrochemically variable charge states and electronic spectra. The charge states assigned herein reflect those of the as-obtained materials, as do all other spectroscopic and compositional measurements. The most abundant core masses (metallic core mass) identified and compositions $[Au_N(SPh)_M]^{z-}$ estimated by mass spectrometry correlated with ^1H NMR and elemental analysis (see Supporting Information) are 28 kDa $[140,78]^{3-}$ and 22 kDa $[110,62]^{6-}$. A minor acetonitrile-soluble fraction with optical properties resembling those of $Au_{28}(glutathione)_{16}Cl_x$ is assigned core mass 5.5 kDa.[6] Further oxidative etching of the 22 or 29 kDa clusters efficiently yields 8.7 kDa core cluster $[44,28]^{2-}$, determined from its anionic parent mass peak at 12190 amu (see Supporting Information). Tetraoctylammonium groups balance the negative charge on the Au−thiolate cores, as MS and ^1H NMR reveal no evidence of Br^- or TOABr. Anionic cluster complexes from reductive preparations are not novel. Stable $[Pt_{44}(CO)_{47}]^{4-}$ and $[Pt_{38}(CO)_{44}]^{2-}$ clusters are known and crystallographically characterized.[7]

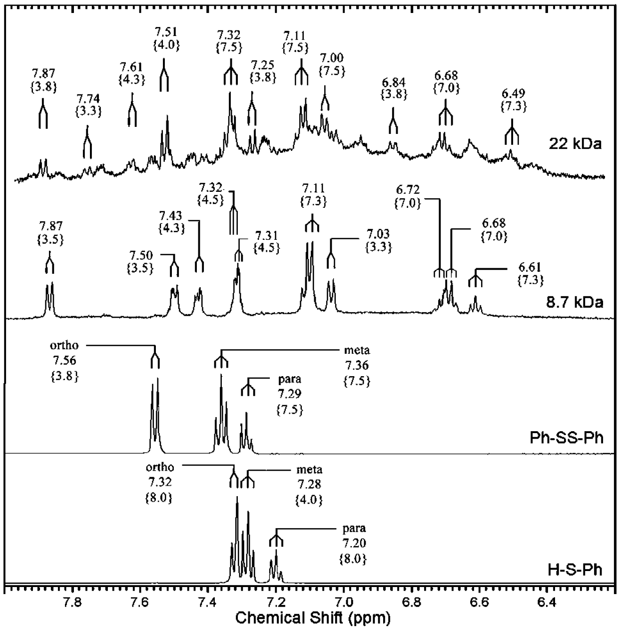

Figure 1. ^1H NMR of 22 and 8.7 kDa core mass Au:SPh clusters with diphenyl disulfide and benzenethiol. Chemical shifts with coupling constants {Hz} are shown for clarity. The samples were prepared as saturated solutions in CD_2Cl_2 and analyzed with a Bruker DRX-500 spectrometer.

The 22 and 8.7 kDa clusters have *distinct ^1H NMR spectra* for $-SC_6H_5$ groups on NMR time scales (Figure 1), indicative of a *unique molecular species and structure* for the 8.7 kDa species. The ~3.5 Hz coupling constants of the 8.7 kDa cluster ortho proton doublets closely approach the 3.8 Hz of diphenyl disulfide and are very dissimilar to the 8.0 Hz found for benzenethiol. Sharp, shifted ^1H NMR features are also present in cadmium sulfide: benzenethiolate molecular clusters.[8] Correlated NMR spectroscopy provides further insight into Au−benzenethiolate bonding. Each material is a c*ompact molecular solid*, reversibly precipitated and/or dried. Small-angle X-ray diffraction (see Supporting Information) indicates 1.92, 2.16, and 1.78 nm center-to-center spacing for the 29, 22, and 8.7 kDa clusters, respectively. These represent the smallest distances yet reported. Each possesses a unique *electronic spectrum* (Figure 2) revealing structured absorption bands characteristic of nanometer-scale Au cluster cores and *vibrational spectra* (Figure 3). The unusually high absorption onset energy at 1.6 eV for the 8.7 kDa cluster may indicate a highly symmetric core structure. The vibrational spectra display shifts of the aryl C=C stretches (1584, 1478, 1442 cm^{-1}) to lower energies by 2−8

10.1021/ja053968+ CCC: $30.25

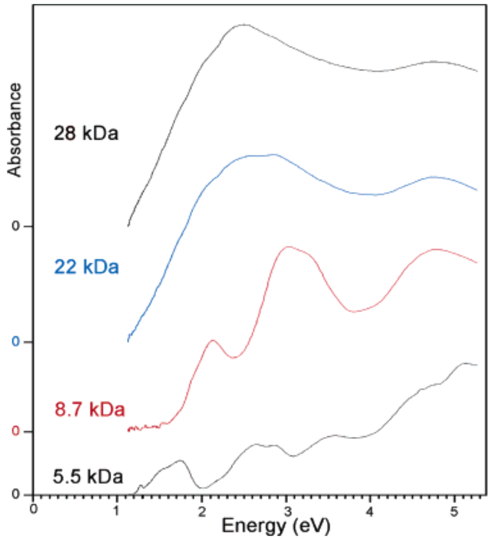

Figure 2. Optical electronic spectrum of the top three Au:SPh clusters in dichloromethane. The 5.5 kDa clusters are in acetonitrile.

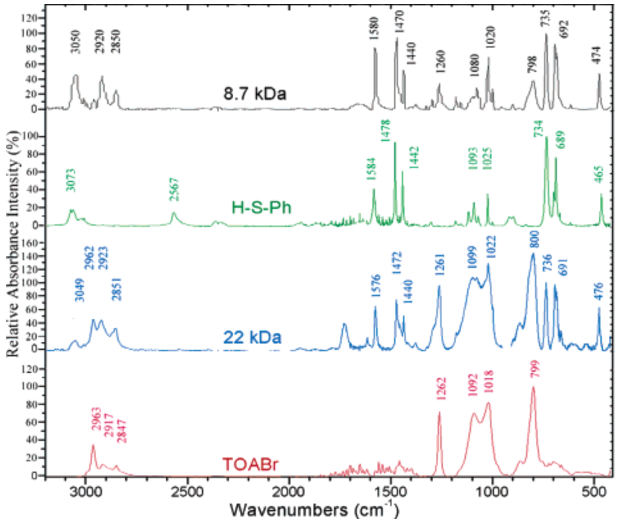

Figure 3. Vibrational spectra for 8.7 kDa Au:SPh clusters, benzenethiol, 22 kDa Au:SPh clusters, and tetraoctylammonium bromide (top to bottom). Thiolate species intensities are normalized to the intense aryl C−H bend at 734 cm^{-1}.

cm^{-1} and an increase of the C−S bend from 465 to ~475 cm^{-1}. Similar shifts have been previously reported for benzenethiol on bulk gold[9a] and gold(I) benzenethiolate molecular complexes.[9b]

Establishing the molecular basis for the remarkable features of the all-aromatic MPCs relative to those containing proximal methylene groups is vital. The PhS− group possesses much higher electronegativity than alkanethiolates, manifested clearly in the enhanced acidity of PhSH ($pK_a = 6.6$, vs 9.4 for $PhCH_2SH$), the enhanced polarity of the PhS−X bond in various compounds, and the increased reduction potential of PhSSPh. Under reducing conditions, these properties favor generation of anionic gold-cluster thiolates, balanced by essential countercations. The compounds are preferentially generated and soluble in weakly polar solvents, such as dichloromethane. The higher lipophilicity of the toluene-soluble 22 kDa clusters must be attributed to the *n*-octyl groups of the six counterions (see Supporting Information). A full accounting of these and other aspects of the generation and etching mechanisms and separations by differential solubility will be presented in a subsequent report.

In conclusion, we have described a successful method for generation of this important class of molecular-metal systems that is simple and general, in that it is extendable to a rich group of *hetero-aromatic* and *substituted aromatic* groups. The conformational inflexibility of the phenyl group gives an appealing simplicity of the products and leads to their greatly reduced solubility (enhanced crystallinity), particularly when the TOA^+ counterions are exchanged for rigid cations. It is anticipated that cationic exchange will facilitate single-crystal growth and thereby total-structure determination of the identified $[Au_{44}(SPh)_{28}]^{2-}$ complex, much as occurred in the case of the 1.65 nm $Pd_{145}(CO)_x(PEt_3)_{30}$ molecule and the similarly sized 1.5 nm CdS $[Cd_{32}S_{14}SPh_{36}]$ molecule.[10] In this way, the unique geometrical and electronic-structure factors, underlying the stability and exceptional electronic properties, of the Au−MPC systems can finally be determined and thereby put on a fundamentally sound chemical molecular basis.

Acknowledgment. The following contributions are hereby acknowledged: Dr. T. G. Schaaff provided essential guidance in the earliest stages (2003 into early 2004) of this research, and obtained the first versions of the mass spectra presented. Dr. L. Gelbaum obtained the ^1H and 2D (not shown) NMR spectra. Technical support and advice were provided Prof. P. First and by M. Arredondo, R. Wyrwas, and J. Bradshaw. Funding was provided by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-FG02-02ER45956.

Supporting Information Available: Preparative methods, powder XRD patterns, elemental analysis data, mass spectral data, and additional ^1H NMR data. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) Daniel, M.; Astruc, D. *Chem. Rev.* **2004**, *104*, 293.
(2) Previous reports of gold:arylthiolate clusters include the following. (a) 4.6−5.1 nm Au:S-Ph-X MPCs: Johnson, S.; Evans, S.; Brydson, R. *Langmuir* **1998**, *14*, 6639. (b) 1.9 and 6.5 nm Au:S-Ph MPCs: Chen, S.; Murray, R. *Langmuir* **1999**, *15*, 682. (c) 4−6 nm Au:S-Ph-OH MPCs: Chen, S. *Langmuir* **1999**, *15*, 7551. (d) 1.1 nm Au:SC_2Ph MPCs with −S−Ph−X partially exchanged onto clusters: Guo, R.; Song, Y.; Wang, G.; Murray, R. *J. Am. Chem. Soc.* **2005**, *127*, 2752.
(3) (a) Wuelfing, P.; Murray, R. *J. Phys. Chem. B* **2002**, *106*, 3139. (b) Donkers, R.; Lee, D.; Murray, R. *Langmuir* **2004**, *20*, 1945. (c) Song, Y.; Harper, A.; Murray R. *Langmuir* **2005**, *21*, 5492.
(4) Brust, M.; Walker, D.; Bethel, D.; Schiffrin, D.; Whyman, R. *J. Chem. Soc.* **1994**, 801.
(5) (a) Schaaff, G.; Whetten, R. *J. Phys. Chem. B* **1999**, *103*, 9394 (b) Song, Y.; Murray, R. *J. Am. Chem. Soc.* **2002**, *124*, 7096. (c) Wilcoxon, J.; Provencio, P. *J. Phys. Chem. B* **2003**, *107*, 12949.
(6) Negishi, Y.; Takasugi, Y.; Sato, S.; Yao, H.; Keisaku, K.; Tsukuda, T. *J. Am. Chem. Soc.* **2004**, *126*, 6518.
(7) Roth, J.; Lewis, G.; Safford, L.; Jiang, X.; Dahl, L.; Weaver, M. *J. Am. Chem. Soc.* **1992**, *114*, 6159.
(8) (a) Sachleben, J.; Colvin, V.; Emsley, L.; Wooten, E.; Alivasatos, A. *J. Phys. Chem. B* **1998**, *102*, 10117. (b) Torimoto, T.; Kontani, H.; Shibutani, Y.; Kuwabata, S.; Sakata, T.; Mori, H.; Yoneyama, H. *J. Phys. Chem. B* **2001**, *105*, 6838.
(9) (a) Wan, L.; Terashima, M.; Noda, H.; Osawa, M. *J. Phys. Chem. B* **2000**, *104*, 3563 (b) Carron, K.; Hurley, G. *J. Phys. Chem.* **1991**, *95*, 9979.
(10) (a) Tran, N.; Powell, D.; Dahl, L. *Angew. Chem., Int. Ed.* **2000**, *39*, 4121. (b) Herron, N.; Calabrese, J.; Farneth, W.; Wang, Y. *Science* **1993**, *259*, 1426.

JA053968+