

Research Article

Protected Gold Nanoparticles with Thioethers and Amines As Surrogate Ligands

M. Rafiq H. Siddiqui

Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia

Correspondence should be addressed to M. Rafiq H. Siddiqui; rafiqs@ksu.edu.sa

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Dodecyl sulfide, dodecyl amine, and hexylamine were shown to act as surrogate ligands (L) via metastable gold nanoparticles. By collating analytical and spectroscopic data obtained simultaneously, empirical formula $Au_{24}L$ was assigned. These impurity-free nanoparticles obtained in near quantitative yields showing exceptional gold assays (up to 98% Au) were prepared by a modification of the two-phase method. Replacement reactions on the $Au_{24}L$ showed that Au:L ratios may be increased (up to $Au_{55}:L$ ($L = (H_{25}C_{12})_2S$)) or decreased ($Au_{12}:L$ ($L = H_2NC_{12}H_{25}$ and $H_2NC_6H_{13}$)) as desired. This work encompassing the role of analytical techniques used, that is, elemental analysis, variable temperature 1H NMR, FAB mass spectrometry, UV-Vis spectroscopy, thin film X-ray diffraction, and high-resolution electron microscopy (HREM) has implications in the study of size control, purity, stability, and metal assays of gold nanoparticles.

1. Introduction

Nanoparticles are the building blocks for nanostructures that have applications ranging from corrosion science to molecular recognition and nanotechnology. The progress reported so far to derive maximum electronic function from nanoparticles appears to be impeded by limitations in controlling their size and sometimes difficulties in freeing them from impurities or instability.

Attempts are continuing from physicists, chemists, and biologists to use monolayer protected clusters [1] (MPCs, nanoparticles) as building blocks in sensor and other devices [1–4]. However, the composition and concomitant molecular electronic properties of MPCs seem difficult to control because of size distribution, the nature of self-assembly, differences in preparative techniques, and sometimes instability. Processes developed to make monodisperse or size-controlled gold nanoparticles have been outlined [5, 6]. Recently, the merits and potential of using ligands (L) such as thioether and amines [7, 8] were discussed, and comparisons with thiol-capped gold nanoparticles have been made. Progress in this direction seems to be limited by challenges in synthesizing the pure analogues and exploiting them due to instability [7–9]. Due to our continued interest in gold chemistry

and specially its applications in catalysis [10–14], we have been studying methods of synthesizing and stabilizing gold nanoparticles. Herein, methods to obtain gold nanoparticles with high metal content and purity, using them as preparatively convenient but readily replaceable (surrogate) ligands, are described. The importance of concurrent spectroscopic, analytical, and structural studies is emphasized. On this basis empirical formulae $Au_{24}(S(C_{12}H_{25})_2)$, $Au_{24}(NH_2C_{12}H_{25})$, and $Au_{24}(NH_2C_6H_{13})$ were assigned. These nanoparticles were *metastable*, which could be converted into both particles of higher Au:L or lower Au:L ratios.

2. Experimental

2.1. Synthetic Procedure. The preparation of dodecyl sulphide-capped gold nanoparticles typifies the synthetic procedure. Addition of dodecyl sulfide (0.028 g, 0.075 mmol) to a red toluene solution (25 mL) from the phase transfer reaction between $HAuCl_4 \cdot 3H_2O$ (0.147 g, 0.373 mmol) and $[N(C_8H_{17})_4]Br$ (0.245 g, 0.448 mmol) showed no visible change in colour. This was added dropwise (15 min) to a gently stirred freshly prepared aqueous (100 mL) solution of $NaBH_4$ (0.138 g, 3.732 mmol). From the first addition, a

dense ruby red organic layer begins to form, and after 2 h, the aqueous phase was rejected. The organic layer was washed gently with water (2×50 mL) and dried over MgSO_4 (5 g) and the total volume reduced to 15 mL by evaporation at room temperature to give a fine black lustrous solid in 2 h. The colourless mother liquor was decanted and the product washed with EtOH (3×50 mL), decanted and dried in air. Yield 75 mg (95% based on gold).

Following the same procedure and using an 8-fold excess of hexylamine, $\text{Au}_{24}(\text{H}_2\text{NC}_6\text{H}_{13})$ was obtained only in 43% yield (22 mg) (i.e., $[\text{N}(\text{C}_8\text{H}_{17})_4][\text{AuBr}_4]$ (0.250 g, 0.254 mmol, in toluene, 20 mL; $\text{NH}_2\text{C}_6\text{H}_{13}$ 0.205 g, 0.28 mL, 2.03 mmol; NaBH_4 0.1 g, 2.7 mmol, in water 200 mL)).

Au_3L (L = $\text{HSC}_{12}\text{H}_{25}$), the prototype gold nanoparticles were prepared by the two-phase method of Brust et al. [1]. Au_{24}L (L = $(\text{C}_{12}\text{H}_{25})_2\text{S}$, $\text{H}_2\text{NC}_{12}\text{H}_{25}$ and $\text{H}_2\text{NC}_6\text{H}_{13}$) reported in this paper were prepared by a modification of the two-phase method. $\text{Au}_{24}(\text{S}(\text{C}_{12}\text{H}_{25})_2)$ and its derivatives, $\text{Au}_x(\text{S}(\text{C}_{12}\text{H}_{25})_2)$ where $X = 26, 30, 55$ having empirical compositions of $\text{Au}_{26}(\text{S}(\text{C}_{12}\text{H}_{25})_2)$, $\text{Au}_{30}(\text{S}(\text{C}_{12}\text{H}_{25})_2)$ and $\text{Au}_{55}(\text{S}(\text{C}_{12}\text{H}_{25})_2)$ and its precursor, $[\text{N}(\text{C}_8\text{H}_{17})_4][\text{AuBr}_4]$, and dodecyl sulfide are described.

2.2. Analytical Techniques. ^1H NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. 5 to 10 mg of sample of the gold nanoparticles dissolved in 0.7 mL of the appropriate solvent was examined using 5 mm NMR tubes. The spectra were recorded straight away or at intervals described. Mass spectra (FAB +ve) were obtained according to previously reported methods [15]. The sulfur content was determined on a spectroscopic charged chip detector ICP atomic emission spectrometer. Carbon, hydrogen, and nitrogen were analyzed on Carlo Erba Instruments Co. elemental analyser (Model 1106). Gold analyses were carried out from samples digested in aqua regia and the metal estimated against a BDH standard by atomic absorption spectroscopy. The halogens were determined by potentiometric titrations using AgNO_3 solutions. Powder XRD patterns were obtained using a Siemens D5005 X-ray diffractometer. Data was collected in the 36–110 (2θ) range with a step scan of $2\theta = 0.036$ and a step size of 1 s. using $\text{Co K}\alpha$ ($\lambda = 1.789 \text{ \AA}$) radiation. Thin solid films were prepared from freshly made and analyzed samples of $\text{Au}_{24}(\text{S}(\text{C}_{12}\text{H}_{25})_2)$ and $\text{Au}_{24}(\text{H}_2\text{NC}_{12}\text{H}_{25})$, and a saturated solution in CHCl_3 containing 50 mg/mL and 25 mg/mL, respectively, was deposited with a micropipette on a transparent glass disc (*dia.* 16 mm) to obtain uniform translucent films. The red solution which on drying spontaneously leaves lustrous golden sheen was subjected to the X-rays immediately or periodically as required. In order to ensure that the nanoparticle aggregation was not influenced by the X-ray beam, thin films aged separately in air were also examined. The observed diffraction patterns correspond to *fcc* gold based on the bulk lattice constants (powder diffraction file 04-0784) for the type of radiation used ($\text{Co K}\alpha$). A sample of gold dust (BDH) was also examined (48.7 nm) and used as a further reference. The size of the nanoparticles was calculated from the diffraction peak line-width broadening using the Scherrer equation. Samples for electron microscopy

examination were dispersed in a dry state onto a holey carbon film supported on a 3.05 mm diameter Cu mesh grid. High-resolution electron microscopy (HREM) was performed in a JEOL 2000EX microscope operating at 200 kV.

3. Results and Discussion

All nanoparticles were formulated based on elemental analysis and FAB mass. The air-dried product for the dodecyl sulphide-, dodecyl amine-, and hexylamine-capped gold nanoparticles were analyzed immediately and simultaneously by ^1H NMR, elemental analysis and +ve FAB mass spectrometry to confirm total exclusion of free ligand $[\text{N}(\text{C}_8\text{H}_{17})_4]\text{Br}$, halides and solvent(s). The elemental analysis data and FAB mass of various gold compounds are given below.

Analysis for $\text{Au}_{24}(\text{S}(\text{C}_{12}\text{H}_{25})_2)$ C: 5.8; H: 0.9; S: 0.6 and Au: 92.6% an average empirical formula of $\text{Au}_{24}(\text{S}(\text{C}_{12}\text{H}_{25})_2)$ would require C 5.65; H: 0.99; S 0.63 and Au: 92.73%. MS (70 eV) (FAB +ve): $m/z(\%)$ 371.4 (100) $\{\text{S}(\text{C}_{12}\text{H}_{25})_2 + \text{H}\}^+$, 369.4 (85%) $[\text{S}(\text{C}_{12}\text{H}_{25})_2 - \text{H}]^+$.

Analysis for $\text{Au}_{24}(\text{H}_2\text{NC}_{12}\text{H}_{25})$ C: 3.01; H: 0.52; N: 0.26 and Au: 95.9%. $\text{Au}_{24}(\text{H}_2\text{NC}_{12}\text{H}_{25})$ would require C: 2.94; H: 0.55; N: 0.28 and Au: 96.22%. MS (70 eV): $m/z(\%)$: 186.2 (100) $[\text{C}_{12}\text{H}_{25}\text{N} + \text{H}_3]$, 184.2 (85%) $[\text{C}_{12}\text{H}_{25}\text{N} + \text{H}_2 - \text{H}]$.

Analysis for $\text{Au}_{24}(\text{H}_2\text{NC}_6\text{H}_{13})$ C: 1.39; H: 0.30; N: 0.28 and Au: 98.2%. $\text{Au}_{24}(\text{H}_2\text{NC}_6\text{H}_{13})$ would require C: 1.49; H: 0.31; N: 0.29 and Au: 97.9%. MS (70 eV): $m/z(\%)$: 102.1 (100) $[\text{C}_6\text{H}_{13}\text{N} + \text{H}_3]$, 100.1 (20%) $[\text{C}_6\text{H}_{13}\text{N} + \text{H}_2 - \text{H}]$.

Analysis for $\text{Au}_{24}(\text{H}_2\text{NC}_6\text{H}_{13})$ C: 1.39; H: 0.30; N: 0.28 and Au: 98.2%. $\text{Au}_{24}(\text{H}_2\text{NC}_6\text{H}_{13})$ would require C: 1.49; H: 0.31; N: 0.29 and Au: 97.9%. MS (70 eV): $m/z(\%)$: 102.1 (100) $[\text{C}_6\text{H}_{13}\text{N} + \text{H}_3]$, 100.1 (20%) $[\text{C}_6\text{H}_{13}\text{N} + \text{H}_2 - \text{H}]$.

The presence of MPCs was confirmed by the characteristic peak at 525 nm in the Uv-Vis spectra (shown in Figure 1) and that of the bound ligand was determined by the broad features in the ^1H NMR (CDCl_3 solution). Empirical formulae $\text{Au}_{24}(\text{S}(\text{C}_{12}\text{H}_{25})_2)$, $\text{Au}_{24}(\text{H}_2\text{NC}_{12}\text{H}_{25})$, and $\text{Au}_{24}(\text{H}_2\text{NC}_6\text{H}_{13})$ were based on reproducible analytical and spectroscopic data.

The high-resolution electron microscopy (HREM) of $\text{Au}_{24}(\text{S}(\text{C}_{12}\text{H}_{25})_2)$ (Figure 2) showed that the nanoparticles were uniform in shape and have a size of 3–5 nm diameter.

3.1. Properties and Storage Techniques for Au_{24}L . $\text{Au}_{24}(\text{S}(\text{C}_{12}\text{H}_{25})_2)$, $\text{Au}_{24}(\text{H}_2\text{NC}_{12}\text{H}_{25})$, and $\text{Au}_{24}(\text{H}_2\text{NC}_6\text{H}_{13})$ are insoluble in water, acetonitrile, dichloromethane, ethanol, and acetone but soluble in hexane, benzene, toluene, and tetrahydrofuran and extremely soluble in chloroform to give intensely red solutions. Their saturated solutions (unlike the thiol-capped analogues) when evaporated on flat glass or metal surfaces spontaneously formed lustrous golden films. Figure 3 shows X-ray diffraction pattern of thin films of $\text{Au}_{24}(\text{S}(\text{C}_{12}\text{H}_{25})_2)$ nanoparticles measured fresh and after one hour. The crystallite sizes as calculated by the Scherrer equation were between 5–15 nm for different samples, which is in very good agreement with the microscopy data. All these MPCs can be kept unchanged in the solid state for few

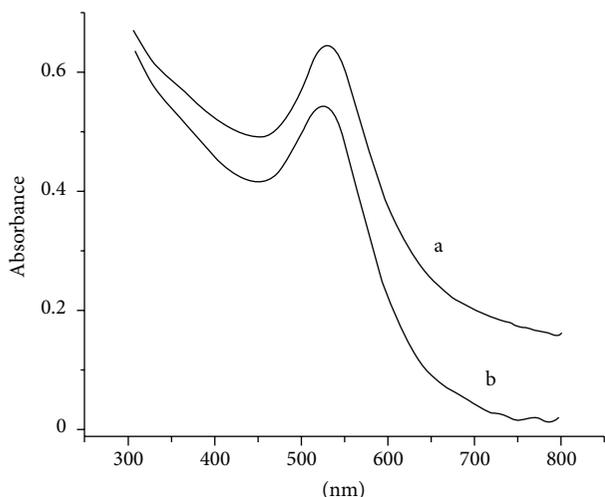


FIGURE 1: The UV-Vis spectra of (a) $\text{Au}_{24}(\text{S}(\text{C}_{12}\text{H}_{25})_2)$ and (b) $\text{Au}_{24}(\text{2HNC}_{12}\text{H}_{25})$ in toluene showing the peak at 525 nm.

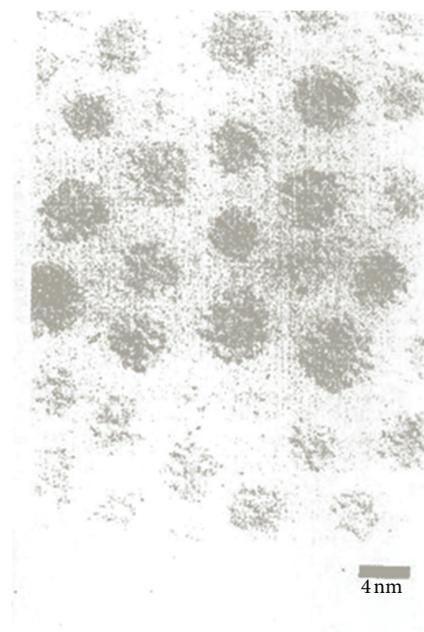


FIGURE 2: The HRTEM micrograph of $\text{Au}_{24}(\text{S}(\text{C}_{12}\text{H}_{25})_2)$ nanoparticles.

hours but aggregate irreversibly unless completely covered in ethanol and in this way can be stored for several months.

3.2. Chemistry of Metastable Gold Nanoparticles. The significance of selecting thioether and amines for ligand capping to gold cores has been outlined previously [16]. A modified two-phase method was employed here under extremely gentle conditions and using ratios of ligand ($\text{L} = (\text{C}_{12}\text{H}_{25})_2\text{S}$, $(\text{C}_6\text{H}_{13})_2\text{S}$, $\text{H}_2\text{NC}_{12}\text{H}_{25}$ and $\text{H}_2\text{NC}_6\text{H}_{13}$) and $[\text{N}(\text{C}_8\text{H}_{17})_4]\text{Br}$ to Au considerably smaller than is conventionally reported. The reduction process was conducted at the interphase

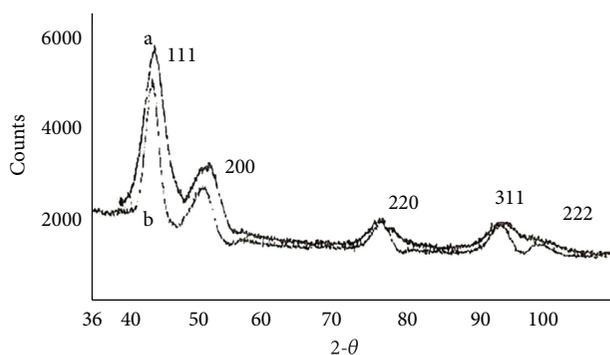


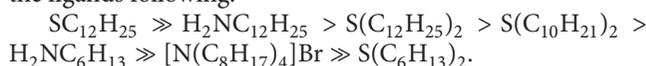
FIGURE 3: X-ray diffraction of thin film of $\text{Au}_{24}(\text{S}(\text{C}_{12}\text{H}_{25})_2)$ nanoparticles: (a) fresh, (b) after 1 h.

by dropwise addition of Au^{III} and L containing reaction mixture in toluene into aqueous NaBH_4 . Due to the relatively weaker coordinating ability of thioether and amine ligands in nanoparticles compared to thiols, it was found necessary to avoid vigorous stirring or any other mechanical stress that might cause ligand desorption, such as removal of solvent under reduced pressure (often at elevated temperatures), ultrasonication, vacuum drying, or centrifugation.

3.3. Reagent Stoichiometries and Ligand Strengths. From a range of stoichiometries studied using dodecyl sulfide, at only $\text{Au}^{\text{III}} : [\text{N}(\text{C}_8\text{H}_{17})_4]\text{Br} : \text{S}(\text{C}_{12}\text{H}_{25})_2 : \text{NaBH}_4$ ratios 1 : 1.2 : 0.2 : 10 impurity-free gold nanoparticles were obtained in 95% yield (based on gold). For the amine-capped MPCs, $[\text{N}(\text{C}_8\text{H}_{17})_4][\text{AuBr}_4]$ was used as the precursor thus permitting lower $\text{Au}^{\text{III}} : \text{L} [\text{N}(\text{C}_8\text{H}_{17})_4]$ ratios as low as 1 : 1.

3.4. Thioether and Amines as Surrogate Ligands. Surrogacy of the thioether and amine ligands is clearly demonstrated by treatment of $\text{Au}_{24}(\text{S}(\text{C}_{12}\text{H}_{25})_2)$, $\text{Au}_{24}(\text{H}_2\text{NC}_{12}\text{H}_{25})$, and $\text{Au}_{24}(\text{H}_2\text{NC}_6\text{H}_{13})$ with an 8-fold excess of dodecanethiol. The thiol substituted products that were isolated showing no traces of the parent ligands in their ^1H NMR and FAB +ve spectra. This technique has applications in metal chemical vapour deposition (MCVD) techniques where molecular complexes are purified [17] selectively using the coordination strengths of ligands.

We were unable to obtain hexyl sulphide-capped gold nanoparticles by this method, and yields were roughly halved for hexylamine (43%) compared with dodecylamine (75%), indicating that they are weaker ligands. More work is required for a further understanding of ligand-exchange reactions from soluble metal cores. However, from experimental data available so far for the isolated nanoparticles, we see a stability trend emerging for capped gold MPCs depending upon the coordination strength and steric and inductive effects from the ligands following:



4. Conclusions

The formation chemistry and subsequent surface reactions studied give an indication of the nature and strength of bonding in ligand-capped gold nanoparticles, in particular, and may contribute towards further understanding of the dynamics of metal/ligand interactions in self-assembled monolayers in general. This work would open vistas to the role of thioether and amines as surrogate ligands or on their own to provide routes to impurity-free metal-rich, size-controlled and stable gold nanoparticles and for mixed ligand capping.

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