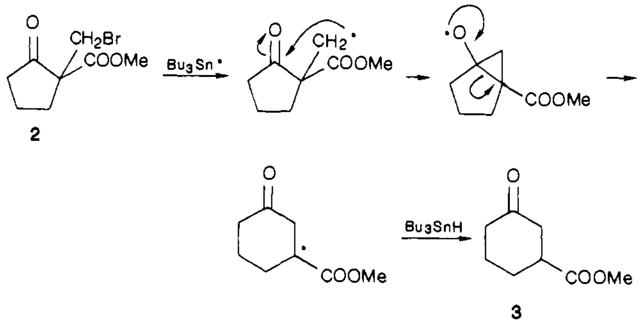
Scheme I



In addition to the insertion product, we also observe the direct reduction products **7** and **11** in the seven- and eight-membered ring-forming reactions. This undesired branch in the reaction can be completely suppressed by carrying out the reaction under dilute conditions in which the tri-*n*-butyltin hydride is added slowly with a syringe drive. Direct reduction is not a problem with the five-membered ring (Table I, entry a) which undergoes ring expansion under normal conditions of concentration (5 mM). In this instance, ring closure is fast relative to the chain transfer that leads to unrearranged reduction product.

There is an interesting sidelight. As noted above, we find that the Schiff base **16** rearranges readily under these circumstances. The latter does not rearrange (in a parallel investigation[12]) upon treatment with vitamin B_{12s}, whereas the α-keto ester **13** rearranges when treated with either tri-*n*-butyltin hydride or with vitamin B_{12s}.

The transformation reported here constitutes an alternative to the Nagata reaction and may be useful in instances where the appropriate α,β-unsaturated ketone is not readily available.

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Observation of Plasmon Frequency in the Optical Spectrum of $Au_{18}Ag_{20}$ Cluster: The Beginning of the Collective Phenomenon Characteristic of the Bulk?

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Recently there has been considerable interest in the fundamental question of when, where, and how the metallic character begins and ends.[2-7] In other words, how many metal atoms must one put together in a cluster before it begins to look and behave like a metal? Conversely, how fine a metal particle must be before it ceases to be a metal? As cluster size increases from $\sim 10^2$ atoms to $\sim 10^3$ atoms, there is a transition from one extreme of chemical and physical behavior of molecular species to the other extreme of bulk properties. It is generally believed, and in many cases has been demonstrated, that unusual size-dependent properties can occur in the intermediate size range, the quantum size regime,[2-7] where there are tens to thousands of atoms. The fact that discrete metal clusters[8] of definitive size and shape provide an opportunity to study the evolution of band structure from the atomic to the solid state has sparked intense interest in the synthesis and characterization of high-nuclearity metal-cluster systems.

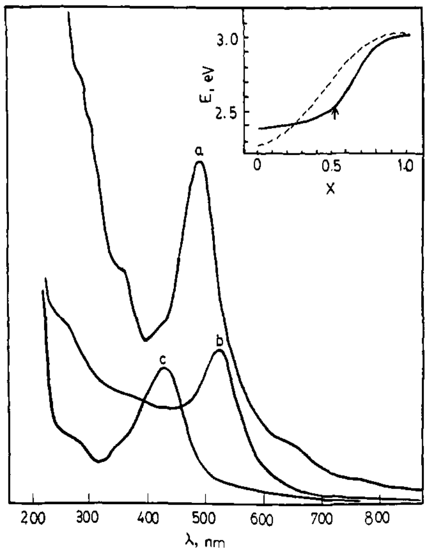

Figure 1. Optical (UV–vis) spectra of (a) $(Ph_3P)_{12}Au_{18}Ag_{20}Cl_{14}$ (**1**) in ethanol, (b) colloidal Au particles in aqueous solution, and (c) colloidal $Au_{0.22}Ag_{0.78}$ particles in aqueous solution. Inset: solid curve, composition dependence of the energy of plasmon frequency of colloidal Au–Ag particles in aqueous solution; dashed curve, computer simulation. The arrow indicates the position for the $Au_{18}Ag_{20}$ (**1**) cluster.

Recently we reported the synthesis and structure of a novel 38-atom cluster $(Ph_3P)_{12}Au_{18}Ag_{20}Cl_{14}$ (**1**).[9] The metal framework can be described as a *three*-centered icosahedra sharing three vertices in a cyclic (triangular) manner plus two capping atoms on the 3-fold axes (nuclearity = 3 × 13 − 3 + 2 = 38), measuring approximately 15 Å in diameter. Its optical spectrum is depicted in Figure 1, curve a. The most striking feature is the 495-nm absorption maximum in the visible region responsible for the intense cherry-red color of the solution.[10] This absorpton fre-

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(10) To date, attempts to observe the fine structure of the 495-nm peak at low temperatures were unsuccessful.

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quency is very similar to the plasmon frequency[11] of 520 nm of colloidal Au particles with an average diameter of approximately 200 Å[12,13] (Figure 1, curve b). Is such similarity an indication of the beginning of the collective phenomenon characteristic of the bulk?

To help shed light on the question, we also prepared aqueous bimetallic colloidal $Au_{1-x}Ag_x$ alloy solutions of 200–400 Å via standard methods[14] and obtained their absorption spectra. The optical spectrum of the $Au_{0.22}Ag_{0.78}$ colloidal solution is depicted in Figure 1, curve c. We found that the frequency of the absorption maximum is highly composition dependent. It varies monotonically from 520 nm (2.4 eV) in Au particles to 400 nm (3.1 eV) in Ag particles as shown in Figure 1, inset, solid curve. The fact that we did not observe two distinct absorption maxima at 520 and 400 nm for the bimetallic ($Au_{1-x}Ag_x$) colloidal solutions argues strongly against segregated Au and Ag particles.[15]

As indicated by the arrow in Figure 1, inset, solid curve, the optical absorption of cluster **1** at 2.5 eV with Ag mole fraction of 0.53 virtually coincides with that of Au bimetallic colloidal particles. This is a strong indication that the 495-nm absorption observed in **1** can be interpretated as a plasmon frequency similar to that of colloidal particles. We believe that, even at the level of a few dozen metal atoms, a cluster, under appropriate ligand environment and suitable molecular architecture and symmetry, may already exhibit collective electronic behavior characteristic of that of the bulk.[16]

To further our understanding of the optical behavior of the colloidal $Au_{1-x}Ag_x$ particles, we performed a semiquantitative computer simulation of the composition dependence of plasmon frequency (Figure 1, inset, dashed curve). Following Mie's theory,[17] the frequency of the absorpton peak is proportional to $\epsilon_2/[(\epsilon_1 + 2\epsilon_0)^2 + \epsilon_2{}^2]$ where ϵ_1 and ϵ_2 are the real and imaginary parts of the dielectric constant and ϵ_0 is the dielectric constant of the medium. Here we take ϵ_1 and ϵ_2 to be the composition-weighted averages[18] of the bulk dielectric constants of Au and Ag (viz., $\epsilon_i = (1 - x)\epsilon_i{}^{Au} + x\epsilon_i{}^{Ag}$ for $i = 1, 2$) and ϵ_0 to be the dielectric constant of water (1.333^2). While the theory predicts quite satisfactorily the general trend of the composition dependence of the plasmon frequency, quantitative agreement is lacking. We believe that the discrepancy is largely due to (1) the inappropriateness of using bulk dielectric constants for these small particles and (2) the neglect of the effect caused by the smallness of the particle size compared with the electron mean free path λ. We note that these particles (15 Å for **1** and 200–400 Å for the colloidal particles) are of dimensions less than λ (~500 Å) which in turn is less than the wavelength of light (~5000 Å). In other words, the electron mean free path of either the molecular or the colloidal systems discussed here is limited by the small size of the cluster or particle.

We conclude that the observation of the plasmon frequency of the 38-atom cluster **1** of approximate 15 Å in diameter (metal core only) is a strong indication that the cluster possesses the free electron quasi-band structure behavior characteristic of bulk metal (viz., entering the quantum-size regime).[19] In other words, the ensemble of the electrons, responsible for the optical absorption, can be considered collectively as a whole in much the same way as in the metal. Further experimental and theoretical studies are in progress.[20]

Acknowledgment. We thank Drs. L. Brus, J. C. Phillips of AT&T Bell Laboratories, Prof. P. A. Lee of MIT, and M. C. Hong and H. Zhang of the University of Illinois at Chicago for helpful discussions. We are also indebted to Drs. S. Woronick and A. Goldman of SUNY, Stony Brook and X. T. Wu of Fujian Institute of Research on the Structure of Matter, Academia Sinica, PRC, for programming assistance.

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(15) The penetration depth is much greater than the size of the particles. If the metallic components in the particles indeed segregate, either on the surface or inside the particle, there should be two distinct absorption peaks. Our observation of a single peak thus gives a strong indication of homogeneously organized clusters.

(16) While such a connection between "large" metal cluster compounds containing $\lesssim 10^2$ atoms and "small" metal particles containing $\gtrsim 10^6$ atoms is rather striking, we note that the similar conclusion that the magnetic behavior of metal clusters containing $\lesssim 10^2$ atoms and reaching a certain size and shape begins to resemble that of colloidal particles or the bulk have also been reported recently.[2,3]

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(19) To what extent electrons in a metal cluster are localized (or delocalized) is difficult to assess. In view of the similar interatomic distance between the metal atoms in **1** as compared to that in bulk Au or Ag, we believe that electrons are delocalized.

(20) Conduction electron spin resonance (CESR) can be a useful means of providing information on the collective behavior of the electrons in metal-cluster systems. The line width of CESR will decrease because the spin-relaxation rates may be limited due to the discreteness of electronic states (thereby making CESR easier to be observed in small particles than in the bulk). However, such a change in line width is complicated by several factors, e.g., spin–orbit coupling, electron–phonon interaction, surface scattering, etc. The line-width variation as a function of particle size, for instance, depends on the strength of spin–orbit coupling. Moreover, when the particle size falls below 30 Å, the number of conduction electrons in a cluster may be so low as to make CESR difficult to observe.

Double-Cubane-Type Molybdenum–Sulfur Cluster Aqua Ion, $[(H_2O)_9Mo_3S_4MoS_4Mo_3(H_2O)_9]^{8+}$

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We have recently reported that the reaction of the incomplete cubane-type $Mo_3S_4{}^{4+}$ aqua ion (**1**) with metallic iron gives the cubane-type $Mo_3FeS_4{}^{4+}$ aqua ion, the core structure of which has been verified by the X-ray structure analysis of $[Mo_3FeS_4(NH_3)_9(H_2O)]Cl_4$ derived from the aqua ion and ammonia water.[1]

We will describe here the preparation, properties, and X-ray structure analysis of a double-cubane-type cluster compound, $[(H_2O)_9Mo_3S_4MoS_4Mo_3(H_2O)_9](CH_3 \cdot C_6H_4 \cdot SO_3)_8 \cdot 18H_2O$, prepared from the aqua ion **1** and metallic magnesium.

Magnesium foil (5 g) was put into a conical flask containing the aqua ion **1** (0.2 M in 50 mL of 6 M HCl) placed in an ice bath. The color of the solution turned rapidly from green to brown. After 1 day, HCl (1 M, 400 mL) was added to the brown solution, which was allowed to stand for several days. Then the solution was filtered and Sephadex G-10 column chromatography was applied (1 M HCl). The second[2] band (dark brown) from the column was absorbed on a Dowex 50W-X2 cation exchanger, which was washed with 1 M HCl. Then the purple solution obtained by use of 2 M HCl[3] was absorbed on the cation exchanger again and eluted with 4 M HPTS (*p*-toluenesulfonic acid). The resultant purple solution was kept in a refrigerator. Black-purple crystals were obtained in a week.[4]

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(2) The first band contains $Mo_4S_4{}^{5+}$ aqua ion. (The yield was ca. 45% based on the starting aqua ion **1**.)

(3) Elution with 6 M HCl gives a brown solution which is converted to a purple solution containing **2** by passing air through it.

(4) Anal. Found (Calcd): Mo, 22.68 (22.79); C, 23.68 (22.83); H, 4.05 (4.37). The yield was ca. 15% based on the starting aqua ion **1**.

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