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### Abstract

A systematic exploration of the growth of Au clusters has revealed a critical size for the formation of stable assemblies. Mass-spectrometric measurements of clusters, as grown in the presence of an excess of weakly binding long-chain n-alkylthiol(ate) groups, show high yields of new compounds with core masses near the 15k minimum ( $\approx 75$  Au atoms;  $k = 10^3$  amu), and also at 23k, and 29k. Structural analyses establish their cores as compact metal nanocrystals of the corresponding effective diameters (1.4 to 1.7 nm), probably of decahedral close-packing and morphology. The precise identities of this sequence of special structures can now be sought.

### 1. Introduction

In the earliest stages of the assembly of material forms from atoms, the rate of growth can be drastically slowed down, or effectively halted, at certain levels of aggregation corresponding to the formation of structures of singular stability, thereby leading to the accumulation of such species. This effect can be strongly enhanced by the action of a reverse process, such as etching, which is more selective than purely thermal disintegration [1,2]. Furthermore, the capture of these entities can be accomplished through suitably gentle handling, e.g., by use of mild passivating agents, to protect against casual (contact) coalescence. It is by now well established that these principles can give rise to some extraordinarily selective phenomena, the best known of which is the high-yield formation of certain carbon-fullerenes [3,4] sharing a special structural characteristic (non-adjacent pentagonal rings), despite a marginal thermodynamic advantage over alternative forms and an absolute instability with respect to larger fullerene structures (or

graphite). A second example, for which the underlying structural principle has not been so definitively clarified, is the case of certain early transition-metal carbides ('metcars')[5].

In this Letter, we describe new experiments designed to reveal the existence of the smallest gold clusters, Au<sub>n</sub>, that possess this kind of extraordinary stability. Our method for approaching this question contains both common and unusual aspects, some of which may make it inapplicable to other kinds of substances. In brief, the growth starts from an atomic-level dispersion, and takes place in the presence of a weakly binding passivating agent, that also acts as a mild etchant, in an otherwise inert environment. Those clusters that can act as growth traps, or thermochemical sinks, accumulate in high abundance, as can readily be detected by a suitable form of mass spectrometry. By careful regulation of the growth conditions, these special forms can be obtained as the essentially exclusive products of the entire, complex formation process. That these species actually are pure gold clusters, substantially unaf-

fects by the retention of a weakly bound surface-passivating monolayer, can be established by structural, spectroscopic and chemical analyses.

The specific aspects of our approach are motivated by the thermodynamics and known chemistry of gold. Gold clusters, nanocrystals, and their colloidal and compound forms are collectively the best known finite metallic system [6]. The situation is favorable not only because of gold's chemical inertness but also its low surface energy, which on a per-surface-atom basis is only about one-tenth of the bulk cohesive energy (3.9 eV per atom). Small gold crystallites can therefore have an unusual degree of stability with respect to the bulk. Indeed, recent calculations [7,8] of the binding energy of relaxed gold clusters show that 90 percent of the bulk cohesion is achieved by certain clusters containing as few as 75 atoms, instead of the  $\approx 60$  percent normal at that degree of aggregation. (The fullerenes are exceptional:  $I_b$ -C<sub>60</sub> recovers fully 95 percent of graphite's cohesion per atom [9,10].) Consequently, weakly binding groups, such as the alkylthiolates (SR), may be used for protecting the nanometer-scale gold surfaces of sufficiently large clusters. This combination (generically Au:SR) has already yielded the following diverse facts:

(i) On extended Au surfaces, one finds the uniform protection of a surface without modification of its essential structural and electronic properties [11]. n-Alkylthiolates (SC) form compact, ordered monolayers in which thiolates (-SR) or dialkyldisulfides (RSSR) reversibly attach to various Au surfaces; their spontaneous assembly is driven by favorable interactions among the long, ordered alkane chains, in concert with a weak chemisorption of the sulfur head group to the metal surface (ca. 0.2 eV per surface Au atom, based on the measured  $\approx 1.2$  eV per RSSR unit desorbed and the six Au atoms covered by this unit) [11]. A recent structural investigation of the surface chemical bond implicates interactions of the Au surface atoms with the non-bonding S orbitals of an intact RSSR molecule [12].

(ii) However, discrete XAu(SR)<sub>m</sub> compounds and small clusters are unstable [13] with respect to elimination of disulfide (RSSR) units – the same channel as described above for the surface system. (By contrast, the strong phosphine (Au:PR<sub>3</sub>) system includes many known mononuclear and cluster compounds,

including the Au<sub>39</sub> cluster (of near-ideal hcp structure) [14] that is the largest elemental cluster outside the carbon-fullerenes to have an unambiguously determined structure.)

(iii) The existence of stable Au:SR nanocrystals, or larger Au<sub>N</sub>(SR)<sub>M</sub> clusters ( $N \gg M$ ) above some size, is implied by the stability of extended-surface systems (point (i) above) and the instability of mononuclear or small cluster compounds (ii). This would mark the size at which the cluster surface appears locally flat to the RSSR units. This logic formed the core of the proposal [2] that precisely such larger cluster- or nanocrystal-based monolayer systems should be based on surfactants capable of forming compact, ordered structures on extended surfaces [11]. The subsequent discovery [15,16] and wide exploration [7,18–21] of the Au:SR nanocrystal systems over the past three years has established the stability and many properties of these systems.

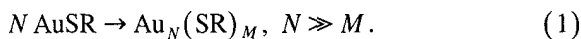
The Au:SR nanocrystals are charge-neutral entities, comprised of a compact core of close-packed metal atoms and a dense mantle of straight-chain groups bound by interactions of the same strength as described above (i), and can be obtained quantitatively by distinct methods [15–17] effective across the  $\approx 1.5$  to 4 nm core diameter range ( $\approx 100$  to 2000 atoms). Their chemical properties are determined mainly by the surfactant tail-group (usually CH<sub>3</sub>), resulting in high inertness; the groups initially adsorbed can subsequently be exchanged [20]. Their electronic and optical properties are characteristic of a small metal particle surrounded by a condensed dielectric (or tunnelling) medium [17,18,23]. Finally, the raw mixtures as prepared contain enhanced abundances at certain sizes, associated with filled shells of Au atoms; the components can be fractionated according to size and then handled as purified molecular substances in ordered (molecular crystals) and dispersed phases [7,20,22]. Considerable insight into the nature of these assemblies and their interactions has recently been provided by realistic simulations [21].

In the research just described, the minimum core-size is not addressed, partly because characterization methods could only provide evidence for the tail of a broad (or continuum) distribution of sizes below 2.0 nm core diameter ( $\approx 300$  atoms) [15,17–19]. From fractionated samples, a lightest purifiable fraction

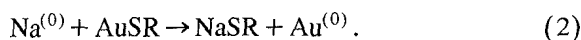
with a core-mass near 30k ( $\approx 150$  Au atoms) has been obtained [7,20], but only in low yield (below one percent of the total nanocrystal abundance). The SC, variant crystallizes well and has therefore been subjected to structural analysis [8,22]. We have only recently found the regulated growth conditions that can reveal the smallest stable forms, which are thereby obtained exclusively.

## 2. Methods

The method used to form selectively the smallest gold clusters is a controlled, stepwise variant of those used to prepare Au:SR nanocrystal materials [15]. In this variant, the growth stage is simply an eliminative condensation process starting from unstable AuSR (stoichiometric) molecules, in the presence of excess RSSR:



This process can be stimulated at room temperature by the action of a gradually added reducing agent, e.g. dispersed Na, expressed in simplified form as



A great excess of this agent is added to assure that growth (1) is driven to its natural completion. Alternatively, elevated temperatures or ultraviolet radiation could be used. The liberated gold atoms combine to form growing clusters, but their accretion rate is limited by the controlled release of Au atoms (2), and coalescence of cluster pairs is eliminated by the presence of excess RSSR groups bound weakly to the cluster surfaces. Here R represents the various choices of n-alkyl groups ( $n\text{-C}_n\text{H}_{2n+1}$ ) denoted by  $C_4$ ,  $C_6$ ,  $C_{12}$ , and  $C_{18}$ .

To obtain first the AuSR species (and excess disulfide RSSR) in toluene, we use the two-phase method [15] in which gold(III) chloride ions are transported into an organic solvent (toluene) containing thiol RSH. At reaction ratios of 3:1(S: Au) or higher, a stoichiometric process [13] goes to completion,  $\text{Au(III)} + 3\text{RS} \rightarrow \text{AuSR} + \text{RSSR}$ , where the charge-balancing protons and chlorides have been omitted for clarity. (The exact nature of the metastable product AuSR species produced is not clear; but this process is described as resulting in

non-metallic 'polymers'  $(\text{AuSR})_n$ , bound by bridging SR groups, that are used as the active precursor in gold paints and in anti-arthritis drugs, depending on the identity of R [4].) The oil phase obtained thus serves as the starting point for process (1) as stimulated by (2). This should be contrasted with preparative methods employing lower S:Au ratios (typically 1:1) [15,18-20], and thus an incomplete preliminary stage prior to the introduction of a reducing agent; the consequences are weakly controlled growth and broadly dispersed larger clusters, typically centered around 2.5 nm (500 Au atoms).

In order to analyze the clusters grown, the quantitatively obtained oil-soluble material is first dried and subsequently washed repeatedly with ethanol to remove all the excess surfactant. The clusters can then be examined as a crude mixture, or can be fractionated according to size by procedures described previously [20]. With slow addition to reasonably concentrated solutions ( $\approx 1$  mmol Au per 0.02 l oil phase), we find that the key control parameters are the surfactant chain-length and the S:Au molar reaction ratio.

The composition of crude mixtures and separated fractions is rapidly assessed by mass-spectrometric analysis using the laser-desorption time-of-flight method described elsewhere [24]. Briefly, a concentrated solution is applied to the laser-target probe tip and rapidly vacuum dried, leaving a continuous neat film of passivated gold clusters, suitable for extended laser desorption and cluster beam experiments. In the custom-built mass spectrometer, pulsed radiation from a collimated XeCl laser strikes the target, and the negatively charged clusters desorbed are accelerated in a high-field, low-resolution time-of-flight spectrometer without any further ionization process. High-resolution mass spectra confirming that the observed peak onsets correspond to essentially totally depassivated gold clusters, as described earlier [24], will be reported separately. Our procedures for X-ray diffraction (XRD) [8,20,22], high-resolution electron microscopy (HREM) [20], and optical spectroscopy [23] have all been described elsewhere.

## 3. Results and discussion

The main results are illustrated in Figs. 1 and 2 by laser-desorption mass spectra (LDMS) obtained with

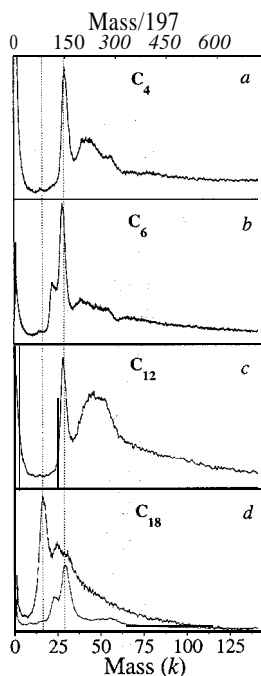


Fig. 1. Examples of low-resolution laser-desorption mass spectra obtained from crude (unfractionated) gold clusters prepared using thiols of various chain-lengths (SC..). All these gold clusters have been prepared under well regulated growth conditions (starting from 3:1S: Au composition), except the lower spectrum in frame *d*, for which 2.5: 1 has been used. The time-of-flight mass spectra have been converted to mass using biomolecular calibrants, and are displayed linearly in  $k$  ( $= 1000$  amu, lower axis) and in units of the Au atomic mass (197 amu, upper axis) [20,24]. The features tracked by vertical dashed lines have rising edges centered around 15k, 23k, and 29k, respectively. The spectra have been obtained in negative-ion mode.

from neat (matrix-free) thick films. Fig. 1 shows examples of mass spectra of massive negatively charged ions [22] generated from crude mixtures (without fractionation) that are obtained using the various chain-length SC, thiol(ate)s in reaction ratios near or exceeding the stoichiometric one (3:1). In every case, these show strong features at masses (sizes) well below the mean-size found earlier,  $\approx 80k$  (400 atoms) [20], which have onsets near 15k, 23k, and 29k (see also Fig. 2). In Fig. 1(d), a comparison is made to the results obtained using a slightly lower ( $\approx 2.5: 1$ ) composition, which results in a drastic depletion of the 15k peak, and brings out prominently the 23k and 29k features.

Separation of such mixtures yields dominant fractions that give clearer LDMS results, Fig. 2, by removing the small quantities of larger clusters. For the shorter chain-lengths, the main fractions contain almost exclusively the 29k cluster; the higher-mass features ( $> 30k$ ) in Fig. 2 result from simple coalescence occurring during the laser-desorption process, as described previously [15,20]. For longer chains (SC<sub>18</sub>, Fig. 2c), the dominant fraction shows principally the 15k peak, with about a 20 percent residual of 23k, and essentially no 29k, as all features above 23k are combinations and multiples of the 15k and 23k masses. These essential results have also been verified with positive-ion detection, and with photoionization mass spectrometry of laser-desorbed neutrals; the negative-ion mass spectra are usually of superior quality, probably because of the very high and nearly uniform electron affinities of Au<sub>N</sub><sup>-</sup> clusters (3-4.5 eV for essentially all  $N > 8$ ) [25].

Although the peaks in such low-resolution spectra are quite broad (enough to conceal a range of clusters sizes), their invariance in location and shape, with respect to changes in formation and extent of

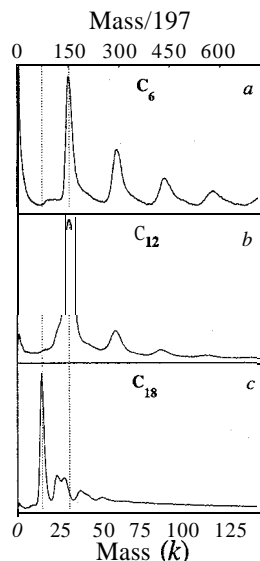


Fig. 2. Mass spectra (see Fig. 1) of the main fractions obtained from the crude mixtures analyzed as in Fig. 1. The absence of small clusters under the mild desorption used is evident in the mass spectra. The step seen near 8k (frame c) is usually clearly seen in such fractionated samples, but could not be enhanced by varying preparation conditions, nor could it be obtained as a fractionated sample.

fractionation, indicates that each is associated with one dominant cluster of definite size ( $N$ ).

In systematic exploration of the reaction conditions (composition, rate of condensation, temperature) we have not been able to modify the essential results illustrated by Figs. 1 and 2, namely that the same three sizes appear as the smallest clusters that can be accumulated in any appreciable abundance. In fact, by comparison with earlier results, Fig. 3, we can confirm that these same three light clusters are probably obtained, although in minute abundance, from every gold cluster growth experiment. The spectra shown in Fig. 3 are the lightest fractions obtained in very low abundance (much less than one percent) from repetitive separation steps performed on a crude mixture obtained from the poorly controlled cluster growth (1: 1 ratio) [20]. The low-mass peaks in each of these can be matched to the three features in Fig. 1. Frames a-c of Fig. 3 show a mixed fraction (a) and its two components (b and c) obtained by further fractionation. This extensive experience, over a period longer than one year, leads us to conclude that there are always three low-mass fractions, and *none* lighter.

The remaining results described here are provided to overcome (perceived) weaknesses of the mass-

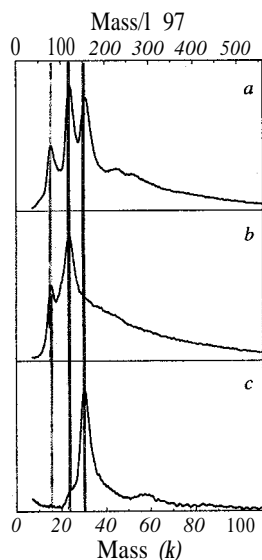


Fig. 3. Mass spectra, as in Figs. 1 and 2, but here for the lightest fractions prepared using  $SC_{12}$  as described also in [20]. See text for discussion.

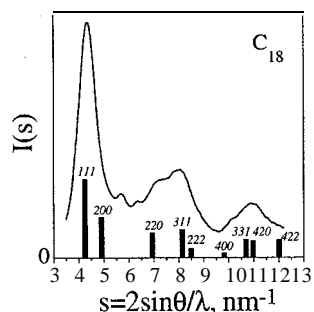


Fig. 4. Large-angle X-ray diffraction pattern obtained from a thick-film sample of a crude mixture prepared using  $(SC_{18})$  in high S:Au molar ratio (2: 1). The results shown are obtained using a Scintag powder diffractometer in the  $(\theta, 219)$  reflection mode using  $CuK\alpha$  radiation with  $\lambda = 1.54 \text{ \AA}$ , and have been corrected for polarization and for an independently measured background from the Si wafer substrate. The bars indicate the positions and relative intensities of the bulk fcc-Au reflections.

spectrometric method and in support of the basic picture of extraordinary accumulation of precisely these sizes of compact gold clusters passivated by very weak surface interactions. We have used XRD analysis as our primary means of determining the Au cluster core-sizes and -structures present in such mixtures and fractions. Earlier experience in correlating LDMS with XRD and HREM results suggests [20,24] that the core-mass can be determined from the steeper rising edge of each main peak in the low-resolution mass spectra, so that crude estimates for the number of Au atoms present are  $\approx Au_{115}$ ,  $\approx Au_{115}$ ,  $\approx Au_{115}$ . A typical XRD pattern is shown in Fig. 4, as obtained from a thick film sample of a crude mixture of  $SC_{18}$  that is rich in all three light species. The location and breadths of all the peaks observed correlate well with those of close-packed, elemental Au, in which the estimated (mean) diameter lies near 1.6 nm ( $\approx 120$  atoms calculated using the bulk density). Besides agreeing roughly with the average mass from LDMS analysis, this quantitative XRD pattern rules out any significant contribution either from massive Au clusters in the sample (as occurs, for example, with ratios S:Au < 2:1) or from other known structural phases, such as cubic  $Au_2S$ , which have principal reflections at quite distinct  $s$ -values [26]. The patterns observed from all these light  $SC_{n}$  mixtures and fractions differ systematically from those of monocrystalline (fcc) Au in ways

that are consistent with those expected for multiply-twinned close-packed structures with decahedral and icosahedral morphology), much as described previously [8,27].

Other measurements sensitive to the presence and size of elemental Au clusters also give results consistent with the above picture. Fig. 5 shows an optical absorption spectrum of a crude Au:SC<sub>18</sub> mixture measured in dilute solution at room temperature. The spectrum shows an absorption onset (or kink) near 1.7 eV, hardly any remnant of the plasmon band, and few other discernable features, and is thus inconsistent with spectra obtained on larger Au clusters (> 2 nm diameter). HREM observations on crude mixtures show a preponderance of very small cores in the 1.2-1.7 nm range. Elemental analysis of an unfractionated sample of Au:SC<sub>6</sub> clusters gives a Au:S ratio near 2.5: 1, the lowest yet reported (consistent with the high surface-to-volume ratio of very small clusters), and complete consistency with the formula Au<sub>N</sub>(SR)<sub>M</sub> (no unexpected impurities or decomposition).

Finally, tests of thermal and chemical stability suggest that the passivating interaction has the weak character already established for the larger (> 2 nm or > 300 atom) Au clusters and extended monolayers [11,20]. The thermal kinetics of (RSSR) desorption on larger clusters passivated by long-chain thiol(ate)s indicated a typical binding energy near 1.3 eV, and experiments on smaller clusters indicate an energy no greater than this. More telling is the chain-length dependence of the stability. Whereas the lights clusters with long-chains are indefinitely stable at 'room temperature, clusters with SC<sub>6</sub> chains

lose their passivating layer on the timescale of days, when stored dilute in toluene, and those with SC<sub>18</sub> chains are insufficiently stable in dilute form to permit attempts at separation. This suggests that a substantial binding energy lies in the dispersion interactions among the chains, as is known for extended monolayers, so that 1 eV likely represents an upper bound for the (RS)<sub>2</sub>-Au cluster interaction. The implied weakness of this interaction's effect on the gold cluster structure can be appreciated by the fact that one RSSR unit covers six surface gold atoms on close-packed surfaces, or approximately four surface atoms on open (100) or highly curved surfaces (very small crystallites)[11,21]. This suggests that the observed critical sizes, and underlying structures, observed here are not significantly determined by the surfactant.

The extent to which these special clusters prevent the accumulation of others is remarkable. By our best estimates based on quantitative separations and analysis, not less than 90 percent of all gold clusters grown can be shown to lie in the three major peaks between 15 and 30k. This behavior implies the existence of a definite 15k molecular Au assembly capable of acting as an efficient thermochemical 'trap' or 'sink', stable against growth or dissolution, in the co-assembly process. The 23k and 30k molecules act as further sinks, should the growth proceed much beyond the 15k minimum. It is relevant here that, as part of self-assembly on extended Au surfaces, thiols are well established to act as etchants capable of removing ≈ 0.5 monolayers of Au into solution [28]. Such etching provides an obvious mechanism for refining Au cluster structures during co-assembly, helping to account for the exceptional yield of certain light compounds. Similar considerations may explain phenomenal yields of apparently well defined compounds claimed in certain preparations of large metal clusters ('Pt<sub>309</sub>', 'Pd<sub>561</sub>' etc.) [29,30].

The central question posed by these results concerns the special structural characteristics shared by the critical clusters. A definite answer to this question, and to others concerning precise structures and compositions, must await structural analysis of rigorously separated clusters. However, a recently published analysis, carried out by some of us [8,22], of the structural evidence obtained from a small sample of 29k Au:SC<sub>6</sub> (purified as a minor fraction of a

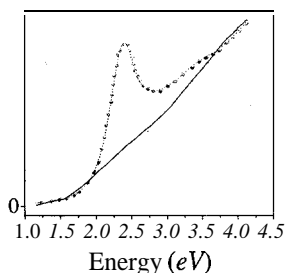


Fig. 5. Optical absorption spectrum of the mixture (solid line) produced using SC<sub>18</sub> as described in Fig. 4, with the spectrum of a standard 10 nm gold colloid (dashed line, Sigma, item 7440-57-5) included for reference.

large-scale preparation), indicated that it is consistent with a truncated-decahedral (pentagonal-bipyramidal) structure of exceptionally high predicted cohesion (92 percent of the bulk) [8], and *not* with icosahedral or fcc single-crystal or twinned structures. Therefore a reasonable hypothesis is that all three share this structural motif. Wales and coworkers have recently discussed theoretically a 75 atom structure of this type [31], also known as Marks decahedra [32], which was found to have unusually high stability over a wide range of empirical pair-potentials. This general morphology has been claimed by Marks to be the equilibrium ('annealed') shape of small Au nanocrystals supported on carbon substrates [32]. Inspection of the rules for generating this type of structure show that 75 is indeed the smallest possible number of atoms capable of forming such a structure, which would provide an elegant explanation for the smallest critical size at 15k.

#### 4. Conclusions and implications

New experiments have revealed the existence of the smallest gold clusters, Au<sub>n</sub>, that possess the kind of extraordinary stability to resist, with minimal assistance, further growth in the presence of reactive gold species (such as atoms). Under appropriately controlled conditions, these clusters have been shown to act as growth traps, or sinks, so that they accumulate in high abundances, and thus can be obtained as the essentially exclusive products of the entire, complex formation process.

Our specific methods for demonstrating this result, involving growth initiated from an atomic-level dispersion in the presence of a weakly binding etching-passivating agent and detection by high-mass spectrometry and an array of supporting structural-spectroscopic techniques, are somewhat unusual specific to gold, but are justified a posteriori by the properties of the resulting clusters.

The most striking finding here is that a heretofore unpredicted Au<sub>N</sub>(SR)<sub>M</sub> compound of  $\approx 15k$  core-mass ( $\approx 75$  atoms) is always found, independent of preparation conditions and chain-length used, as the smallest observable cluster. Its abundance and subsequent stability further show dramatic enhancements under optimal conditions of chain-length and molar

S:Au ratio, without the concomitant emergence of smaller entities. These results point to the existence of a series of special structures, with preliminary evidence that they will belong to the truncated-decahedral family, as described already [8] for the largest (29k) of the three, but considerable further experiments will be needed to determine the precise number of metal atoms and the detailed structures of these special assemblies.

In the absence of this crucial information, we conclude-by indicating more narrowly how a critical size for co-assembly and stability in the Au:SR system may have implications beyond cluster and surface chemical physics. First, in mining technology, long-chain alkylthiols (C<sub>12</sub>S) are used in particular to recover ultrafine gold grains from crushed ore dispersed in biphasic (frothing) media [33]; our results suggest a distinct critical (minimum) size for such recovery. Second, there is strong evidence that the metabolism of certain micro-organisms plays a key role in transforming Au ions [Au(I, III)  $\rightarrow$  Au(O)] into placer deposits of pure gold, for which process a cysteine- (cystine-)rich protein is invoked [34]; if the interior of such a protein is extremely thiol-rich, as seems likely [34], then a critical nucleus for this process may resemble the core of the 15k compound described above. The ease of preparation and good stability of these light gold compounds further suggests their potential as model compounds for supported Au catalysts, and also for their potential exploitation as well-defined active elements (double tunnel-junctions) in high-temperature mesoscopic and microelectronics research, since 1.2 nm gold crystallites may act as nearly ideal electron reservoirs [25,35] and the requisite phenomena (Coulomb staircase) are barely observable at room temperature in larger particles ( $\approx 1.8$  nm) [17].

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