Density Functional Theory Studies of the Electronic Structure and Muon Hyperfine Interaction in [Au\textsubscript{25}(SR)\textsubscript{18}]\textsuperscript{0} and [Au\textsubscript{25}(SeR)\textsubscript{18}]\textsuperscript{0} Nanoclusters

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ABSTRACT: Density functional theory computational investigation was performed to study the electronic structures, muon sites, and the associated hyperfine interactions in [Au\textsubscript{25}(SR)\textsubscript{18}]\textsuperscript{0} and [Au\textsubscript{25}(SeR)\textsubscript{18}]\textsuperscript{0} where R is phenylethane. The calculated electronic structures show inhomogeneous spin density distribution and are also affected by different ligands. The two most stable muon sites near Au atoms in the thiolated system are MAu\textsubscript{11} and MAu\textsubscript{6}. When the thiolate ligands were replaced by selenolate ligands, the lowest energy positions of muons moved to MAu\textsubscript{6} and MAu\textsubscript{5}. Muons prefer to stop inside the Au\textsubscript{12} icosahedral shell, away from the central Au and the staple motifs region. Muonium states at phenyl ring and S/Se atoms in the ligand were found to be stable and the Fermi contact fields are much larger as compared to the field experienced by muons near Au atoms.

INTRODUCTION

Magnetic properties of gold nanoparticles and nanoclusters have vast potential in various applications. However, the magnetism of these materials is still unclear, as discussed by Agrachev et al.\textsuperscript{1} Contradictory results of various experimental and theoretical investigations could be due to different ligands that cap the gold nanoclusters.\textsuperscript{2} Thiolate-passivated gold nanoclusters with icosahedral geometry Au\textsubscript{25}(SR)\textsubscript{18} have been extensively studied because of their high stability, intriguing properties, and ease of synthesis.\textsuperscript{3−9} There are three possible charge states for the stable redox species of Au\textsubscript{25}(SR)\textsubscript{18}, that is, q = −1, 0, and +1.\textsuperscript{10−15} The superatomic electron configurations of the three charge state nanoclusters are 1s\textsuperscript{2}1p\textsuperscript{6}, 1s\textsuperscript{2}1p\textsuperscript{5}, and 1s\textsuperscript{2}1p\textsuperscript{4}, which are diamagnetic, paramagnetic, and diamagnetic, respectively.

Previous studies have reported that when the thiolate ligands are substituted with selenolate ligands, the stability in reactions involving dissociation of the gold–ligand bond increases, but the stability of the nanoclusters in reactions involving intramolecular dissociation of the ligand is reduced.\textsuperscript{16−18} This will produce gold nanoclusters with selenolate ligands that are more stable against degradation in solution than the thiolate-protected gold nanoclusters. Among chalcogens, selenolates and tellurides are considered as substitutes for thiolates in the gold nanocluster systems. However, because of the limited stability of tellurium-based monolayers, selenolate appears to be a more suitable candidate.\textsuperscript{19}

Goikolea et al. were the first to report the magnetic properties of thiolated-gold nanoparticles probed by muon spin relaxation (μSR) measurement, using 2.1 nm of dodecanethiol-capped Au nanoparticles.\textsuperscript{20} They have estimated the internal field at the muon stopping site to be around 0.4 T from the observation of the muon-spin precession. However, this result is unreliable because they used a pulsed muon which has a 70 ns pulse width that gives the detection limit of the internal field at the muon site to be 1 kOe at most.\textsuperscript{21} Recently, more explicit evidence for magnetism was found using μSR measurement in butanethiol-capped gold nanoparticles with 2.2 nm in diameter.\textsuperscript{2} Their results also indicated the presence of a broad range of internal magnetic fields at the muon stopping site, which is consistent with a spatially inhomogeneous distribution of magnetic moments.

Computed electronic structures of muonated systems can provide an insight into the distribution of spin as well as the Fermi contact and dipolar contributions to the hyperfine field experienced by the implanted muon. In this regard, we have

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previously reported our computational work on muon sites in \([\text{Au}_{25}(\text{SR})_{18}]^0\) nanocluster, where R is a hexyl group.\(^{22}\) In the current work, we present the results of our density functional theory (DFT) computational investigations on the electronic structure, muon sites, and hyperfine interactions in two nanocluster systems, \([\text{Au}_{25}(\text{SR})_{18}]^0\) and \([\text{Au}_{25}(\text{SeR})_{18}]^0\), where R is a phenylethane group. As to gauge the effects of different ligands on the electronic structure, muon sites, and muon hyperfine interactions, two chalcogen atoms, sulfur and selenium, were used. The detailed structures used and the computational approach are given in the next section.

**RESULTS AND DISCUSSION**

**Spin Density.** We now present the spin density distribution in \([\text{Au}_{25}(\text{SR})_{18}]^0\) and \([\text{Au}_{25}(\text{SeR})_{18}]^0\) nanoclusters. A comprehensive understanding of the spin density distribution in the host systems could provide a general insight into the muon hyperfine interaction in the systems. Figure 1 shows the spin density distribution, viewed in the Au$_8$S$_6$/Au$_8$Se$_6$ plane. To demonstrate the difference in the spin density distribution of \([\text{Au}_{25}(\text{SR})_{18}]^0\) and \([\text{Au}_{25}(\text{SeR})_{18}]^0\) nanoclusters, the orientations of the Au$_8$S$_6$ and Au$_8$Se$_6$ plane in Figure 1a,b are kept the same.

As can be seen in Figure 1, the distributions of spin density in both systems are rather inhomogeneous and span almost vertically across the Au$_8$S$_6$/Au$_8$Se$_6$ plane but slightly inclined in different directions. A closer look at the spin distribution in the two systems reveals that the selenolate system (Figure 1b) has a more localized spin density distribution, centered in the vicinity of the central core (Au1). These are expected as the optimized geometrical structures of the two systems are not the same due to different coordinating ligands.\(^{23}\) The anisotropic effects of these Au nanoclusters were previously reported by Fortunelli et al.,\(^{24}\) whose work focused on optical and photoluminescence properties. According to Tofanelli et al.,\(^{15}\) the inhomogeneity of the spin densities for both systems is due to the molecular symmetry distortions, corresponding to the Jahn–Teller symmetry breaking, which is prominent in \([\text{Au}_{25}(\text{SR})_{18}]^0\) nanoclusters. The deviation from the idealized polyhedral shape increases as the charge state of Au$_{25}(\text{SR})_{18}$ systems changes from $-1$ to $+1$. Previous DFT\(^ {25,26}\) studies and vibrational analysis\(^ {27}\) reported that the use of certain ligands could also destroy the inversion symmetry and causes significant distortions to the Au$_{25}$S$_{15}$ frameworks. Tlalhuize-Flores et al.,\(^ {25}\) however, revealed that low-polarity R groups such as phenylethane ligand in the \([\text{Au}_{25}(\text{SR})_{18}]^{-}\) nanocluster have no significant effect on the structure.

The result of a recent $\mu$SR experiment on nanogold particles also indicates inhomogeneity in the spin distribution.\(^ {2}\) Dehn et al. have observed a significant $\mu$SR in butanethiol-capped gold nanoparticles, indicating the presence of a broad range of internal magnetic fields at the muon stopping site, which is consistent with a spatially inhomogeneous distribution of magnetic moments.\(^ {2}\) They also suggested that the magnetic properties of the nanoparticles are dependent on the number of electrons or density of states at the Fermi level, which in turn depends on the type and number of ligands.

The spin densities of the positively and negatively charged (staple motifs and Au$_{13}$ core) components for the \([\text{Au}_{25}(\text{SR})_{18}]^0\) and \([\text{Au}_{25}(\text{SeR})_{18}]^0\) molecular systems are summarized in Table 1. The spin density distributions in the staple motifs, \([-(\text{SR})-\text{Au}-(\text{SR})-\text{Au}-(\text{SR})-]_6/\text{phenylethane component}\) and selenolate component are given separately in Table 1. In general, spin density distribution in the thiolated system was found to be more delocalized compared to the system with Se ligands. For both systems, most of the spin densities are distributed inside the icosahedral Au$_{13}$ region, 62, and 75% for the thiolated and selenolated systems, respectively. Furthermore, the spin densities are mainly concentrated around the central gold atom Au1. In both systems, $-0.17$ of spin density is distributed over the Au$_{12}$ icosahedral shell area, consisting of 12 Au atoms, Au2--Au13. Spin densities of about 0.02 and $-0.11$ for each thiolate-- and selenolate--gold nanoclusters are spread over a large area throughout the phenylethane components.

**Charge Density.** Figure 2a,b shows the isosurface plots of charge densities for thiolate-- and selenolate--gold nanoclusters, indicating the distribution of partial charge densities throughout the systems. The charge densities were calculated using the natural bond orbital (NBO) method, and the values for essential components of the molecular systems are tabulated in Table 1. The similar proportions of total charge densities of the negative (Au$_{13}$) and positive \([\text{Au}_{25}(\text{SR})_{18}]^{-}\) or

| structural components | spin density | charge density |
|------------------------|-------------|---------------|
| \([\text{Au}_{25}(\text{SR})_{18}]^0\) | 0.62 | 0.75 |
| \([\text{Au}_{25}(\text{SeR})_{18}]^0\) | $-0.17$ | $-0.17$ |
| \([-(\text{SR})-\text{Au}-(\text{SR})-\text{Au}-(\text{SR})-]_6/\text{phenylethane component}\) | 0.38 | 0.25 |
| \([\text{CH}_2\text{CH}_2\text{Ph}]_{18}\) | 0.02 | $-0.11$ | 0.63 | $-0.23$ |
Au(SR)\textsubscript{18} species indicate that there is a strong intermolecular force in the form of electrostatic interaction between the positive species and the negative species in both systems. This result is similar to the findings of previous DFT studies,\textsuperscript{18,20} that a significant difference exists in the charge distribution at Au\textsubscript{13} core atoms and the outer Au\textsubscript{12} atoms in the staple motifs. In particular, the superatomic Au\textsubscript{13} core is more electron rich. On the other hand, because of electron transfer to the sulfur of the thiolate ligand, the exterior Au\textsubscript{12} atoms in the staple motifs are electron deficient.\textsuperscript{18} The charges on Au\textsubscript{1} atom are \(-1.44\) and \(-1.46\) for the thiolated and selenolated systems, respectively. The other Au atoms in the icosahedron are relatively neutral.

Figure 3 shows the contour plots of electron density distribution on the Au\textsubscript{S}/Au\textsubscript{Se} plane. Significant differences in the distribution of electrons could be noticed between the Au\textsubscript{13}(SR)\textsubscript{18} and Au\textsubscript{13}(SeR)\textsubscript{18} regions.

The calculated average Au\textsubscript{1}–Au\textsubscript{X} bond distances, where X = 2–13 represents the Au atoms in the icosaedral shell, are 2.869 and 2.872 Å for the thiolate– and selenolate–gold systems, respectively, while the corresponding average Au\textsubscript{X}–Au\textsubscript{Y} bond distances among the nearest neighbor gold atoms in the Au\textsubscript{13} icosaedral shell are 3.018 and 3.021 Å.

The calculated average bond distances between the gold atoms in the Au\textsubscript{12} icosaedral shell and the chalcogenide ligands, Au–S and Au–Se, are 2.456 and 2.539 Å. In comparison, the Au–S and Au–Se average bond distances for Au in the staple motifs are slightly shorter, 2.384 and 2.489 Å, respectively. The average charge on the Au atoms in the Au\textsubscript{12} icosaedral shell is \(+0.26\) e\textsuperscript{−}, while for the sulfur atoms in the ligands is \(-0.17\) e\textsuperscript{−}, leading to a relatively significant electronegativity difference. Previous experimental and computational data reported that the Au–S bonds in the coordinating ligands exhibit weak charge polarization (Au\textsuperscript{6+}–S\textsuperscript{2−}), implying that Au(I)–thiolate bonding character is present\textsuperscript{33} with the possibility of partial ionic character.\textsuperscript{18} In contrast, the difference of electronegativity between the Au and Se ligand in the selenolated gold nanocluster is not that significant.

Molecular electrostatic potential (MEP) map can visually analyze the negatively and positively charged region of a molecule. The varying intensities of the electrostatic potential (ESP) mapped surface plots demonstrate the ESP energy values; the red area represents the region where the potential is negative due to high electron density, while the blue area indicates the opposite. The green and yellow regions represent intermediary potentials. In this work, MEP was utilized as an initial prediction tool to determine possible muon stopping sites in both nanocluster systems. A muon that carries one positive charge can be considered an electrophile and is therefore attracted to electron-rich regions in the host systems.

Figure 4a,b show the MEP surface plots for the [Au\textsubscript{25}(SR)\textsubscript{18}]\textsuperscript{0} and [Au\textsubscript{25}(SeR)\textsubscript{18}]\textsuperscript{0} nanoclusters. As shown in the figures for both systems, the Au\textsubscript{13} inner core regions are filled with red, an indication of favorable sites for the electrophilic attack. Additionally, there are also electron-rich spots in the coordinating ligands around the phenyl groups. Hence, for further muon site investigation, a total of 16 possible muon stopping sites comprising 14 sites near the Au atoms were considered. We have also investigated possible muonium (Mu) states at five sites in the ligand region. They are ortho-, meta-, and para-positions at the phenyl ring and two sites near sulfur (selenium) atoms.

**Muon Site Estimation and Hyperfine Interaction.**

Table 2 summarizes the main findings of our computational investigations on muon stopping sites and their associated hyperfine interactions in [Au\textsubscript{25}(SR)\textsubscript{18}]\textsuperscript{0} and [Au\textsubscript{25}(SeR)\textsubscript{18}]\textsuperscript{0} nanoclusters. The “initial site” column specifies the initial muon site before geometry optimization. The initial \(\mu\)-Au was set to 1.640 Å. The second column, “converged muon site” displays the stable muon site after the geometry optimization procedure. The site with the lowest total energy for each particular system was made as the reference energy for all muon sites in a particular nanocluster. Thus, its relative energy was taken as zero. We will discuss the two most stable muon sites in each system in detail, where the relative energy is less than 0.01 and 0.02 eV, respectively, for the muonated [Au\textsubscript{25}(SR)\textsubscript{18}]\textsuperscript{0} and [Au\textsubscript{25}(SeR)\textsubscript{18}]\textsuperscript{0} nanoclusters.

Out of the 16 possible muon sites investigated in this work, \(M_{Au11}\) is the site that has the lowest energy in the

![Figure 2](image1.png)

Figure 2. Charge density distribution of the (a) [Au\textsubscript{25}(SR)\textsubscript{18}]\textsuperscript{0} and (b) [Au\textsubscript{25}(SeR)\textsubscript{18}]\textsuperscript{0} nanoclusters using NBO population analysis. The color range was set to +1.00 to −1.00. Charge density values at individual atoms are given in Table S1 in the Supporting Information section.

![Figure 3](image2.png)

Figure 3. Contour plots of electron density distribution of (a) [Au\textsubscript{25}(SR)\textsubscript{18}]\textsuperscript{0} and (b) [Au\textsubscript{25}(SeR)\textsubscript{18}]\textsuperscript{0} nanoclusters on the Au\textsubscript{S}/Au\textsubscript{Se} plane.

![Figure 4](image3.png)

Figure 4. MEP map generated from the calculated total electron density of (a) [Au\textsubscript{25}(SR)\textsubscript{18}]\textsuperscript{0} and (b) [Au\textsubscript{25}(SeR)\textsubscript{18}]\textsuperscript{0} nanoclusters. Both maps are displayed as viewed in the Au\textsubscript{S}/Au\textsubscript{Se} planes.

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Table 2. Relative Energy, Spin Densities, and the Distance between $\mu$ and Its Nearest Host Atom of the Sixteen Muon Sites for Thiolate $-$ and Selenolate $-$ Gold Nanoclusters $^{a}$

| Site                | $\Delta E$ (eV) | $\mu$-host atom $\Delta$E (eV) | $B_{iso}$ (MHz) | $B_{aniso}$ (MHz) |
|---------------------|-----------------|---------------------------------|-----------------|-------------------|
| $^{a}$Au$_{25}$(SR)$_{18}$ |                 |                                 |                 |                   |
| M$_{Au6}$           | 12.10           | 6.44                            |                 |                   |
| M$_{Au6}$           |                  |                                 |                 |                   |
| M$_{Au6}$           | 7.37            | 6.44                            |                 |                   |
| M$_{Au11}$          | 12.67           | 7.12                            |                 |                   |
| M$_{Au11}$          | 12.95           | 7.46                            |                 |                   |
| M$_{Au12}$          | 10.07           | 9.47                            |                 |                   |
| M$_{Au12}$          | 10.92           | 7.80                            |                 |                   |
| M$_{Au13}$          | 12.10           | 7.12                            |                 |                   |
| M$_{Au13}$          | 12.67           | 7.12                            |                 |                   |
| M$_{Au13}$          | 12.95           | 7.46                            |                 |                   |
| M$_{Au14}$          | 10.07           | 9.47                            |                 |                   |
| M$_{Au14}$          | 10.92           | 7.80                            |                 |                   |
| M$_{Au15}$          | 12.10           | 7.12                            |                 |                   |
| M$_{Au15}$          | 12.67           | 7.12                            |                 |                   |
| M$_{Au15}$          | 12.95           | 7.46                            |                 |                   |
| M$_{Au16}$          | 10.07           | 9.47                            |                 |                   |
| M$_{Au16}$          | 10.92           | 7.80                            |                 |                   |

The corresponding hyperfine coupling constant ($B_{iso}$) and dipolar coupling constants ($B_{aniso}$) for all muon sites are also given in the table.

$^{a}$The corresponding hyperfine coupling constant ($B_{iso}$) and dipolar coupling constants ($B_{aniso}$) for all muon sites.

Figure 5. (a) Lowest energy muon site in $^{[\text{Au}_{25}$(SR)$_{18}$]$^2$, M$_{Au11}$. (b) Magnified picture of the corresponding site showing the bond distance between $\mu$ and Au11 as well as between $\mu$ and other neighboring atoms, Au1 and Au7. (c) Au1, Au11, and Au7 interatomic distances before the introduction of a muon into the host system.
The hyperfine coupling constant (hfcc) values at the various muon sites differ greatly due to a large variation in the contribution of the Fermi contact component. The sign of the Fermi contact coupling constant is negative at some sites where the polarization effect prevails, such as at the three lowest energy sites in the thiolated system. For most sites near Au atoms, the variation in the dipolar field is not so pronounced.

The ordering of muon sites’ stability based on the relative energy for the [Au25(SR)18]0 nanocluster is different from that for the [Au25(SeR)18]0. Moreover, all similar sites such as M_{Au5}, M_{Au5}′, and M_{Au5}″ are grouped together in the ordering list. The lowest energy muon site in the [Au25(SeR)18]0 nanocluster is M_{Au6}, where μ−Au6 distance is 1.772 Å, as shown in Figure 8. This site has the second-lowest relative energy in the [Au25(SR)18]0 nanocluster. Comparing the data in Figure 8 with Figures 6 and 7, one can notice that there are only small differences in the Au−Au interatomic distances, and the expansion of Au−Au distances to accommodate the presence of a muon are very similar to the ones for the [Au25(SR)18]0 nanocluster. The Fermi contact coupling constant at the M_{Au6} site is only 2.85 MHz, and the sign, which is positive, is opposite to the case in the [Au25(SR)18]0 nanocluster. The anisotropic component B_{aniso} is 7.12 MHz, that is exactly the same as the one in the [Au25(SR)18]0 system.

The muon site with the second-lowest energy in [Au25(SeR)18]0 is M_{Au5} in which the relative energy is 0.02 eV. A muon that was initially placed near Au1 and Au2 also moved closer toward Au5, indicated as M_{Au5}′ and M_{Au5}″ in Table 2. At this M_{Au5} site, the μ−Au5 distance is 1.770 Å, and the distance from Au1, Au2, and Au5 planes is 0.613 Å. Figure 9 shows the surrounding environment of M_{Au5}. Generally, the optimized μ−Au distance [Au25(SeR)18]0 is slightly longer as compared to the μ−Au distance in [Au25(SR)18]0. The Fermi contact and dipolar coupling constants at M_{Au5} are −3.13 MHz and 7.29 MHz. Note that the isotropic component sign is negative, in contrast to that found at [Au25(SR)18]0 nanocluster, where the sign is positive and with a much larger magnitude of 21.35 MHz. In the [Au25(SR)18]0 nanocluster, M_{Au5} is the fourth-lowest energy muon site.

The asymmetry and longitudinal field (LF) μSR spectra measured by Dehn et al. show loss of initial amplitude at low temperature which they attributed to a small fraction of muons experiencing very large internal fields. Their spectra at 1.8 K in which the LF ranges from 2 G to 2 kG indicates that the initial symmetry that was suppressed at low field recovered as the field was increased. Goikolea et al. describe spectra, on the other hand, that show missing initial asymmetry, and they suggested that this could be due to the formation of muonium (Mu) states in the ligand. Thus, we have investigated the hyperfine interaction of a Mu at possible sites in the ligand region. Three Mu sites at the phenyl ring, ortho-, meta-, and para-positions, were considered where the double bonds in the ring provide a high electron density region for a Mu to attack. In addition, Mu sites at two sulfur (selenium) atoms in the
The calculated Mu hfcc at S1 and S2 sites are $-0.01$ MHz and 40.01 MHz for the doublet state. In the triplet state, the values increase to 140.11 and 58.00 MHz, respectively. The average Mu–S bond order for the two sulfur sites is 0.867, higher than that for the Mu–C bond order of 0.840. In both thiolated and selenolated systems, the increase in the hfcc values is mainly due to the large Fermi contact contribution, which is typical for Mu hyperfine interaction in organic systems.

**CONCLUSIONS**

The results of our present work show that ligand effects are quite significant in affecting the position of the muon in Au nanocluster. In $[\text{Au}_{25}(\text{SR})_{18}]^{10}$, the most stable muon Au site is $\text{M}_{\text{Au10}}$, while in $[\text{Au}_{25}(\text{SeR})_{18}]^{10}$, $\text{M}_{\text{Au5}}$ is the one with the lowest energy. In our previous work using the hexanethiol ligands, $\text{S(CH}_2\text{)}_5\text{CH}_3$, the most stable muon site was found to be $\text{M}_{\text{Au10}}$. There are of course possibilities that muons stop at multiple Au sites due to the small energy differences among the various Au sites. In terms of hyperfine interaction, the anisotropic component does not change much at different muon Au sites. On the other hand, the isotropic component was found to be quite sensitive to different ligands, varying in both magnitudes and signs. It was found that the hfcc for the most stable Au sites in the $[\text{Au}_{25}(\text{SR})_{18}]^{10}$ and $[\text{Au}_{25}(\text{SeR})_{18}]^{10}$ are $-5.66$ MHz and 9.57 MHz, respectively.

Our investigation on Mu state in the ligand region indicates that the ortho-, meta-, and para-positions at the phenyl rings, as well as Mu trapping sites at sulfur and selenium atoms are

| Mu site | bond order | $A_{iso}$ (MHz) | $B_{iso}$ (MHz) | hfcc (MHz) |
|---------|------------|----------------|----------------|------------|
| $\text{M}_{\text{ortho}}$ | 0.779 | 254.35 | 6.95 | 261.31 |
| $\text{M}_{\text{meta}}$ | 0.811 | 279.41 | 9.94 | 288.90 |
| $\text{M}_{\text{para}}$ | 0.783 | 222.90 | 8.31 | 231.21 |
| $\text{M}_{\text{s1}}$ | 0.895 | 1.362 | $-0.85$ | 0.85 | 0.01 |
| $\text{M}_{\text{s2}}$ | 0.847 | 38.15 | 1.86 | 40.01 |

**Figure 9.** (a) Second most energetically favorable muon stopping site in the selenolated system, which is located at the $\text{M}_{\text{Au5}}$ site. (b) Magnified picture of the corresponding site, showing the bond distance between $\mu$ and Au5 as well as between $\mu$ and other neighboring atoms, Au1 and Au2. (c) Au1, Au2, and Au5 interatomic distances before the introduction of a muon into the host system.
energetically stable. The hfcc values at these Mu sites in the triplet state are high due to a large Fermi contact field. It should be noted that both Goikolea et al. and Dehn et al. systems do not contain any phenyl ring in the ligand, but there are sulfur atoms that can provide multiple Mu trapping sites. Thus, the large Mu Fermi contact field at sulfur sites is a factor that could explain the loss of initial asymmetry observed in the µSR spectra.

**Computational Details.** The initial geometry of the \([\text{Au}_{15}(\text{SR})_{18}]^0\) nanocluster used in this investigation was taken from the crystal structure data where \(R\) is phenyl-ethane. The crystal structure of the system is triclinic with the \(P\bar{1}\) space group. The starting geometry for the \([\text{Au}_{15}(\text{SeR})_{18}]^0\) nanocluster was modified from the thiolated system, where all sulfur atoms were replaced with selenium atoms. As shown in Figure 10a, the system possesses a core–shell structure of 13 gold atoms, comprising one central Au encapsulated by the \(\text{Au}_{12}\) icosahedral shell. The basic framework of the system contains three interlocked \(\text{Au}_{8}\text{S}_6/\text{Au}_{8}\text{Se}_6\) rings indicated using different color codes, as shown in Figure 10b. All rings have two orthogonal staple motifs, each of which consists of a (−RS−Au−RS−Au−SR−) dimer. For labeling purposes, the rings are divided into two semi-rings labeled as D1, D2, D3, D4, D5, and D6. There is a total of nine crystallographically independent phenylethane ligands, and each is bonded to a sulfur atom or a selenium atom in the staple motifs. A full geometry optimization without symmetry constraints was performed for each nanocluster system to obtain its minimum total energy. This optimized geometry was subsequently utilized as the host system to study possible muon trapping sites.

DFT in the B3LYP framework was employed for all calculations in this work. LanL2DZ basis sets were used for Au atoms with the inclusion of scalar relativistic effects. For other atoms, the calculations were carried out using 6-31G++(d,p) basis sets. Because of significant dispersion forces in gold atoms, Grimme’s dispersion with Becke–Johnson damping model was included in all calculations to take into account the empirical dispersion corrections to the DFT hybrid functional. All calculations were performed using G16 Revision B0.1 software package installed at the RIKEN Hokkaido GreatWave Supercomputing facility. The setting up of the input file, as well as output analysis and graphical illustration, were accomplished using GaussView and Mercury software. The spin densities were examined using Mulliken population analysis, whereas the charge distribution was obtained using natural population analysis.

There is a total of 25 inequivalent Au atoms and 18 inequivalent S/Se atoms in the nanocluster, which allow a muon to be trapped near these sites. Based on our previous work and because of the computational cost, we have visually analyzed the MEP map to identify potential muon stopping sites. The MEP was generated using the host systems without the presence of a muon. This is similar to the minimum ESP search adopted by other works where the map is generated using an unperturbed environment. As a result, there are 13 sites near Au atoms in the icosahedral core and one site near Au in the staple motif that were considered in the search for stable muon sites. For identification purposes, the muon sites inside the icosahedral core are labeled as \(M_{\text{Au1}}\) to \(M_{\text{Au13}}\) and the one in the staple motif is labeled as \(M_{\text{Au14}}\). Muon sites near two sulfur/selenium atoms in the staple motifs are designated as \(M_{\text{S1}/M_{\text{Se1}}}\) and \(M_{\text{S2}/M_{\text{Se2}}}\). In Figure 10a, the S1/Se1 atom is indicated as S central, while the S2/Se2 is shown as S terminal. As is customary in muon site calculation, hydrogen with the mass of muonium was used to mimic muonium. After a positive muon was introduced into the host systems, we performed another geometry optimization that allowed the muon and several host atoms in its vicinity to move. This condition is to allow those atoms to relax into new positions and to stabilize the muon stopping sites.

![Figure 10.](https://pubs.acs.org/doi/10.1021/acsomega.0c04937)

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04937.

Spin density and natural charge density distributions of individual atoms in \([\text{Au}_{15}(\text{SR})_{18}]^0\) and \([\text{Au}_{15}(\text{SeR})_{18}]^0\) systems

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Notes
The authors declare no competing financial interest.

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■ REFERENCES
(1) Agrachev, M.; Antonello, S.; Dainese, T.; Ruzzi, M.; Zoleo, A.; Aprà, E.; Govind, N.; Fortunelli, A.; Sementa, L.; Maran, F. Magnetic Ordering in Gold Nanoclusters. ACS Omega 2017, 2, 2607−2617. (2) Deyn, M. H.; Arsenneau, D. J.; Buck, T.; Courtie, D. L.; Fleming, D. G.; King, S. R.; MacFarlane, W. A.; McDonagh, A. M.; McCadden, R. M. L.; Mitchell, D. R. G.; Kiefl, R. F. Nature of magnetism in thiol-capped gold nanoparticles investigated withMuon spin rotation. Appl. Phys. Lett. 2018, 112, 053105. (3) Jin, R. Quantum-sized, thiolate-protected gold nanoclusters. Nanoscale 2010, 2, 343−362. (4) Katla, S. K.; Zhang, J.; Castro, E.; Bernal, R. A.; Li, X. Atomically Precise Au125(SR)18 Nanoclusters: Rapid Single-Step Synthesis and Application in Photothermal Therapy. ACS Appl. Mater. Interfaces 2018, 10, 75−82. (5) Chen, Y.-S.; Choi, H.; Kamat, P. V. Metal-Cluster-Sensitized Solar Cells. A New Class ofThiolated Gold Sensitizers Delivering Efficiency Greater Than 2%. J. Am. Chem. Soc. 2013, 135, 8822−8825. (6) Chen, Y.-S.; Kamat, P. V. Glutathione-Capped Gold Nanoclusters as Photosensitizers. Visible Light-Induced Hydrogen Generation in Neutral Water. J. Am. Chem. Soc. 2014, 136, 6075−6082. (7) Stemplecoksie, K. G.; Kamat, P. V. Size-Dependent Excited State Behavior of Glutathione-Capped Gold Clusters and Their Light-Harvesting Capacity. J. Am. Chem. Soc. 2014, 136, 11093−11099. (8) Abbas, M. A.; Kamat, P. V.; Bang, J. H. Thiolated Gold Nanoclusters for Light Energy Conversion. ACS Energy Lett. 2018, 3, 840−854. (9) Kurashige, W.; Nihori, Y.; Sharma, S.; Negishi, Y. Recent Progress in the Functionalization Methods of Thiolate-Protected Gold Clusters. J. Phys. Chem. Lett. 2014, 5, 4134−4142. (10) Negishi, Y.; Nobusada, K.; Tsukuda, T. Glutathione-Protected Gold Clusters Revisited: Bridging the Gap between Gold(1)−Thiolate Complexes and Thiolate-Protected Gold Nanocrystals. J. Am. Chem. Soc. 2005, 127, 5261−5270. (11) Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. Crystal Structure of the Gold Nanoparticle [N(C6H5)2]+[Au125(SCH2CH2Ph)18]. J. Am. Chem. Soc. 2008, 130, 3754−3755. (12) Zhu, M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. Correlating the Crystal Structure of a Thiol-Protected Au125 Cluster and Optical Properties. J. Am. Chem. Soc. 2008, 130, 5883−5885. (13) Zhu, M.; Lanni, E.; Garg, N.; Bier, M. E.; Jin, R. Kinetically Controlled, High-Yield Synthesis of Au125 Clusters. J. Am. Chem. Soc. 2008, 130, 1138−1139. (14) Parker, J. F.; Weaver, J. E. F.; McCallum, F.; Fields-Zima, C. A.; Murray, R. W. Synthesis of Monodisperse [Oct4N]+[Au32(SR)18] Nanoparticles, with Some Mechanistic Observations. Langmuir 2010, 26, 13650−13654. (15) Tofanelli, M. A.; Salorinne, K.; Ni, T. W.; Malola, S.; Newell, B.; Phillips, B.; Häkkinen, H.; Ackerson, C. J. Jahn–Teller effects in Au125(SR)18. Chem. Sci. 2016, 7, 1882−1890. (16) Monnelli, J. D.; Stapleton, J. J.; Dirk, S. M.; Reinerth, W. A.; Tour, J. M.; Allara, D. L.; Weiss, P. S. Relative Conductances of Alkaneselenolate and Alkanethiolate Monolayers on Au[111]. J. Phys. Chem. B 2005, 109, 20343−20349. (17) Kurashige, W.; Yamaguchi, M.; Nobusada, K.; Negishi, Y. Ligand-Induced Stability of Gold Nanoclusters: Thiolate versus Selenolate. J. Phys. Chem. Lett. 2012, 3, 2649−2652. (18) Ossowska, J.; Wächter, T.; Silies, L.; Kind, M.; Noworolska, A.; Bobe, F.; Gnojets, D.; Rys, J.; Bolte, M.; Feulner, P.; Terfort, A.; Cyganik, P.; Zhar nikov, M. Ligand Induced Stability of Gold Nanoclusters: Thiolate versus Selenolate: Structure, Stability, and Charge Transfer Properties. ACS Nano 2015, 9, 4508−4526. (19) Weidner, T.; Shaparenko, A.; Müller, J.; Höltig, M.; Terfort, A.; Zhar nikov, M. Self-Assembled Monolayers of Aromatic Tellurides on(111)-Oriented Gold and Silver Substrates. J. Phys. Chem. C 2007, 111, 11627−11635. (20) Goikolea, E.; Garitaonandia, J. S.; Insauti, M.; Lago, J.; Gil de Muro, I.; Salado, J.; Bermejo, F. J.; Schmool, D. Evidence of intrinsic ferromagnetic behavior of thiol capped Au nanoparticles based on μSR results. J. Non-Cryst. Solids 2008, 354, 5210−5212. (21) Asih, R.; Adan, N.; Mohd-Tajudin, S. S.; Sari, D. P.; Matsuura, K.; Guo, H.; Wakeshima, M.; Inhatu, Y.; Nakano, T.; Nozue, Y.; Sulaiman, S.; Mohamed-Ibrahim, M. I.; Biswas, P. K.; Watanabe, I. Magnetic moments and ordered states in pyrochlore iridates Na₂Ir₂O₇ and Sm₂Ir₂O₇ studied by Muon-spin relaxation. J. Phys. Soc. Jpn. 2017, 86, 024705. (22) Ahmad, S. N. A.; Sulaiman, S.; Baseri, D. F. H.; Ang, L. S.; Yahaya, N. Z.; Arsad, H.; Watanabe, I. Density Functional Theory Studies of Muon Stopping Sites and Hyperfine Interaction in[Au32(SR)18]− Nanocluster. J. Phys. Soc. Jpn. 2019, 89, 014301. (23) Song, Y.; Zhong, J.; Yang, S.; Wang, S.; Cao, T.; Zhang, J.; Li, P.; Hu, D.; Pei, Y.; Zhu, M. Crystal structure of Au125(SePh18) nanoclusters and insights into their electronic, optical and catalytic properties. Nanoscale 2014, 6, 13977−13985. (24) Fortunelli, A.; Sementa, L.; Thanthinge, V. D.; Jones, T. C.; Stener, M.; Gagnon, K. J.; Dass, A.; Ramakrishna, G. Au21S(Aldm)−5: An Anisotropic Gold Nanomolecule. Optical and Photo-luminescence Spectroscopy and First-Principles Theoretical Analysis. J. Phys. Chem. Lett. 2017, 8, 457−462. (25) Tlahuice-Flores, A.; Whetten, R. L.; Jose-Yacaman, M. Ligand Effects on the Structure and the Electronic Optical Properties of Anionic Au125(SR)18 Nanoclusters. J. Phys. Chem. C 2013, 117, 20867−20875. (26) Tlahuice-Flores, A. Ligand effects on the optical and chiroptical properties of the thiolated Au125 cluster. Phys. Chem. Chem. Phys. 2016, 18, 27738−27744. (27) Tlahuice-Flores, A. Ligand effects on the structure and vibrational properties of the thiolated Au125 cluster. Prog. Nat. Sci.: Mater. Int. 2016, 26, 510−515. (28) Zhu, Y.; Qian, H.; Drake, B. A.; Jin, R. Atomically Precise Au25(SR)18 Nanoparticles as Catalysts for the Selective Hydrogenation of α,β-Unsaturated Ketones and Aldehydes. Angew. Chem., Int. Ed. 2010, 49, 1295−1298.
(29) Okumura, M.; Kitagawa, Y.; Kawakami, T.; Haruta, M. Theoretical investigation of the hetero-junction effect in PVP-stabilized Au11 clusters. The role of PVP in their catalytic activities. Chem. Phys. Lett. 2008, 459, 133–136.

(30) Reimers, J. R.; Ford, M. J.; Halder, A.; Ulstrup, J.; Hush, N. S. Gold surfaces and nanoparticles are protected by Au(I)-thiol species and are destroyed when Au(I)-thiolates form. Proc. Natl. Acad. Sci. U.S.A. 2016, 113, E1424–E1433.

(31) Pakiari, A. H.; Janshidi, Z. Nature and Strength of M–S Bonds (M = Au, Ag, and Cu) in Binary Alloy Gold Clusters. J. Phys. Chem. A 2010, 114, 9212–9221.

(32) Roduner, E.; Brinkman, G. A.; Louwerier, P. W. F. Muonium-substituted organic free radicals in liquids. Muon-electron hyperfine coupling constants and the selectivity of formation of methyl and fluorine-substituted cyclohexadienyl type radicals. Chem. Phys. 1982, 73, 117–130.

(33) Roduner, E.; Brinkman, G. A.; Louwerier, P. W. F. Muonium-substituted organic free radicals in liquids. Isomer distribution and end-of-track radiolytic processes determined from studies of cyclohexadienyl radicals derived from substituted benzenes. Chem. Phys. 1984, 88, 143–153.

(34) Grimm, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. J. Comput. Chem. 2011, 32, 1456–1465.

(35) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, G. B.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams, D. F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Cross, J. B.; Fox, D. J. Gaussian 16 Rev. B.01, Wallingford, CT, 2016.

(36) Dennington, R.; Keith, T. A.; Millam, J. M. GaussView, Version 6; Semichem Inc.: Shawnee Mission, KS, 2016.

(37) Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. Mercury CSD 2.0-new features for the visualization and investigation of crystal structures. J. Appl. Crystallogr. 2008, 41, 466–470.

(38) Mulliken, R. S. Electronic Population Analysis on LCAO-MO Molecular Wave Functions. I. J. Chem. Phys. 1955, 23, 1833–1840.

(39) Glendening, E. D.; Badenhoop, K. J.; Reed, A. E.; Carpenter, J. E.; Bohmann, J. A.; Morales, C. M.; Lands, C. R.; Weinhold, F. Natural Bond Orbital Analysis; Theoretical Chemistry Institute, University of Wisconsin: Madison, 2013.

(40) Stummel, O.; Liborio, L.; Computational Prediction of Muon Stopping Sites: a Novel Take on the Unperturbed Electrostatic Potential Method. 2020, arXiv preprint arXiv:2005.02024.

(41) Adam, N.; Supravaya, E.; Adiperdana, B.; Guo, H.; Tanida, H.; Mohd-Tajudin, S. S.; Kobayashi, R.; Sera, M.; Nishikawa, T.; Matsumura, M.; Sulaiman, S.; Mohamed-Ibrahim, M. I.; Watanabe, I. Muon sites in Ce(Ru,Rh)2Al10 investigated by using Density Functional Theory from the view point of electronic potential. J. Phys.: Conf. Ser. 2014, 551, 012053.

(42) Mohd-Tajudin, S. S.; Ahmad, S. N. A.; Hasan-Baseri, D. F.; Supravaya, E.; Adam, N.; Rozlan, A. F.; Sulaiman, S.; Mohamed-Ibrahim, M. I.; Watanabe, I. An investigation of muon sites in YBa3Cu4O8 by using Density Functional Theory. J. Phys.: Conf. Ser. 2014, 551, 012052.

(43) Sulaiman, S. B.; Srinivas, S.; Sahoo, N.; Hagelberg, F.; Das, T. P.; Torikai, E.; Nagamine, K. Theory of the location and associated hyperfine properties of the positive muon in La2CuO4. Phys. Rev. B: Condens. Matter Mater. Phys. 1994, 49, 9879–9884.

(44) Möller, J. S.; Bonfà, P.; Ceresoli, D.; Bernardini, F.; Blundell, S. J.; Lancaster, T.; De Renzi, R.; Marzari, N.; Watanabe, I.; Sulaiman, S.; Mohamed-Ibrahim, M. I. Playing quantum hide-and-seek with the muon: localizing muon stopping sites. Phys. Scr. 2013, 88, 068510.

(45) Sulaiman, S. B.; Sahoo, N.; Das, T. P.; Donzelli, O.; Torikai, E.; Nagamine, K. Theory of copper hyperfine interactions in the La2CuO4 system. Phys. Rev. B: Condens. Matter Mater. Phys. 1991, 44, 7028–7033.

(46) Zaharim, W. N.; Sulaiman, S.; Abu Bakar, S. N.; Ismail, N. E.; Rozak, H.; Watanabe, I. The Effects of Split Valence Basis Sets on Muon Hyperfine Interaction in Guanine Nucleobase and Nucleotide Structures. Mater. Sci. Forum 2019, 966, 222–228.