



# Empirical-potential global minima and DFT local minima of trimetallic $\text{Ag}_l\text{Au}_m\text{Pt}_n$ ( $l + m + n = 13, 19, 33, 38$ ) clusters



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## ARTICLE INFO

### Article history:

Received 19 May 2017

Received in revised form 2 September 2017

Accepted 11 September 2017

### Keywords:

Trimetallic clusters

Global optimization

Empirical potentials

First-principles calculation

## ABSTRACT

Using a basin-hopping global optimization method, an exhaustive global search of the potential energy surface (PES) of trimetallic Ag-Au-Pt clusters is performed at the empirical potential (Gupta) level. The clusters contain a total of  $N = 13, 19, 33, 38$  atoms while the Ag, Au, Pt content range from 0% to 100%. A broad region of the PES of these systems is sampled, finding a menagerie of geometries, which are catalogued into structural families according to geometrical considerations. The structural families so defined contain a fixed number of Pt atoms while the loading of Ag and Au atoms varies, and indicate that selective Pt doping can stabilize Ag-Au subnanometer clusters. Structural stability trends are identified thus obtaining the optimal composition for each cluster size. Segregation is analyzed through a chemical order parameter, and found to exhibit a size-dependent behavior, with a transition from mixed to segregated structures clearly evidenced at 38-atom cluster size. Optimal composition structures of the Gupta global minima and a few isomers are subjected to DFT reoptimization, which is found to predict qualitatively similar atomic arrangements with a certain degree of deformation, especially for 38-atom clusters, and to introduce changes in the energy ordering among structures with respect to the Gupta potential predictions, although the stabilizing effect of Pt and a cross-over character of 38-atom size seem confirmed.

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## 1. Introduction

Science and technology is advancing in the development of nanotechnological devices with exceptional performances to tackle many current problems in diverse areas such as medicine, chemical industry and electronics, etc. [1]. In this context, mono- and bimetallic nanoclusters play an important role and have been extensively studied, because of two main reasons: first, because nanoscale systems exhibit properties different from those of their counterpart massive solids, and, second, because the physicochemical properties of such clusters vary as a function of composition, size, shape, and chemical ordering [2], which make them excellent laboratories to understand the basic phenomena occurring when these characteristics are modified.

Experimental studies have shown for example that the catalytic activity of metal nanoaggregates can be enhanced when a second

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chemical element is introduced into unary clusters, and a number of studies related to binary clusters or nanoparticles investigated in different catalytic reactions exist [3]. There is also evidence that, for some ternary noble/transition metal clusters, the catalytic activity is superior to that of unary and binary clusters [4]. Computationally, the problem of describing the potential energy surface (PES) and thus e.g. finding and enumerating local and global minima of the PES in binary clusters is harder than in unary clusters, and this combinatorial complexity increases even more drastically in ternary systems. For example, considering  $N$  atoms and a given structural framework, the number of isomers in binary clusters  $\text{A}_l\text{B}_m$  ( $l + m = N$ ) is  $(l + m)!/(l!m!)$ , while in ternary clusters  $\text{A}_l\text{B}_m\text{C}_n$  ( $l + m + n = N$ ) the number of isomers amounts to  $(l + m + n)!/(l!m!n!)$  [5]. Such isomers sharing structure and differing in compositions are called 'homotops' [6]. This increase in complexity represents a major issue when using high-level theoretical approaches to explore the PES of large clusters and a convenient protocol to overcome this issue is to use computational schemes employing empirical potentials (EP) to obtain candidate structures

that are subsequently analyzed with wave-function or electron-density-based schemes [7].

However, cluster optimizations using first principle approaches, though relatively abundant in mono- and bimetallic clusters, are scarce in ternary systems. Noble- and transition-metal ternary clusters have been analyzed using DFT in, for example, the study of magnetic, electronic, and structural properties of  $\text{Fe}_x\text{Co}_y\text{Ni}_z$  ( $x + y + z = 7$ ) trimetallic clusters [8]. In this work, DFT was used to analyze reactivity and stability as a function of concentration. Similarly, structural, electronic, and magnetic properties have been calculated for  $\text{FeAlAu}_n$  ( $n = 1-6$ ) clusters [9], finding an odd-even oscillation effect related to gold loading. The interaction of  $\text{Pt}_x\text{Ru}_y\text{M}_z$  ( $M = \text{Fe, Ni, Cu, Mo, Sn, } x + y + z = 4, x \geq 1, y \geq 1$ ) clusters with  $\text{O}_2$  was described through molecular orbital and natural bond population analysis within a DFT scheme [10], and recently, a combined (EP + DFT) potential energy surface search was carried out on  $\text{Cu}_l\text{Ag}_m\text{Au}_n$  ( $l + m + n = 6$ ) trimetallic clusters [11]. In all these cases, the studied clusters are composed by only few atoms, mainly because DFT optimizations require a significant computational effort. It is worth mentioning that, for atomic clusters deposited on a support, the problem is even more complex because of the increase in the number of atomic interactions which significantly affect cluster structure [12].

Embedded-atom method (EAM) and Gupta potential are two popular empirical many-body potentials for modeling interatomic interactions in noble- and transition-metal clusters [13,14]. Both were proposed to take into account the physical principles that describe bonding of these types of atoms, and are versatile enough to model polyatomic metallic clusters. They can be used in combination with global-minimum optimization algorithms in the search of lower-energy cluster structures. Several studies have analyzed structural and energetic properties of trimetallic clusters using these empirical potentials. For example, Helmholtz free energy minimization using Metropolis Monte Carlo was implemented [15] to study equilibrium structures at different temperatures of binary and ternary Ag-Cu-Co clusters of 200–1300 atoms, modeled through EAM potential, finding that Ag atoms segregate forming a surface layer and that Cu and Co distributions depend on the thickness of this layer. An adaptive immune optimization algorithm combined with the Gupta potential was employed to find the putative global minima of Cu-Ag-Au clusters [16], predicting that, in stable structures of 19 and 55 atoms, Cu and Ag atoms are located on the inner-shell and cluster surface, while Au atoms tend to mix with Cu and Ag atoms, occupying the middle shell. More recently, selected compositions were chosen to study stable structures and thermal stability of up to 561-atom Au-Pd-Pt clusters, performing semi-grand-canonical ensemble Monte Carlo and Molecular Dynamics computations together with the Gupta potential. The stable structures were described and a detailed finite-temperature analysis was provided [17]. For the low-lying structures, it was found that Au atoms locate on the cluster surface, while surface and third inner layers are occupied by Pd atoms, and Pt atoms form the subsurface layer and inner core of clusters. Dynamic lattice searching and adaptive immune optimization (AIO) algorithms were utilized to explore the potential energy surface minima in 50- and 79-atom Au-Pd-Pt clusters [18] described through the Gupta potential, comparing segregation with the bimetallic Au-Pd, Au-Pt, and Pd-Pt. The AIO algorithm combined with the Gupta potential was also used to find the equilibrium structures of 38-atom Au-Pd-Pt clusters [19]. Segregation properties were analyzed, and morphology was categorized into five different shapes. Other algorithms, such as particle swarm optimization and genetic algorithms, have also been used to study trimetallic clusters comprising from hundreds to thousands of atoms [20,21]. Very recently also quaternary Ag-Au-Pd-Pt clusters have been studied employing a Gupta empirical potential and an

adaptive immune optimization algorithm [22]. Compositions were investigated comprising 6 atoms of each of 3 elements while the number of atoms of the fourth element was varied between 1 and 20 for a final total cluster size of up to 38 atoms. A segregation tendency with surface Ag, outer-shell Au, intermediate Pd and inner Pt was singled out.

In this work, we use the basin-hopping global optimization method and the Gupta empirical potential to investigate gas-phase (13, 19, 33, 38)-atom Ag-Au-Pt clusters. Global optimizations are carried out over the entire compositions range. These sizes are interesting because they correspond to magic number of atoms for the icosahedron, double-icosahedron, dodecahedron, and truncated octahedron, respectively. Besides, the search for minimum energy structures is computationally affordable using empirical potentials, while ab initio calculations of predicted global minima structures are still feasible with a reasonable computational time [23]. A collection of structural motifs is obtained from our global optimizations, and structural and energetic trends are explored and illustrated as a function of composition. For each cluster size, structural families are identified via an analysis of both global and local cluster stability functions, from which the optimal compositions and the corresponding putative global minima structures are derived. At such optimal composition DFT reoptimization is then performed on the putative global minima structures and a few isomers [7]. From the comparison between Gupta and DFT results via energy difference analysis and a structural similarity test, it is found that DFT can significantly change geometric and energetic details, but some qualitative features seem confirmed, and the approach of combining a Gupta systematic search with DFT re-optimization appears as a valuable tool to explore the potential energy landscape of such complex systems.

## 2. Model and computational details

### 2.1. The Gupta potential for ternary clusters

The many-body Gupta potential is used for the modeling of the interatomic interactions. According to Cleri and Rosato [24], the term describing  $n$ -body bonding effects on the  $i$ -th atom is associated to the attractive contribution and has the form:

$$E_i^b = - \left[ \sum_{j \neq i}^n \xi^2(i, j) e^{-2q(i, j) \left[ \frac{r_{ij}}{r_0(i, j)} - 1 \right]} \right]^{1/2} \quad (1)$$

To ensure structural stability a repulsive Born-Mayer type term is included, given by:

$$E_i^r = \sum_{j \neq i}^n A(i, j) e^{-p(i, j) \left[ \frac{r_{ij}}{r_0(i, j)} - 1 \right]} \quad (2)$$

Thus, the atomic cluster cohesive energy is:

$$E_{\text{Cluster}} = \sum_{i=1}^n (E_i^r + E_i^b) \quad (3)$$

In both attractive and repulsive interactions, indices  $i$  and  $j$  are related to the atomic species and  $r_{ij}$  is the interatomic distance. The parameters  $A(i, i)$ ,  $r_0(i, i)$ ,  $p(i, i)$ ,  $q(i, i)$  and  $\xi(i, i)$  for homoatomic interactions (Ag-Ag, Au-Au and Pt-Pt) are adjusted to experimental values of the cohesive energy, lattice parameters and independent elastic constants for the corresponding bulk metals at 0 K [24]. The cross-interaction parameters  $A(i, j)$ ,  $r_0(i, j)$ ,  $p(i, j)$ ,  $q(i, j)$  and  $\xi(i, j)$  are obtained by fitting the solubility energies of atomic species A and B (A in B and B in A) [25]. For the ternary system under study, no parameters set has been obtained either from experimental phase diagrams or by ab initio fitting to calculated properties.

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