DISSRETATION

APPICATIONS OF SUPERATOM THEORY IN METAL CLUSTER CHEMISTRY

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ABSTRACT

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One of the largest modern scientific debates is understanding the size dependent properties of a metal. While much effort has been performed on understanding metal particles from the top down to much less work has been accomplished from the bottom up. This has lead to a great deal of interest in metal clusters. Metal clusters containing 20 to 200 metal atoms are similar yet strikingly different to both to normal coordination chemistry and continuous bulk systems, therefore neither a classical understanding for bulk or molecular systems appears to be appropriate.

Superatom theory has emerged as a useful concept for describing the properties of a metal cluster in this size range. In this model a new set of 'superatomic' orbitals arises from the valence electrons of all the metals in a cluster. From superatom theory the properties of a metal cluster, such as stability, ionization energy, reactivity, and magnetism, should depend on valence of the superatomic orbitals, similar to a normal atom. However superatom theory has largely been used to describe the high stabilities of metal clusters with completed electronic configurations. Thus many features of superatom theory have remained largely untested and the extent that the superatom model truly applies has remained in question for many years.

Over the past decade increases in synthetic and analytical techniques have allowed for the isolation of a series of stable monodisperse gold thiolate monolayer protected clusters (MPCs) containing from 10 to 500 gold atoms. The wide range in sizes and high stability of gold thiolate

clusters provides an instrumental system for understanding superatom theory and the transition from molecular-like cluster to bulk-like system.

In the first part of this thesis the effects of the superatomic valence is investigated under superatomic assumptions. $Au_{25}(SR)_{18}$ (where SR= any thiolate) can be synthesized in 3 different oxidation states without any major distortions to the geometry of the cluster, thus it is possible to test 3 different superatomic configurations for a single cluster. These studies show that the superatom model correctly predicts changes observed in the stability, absorption spectrum, crystal structures, and magnetic susceptibility for each charge state of $Au_{25}(SR)_{18}$. In addition, the superatom model is shown to also apply to the isoelectronic $PdAu_{24}(SR)_{18}$ superatomic cluster. This work is discussed in Chapters 2, 3, and 4.

The second part of this thesis focuses on the transition from superatomic metal clusters to metal nanoparticles. $Au_{144}(SR)_{60}$ is studied in order to understand this transition. Although the plasmon is not immediately apparent through linear absorption spectroscopy, a plasmonic feature is observed in transient absorption spectroscopy. This observation in combination with the absence of a HOMO-LUMO gap suggests that $Au_{144}(SR)_{60}$ can be treated with bulk assumptions. However $Au_{144}(SR)_{60}$ shows quantized behavior and powder x-ray diffraction reveals that symmetry of the metal core does not represent what is observed in the bulk. $Au_{144}(SR)_{60}$ appears to show both superatomic and bulk behavior making it an instrumental tool for understanding the transition from superatomic to bulk behavior. This work is discussed in Chapters 2, 5, and 6.

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Chapter 1

An Introduction to Metal Cluster Chemistry

During the past 50 years a new major area of chemistry has developed focused on metal clusters containing from several to several hundred metal atoms. In this size range the physiochemical properties are highly dependent on the symmetry and exact atomic count of cluster. This has allowed for an incredibly diverse set of applications to be envisioned for metal clusters such as high temperature superconducting, multi-dimensional theranostics, and catalysis.¹⁻⁴ However before the full potential of metal cluster chemistry can be realized a better understanding of these systems is required.

Interest in metal cluster expands over a diverse set of fields as they have been observed in solids, solutions, and gases. Initially it was believed that each cluster was a unique molecule because the properties varied so much from cluster to cluster. Nevertheless in the mid 1980's it was found that the behavior of ligated inorganic clusters followed rules developed by Wade and Mingos, and that these could even be extended to metal clusters in the solid state.^{1,5,6} Thus it is possible to relate clusters containing different metals and in different phases. Early in the studies preformed on metal MPC crude characterization techniques made it difficult to study clusters containing much more than 12 metal atoms. As advancements in characterization techniques progressed it was possible to study monodisperse clusters up to several hundred atoms. However once a metal cluster becomes much larger than about 12 atoms the Wade-Mingos rules no longer appear to hold valid. A new model is required in order to understand metal clusters larger than 12 metal atoms but still significantly smaller than bulk material.

During the 1960's new methods were developed to produce gas phase metal clusters in order to elucidate the properties isolated metal clusters. Results from these studies revealed that metal clusters with specific atomic counts were much more abundant than others and this was attributed to a high stability of these clusters. Initially it was not well understood what gave rise to the enhanced stability of these metal clusters. In 1984 Knight and coworkers realized that the nuclear shell model correctly predicted the stability of gas phase sodium metal clusters.⁷ This lead theoreticians to apply a similar model developed by Nilsson. In the model developed for metal clusters the s and p valence electrons are considered to be delocalized over the entire cluster and experience a spherically symmetric square well potential. Solving the Schrödinger equation with these approximations gives rise to a new set of molecular orbitals that have the same symmetry as normal atomic orbitals, thus this model has coined the name superatom'theory.⁸ The new 'superatomic' orbitals derived from this mode appear as |1S²|, $|1S^{2}1P^{6}|, |1S^{2}1P^{6}1D^{10}2S^{2}|, |1S^{2}1P^{6}1D^{10}2S^{2}1F^{14}2P^{6}|...$ corresponding to electron counts of 2, 8, 20, 40 . . . , respectively, as shown in Figure 1.1.⁷ When the number of valence electrons in a metal cluster fills a 'superatomic' orbital stability is gained, similar to a normal atom, Superatom theory has since been successfully applied to many other gas phase clusters. ⁹⁻¹¹ However superatom theory could not be used to rationalize the stability of all metal clusters observed. It was soon discovered that in many cases these numbers corresponded to a completed geometric shell.^{12,13} By completing a geometric shell it is possible to obtain the minimum surface energy and the maximum coordination for each atom in the system. Thus the stability of gas phase metal clusters can be understood to be as a competition between electronic and geometric shell closures.

Most of the early studies on gas phase metal cluster focused on describing the stability of the most prominent clusters, while much less effort was put forth toward understanding the properties of a cluster. Superatom theory can also be used to predict other physical and chemical properties such as electronegativity, reactivity, magnetism, and even Jahn-Teller type distortions, based on the superatomic valence.^{4,8} For example Al₁₄ has been produced and has two more valence electrons than is required to fill its superatomic 2P shell. Due to this the reactivity and ionization potentials observed for Al₁₄ mimic that of an alkaline earth metal.¹⁴ Although the short lifetimes of even the stable gas phase clusters make many experiential tests nearly impossible to perform.



Figure 1.1. A) shows the energy of the electronic orbitals using a Coulombic potential. B) shows the energy diagram of the using a square well potential.

Over the past decade it has been shown that many of the concepts gained from the gas phase work could be applied to metal MPCs.¹⁵⁻¹⁸ Similar to the gas phase clusters the stability of the large metal MPCs can be attributed to a completed electronic or geometric shell, however unlike the gas phase clusters the ligand layer grants a great deal of stability to a cluster. Initially

it was not well understood how the passivation of the surface, geometry, and electronic shell closures combine to form stable MPCs. Fortunately a series of crystal structures have been reported which helped to elucidate many important features of the ligand layer,^{15,19-21} an example of a gold thiolate MPC is shown in Figure 1.2. The most important feature is that each surface is passivated by a chemically bound ligand. In addition each ligand provides steric shielding of foreign molecules or other clusters.

Since metal MPCs contain chemically bound ligands the electron counting rules change slightly compared to the gas phase clusters.¹⁵ The bound ligands can localize electrons from a metal MPC either through ionic or covalent type bonds (X), or a cluster can be stabilized through dative bonds (L), which do not remove electrons. The electron count of a metal MPC formulated $(L_sA_MX_N)^z$, where A is the metal atom present and z is the oxidation state of the cluster, can be calculated by equation [1] below.

$$n^* = MV_a - N - z$$
^[1]

 V_a represents the valence of the metal atom (which only considers the s and p electrons).¹⁵ When n* is equivalent to the number of electrons required to close a superatomic shell a high stability is observed, analogous to the high stability of noble gases.¹⁵

Gold thiolate MPCs are among the most studied clusters as they generally have a much higher stability than other MPCs allowing for the synthesis and isolation of a wide variety of gold MPCs containing from 10 to more than 500 gold atoms.^{22,23} Thus gold thiolate clusters provide many advantages toward further expanding the understanding of metal cluster chemistry and the subsequent transition to bulk material. One feature of gold thiolate MPCs that help to elucidate the nature of metal clusters is that in many cases undergo reversible charging events in electrochemistry, making it possible to compare the effects of the superatomic valence for a single cluster. Most notably superatom theory has been able to correctly predict the magnetic properties of $Au_{25}(SR)_{18}$ in the -1 and 0 charge states. Electron paramagnetic resonance spectroscopy (EPR) has revealed that $Au_{25}(SR)_{18}^{-1}$ is diamagnetic due to a completed superatomic orbital $(1S^21P^6)$, while $Au_{25}(SR)_{18}^{0}$ $(1S^21P^5)$ is paramagnetic resulting from one unpaired.^{24,25} Unfortunately the effects of the superatomic valence have remained largely untested for gold thiolate MPCs.



Figure 1.2. Shown above is the crystal structure of $Au_{25}(SC_8H_9)_{18}PF_6$. Gold is colored yellow, sulfur is orange, carbon is black, fluorine is blue, and phosphorus is in light orange. In **A** the gold core is shown. **B** depicts the bonding of the sulfur to the core. **C** shows the entire structure of $Au_{25}(SC_8H_9)_{18}PF_6$.

Since it is possible to isolate gold thiolate MPCs all the way up to bulk-like nanoparticles, gold clusters provide valuable insight into the transition from molecular to bulk material. As a gold thiolate cluster grows in size the HOMO-LUMO gap decreases and electronic stabilization imparted from superatomic effects become weak. The largest cluster to still have an observable HOMO-LUMO gap is Au₁₀₂(SR)₄₄, thus this cluster is expected to be the largest cluster

stabilized through superatomic effects, while larger clusters are stabilized through geometric effects.¹⁵ However it is not readily apparent at what point superatomic effects give way to bulk material. The largest cluster to still have an observable HOMO-LUMO gap is $Au_{102}(SR)_{44}$, thus this cluster is expected to be the largest cluster stabilized through superatomic effects, while larger clusters are stabilized through geometric effects. Another question that remains for clusters on the verge of bulk material is the symmetry that the metal cluster adopts. Bulk gold adopts a face center cubic lattice, which has an octahedral symmetry, however the observed symmetry for many metal clusters is near icosahedral. Therefore at some size a metal cluster will adopt the geometry affects the properties of a metal cluster. It has proven difficult to determine crystal structures for clusters larger than $Au_{102}(SR)_{44}$, however it is expected that clusters in this size range mark the transition from superatomic to bulk system making it possible to study the evolution of a metal particle from molecular to bulk material one step at a time.

Early studies on gas phase metal clusters revealed many valuable insights into metal bonding. Unfortunately, the "stable" gas phase clusters often exist for seconds or less, making many empirical tests impossible. Recently, it has been shown that many of the concepts that have been developed for gas phase clusters can be extended to solution-stable MPCs. The most notable are gold thiolate MPCs, due to the high stability and wide range in sizes that can be produced. In combination with the advancements made in characterization techniques research into gold thiolate MPCs provide valuable insights into the fundamental nature of metallic bonding between the bulk and molecular systems.

References

- (1) Mingos, M.; Wales, D. Introduction to Cluster Chemistry; Prentice-Hall, 1990.
- Hagel, J.; Kelemen, M. T.; Fischer, G.; Pilawa, B.; Wosnitza, J.; Dormann, E.; Löhneysen,
 H. v; Schnepf, A.; Schnöckel, H.; Neisel, U.; Beck, J. J. Low Temp. Phys. 2002, 129 (3–4), 133–142.
- (3) Castleman, A. W.; Khanna, S. N. J. Phys. Chem. C 2009, 113 (7), 2664–2675.
- (4) Jena, P. J. Phys. Chem. Lett. 2013, 4 (9), 1432–1442.
- (5) Mingos, D. M. P. Acc. Chem. Res. **1984**, *17* (9), 311–319.
- (6) Corbett, J. D. Inorg. Chem. 2000, 39 (23), 5178–5191.
- Knight, W. D.; Clemenger, K.; de Heer, W. A.; Saunders, W. A.; Chou, M. Y.; Cohen, M. L. *Phys. Rev. Lett.* **1984**, *52* (24), 2141–2143.
- (8) de Heer, W. A. Rev. Mod. Phys. 1993, 65 (3), 611–676.
- (9) Schriver, null; Persson, null; Honea, null; Whetten, null. *Phys. Rev. Lett.* 1990, 64 (21), 2539–2542.
- (10) Brack, M.; Genzken, O.; Hansen, K. Z. Für Phys. At. Mol. Clust. 19 (4), 51-53.
- Katakuse, I.; Ichihara, T.; Fujita, Y.; Matsuo, T.; Sakurai, T.; Matsuda, H. Int. J. Mass Spectrom. Ion Process. 1986, 69 (1), 109–114.
- (12) Rayane, D.; Benamar, A.; Melinon, P.; Tribollet, B.; Broyer, M. Z. Für Phys. At. Mol. Clust. 19 (4), 191–193.
- (13) Rayane, D.; Melinon, P.; Cabaud, B.; Hoareau, A.; Tribollet, B.; Broyer, M. *Phys. Rev. A* 1989, *39* (11), 6056–6059.
- (14) Bergeron, D. E.; Roach, P. J.; Castleman, A. W.; Jones, N. O.; Khanna, S. N. *Science* 2005, *307* (5707), 231–235.

- Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.;
 Whetten, R. L.; Grönbeck, H.; Häkkinen, H. *Proc. Natl. Acad. Sci.* 2008, *105* (27), 9157–9162.
- (16) Lopez-Acevedo, O.; Clayborne, P. A.; Häkkinen, H. Phys. Rev. B 2011, 84 (3), 35434.
- (17) Joshi, C. P.; Bootharaju, M. S.; Alhilaly, M. J.; Bakr, O. M. J. Am. Chem. Soc. 2015, 137
 (36), 11578–11581.
- (18) Aluminum(I) and Gallium(I) Compounds: Syntheses, Structures, and Reactions Dohmeier 2003 Angewandte Chemie International Edition in English Wiley Online
 Library

http://onlinelibrary.wiley.com/doi/10.1002/anie.199601291/abstract?systemMessage=Wile y+Online+Library+will+be+disrupted+on+21st+March+from+10%3A30+GMT+%2806% 3A30+EDT%29+for+up+to+six+hours+for+essential+maintenance.++Apologies+for+the +inconvenience. (accessed Mar 20, 2015).

- (19) Dainese, T.; Antonello, S.; Gascón, J. A.; Pan, F.; Perera, N. V.; Ruzzi, M.; Venzo, A.;
 Zoleo, A.; Rissanen, K.; Maran, F. *ACS Nano* 2014, *8* (4), 3904–3912.
- (20) Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. J. Am. Chem. Soc.
 2008, 130 (12), 3754–3755.
- (21) Zeng, C.; Chen, Y.; Kirschbaum, K.; Appavoo, K.; Sfeir, M. Y.; Jin, R. Sci. Adv. 2015, 1
 (2), e1500045.
- Negishi, Y.; Nakazaki, T.; Malola, S.; Takano, S.; Niihori, Y.; Kurashige, W.; Yamazoe,
 S.; Tsukuda, T.; Häkkinen, H. J. Am. Chem. Soc. 2015, 137 (3), 1206–1212.
- (23) Dass, A. J. Am. Chem. Soc. 2011, 133 (48), 19259–19261.

- (24) Venzo, A.; Antonello, S.; Gascón, J. A.; Guryanov, I.; Leapman, R. D.; Perera, N. V.;
 Sousa, A.; Zamuner, M.; Zanella, A.; Maran, F. *Anal. Chem.* 2011, *83* (16), 6355–6362.
- (25) Akbari-Sharbaf, A.; Hesari, M.; Workentin, M. S.; Fanchini, G. J. Chem. Phys. 2013, 138
 (2), 24305-024305-5.
- (26) Lopez-Acevedo, O.; Akola, J.; Whetten, R. L.; Grönbeck, H.; Häkkinen, H. J. Phys. Chem. C 2009, 113 (13), 5035–5038.
- (27) Dass, A.; Theivendran, S.; Nimmala, P. R.; Kumara, C.; Jupally, V. R.; Fortunelli, A.;
 Sementa, L.; Barcaro, G.; Zuo, X.; Noll, B. C. *J. Am. Chem. Soc.* 2015, *137* (14), 4610–4613.

Chapter 2

Superatom Electron Configuration Predicts Thermal Stability of Au₂₅(SR)₁₈ Nanoclusters^{*}

2.1 Synopsis

The exceptional stability of ligand-stabilized gold nanoclusters such as $Au_{25}(SC_6H_{13})_{18}^{-1}$, $Au_{39}(PR_3)_{14}X_6^{-1}$, and $Au_{102}(SR)_{44}$ arises from the total filling of superatomic electron shells resulting in a "noble-gas superatom" electron configuration. Electrochemical manipulation of oxidation state can add or remove electrons from superatom orbitals creating species electronically analogous to atomic radicals. Herein we show that oxidizing the $Au_{25}(SR)_{18}^{-1}$ superatom from the noble gas like $1S^2 1P^6$ to the open shell radical $1S^2 1P^5$ and diradical $1S^2 1P^4$ electron configurations results in decreased thermal stability of the compound, as measured by differential scanning calorimetry. Similar experiments probing 5 oxidation states of the putatively geometrically stabilized $Au_{144}(SR)_{60}$ cluster suggest a more complex relationship between oxidation state and thermal stability for this compound.

2.2 Introduction

The electron configurations of elements predict a remarkable set of properties, including ionization energy, electronegativity, and bonding valency. The superatomic electron configurations of metal clusters predict stable molecular formulas, which are associated with

^{*} The work presented herein is published in the Journal of the American Chemical Society with Marcus A. Tofanelli and Christopher J. Ackerson as coauthors. Marcus Tofanelli's include experimental design, data analysis, and synthetic development and characterization of gold nanoclusters and assemblies. Permission to reprint this material was granted by the American Chemical Society. © 2012 American Chemical Society. J. Am. Chem. Soc., 2012, 134 (41), 16937–16940.

noble-gas-like superatomic electron configurations.^{1,2} Geometric shell closing can also stabilize metal nanoclusters, making electronic and geometric shell closures competing modes of nanoparticle stabilization. Smaller nanoparticles tend toward stabilization by superatomic shell closing, while larger nanoparticles tend toward stabilization by geometric shell closing.³ The theory of metal clusters as electronic superatoms has been most widely deployed for gas-phase clusters.⁴

The extension of superatom theory from gas-phase clusters to soluble, stable, ligated clusters is recent¹ and has been best developed for ligated gold nanoclusters,^{5,6} although it is being increasingly applied to ligated clusters of other transition metals.⁷ Structural and theoretical data for gold–thiolate nanocluster compounds suggest that geometric shell closures dominate the stability of $Au_{144}(SR)_{60}$ and larger,⁸⁻¹¹ while electronic shell filling stabilizes $Au_{102}(SR)_{44}$ and smaller.^{12,13}

The solution of the Schrodinger equation for a spherically symmetric square-well potential defines the superatomic orbitals for approximately spherical particles.² The spherical superatom orbitals are 1S, 1P, 1D, 2S 1F, 2P 1G, 2D 1H 3S, ... Thus, the electron counts that achieve a particularly stable (noble-gas-like) configuration are 2, 8, 18, 34, 58, 92, ... For a metal cluster formulated as $(L_s \cdot A_N X_M)^z$, where A and X represent metal atoms and electron-withdrawing ligands with *N* and *M* being their respective numbers, L represents dative ligands, *s* the number of dative ligands, and *z* represents the overall charge on the compound, the number of superatomic electrons is:

$$n^* = NV_{\rm A} - M - z \tag{1}$$

where V is the valence of the metal atom (V = 1 for Au, which donates its 6s electron). When n^* is equivalent to the number of electrons required to close a superatomic shell (i.e., a magic number), special stability is observed, analogous to the special stability of noble gases.

Implicit in the superatom description of nanoclusters is that filled electronic shells produce highly inert, noble-gas-like compounds, while open-shell compounds may be more reactive. Castleman and Khanna extended the superatom theory to show that ion pairs¹⁴ and extended solid-state networks^{15,16} can be formed from open-shell Al and As clusters that are soft-landed from the gas phase.

Compared with the work on soft-landed gas-phase clusters, the application of superatom theory to ligated clusters is more limited and to date has been used in two notable ways. First, superatom theory has been used to explain the special stability of compounds such as $Au_{25}(SR)_{18}^{-1}$, $Au_{39}(PPh_3)_{14}Cl_6^{-1}$, $Au_{68}(SR)_{34}$, and $Au_{102}(SR)_{44}$ as resulting from total fillings of the 2P, 1F, 1F, and 1G shells (i.e., n = 8, 34, 34, and 58), respectively. ^{1,13,17-21}. Second, the observed paramagnetism of the $Au_{25}(SR)_{18}^{0}$ species has been explained in terms of an unpaired superatomic electron arising in a $1S^2 1P^5$ superatomic electron configuration. ^{6,17}

Here we performed a direct experimental test of the superatom theory as applied to ligated metal clusters and established that superatomic electron configurations of $Au_{25}(SC_6H_{13})_{18}$ are predictive of the thermal decomposition temperature of this compound. For comparison, we also established the thermal stability of charge states of the putatively geometrically stabilized^{8,22} compound $Au_{144}(SC_6H_{13})_{60}$.

2.3 Methods

 $Au_{25}(SC_6H_{13})_{18}$ and $Au_{144}(SC_6H_{13})_{60}$ were prepared by the methods of Murray²³ and Jin²⁴ respectively with minor modifications detailed in the supporting information. Differential pulse voltammetry was done on a Bioanalytical Systems BAS 100B potentionstat using 100mmol TBAPF₆, or about 50 mmol TEABF₄ in dichloromethane as electrolyte and solvent, similar to the previous work of Murray²⁵⁻²⁹.

Bulk electrolysis was performed under air in a two frit, three chamber electrochemical cell, controlled by the same potentiostat used for the DPV experiments.

Differential Scanning Calorimetry (DSC) was accomplished with TA Intruments 2920 modulated DSC. All products were redissolved in a minimal amount of DCM and then deposited into an aluminum hermetic DSC pan and allowed to air dry in order to achieve uniform coverage of the pan. Vacuum was applied for 10 min to ensure complete removal of DCM. Greater experimental detail may be found in the supporting information.

2.4 Results and Discussion

We prepared Au₂₅(SC₆H₁₃)₁₈ in the -1, 0, and 1 charge states and Au₁₄₄(SC₆H₁₃)₆₀ in the -1, 0, 1, 2, and 3 charge states. The preparation of each formal charge state proceeded by initial collection of a differential pulse voltammogram and verification that the as-prepared clusters showed the expected electrochemical response (Figure 2.1). Following the DPV measurement, analytical amounts (1–3 mg) of each cluster in each targeted formal charge state were prepared by bulk electrolysis. To isolate the stability effect of the cluster core charge from the effect of counterions, we executed bulk electrolysis with two different electrolytes, TBAPF₆ and TEABF₄. Success of the bulk electrolysis preparation was verified by resting potential measurements. The

integrity of the electrolyzed cluster preparations was also confirmed by postelectrolysis DPV measurements, and in the case of $Au_{25}(SC_6H_{13})_{18}$, additional confirmation was provided by the fact that the spectra we observed for various charge states reproduced the spectra measured in other laboratories (Figure 2.1 inset).^{23,24} Analyses of $Au_{25}(SC_6H_{13})_{18}$ in the +2 or -2 charge state were not attempted because of the apparent instability of the cluster in these charge states; In fact, even the +1 charge state required careful handling (Figure S1 in the SI). More negative formal charges for Au_{144} were difficult to prepare stably because of our inability to exclude oxygen from the calorimeter completely, while more positive charge states of Au_{144} appeared to revert spontaneously to lower formal charge states during the course of the experiment as judged by resting potential measurements.



Figure 2.1. Main figure shows differential pulse voltammetry for the as-prepared $Au_{25}(SR)_{18}$ (bottom trace, orange) and $Au_{144}(SR)_{60}$ (top trace, brown). Potentials are relative to Standard Caloumel Electrode. Inset shows the relative UV/VIS absorbance of the -1, 0 and +1 bulk electrolysis preparations of $Au_{25}(SR)_{18}$ in blue, red and green respectively.

Au₂₅(SC₆H₁₃)₁₈ should be most stable in the $1S^21P^6$ configuration, corresponding to the molecular anion. Thus, the superatomic electron configurations of the three Au₂₅(SC₆H₁₃)₁₈ species that we prepared are $1S^21P^6$, $1S^21P^5$, and $1S^21P^4$. The thermal characteristics, including the thermal stability, of Au₂₅(SC₆H₁₃)₁₈ in each of these electron configurations were measured in DSC experiments. For every compound tested there was a major thermal event, corresponding to what we believe to be the desorption of the ligand shell and subsequent decomposition of the cluster. We interpret the temperature at which this major thermal event occurs as an indicator of the thermal stability of the cluster; clusters that decompose at higher temperatures are thus more thermally stable. By this metric of stability, Au₂₅(SC₆H₁₃)₁₈⁰ radical, which in turn is more stable than the Au₂₅(SC₆H₁₃)₁₈⁺ superatomic diradical (Figure 2.2), with each additional electron removal causing ca. 10 °C of destabilization. At least three measurements were made for each preparation.



Figure 2.2. Scanning Calorimetry of the -1, 0 and +1 charge states of $Au_{25}(SC_6H_{13})_{18}$ compound. The bottom, middle and top traces in blue red and green respectively are for the indicated electron configuraitons of $Au_{25}(SC_6H_{13})_{18}$. Thermal decomposition events for each are observed at 229, 221, and 207 °C.

For the $Au_{25}(SC_6H_{13})_{18}^0$ and $Au_{25}(SC_6H_{13})_{18}^+$ charge states, different electrolytes gave indistinguishable stability measurements when the standard error was taken into account. The $Au_{25}(SC_6H_{13})_{18}^-$ charge state appeared to be slightly stabilized by the tetrabutylammonium counterion relative to the tetramethylammonium or tetraethylammonium counterion, although the effect of the electrolyte was small in comparison with the effect of the charge state. The Figure 2.2 inset reports the results of the DSC runs for all of the electrolytes with standard error. Figure S2 shows the separate effects of the electrolyte and charge on the thermal stability.

We also measured the charge-state-dependent thermal stability of $Au_{144}(SC_6H_{13})_{60}$ for the five prepared charge states of this compound. The charge state and thermal stability do not appear to be closely linked for this compound (Figure 2.3) Moreover, the counterion retained by the $Au_{144}(SC_6H_{13})_{60}$ nanocluster after bulk electrolysis could in many cases exert a dramatic effect on the nanocluster thermal stability (data not shown), consistent in part with the description of this compound as stabilized in part by an electrical double layer.²⁵ While superatomic orbital effects are presently not considered to be as important as the filling of geometric closed shells for conferring stability to $Au_{144}(SC_6H_{13})_{60}$, we suggest below how superatomic electron effects may account in an unpredictable manner for the absence of a trend in the thermal stability as a function of oxidation state for $Au_{144}(SC_6H_{13})_{60}$.

Geometric stabilization of $Au_{144}(SC_6H_{13})_{60}$ is suggested by a widely cited density functional theory (DFT) model of $Au_{144}(SC_6H_{13})_{60}$,⁸ by the inexplicability of the cluster's formula and electronic structure in terms of superatom theory,¹ and by the observation of a single symmetry environment by NMR spectroscopy, which is consistent with the DFT model.^{10,26} In contrast, superatomic-stabilized clusters show multiple symmetry environments as judged by NMR spectroscopy.¹⁰ The ligand symmetry environment of $Au_{144}(SC_6H_{13})_{60}$ appears to change



Figure 2.3. Differential Scanning Calorimetry of representative samples of $Au_{144}(SC_6H_{13})_{60}$ in +3, +2, +1, 0, and -1 oxidation states. Inset shows the decomposition temperature for multiple masurements at each oxidation state, with error bars representing the standard deviation for the set of measurements. Only one measurement was made for the +3 oxidation state.

reversibly upon oxidation and reduction of the $Au_{144}(SC_6H_{13})_{60}$ cluster.²⁶ Taken together, the unpredictable counterion- and charge-dependent thermal stability and the apparent breakdown of symmetry in some oxidation states leads us to speculate that residual superatom electronic effects may provoke Jahn–Teller-type distortion of these structurally obscure clusters. This means that competing superatomic effects may alter the structure and electronic and thermal stability of these clusters in unpredictable ways that depend on the interplay of geometric, ligand-steric, and electronic effects.

In contrast to $Au_{144}(SC_6H_{13})_{60}$, the outer coordination shell [SR-Au(I)-SR-Au(I)-SR units] of $Au_{25}(SC_6H_{13})_{18}$ may act in concert with the organic ligands of this cluster to constrain the geometry even when the superatomic electron configuration favors Jahn-Teller-type distortion. Thus, there are no significant distortions between $Au_{25}(SC_6H_{13})_{18}^-$ and $Au_{25}(SC_6H_{13})_{18}^{0}$ in single-crystal X-ray structures,^{13,18,27} while we observe stability trends predicted by the superatomic electron configuration. While the low rates of electron transfer for $Au_{25}(SR)_{18}^{0/-1}$ noted by Murray and Maran²³ suggest a charge-state-dependent distortion, the totality of current evidence suggests that this distortion is small.

In conclusion, we have shown that the superatom electron configuration predicts a thermal stability trend for noble-gas, radical, and diradical superatom electron configurations of $Au_{25}(SR)_{18}$. Clear trends were not observed for $Au_{144}(SR)_{60}$, leading us to speculate that a complex interplay of electronic and geometric effects may be of importance. The extension of superatom theory to predict other properties of ligated clusters, such as superatomic valency and catalytic reactivity, remain largely open questions.

References

- (1) Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Whetten, R. L.; Grönbeck, H.; Häkkinen, H. *Proc. Natl. Acad. Sci.* **2008**, *105* (27), 9157–9162.
- (2) de Heer, W. A. *Rev. Mod. Phys.* **1993**, *65* (3), 611–676.
- (3) Martin, T. P.; Bergmann, T.; Goehlich, H.; Lange, T. J. Phys. Chem. **1991**, 95 (17), 6421–6429.
- (4) Castleman, A. W. J. Phys. Chem. Lett. 2011, 2 (9), 1062–1069.
- (5) Häkkinen, H. Chem. Soc. Rev. 2008, 37 (9), 1847–1859.
- (6) Zhu, M.; Aikens, C. M.; Hendrich, M. P.; Gupta, R.; Qian, H.; Schatz, G. C.; Jin, R. J.
 Am. Chem. Soc. 2009, 131 (7), 2490–2492.
- (7) Clayborne, P. A.; Lopez-Acevedo, O.; Whetten, R. L.; Grönbeck, H.; Häkkinen, H. *Eur. J. Inorg. Chem.* 2011, 2011 (17), 2649–2652.
- (8) Lopez-Acevedo, O.; Akola, J.; Whetten, R. L.; Grönbeck, H.; Häkkinen, H. J. Phys.
 Chem. C 2009, *113* (13), 5035–5038.
- (9) Dass, A. J. Am. Chem. Soc. 2011, 133 (48), 19259–19261.
- (10) Wong, O. A.; Heinecke, C. L.; Simone, A. R.; Whetten, R. L.; Ackerson, C. J. *Nanoscale* **2012**, *4* (14), 4099.
- (11) Qian, H.; Zhu, Y.; Jin, R. Proc. Natl. Acad. Sci. 2012, 109 (3), 696–700.
- (12) Lopez-Acevedo, O.; Tsunoyama, H.; Tsukuda, T.; Hannu Häkkinen; Aikens, C. M. J.
 Am. Chem. Soc. 2010, 132 (23), 8210–8218.
- (13) Zhu, M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. J. Am. Chem. Soc. 2008, 130 (18), 5883–5885.

- (14) Bergeron, D. E.; Castleman, A. W.; Morisato, T.; Khanna, S. N. Science 2004, 304
 (5667), 84–87.
- (15) Castleman, A. W.; Khanna, S. N. J. Phys. Chem. C 2009, 113 (7), 2664–2675.
- (16) Claridge, S. A.; Castleman, A. W.; Khanna, S. N.; Murray, C. B.; Sen, A.; Weiss, P. S.
 ACS Nano 2009, 3 (2), 244–255.
- (17) Nealon, G. L.; Donnio, B.; Greget, R.; Kappler, J.-P.; Terazzi, E.; Gallani, J.-L. *Nanoscale* **2012**, *4* (17), 5244–5258.
- (18) Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. J. Am. Chem. Soc.
 2008, 130 (12), 3754–3755.
- (19) Teo, B. K.; Shi, X.; Zhang, H. J. Am. Chem. Soc. 1992, 114 (7), 2743–2745.
- (20) Dass, A. J. Am. Chem. Soc. 2009, 131 (33), 11666–11667.
- (21) Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. Science
 2007, 318 (5849), 430–433.
- (22) Kumara, C.; Dass, A. Nanoscale 2011, 3 (8), 3064–3067.
- (23) Parker, J. F.; Fields-Zinna, C. A.; Murray, R. W. Acc. Chem. Res. 2010, 43 (9), 1289–1296.
- (24) Venzo, A.; Antonello, S.; Gascón, J. A.; Guryanov, I.; Leapman, R. D.; Perera, N. V.;
 Sousa, A.; Zamuner, M.; Zanella, A.; Maran, F. *Anal. Chem.* 2011, *83* (16), 6355–6362.
- (25) Murray, R. W. Chem. Rev. 2008, 108 (7), 2688–2720.
- (26) Song, Y.; Harper, A. S.; Murray, R. W. Langmuir 2005, 21 (12), 5492–5500.
- (27) Zhu, M.; Eckenhoff, W. T.; Pintauer, T.; Jin, R. J. Phys. Chem. C 2008, 112 (37), 14221–
 14224.

(28) Parker, J. F.; Weaver, J. E. F.; McCallum, F.; Fields-Zinna, C. A.; Murray, R. W. Langmuir **2010**, *26* (16), 13650–13654.

(29) Qian, H.; Jin, R. Chem. Mater. 2011, 23 (8), 2209–2217.

(30) Gold Nanoelectrodes of Varied Size: Transition to Molecule-Like Charging | Science https://secure.colostate.edu/content/280/5372/,DanaInfo=science.sciencemag.org+2098
 (accessed May 24, 2016).

- (31) Ingram, R. S.; Hostetler, M. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Whetten, R.
 L.; Bigioni, T. P.; Guthrie, D. K.; First, P. N. J. Am. Chem. Soc. 1997, 119 (39), 9279–9280.
- (32) García-Raya, D.; Madueño, R.; Blázquez, M.; Pineda, T. J. Phys. Chem. C 2009, 113
 (20), 8756–8761.
- (33) Quinn, B. M.; Liljeroth, P.; Ruiz, V.; Laaksonen, T.; Kontturi, K. J. Am. Chem. Soc.
 2003, 125 (22), 6644–6645.

Chapter 3

Jahn–Teller effects in Au₂₅(SR)₁₈*

3.1 Synopsis

The relationship between oxidation state, structure, and magnetism in many molecules is well described by first-order Jahn–Teller distortions. This relationship is not yet well defined for ligated nanoclusters and nanoparticles, especially the nano-technologically relevant gold-thiolate protected metal clusters. Here we interrogate the relationships between structure, magnetism, and oxidation state for the three stable oxidation states, -1, 0 and +1 of the thiolate protected nanocluster Au₂₅(SR)₁₈. We present the single crystal X-ray structures of the previously undetermined charge state Au₂₅(SR)₁₈⁺¹, as well as a higher quality single crystal structure of the neutral compound Au₂₅(SR)₁₈⁰. Structural data combined with SQUID magnetometry and DFT theory enable a complete description of the optical and magnetic properties of Au₂₅(SR)₁₈ in the three oxidation states. In aggregate the data suggests a first-order Jahn–Teller distortion in this compound. The high quality single crystal X-ray structure enables an analysis of the ligand–ligand and ligand–cluster packing interactions that underlie single-crystal formation in thiolate protected metal clusters.

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3.2 Intro

The Jahn–Teller theorem establishes that molecular orbitals must be symmetrically occupied by electrons in order for them to be energetically degenerate.¹ Unequal occupation of orbitals leads to breaking of the energetic degeneracy of the orbitals, with concomitant distortions to the symmetry of the molecule, coupled to simultaneous changes in optical and magnetic properties. Jahn–Teller effects are described experimentally for low-nuclearity metal clusters,² carbon clusters such as fullerenes,³ clusters in extended solids,⁴ Zintl phases,⁵ and theoretically for larger nanoclusters.⁶⁻⁸

For nanocluster compounds (here we define a nanocluster as a metal cluster with one or more metal atoms that is neighbored only by other metal atoms) the role of the Jahn-Teller effect is unclear. In this work, we investigate the structural and magnetic properties of Au₂₅(SR)₁₈ in 3 charge states. Of the compounds comprising the Au_x(SR)_y monolayer protected cluster magic number series,⁹ the $Au_{25}(SR)_{18}$ nanocluster^{10,11} is the best understood, both experimentally and theoretically. The compound was initially isolated by Whetten,¹⁰ with the Au₂₅(SR)₁₈ formulation made subsequently by Tsukuda.¹² The single-crystal X-ray structure^{13,14} combined with reliable syntheses^{15,16} preceded the emergence of this compound as a singular subject for understanding the physical and inorganic chemistry of broadly studied and applied^{17,18} thiolate protected gold nanoclusters. Theoretical studies conclude that the frontier orbitals of Au₂₅(SR)₁₈ and many other Au_x(SR)_v compounds as large as Au₁₀₂(SR)₄₄ are well predicted by a spherical superatom model.^{9,19} In this model, $Au_{25}(SR)_{18}^{-1}$ is an 8e⁻ system, corresponding to a noble gaslike $1S^21P^6$ superatom electron configuration. The superatom electron configuration of Au₂₅(SR)₁₈ can be modified through now well established electrochemical methods which allows for stable preparations of Au₂₅(SR)₁₈ in -1, 0 and +1 oxidation states, corresponding to $1S^{2}1P^{6}$,

 $1S^{2}1P^{5}$, and $1S^{2}1P^{4}$ superatom electron configurations, respectively. Several properties including magnetism, optical absorption, catalytic reactivity and stability can be rationalized in terms of superatom electron configuration.^{14,20,21} Of these reports, magnetic studies may give insight into whether Au₂₅(SR)₁₈ is subject to Jahn–Teller effects.

If Jahn–Teller effects do not apply to $Au_{25}(SR)_{18}$, then Hund's rule predicts that the -1, 0, and +1 charge states should be diamagnetic, S = 1/2 paramagnetic and S = 1 paramagnetic, respectively. However, if the cluster has morphological flexibility and can change shape with changing charge, then the superatomic orbitals may lose their degeneracy with changing charge states and the -1, 0 and +1 charge states would become diamagnetic, S = 1/2 paramagnetic, and diamagnetic, respectively. The magnetic properties of thiolate protected gold nanoparticles, however, are controversial, with inconsistent reports of magnetic properties made for apparently similar preparations.²² Indeed, even for the remarkably well defined cluster $Au_{25}(SR)_{18}$ there are conflicting reports of magnetism. Of three prior reports interrogating $Au_{25}(SR)_{18}$ magnetism by EPR or NMR spectroscopy, all reports found that the -1 and 0 oxidation states are diamagnetic and S = 1/2 paramagnetic, consistent with superatom theory for the cluster. There are conflicting reports, however, regarding the nature of the +1 cluster, with two studies concluding diamagnetism and one study concluding paramagnetism.²¹⁻²⁵

Here we present a comprehensive study on the structures, magnetic properties, and optical properties of $Au_{25}(PET)_{18}$ in its three stable charge states. Notably we present the first crystal structure of $\{[Au_{25}(PET)_{18}^{+1}][PF_6^{-1}]\}$, as well as a notably higher resolution crystal structure of $Au_{25}(PET)_{18}^{0}$ relative to a previous report.²⁶ These structures show the same general atomic connectivity as observed in previous structures, with a 13 atom icosahedral core protected by 6 SR–Au–SR–Au–SR "semiring" units. The formal symmetry of the entire molecule,

including the approximately icosahedral core, is T_h .²⁷ In addition, we make the first SQUID magnetometry study of all three charge states, and also present linear absorption spectra from redissolved crystals of each charge state, notably improving upon the previous spectroelectrochemistry of this compound. We observe geometric distortions away from idealized symmetry in the inorganic core, and these distortions increased with decreasing superatomic valence from $1S^21P^6$ to $1S^21P^4$. The evolution of structure, magnetism and optical properties with oxidation state can be understood in terms of Jahn–Teller effects.

3.3 Methods

 $Au_{25}(PET)_{18}$ was synthesized using widely adopted methods.¹³ [$Au_{25}(PET)_{18}$]⁻ [TOA]⁺: $Au_{25}(PET)_{18}$ was synthesized by co-dissolving 1 g of HAuCl₄ and 1.560 g of tetraoctylammonium bromide (TOAB) in 70 ml of THF. This solution was allowed to stir for 15 min over which time the solution turns from yellow to orange. Next 1.8 ml of phenylethanethiol (PET) is added to the solution. The reaction mixture was stirred until it turned clear, which takes about 3 hours. Once the solution turned clear a freshly prepared aqueous solution containing 965 mg of NaBH₄ and 24 ml of water at 0 C ° was prepared. This aqueous solution is than rapidly added to the THF solution under vigorous stirring and was allowed to stir for 2 days. The reaction mixture was loosely covered to prevent the loss of THF over this course of time. $Au_{25}(PET)_{18}$ -¹ can than be oxidized to the $Au_{25}(SR)_{18}$ ⁰ by shaking in the presence of silica gel.

 $Au_{25}(PET)_{18}^{+}$ was synthesized through bulk electrolysis from crystallized $Au_{25}(PET)_{18}^{-}$ or $Au_{25}(PET)_{18}^{-0}$. $Au_{25}(PET)_{18}^{-0}$ was dissolved in a solution of containing 0.1M TBAPF₆ in DCM. Bulk electrolysis was preformed at a constant potential in a three-compartment cell at 300 mV vs SCE. Immediately after the bulk electrolysis was complete, the solution was prepared for

crystallization, as this compound appears to be unstable in solution for short periods of time. Ethanol was added to the DCM solution used in bulk electrolysis until a precipitate formed. This was than centrifuged and the solution was decanted. This was repeated until the precipitated appears to contain $Au_{25}(PET)_{18}^+$, as judged by UV/Vis. Once this $Au_{25}(PET)_{18}^+$ is sufficiently pure the solution will appear green instead of yellow or orange. At this point the $Au_{25}(PET)_{18}^+$ was put into a at -20 °C freezer with no insulation.

 $Au_{25}(PET)_{18}$ was synthesized using previously reported methods.¹³ The as-synthesized product was than oxidized to the $Au_{25}(SR)_{18}^{0}$ by shaking in the presence of silica gel. The cationic form was produced by bulk electrolysis of crystal pure $Au_{25}(SR)_{18}^{0}$. Single crystals of all three charge states formed after slow cooling in a solvent anti-solvent mixture. A more detailed procedure is presented in the SI. Crystals of each form were amenable to total structure determination by single crystal X-ray methods. This resulted in the first crystal structure of $Au_{25}(SR)_{18}^{+1}$ as well as a notably higher quality single crystal x-ray structure of $Au_{25}(SR)_{18}^{+1}$ as well as a notably higher quality single crystal x-ray structure of $Au_{25}(SR)_{18}^{+1}$

We performed density functional theory (DFT) calculations using the GPAW package that implements projector augmented-wave (PAW) method in a real-space grid.²⁵ Electronic structure, charge distribution, magnetic states and optical absorption of the clusters in all charge states were analyzed. Crystal structure coordinates including the full ligand layer were used as such without optimization to the theoretical minimum. The atomic charges were analyzed using the Bader decomposition method²⁶ and the optical absorption spectra were calculated from the linear response time dependent DFT as implemented in GPAW.²⁷ The PBE exchange-correlation functional was used both for the ground-state and optical absorption calculation. The PAW setups for gold include scalar-relativistic corrections.

3.4 Symmetry analysis

We report crystal structure of $Au_{25}(PET)_{18}^{+1}$ and an improved $Au_{25}(PET)_{18}^{0}$ crystal structure.²⁶ Each structure shows the same general atomic connectivity as the observed previously^{13,14,26,28}, with each cluster structure containing a 13 atom filled icosahedral core surrounded by 6 SR-Au-SR-Au-SR semi-rings. A comparison of the structures of the crystallographically resolved charge states of $Au_{25}(PET)_{18}^{-1/0/+1}$ (Figure 3.1) shows that the symmetry of the structure evolves from more ideal to less ideal as charge state increases.

We quantified the distortions from ideal symmetry in two ways: First, by analysis of bond lengths, angles, and dihedral angles; Second, by continuous symmetry measure $(CSM)^{29,30}$ as implemented in SHAPE v2.1. CSM is a method for quantifying the deviation from idealized symmetry. Briefly, the method quantifies the deviation of a shape from its ideal counterpart by calculating the sum of squares of displacement from the ideal geometry. To quantify distortion from ideal geometry through CSM, we developed a 'shell-by-shell' description of the geometric relationships of the atoms in Au₂₅(SR)₁₈ as shown in Figure 3.2.

In the shell-by-shell description, $Au_{25}(PET)_{18}$ is composed of 4 shells of symmetrically related atoms (Figure 3.2). The innermost shell (**I**, Figure 3.2B) is a filled Au_{13} icosahedron. The next most outer shell (**II**, Figure 3.2C) is comprised of 12 sulfur atoms that form the vertices of an icosahedron. The next most outer shell (**III**, Figure 3.2D) is comprised of the 12 Au(I) atoms of $Au_{25}(SR)_{18}$ forming the vertices of a truncated dodecahedron. The outermost shell (**IV**, figure 3.2E) is comprised of 6 sulfur atoms that form the vertices of an octahedron. The atoms in shell **I** are both chemically and geometrically related. In shells **II-IV** the atoms within each shells are related only by geometry. Figure 3.2A shows how these geometric shells are related in the context of chemical bonding in the structure. The geometric relationships of the shells to each other is as follows: The S_{12} icosahedron of shell II caps each of the vertices of shell I. The 12 Au(I) atoms of shell III, in addition to being chemically bonded to II and IV, also cap 12 of the 20 icosahedral faces of shell I. Thus, shell III represents a dodecahedron in which 8 vertices are missing. Chemical bonding forces the S atoms in shell II away from ideal icosahedral symmetry in order to allow for the optimal facecapping of I by III. Thus the aurophilic interactions between shells I and III must be very energetically favorable.

 CSM^{29} reveals shell I to be a nearly perfect icosahedron for $Au_{25}(PET)_{18}^{-1}$. Increasing the oxidation state of $Au_{25}(PET)_{18}$ from the closed electron shell superatom anion to neutral and cationic form causes the icosahedron in shell I to become oblate. CSM values for shell I relative to an ideal icosahedron are 0.067, 0.201 and 0.524 for the -1, 0 and +1 oxidation states, respectively, quantifying an increasing deviation from ideal symmetry with increasing charge state. The deviation from ideal symmetry is also reflected in an increasing bond length variation. Bonds, which in an ideal icosahedron are identical, vary over a range of 0.3 Å, 0.4 Å and 0.7 Å for $Au_{25}(PET)_{18}^{-1}$, $Au_{25}(PET)_{18}^{0}$, and $Au_{25}(PET)_{18}^{+1}$, respectively. The variation in bond lengths is shown in a quantitative heat map of the icosahedral cores of each charge state in Figure 3.3A. A summary of the bond lengths is given in Table S1.

The geometric distortions from I propagate outward to shell II. The CSM values for shell II are 3.407, 3.879, and 4.45, for -1, to 0, and +1, respectively. For shell III, CSM values are difficult to calculate algorithmically. The CSM values for shell IV are 0.138, 0.109, and 0.106, for -1, 0, and +1.

The outer-most shell IV is apparently least affected by charge state, as it is almost ideally octahedral for 0 and +1, while -1 shows the largest deviation from this symmetry. We attribute

the deviation from ideal symmetry in shell IV for the anion to the packing of the tetraoctylammonium cation in the crystal lattice, which appears to provoke the deviation from ideal symmetry in the solid state. In the case of $Au_{25}(PET)_{18}^{+1}$, the lattice position of the PF_6^{-1} ion does not cause deviation from ideal symmetry in shell IV.



Figure 3.1. The crystal structures of $Au_{25}(PET)_{18}$ in the -1 (A), 0 (B), and +1 (C) charge states are shown above. Gold is in yellow and sulfur is in orange. Crystallographically independent ligands are shown in unique color (see Table 1).



Figure 3.2. A) Shows the structure of the inorganic core and semirings of $Au_{25}(PET)_{18}$, with each color highlighting a different symmetry for sulfur or gold. In B-E) the shape that each unique shell forms is displayed.

To fully describe the changes that occur to the semi-rings (II-IV), we examine how each shell distorts with respect to shell I. The symmetry of the inorganic core (shells I-IV) is approximately of the point group D_{2h} .¹⁹ This approximation assumes the semirings on opposite sides of the cluster are coplanar, with the other four semirings lying orthogonal to the plane defined by coplanar semirings. In all structures of $Au_{25}(SR)_{18}$, there is some deviation from this idealized description. The amount of in which the symmetry is lowered, on average, increases with increasing oxidation state. As $Au_{25}(PET)_{18}$ becomes more oxidized the gold atoms in shell



Figure 3.3. A) Heat map of $Au_{25}(PET)_{18}^{-1,0,+1}$. B) An energy level diagram. C) A heat map of distortion away from the face.
III shift toward the edges of shell I in order to stabilize the weaker bonds that arise from an oblate core. As shown in Table S1 the average degree that the atoms in shell III deviate away from the face are 1.91° , 2.06° , and 2.63° for -1, 0, and +1 charge states, respectively. This in turn causes shell II and IV to bend out of the plane. By measuring the dihedral angle the amount that the semirings bend out of the plane can be quantified. The plane of shell I is defined as the very central atom of the icosahedral and the two gold atoms which are bound to the semirings. For the semirings the plane is defined as the atom of interest in the semi-ring, the gold atom in shell I which is bound the semi-ring, and the central atom of shell I. The planes defined for the measurement of the dihedral angle between shells I and II is shown in Figure 3.4. This measurement was performed for each atom in the semi-ring. On average the dihedral angle of the semirings are 7.3° , 8.6° , and 12.8° , for -1, 0, and +1, respectively. The average dihedral angle for each shell is given in Table S2.

Measurement of the dihedral angles shown in Figure 3.4 allows quantification of deviation from the ideal point group. One plane is contained within shell **I** and is defined as the central atom of the icosahedron and the two vertex gold atoms anchoring each side of a semiring (Figure 3.4A). The second plane is defined by the atom of the semi-ring, the gold atom of shell **I** to which the semi-ring is anchored, and the central atom of the cluster (Figure 3.4B).

The deviations from ideal symmetry of **IV** identified by CSM are presently described independently of chemical bonding to other shells. Chemical bonding requirements in the cluster clearly influence the sulfur atoms of shell **IV**. This is most obvious in the dihedral angles of the atoms in the semi-rings. The sulfur atoms in **IV** have the largest average dihedral angle for the +1 (5.1°), followed by -1 (3.9°), and finally 0 (0.8°) oxidation states. Thus, the coordinates of

atoms in shell **IV** appear to be influenced by a combination of counterion, solvent, and underlying inorganic structure.

We previously reported that the thermal stability of $Au_{25}(PET)_{18}$ depends on the superatomic electron configuration,²⁰ with lower stabilities associated with departure from noblegas like superatom electron configuration. This work suggests that the changes in cluster geometry that arise as charge state may be tied to the thermal stability we previously observed. For instance, we observe that the longest (weakest) bond in the icosahedral core is 3 Å, 3.1 Å, and 3.3 Å for -1, 0, and +1, respectively. These effects are also seen in shells II and III.



Figure 3.4. Depicted above is the two planes used to measure the dihedral angles of the semirings. A) Shows the plane defined by the core and(B) shows the plane defined by the semiring. The plane on B) is changed to incorporate the appropriate atom in the semi-ring and is measured on both sides.

3.5 Optical/Electronic Properties of Au₂₅(PET)₁₈^{-1/0/+1}

The absorption spectra of $Au_{25}(PET)_{18}$ evolves notably across each charge state, suggesting changes in the underlying electronic structure after oxidation or reduction of $Au_{25}(SR)_{18}$. The absorption peak around 680 nm (1.81 eV) is attributed to the transition from the 1P to 1D_e and the peak between 450-470 nm (2.76-2.58 eV) has been attributed to the transition of the 1P to 1D_t.¹⁹ The transition at 380-400 nm (3.15-3.08 eV) is attributed to excitation of the semirings to 1D_e orbital. The energy transition from the 1P to 1D_e for the -1, 0, and +1 are 1.78 eV, 1.81 eV, and 1.88 eV, respectively. For the 1P to 1D_t energy gaps of 2.76 eV, 2.68 eV, and 2.58 eV are observed for the -1, 0 and +1, respectively. Finally the energy gap for ligand band to superatomic D orbital transition is 3.08 eV for -1 and 0, and 3.15 eV for +1. These values are summarized in Table S3.

The experimental and theoretical spectra of $Au_{25}(PET)_{18}$ are previously reported.^{14,21,24,26} We improved the experimental spectra for each charge state by forming, isolating and redissolving x-ray quality single crystals of each charge state. We replot our data with previously reported spectroelectrochemical data in Figure 3.5 as previously noted, the linear absorption spectrum changes substantially for each oxidation state. We correlate these changes here to changes in the structure of each oxidation state. Relative to $Au_{25}(PET)_{18}$ the 1P to 1D_e transition shows a slightly decreased energy gap of about 0.03 eV for $Au_{25}(PET)_{18}^{0}$, while the energy of this transition increases for $Au_{25}(PET)_{18}^{-1}$ to $Au_{25}(PET)_{18}^{0}$ is due to one of the 1P orbitals increasing in energy, but still being occupied by one electron, depicted in a qualitative energy level diagram in Figure 3.3. With the removal of a second electron the splitting of the 1P orbitals becomes much greater than thermal energy, and the highest energy 1P orbital becomes unoccupied. The

decrease in the energy gap of the 1P to 1D_t going from with increasing oxidation of $Au_{25}(PET)_{18}$ can be attributed to the splitting of the superatomic D orbitals due to core distortion as previously calculated.¹⁹ This first-order Jahn–Teller distortion is reflected in the distortion from ideal symmetry in the crystal structures.^{19,26} We suggest that the increase in energy gap for the ligand band to 1D_e in $Au_{25}(PET)_{18}^{+1}$ arises from the electron deficient core pulling electron density from the ligand shell. This in-turn increases the bond strength of the core gold to the first sulfur shell, and this is supported by the on average shorter bond lengths of the sulfur to core gold for $Au_{25}(PET)_{18}^{+1}$.

Theoretical optical absorption spectra (Figure S3) show a reasonable qualitative agreement with the experimental data, particularly showing the systematic blue shift of the first absorption peak as the oxidation state increases from -1 to +1. We also calculated the spectrum of +2 state in the experimental configuration of +1. The spectrum is significantly different from



Figure 3.5. The UV/Vis absorption spectrum of $Au_{25}(PET)_{18}^{-1,0,+1}$.

+1 spectrum at low excitation energies and confirm that +2 clusters are not as impurities in the solution of +1.

3.6 Magnetic Properties of Au₂₅(SR)₁₈^{-1/0/+1}

We report the first investigation of magnetism in the Au₂₅(SR)₁₈^{-1/0/+1} cluster by Superconducting Quantum Interference Device (SQUID). Relative to NMR and EPR approaches SQUID incorporates greater sensitivity, allowing observation of smaller molar magnetic susceptibilities (χ_m). SQUID measures the total susceptibility of a sample whereas previous studies were limited to paramagnetic susceptibility. Subtraction of the diamagnetic contribution from χ_m allows determination of the paramagnetic susceptibility (χ_p). χ_p can be used for the comparison of a magnetic moment to that of a free electron. The diamagnetic susceptibilities were approximated from Pascal's diamagnetic corrections.

To determine the charge dependent magnetic behavior of $Au_{25}(SR)_{18}$, temperature was ramped from 4 K to 300 K under a magnetic field of 0.1 Tesla. In this regime, paramagnetic substances show a response that is inversely proportional to the temperature, and diamagnetic substances show a temperature-independent response. Figure 3.6 shows the χ_p vs. temperature. We conclude that $Au_{25}(PET)_{18}$ in -1 and +1 oxidation states is almost ideally diamagnetic. This observation agrees with the computational prediction for the spin-singlet ground state of $Au_{25}(PET)_{18}^+$ (the spin-triplet state is predicted to be +0.39 eV higher in energy). Deviations from ideal behavior are reflected in a very small paramagnetic-type response, observable only at very low temperatures for -1 and +1. Conversely, $Au_{25}(PET)_{18}$ as a neutral compound produces a nearly ideal paramagnetic response that could be observed up to 300 K. The paramagnetic susceptibilities found from SQUID for $Au_{25}(SR)_{18}^{-1/0/+1}$ correspond to 0.01, 1.07, and 0.03 unpaired electrons, respectively.

These values assume ideal paramagnetic behavior, where magnetic anisotropy or magnetic coupling violate the assumption. To determine magnetic anisotropy, measurements were made at low temperatures (2–32 K) and large magnetic fields (1–5 T). Under these conditions, the unpaired electrons within a paramagnetic substance all align with the external field and response is expected to fit to the Brillouin function of magnetism.³¹ The SQUID data for Au₂₅(PET)₁₈⁰ fits the Brillouin function for a spin value of 1/2 and a g-factor of 2.16, as shown in Figure S5. Minimal magnetic anisotropy is thus suggested. Here, the g-factor value indicates spin–orbit coupling, similar to a previous conclusion for this system.^{23,32}



Figure 3.6. The magnetic susceptibilities of $Au_{25}(PET)_{18}^{-1,0,+1}$.

First order Jahn–Teller distortions resulting in the splitting the degeneracy of superatom P orbitals account well for the magnetic behavior of $Au_{25}(PET)_{18}$. However, some paramagnetic susceptibility is observed that is not accounted for by this simple approximation. Previous studies have reported that the gold 5d orbital is partially depleted in its bonding to sulfur.^{9,33} This may

result in a magnetic moment that would correspond to a fraction of an unpaired electron on gold bonded to sulfur, which in the ensemble of an $Au_{25}(SR)_{18}$ molecule is observed as a small magnetic moment for the -1 and +1 oxidation states.

Compared to $Au_{25}(PET)_{18}^{-1}$, $Au_{25}(PET)_{18}^{+1}$ has a slightly larger magnetic susceptibility. We propose that this arises from greater electron deficiency in $Au_{25}(PET)_{18}^{+1}$, which pulls electron density inward, creating larger d holes in the semiring Au(I) atoms compared to $Au_{25}(PET)_{18}^{-1}$. According to the Bader charge analysis, 0.34e and 0.28 are depleted from the core and semiring Au atoms, respectively, when comparing $Au_{25}(PET)_{18}^{+1}$ to $Au_{25}(PET)_{18}^{-1}$ (Table S4). The magnetic behavior of $Au_{25}(PET)_{18}^{0}$ is more complicated. Here we propose that due to the almost degenerate P orbitals, the paramagnetic susceptibility in excess of 1.0 unpaired electrons arises from spin–orbit coupling.^{23,32} We estimate that 1–3% of an unpaired electron arises from the Au–S interaction (d-holes), with the remaining (4–6%) arising from superatomic spin–orbit coupling for $Au_{25}(PET)_{18}^{0}$. Our values for magnetism in the anionic compound are consistent with previously reported results.³³

3.7 Long range order and packing of Au₂₅(PET)₁₈PF₆

The high-quality of the two reported crystal structures prompts the first complete analysis of molecular packing interactions in single-crystals of thiolate protected gold. Indeed, clusters with ligand shells comprised of aromatic ligands such as PET and pMBA account for most crystal structures of ligated gold nanoparticles. In the case of $Au_{25}(SR)_{18}^{-1/0/+1}$, there are substantial differences in the ligand shell structure in the solid state for each charge state. These differences in the ligand layer do not appear to be propagations of the changes in the inorganic core due to charge state; rather, the differences in the ligand layer of $Au_{25}(SR)_{18}^{-1/0/+1}$ arise from

different inter- and intra-molecular ligand-ligand interactions, ligand-counterion interactions, and ligand-solvent interactions (Figure 3.7).

The high quality of the $Au_{25}(SR)_{18}^{+1}$ structure reported here allows a careful analysis of the role of phenylethane thiolate ligands in the packing of $Au_{25}(PET)_{18}^{+1}$ into single crystals. To our knowledge, no similar analysis has been previously reported; the interactions described here, however, appear to be ubiquitous among PET protected AuNC structures.^{13,14,26,34,35,36}. The importance of this analysis is due to the ligand shell of thiolate protected gold nanoparticles largely determining the interaction of the cluster with its external environment, for instance, in biological contexts.^{37,38}

Due to the imposed inversion symmetry of the $P\bar{I}(bar)$ space group, there are nine crystallographically independent PET ligands found on the cluster surface (Figure 3.1) located in three crystallographically independent semirings (S–Au–S–Au–S units) shown in Figure S4 and S5. Table 3.1 summarizes the dominant intra- and inter-molecular interactions of each of the nine symmetry-unique ligands in the Au₂₅(SR)₁₈⁺¹ crystal structure.

Each ligand adopts either anti or gauche conformation on the cluster surface, corresponding to an S–CH₂–CH₂–Ph torsion angle of ~180° or ~60°, respectively (Table 1, Scheme S1, Figure S4). Four of the five gauche ligands (PET1, PET6, PET7 and PET9) fold over the semiring to which they are bonded and form cation–aromatic interactions with the Au¹ atom in the semiring. Specifically, Au¹···π interactions are observed, with average distance of 3.43 Å (Figure S6). A fifth gauche ligand (PET3) does not form cation–phenyl interaction with the Au¹ atom in the unit. Instead it coordinates to the PF₆⁻ counter anion and DCM solvent molecule that sit above the corresponding Au¹ atom (Au3), preventing the Au¹···π interactions observed for other gauche ligands.

The remaining four crystallographically independent ligands (PET2, PET4, PET5 and PET8) form inter-cluster CH--S, CH--Ph and Ph--Ph interactions with the ligands of adjacent Au₂₅ clusters. In addition, these ligands form intermolecular Ph--F, Ph--Cl and CH--F interactions with the PF_6^- anions or DCM solvent molecules within the crystal lattice.

We observe three structural motifs that underlie the intermolecular interactions among adjacent Au₂₅(PET)₁₈⁺¹ clusters. A packing diagram for the crystalline arrangement of clusters is shown in Figure S6 The three motifs that mediate this assembly are: (1) phenyl–phenyl' squares (where the ' denotes a phenyl ring from a neighboring cluster); (2) an extended π -interaction network involving 6 ligands; (3) halogen mediated interactions of PET–PF₆–DCM–PET construction. An example of each of these interactions is shown in Figure 3.7.



Figure 3.7. The π -stacking squares formed by PET4 and PET9 of adjacent clusters are shown in panel (A). The extended π -interaction network of PET1, PET2, and PET8 with PET5, PET6 and PET9 of an adjacent cluster are shown in panel (B). The ligands involved in phenyl–halogen and phenyl–solvent interactions important for crystal packing are shown in (C). Ligands of neighboring clusters are denoted by an apostrophe.

In the phenyl–phenyl' square assembly, PET9 ligands interact with the respective ligands of the neighboring Au₂₅ cluster by forming π --- π and CH--- π inter-cluster interactions (Figure 3.7, panel A). The sides of the square are composed of parallel displaced opposite facing PET9 ligands forming both π --- π (3.34 Å) and CH--- π (2.69 Å) interactions. The other two sides of the square assembly are defined by PET4 ligands, which form a perpendicular edge-to-face π --- π (2.84 Å) interaction with the respective PET9 ligand. A second neighboring Au₂₅ cluster additionally interacts with PET4 ligand from the opposite side by forming tilted edge-to-face π --- π (2.81 Å) interactions with PET5' and PET6' ligands and CH--- π (2.85 Å) interaction with PET7' ligand. Figure 3.7 panel A illustrates this assemblage.

The extended π -interaction network is nucleated by three PET ligands (PET2, PET5 and PET8) in the anti-conformation, which are located at the S2–S5–S8 intersection of the three separate semirings (Figure S5). These ligands form intermolecular interactions with one another and also interact with the ligands of two neighboring Au₂₅ clusters, and also with the PF₆⁻ anion and DCM solvent molecule (Figure 3.7, panel B, DCM solvent not shown). PET2 and PET5 coordinate to one of the adjacent Au₂₅ clusters, forming tilted edge-to-face and edge-to-edge π -m π (2.80 and 2.38 Å) interactions with the neighboring PET6' and PET9' ligands, respectively. In addition to the aromatic interaction, the PET5 ligand quite interestingly also forms PhH-S (2.92 Å) interaction with the sulfur atom of the neighboring PET9' ligand. The PET8 ligand of the nucleating cluster, on the other hand, connects to a second neighboring Au₂₅ cluster by forming perpendicular edge-to-face π -m π (2.83 Å) interaction with its PET1'' ligand. The space between the two neighboring Au₂₅ clusters is occupied by the DCM–PF₆–PF₆–DCM complex (vide infra) and in addition to the prevailing aromatic inter-cluster interactions, PET2 ligand is also available

to form π --HC (2.90 Å) and PhH--F (2.60 Å) interactions with the solvent DCM and PF₆⁻ anion,

respectively.

Table 3.1 Geometric parameters and selected intra- and inter-cluster interactions of the PET ligands of the $Au_{25}(PET)_{18}^{+1}$ crystal structure. ^a Color code of the crystallographically independent PET ligand. ^b g = gauche and a = anti. ^c Ligand intracluster interactions. ^d X = halide (F or Cl). ^e Average distance reported.

Ligand ^a	S-CH2CH2-Ph torsion angle ^b (°)	Ph…Au¹ / CH [∠] (Å)	anion / solvent CH···X ^d coordination and Ph···Ph / CH / S intercluster interactions ^e
PET1 (S1)	64.0 (<i>g</i>)	3.44 (Au2)	PF ₆ anion (2.60 Å)
PET2 (S2)	178.5 (a)	_	PF ₆ anion (2.60 Å), DCM solvent (2.90 Å) tilted edge-to-face (PET6, 2.80 Å)
PET3 (S3)	66.1 (<i>g</i>)	3.84 (C49)	PF ₆ anion (2.59 Å), DCM solvent (2.94 Å) tilted edge-to-face (PET6, 2.86 Å)
PET4 (S4)	173.4 (a)	—	edge-to-face (PET9, 2.84 Å)
PET5 (S5)	174.1 (a)	-	tilted edge-to-face (PET4, 2.81 Å) Ph⋯S9 (PET9, 2.92 Å)
PET6 (S6)	-63.2 (g)	3.35 (Au13)	tilted edge-to-face (PET4, 2.77 Å)
PET7 (S7)	71.6 (<i>g</i>)	3.54 (Au12)	CH…Ph (PET4, 2.85 Å)
PET8 (S8)	-179.3 (a)	_	edge-to-face (PET1, 2.83 Å)
PET9 (S9)	-67.2 (g)	3.39 (Au6)	PF6 anion (2.60 Å) parallel displaced (PET9, 3.34 Å) CH…Ph (PET9, 2.69 Å)

The voids in the distorted simple cubic lattice formed by $Au_{25}(PET)_{18}$ nuclei in the single crystal are occupied by a DCM–PF₆–PF₆–DCM complex that not only fills the available space, but also coordinates to the neighboring PET ligands (PET1, PET2, PET3 and PET9) forming directional aromatic–halide and aromatic–CH weak inter-cluster interactions (Figure 3.7, panel C). As such, one Au₂₅ cluster is surrounded by total of six DCM–PF₆–PF₆–DCM complexes in the crystal lattice. Due to the directional halide–halide and aromatic–halide intermolecular interactions offered by the DCM–PF₆–PF₆–DCM, the complex fills almost perfectly the space between the Au₂₅ clusters in the crystal lattice. This seems to have a strong effect on the crystal packing arrangement and gives an extremely good quality crystal structure which is also seen as the lack of disorder in the ligand layer.

3.8 Conclusions

The determination of the crystal structures of $Au_{25}(PET)_{18}$ in three discrete charge states allows for the first time a comparison of electronic and magnetic differences of all three stable charge states of Au₂₅(SR)₁₈ in the context of their structure. The Jahn-Teller effect is a convenient structural framework to describe the evolution of structure as oxidation state changes. Au₂₅(PET)₁₈⁻¹ has a noble gas-like configuration (1S²1P⁶) underlying its diamagnetism and comparatively high thermal stability. Comparatively, $Au_{25}(PET)_{18}^{0}$ with $1S^{2}1P^{5}$ superatom electron configuration is paramagnetic arising from an unpaired 1P electron. When incomplete, the superatomic 1P become non-degenerate, which is reflected in the structure of the cluster becoming oblate relative to the anion. Oxidation to $Au_{25}(PET)_{18}^{+1}$ (1S²1P⁴) results in larger distortions to the cluster than are observed in either of the other charge states. The electronic distortion results in an unoccupied P orbital in $Au_{25}(PET)_{18}^{+1}$, rendering it diamagnetic. Here we show for the first time that Jahn-Teller effects apply to thiolate protected gold clusters. The superatom driven distortions are primarily observed in the 13 gold atoms of shell I, with subsequent shells reflecting smaller distortions. A Jahn–Teller effect for $Au_{24}X(SR)_{18}$ where X = Pd or Pt was recently reported by another group, based on spectroscopic evidence, while this paper was under revision.³⁹

References

Jahn, H. A.; Teller, E. Proc. R. Soc. Lond. Math. Phys. Eng. Sci. 1937, 161 (905), 220–235.

(2) Cotton, F. A.; Fang, A. J. Am. Chem. Soc. 1982, 104 (1), 113–119.

(3) Chancey, C.C. and O'Brien, M.C.M.: The Jahn-Teller Effect in C60 and Other Icosahedral Complexes (Hardcover). http://press.princeton.edu/titles/6243.html (accessed May 19, **2016**).

(4) Hughbanks, T.; Corbett, J. D. Inorg. Chem. 1988, 27 (12), 2022–2026.

(5) Campbell, J.; Dixon, D. A.; Mercier, H. P. A.; Schrobilgen, G. J. *Inorg. Chem.* 1995, *34*(23), 5798–5809.

(6) Häkkinen, H. Chem. Soc. Rev. 2008, 37 (9), 1847–1859.

(7) de Heer, W. A. *Rev. Mod. Phys.* **1993**, *65* (3), 611–676.

(8) Schooss, D.; Weis, P.; Hampe, O.; Kappes, M. M. Philos. Trans. R. Soc. Lond. Math.
 Phys. Eng. Sci. 2010, 368 (1915), 1211–1243.

Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.;
Whetten, R. L.; Grönbeck, H.; Häkkinen, H. *Proc. Natl. Acad. Sci.* 2008, *105* (27), 9157–9162.

(10) Schaaff, T. G.; Knight, G.; Shafigullin, M. N.; Borkman, R. F.; Whetten, R. L. J. Phys. Chem. B 1998, 102 (52), 10643–10646.

(11) Parker, J. F.; Fields-Zinna, C. A.; Murray, R. W. Acc. Chem. Res. 2010, 43 (9), 1289–1296.

(12) Negishi, Y.; Nobusada, K.; Tsukuda, T. J. Am. Chem. Soc. 2005, 127 (14), 5261-5270.

43

(13) Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. J. Am. Chem. Soc.
2008, 130 (12), 3754–3755.

- (14) Zhu, M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. J. Am. Chem. Soc. 2008, 130 (18), 5883–5885.
- (15) Parker, J. F.; Weaver, J. E. F.; McCallum, F.; Fields-Zinna, C. A.; Murray, R. W. Langmuir **2010**, *26* (16), 13650–13654.
- (16) Zhu, M.; Lanni, E.; Garg, N.; Bier, M. E.; Jin, R. J. Am. Chem. Soc. 2008, 130 (4), 1138–1139.
- (17) Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Chem. Rev.
 2005, 105 (4), 1103–1170.
- (18) Daniel, M.-C.; Astruc, D. Chem. Rev. 2004, 104 (1), 293–346.
- (19) Aikens, C. M. J. Phys. Chem. Lett. 2011, 2 (2), 99–104.
- (20) Tofanelli, M. A.; Ackerson, C. J. J. Am. Chem. Soc. 2012, 134 (41), 16937–16940.
- (21) Antonello, S.; Perera, N. V.; Ruzzi, M.; Gascón, J. A.; Maran, F. J. Am. Chem. Soc. 2013, 135 (41), 15585–15594.
- (22) Nealon, G. L.; Donnio, B.; Greget, R.; Kappler, J.-P.; Terazzi, E.; Gallani, J.-L. *Nanoscale* **2012**, *4* (17), 5244–5258.
- (23) Zhu, M.; Aikens, C. M.; Hendrich, M. P.; Gupta, R.; Qian, H.; Schatz, G. C.; Jin, R. J. *Am. Chem. Soc.* 2009, *131* (7), 2490–2492.
- (24) Venzo, A.; Antonello, S.; Gascón, J. A.; Guryanov, I.; Leapman, R. D.; Perera, N. V.;
 Sousa, A.; Zamuner, M.; Zanella, A.; Maran, F. *Anal. Chem.* 2011, *83* (16), 6355–6362.
- (25) Akbari-Sharbaf, A.; Hesari, M.; Workentin, M. S.; Fanchini, G. J. Chem. Phys. 2013, 138
 (2), 24305.

(26) Zhu, M.; Eckenhoff, W. T.; Pintauer, T.; Jin, R. J. Phys. Chem. C 2008, 112 (37), 14221–14224.

(27) Aikens, C. M. In *Frontiers of Nanoscience*; Häkkinen, T. T. and H., Ed.; Protected Metal ClustersFrom Fundamentals to Applications; Elsevier, **2015**; Vol. 9, pp 223–261.

(28) Dainese, T.; Antonello, S.; Gascón, J. A.; Pan, F.; Perera, N. V.; Ruzzi, M.; Venzo, A.;
Zoleo, A.; Rissanen, K.; Maran, F. *ACS Nano* 2014, *8* (4), 3904–3912.

- (29) Zabrodsky, H.; Peleg, S.; Avnir, D. J. Am. Chem. Soc. 1992, 114 (20), 7843-7851.
- (30) Pinsky, M.; Avnir, D. Inorg. Chem. 1998, 37 (21), 5575–5582.
- (31) Kahn, O. 1942-. Molecular magnetism; VCH, 1993.
- (32) Jiang, D.; Kühn, M.; Tang, Q.; Weigend, F. J. Phys. Chem. Lett. 2014, 5 (19), 3286–3289.
- (33) Negishi, Y.; Tsunoyama, H.; Suzuki, M.; Kawamura, N.; Matsushita, M. M.; Maruyama,

K.; Sugawara, T.; Yokoyama, T.; Tsukuda, T. J. Am. Chem. Soc. 2006, 128 (37), 12034–12035.

- (34) Qian, H.; Eckenhoff, W. T.; Zhu, Y.; Pintauer, T.; Jin, R. J. Am. Chem. Soc. 2010, 132
 (24), 8280–8281.
- (35) Das, A.; Li, T.; Li, G.; Nobusada, K.; Zeng, C.; Rosi, N. L.; Jin, R. *Nanoscale* 2014, 6
 (12), 6458–6462.
- (36) Zeng, C.; Liu, C.; Chen, Y.; Rosi, N. L.; Jin, R. J. Am. Chem. Soc. 2014, 136 (34), 11922–11925.
- (37) Sexton, J. Z.; Ackerson, C. J. J. Phys. Chem. C 2010, 114 (38), 16037–16042.
- (38) Wong, O. A.; Hansen, R. J.; Ni, T. W.; Heinecke, C. L.; Compel, W. S.; Gustafson, D.
 L.; Ackerson, C. J. *Nanoscale* 2013, 5 (21), 10525–10533.

(39) Kwak, K.; Tang, Q.; Kim, M.; Jiang, D.; Lee, D. J. Am. Chem. Soc. 2015, 137 (33), 10833–10840.

Chapter 4

Crystal Structure of the PdAu₂₄(SR)₁₈⁰ Superatom^{*}

4.1 Synopsis

The single-crystal X-ray structure of Pd-doped $Au_{25}(SR)_{18}$ was solved. The crystal structure reveals that in PdAu₂₄(SR)₁₈, the Pd atom is localized only to the centroid of the $Au_{25}(SR)_{18}$ cluster. This single-crystal X-ray structure shows that PdAu₂₄(SR)₁₈⁰ is well conceptualized with the superatom theory. The PdAu₂₄(SR)₁₈⁰ charge state is isoelectronic with $Au_{25}(SR)_{18}^{+1}$ as determined by a first order Jahn–Teller effect of similar magnitude and by electrochemical comparison. The previously reported increased stability of PdAu₂₄(SR)₁₈ can be rationalized in terms of Pd–Au bonds that are shorter than the Au–Au bonds in $Au_{25}(SR)_{18}$.

4.2 Introduction

Many ligand-protected gold clusters, including Au₁₁(PPh₃)₇Cl₃, Au₂₅(SR)₁₈, Au₃₉(PPh₃)₁₄Cl₆, and Au₁₀₂(SR)₄₄, can be described electronically as superatoms.¹ Superatom theory can be extended to describe properties such as stability,² magnetism,³ and *certain* optical properties.⁴ Superatom theory approximates metal clusters as spheres containing the free or valence electrons of the metal atoms comprising the cluster. A valence electron count of 2, 8, 18, 20, 34, 40, 58... corresponds to total filling of superatom orbitals, resulting in noble gas-like electron configurations associated with high stability.⁵ Ligands can either withdraw one electron

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each from the superatom or serve as dative ligands that neither add to nor subtract from the superatom electron count.¹ Overall, this simple approximation remarkably predicts the symmetry and degeneracy of the frontier orbitals of many ligated metal clusters.⁶ Au₂₅(SR)₁₈ and isostructural compounds are intensively studied currently, with detailed understanding of electronic properties available.⁷

An emergent question in the experimental literature is how dopant atoms such as Pt or Pd impact the superatom electron count in ligated bimetallic clusters, such as in the recently reported PdAu₂₄(SR)₁₈, PtAu₂₄(SR)₁₈, Pd₂Au₃₆(SR)₂₄, Ag_xAu_{25-x}(SR)₁₈, and Pd_xAu_{144-x}(SR)₆₀ clusters.^{8,9,10} All of the single-crystal X-ray determined doped or alloy clusters of thiolate-protected metal replace Au with Ag or vice versa, resulting in clusters such as Ag₃₂Au₁₂(SR)₂₄ and Ag_xAu_{144-x}(SR)₆₀.^{11,12,13,14,15} In the case of coinage metals (Cu, Ag, Au), each metal is now understood to donate one electron (i.e., 6s¹ electron of Au). The electron donation behavior of other metals to the superatom is a matter of conjecture. In the case of Pd, for instance, it is expected that the d¹⁰ metal atom will neither add to nor subtract from the superatom electron count.¹⁶ There is no empirical structural evidence so far to support this conjecture.

Another open question in the recent literature concerns the position of dopant or alloy atoms in the cluster. In $Au_{25}(SR)_{18}$ based clusters, there are three possible positions for these dopants: (1) in the centroid of the 13 atom icosahedron that forms the core of the cluster, (2) as one of the vertices of the central icosahedron, or (3) in the semi-ring (i.e., replacing a Au atom in the SR-Au(I)-SR-Au(I)-SR structure. In the case of PdAu₂₄(SR)₁₈, DFT and EXAFS studies place the dopant atom at the centroid position for Au₂₄X(SR)₁₈ clusters where X is Pt or Pd.^{14,16} However, the position of Pd in the Pd₂Au₃₆(SR)₂₄ structure is not speculated as found at the centroid positions of each fused bi-icosihedra.¹⁷ In each case, the positions of heteroatoms are inferred from indirect methods; single-crystal X-ray structures are not yet available for any alloy structure of a gold cluster that does not contain coinage metals.

4.3 Results and Discussion

Here, we present the single-crystal X-ray structure of $PdAu_{24}(SR)_{18}$, localizing the Pd dopant atom to a single location in the crystal structure. Through analysis of electrochemical/spectroscopic data, we assign the solved structure as the $1S^21P^4$ superatom configuration, suggesting that the Pd heteroatom donates no electrons to the superatom electronic structure.

We synthesized $PdAu_{24}(PET)_{18}$ (PET = phenylethanethiol) by methods adopted from Negishi.¹⁸ Crystal diffraction data was collected on an Advanced Light Source Beamline 4.2.2. Synchrotron flux was required for timely collection of data, especially at higher angle diffraction. $PdAu_{24}(PET)_{18}^{0}$ forms a triclinic lattice in the space group P1(bar), as observed for every other crystallographically resolved $Au_{25}(SR)_{18}$ cluster structure.^{19,20,21,22,23} The crystal structure was solved in SHELXTL. The single-crystal X-ray structure of $PdAu_{24}(PET)_{18}$ is shown in Figure 4.1. The structure reveals identical connectivity to the other $Au_{25}(SR)_{18}$ crystal structures so far reported, with a filled 13-atom icosahedral core protected by six SR-Au-SR-Au-SR semi-rings. ^{19,20,21,22,23} Static substitution disorder refinement in SHELX was used to refine the occupancy of Pd in all metal atom positions. In this refinement strategy, Pd refines to less than 10% occupancy or fails to refine to any occupancy except in the centroid of the cluster, where it refines to 92.6% occupancy. Au could completely account for electron density in every other electron density peak, without resulting in "negative density" (Figure S7). We assign the material that crystallized as neutral because no counterions were observed in the crystal lattice.

Linear absorption spectroscopy and electrochemical measurements suggest that the $PdAu_{24}(PET)_{18}$ cluster is isoelectronic with the $Au_{25}(SR)_{18}$ cluster. Electrochemically, $PdAu_{24}(PET)_{18}$ and $Au_{25}(PET)_{18}$ show the same multiplicity of charging events with almost identical spacing between each reduction/oxidation wave. The difference in the voltammograms is a shift of -534 mV for the potentials of $PdAu_{24}(PET)_{18}$ compared to $Au_{25}(PET)_{18}$ (Figure 4.2).²⁴ Likewise, the linear absorption spectra of $PdAu_{24}(PET)_{18}^{0}$ are similar to $Au_{25}(PET)_{18}^{0}$; each compound has a broad band peak centered at 650 and 688 nm with a sharp feature at 380 and 400 nm for $PdAu_{24}(PET)_{18}^{0}$ and $Au_{25}(PET)_{18}^{0}$, respectively. The voltammograms are similar to those previously reported by Murray for the same compound.²⁴ Previous theoretical reports describe modification of the electronic spectra of $Au_{25}(SR)_{18}$ upon doping with Pd. DFT description of the electronic structure suggests that removal of electrons is "softer" for PdAu₂₄(SR)₁₈ as a result of the electronic structure modification upon doping, resulting in a substantially shifted electrochemical response.²⁵



Figure 4.1. Shown in A is the crystal structure of $PdAu_{24}(PET)_{18}$ with gold in yellow, thiol in red and palladium in blue. The carbon chains have been removed for clarity. B is a heat map of the bond lengths of the gold icosahedron.

Despite the similarities, it is obscure which oxidation state of $Au_{25}(PET)_{18}$ is formally isoelectronic with $PdAu_{24}(PET)_{18}^{0}$. In general, only the s and p electrons of a metal are donated to the superatom. With an electron configuration of $5s^{0}4d^{10}$, it is expected that Pd makes no contribution to the superatom electron count. Thus, $PdAu_{24}(PET)_{18}^{0}$ is expected to be "superatom-isoelectronic" with $Au_{25}(PET)_{18}^{+}$.

Assuming this, each event in the square wave voltammogram of $PdAu_{24}(SR)_{18}$ is assigned with the superatomic configuration (Figure 4.2). The resting potential of the $PdAu_{24}(PET)_{18}^{0}$ used in formation of single crystals is at 50 mV vs SCE, suggesting a $1S^{2}1P^{4}$ superatomic configuration for the single-crystal structure. This "open-shell" superatom electron configuration is one in which a Jahn–Teller effect should be observable, analogous to our recent observations of a Jahn–Teller effect that increases with increasing oxidation state for $Au_{25}(SR)_{18}^{-1}$ 1/0/+1 26

Indeed, analysis of the central icosahedron of $PdAu_{24}(SR)_{18}$ reveals that the structure is distorted away from idealized icosahedral symmetry with remarkable similarity to the distortion observed previously in the $Au_{25}(SR)_{18}^{1+}$ ($1S^21P^4$) superatom. In the $1S^2 1P^4$ superatom structure of $Au_{25}(SR)_{18}^{1+}$, bond lengths in the icosahedral core varied from 2.7 to 3.3 Å, whereas for the $1S^21P^6$ configuration, bond lengths vary only from 2.8 to 3.0 Å. The variability in bond lengths observed in $PdAu_{24}(SR)_{18}^{0}$ span an identical range to those of $Au_{25}(SR)_{18}^{+1}$. Continuous symmetry measurement (CSM) can be used to quantify distortion from idealized geometry in terms of root mean squares.²⁷ The CSM values for the central icosahedron of $Au_{25}(SR)_{18}^{-1/0/+1}$ are 0.67, 0.201, and 0.524. The CSM value for the corresponding structure in $PdAu_{24}(SR)_{18}^{0}$ is 0.350, falling between the values previously observed for the neutral and cationic $Au_{25}(SR)_{18}$

Further support of this isolectronic assignment is revealed in the linear absorption spectrum as shown in Figure S8. Absorbance from the icosahedral core is attributed to a feature at 650 nm for PdAu₂₄(PET)₁₈⁰ and 660 for Au₂₅(PET)₁₈⁺,¹⁷ corresponding to the HOMO-LUMO transition. The slightly larger HOMO-LUMO gap observed for PdAu₂₄(SR)₁₈ follows from stronger bonding (shorter crystallographically observed bonds) in the 13-atom core for PdAu₂₄(SR)₁₈. The contraction around Pd results in shortening of the gold-gold bonds of the PdAu₂₄(SR)₁₈ icosahedron by an average of 0.04 Å. In addition, the absorption band at 400 nm for Au₂₅(PET)₁₈⁺ is blue-shifted to 380 nm for PdAu₂₄(PET)₁₈⁰ which suggests that the thiols may also bond more strongly to the icosahedral core.^{15,17} Thus, the higher stability of PdAu₂₄(PET)₁₈⁰ compared to Au₂₅(SR)₁₈ suggested by previous results can than be attributed to an overall stronger bonding of the inorganic core.^{2,24}



Figure 4.2. Shown above are the square wave voltammograms of $PdAu_{24}(PET)_{18}$ and $Au_{25}(PET)_{18}$. The current axis is offset and normalized for comparison.

We isolated the $PdAu_{24}(PET)_{18}$ as the neutral $(1S^21P^4)$ compound without taking any measures to preserve the oxidation state of the cluster. We suggest that the as-synthesized $PdAu_{24}(PET)_{18}$ is in the -2 charge state $(1S^21P^6)$, presumably more stable). We suggest that, similar to $Au_{25}(SR)_{18}$, the compound we studied may be oxidized by ambient atmosphere into the crystallized oxidation state. Because the reduction potentials are shifted to more negative values for $PdAu_{24}(PET)_{18}$ compared to $Au_{25}(PET)_{18}$, oxidaiton in the presence of atmospheric oxygen is expected to be more facile.

Herein we report the crystal structure of $PdAu_{24}(PET)_{18}^{0}$ revealing that Pd is localized to the cluster core, which retains the same atomic connectivity and nearly identical geometry to $Au_{25}(PET)_{18}^{-,0,+}$ clusters. The presence of Pd results in shorter bonds in the 13-atom core and a blue-shift in the UV/Vis spectrum. Furthermore isoelectronic features between $Au_{25}(SR)_{18}$ and PdAu₂₄(SR)₁₈ are clear in their structures, electrochemistry, and linear absorption spectra. Overall we suggest that PdAu₂₄(PET)₁₈, like $Au_{25}(SR)_{18}$ is well predicted by a spherical superatom model.

References

Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.;
 Whetten, R. L.; Grönbeck, H.; Häkkinen, H. Proc. Natl. Acad. Sci. U.S.A. 2008, 105, 9157–9162.

(2) Tofanelli, M. A.; Ackerson, C. J. J. Am. Chem. Soc. 2012, 134, 16937–16940.

(3) Zhu, M.; Aikens, C. M.; Hendrich, M. P.; Gupta, R.; Qian, H.; Schatz, G. C.; Jin, R. J.
 Am. Chem. Soc. 2009, *131*, 2490–2492.

(4) Yi, C.; Tofanelli, M. A.; Ackerson, C. J.; Knappenberger, K. L. J. Am. Chem. Soc. 2013, 135, 18222–18228.

(5) Deheer, W. A. *Rev. Mod. Phys.* **1993**, *65*, 611–676.

(6) Lopez-Acevedo, O.; Clayborne, P. A.; Hakkinen, H. Phys. Rev. B: Condens. Matter Mater. Phys. 2011, 84, 035434.

(7) Aikens, C. M. In Protected Metal Clusters -- From Fundamentals to Applications;
 Tsukuda, T., Häkkinen, H., Eds.; Elsevier, 2015; Vol. 9, pp 223–261.

(8) Kothalawala, N.; Kumara, C.; Ferrando, R.; Dass, A. Chem. Commun. 2013, 49, 10850–10852.

- (9) Qian, H.; Barry, E.; Zhu, Y.; Jin, R. Acta Phys.-Chim. Sin. 2011, 27, 513–519.
- (10) Kwak, K.; Tang, Q.; Kim, M.; Jiang, D.-E.; Lee, D. J. Am. Chem. Soc. 2015, 137, 10833.
- (11) Kumara, C.; Dass, A. Nanoscale **2011**, *3*, 3064–3067.
- (12) Kumara, C.; Aikens, C. M.; Dass, A. J. Phys. Chem. Lett. 2014, 5, 461–466.
- (13) Parker, J. F.; Fields-Zinna, C. A.; Murray, R. W. Acc. Chem. Res. 2010, 43, 1289–1296.
- (14) Christensen, S. L.; MacDonald, M. A.; Chatt, A.; et al. J. Phys.

Chem. C 2012, 116, 26932–26937.

(15) Yang, H.; Wang, Y.; Huang, H.; Gell, L.; Lehtovaara, L.; Malola, S.; Häkkinen, H.;Zheng, N. Nat. Commun. 2013, 4, 2422.

(16) Kacprzak, K. A.; Lehtovaara, L.; Akola, J.; Lopez-Acevedo, O.; Häkkinen, H. Phys. Chem. Chem. Phys. 2009, 11, 7123–7129.

(17) Zhang, B.; Kaziz, S.; Li, H.; Wodka, D.; Malola, S.; Safonova, O.; Nachtegaal, M.;
Mazet, C.; Dolamic, I.; Llorca, J.; Kalenius, E.; Lawson Daku, L. M.; Häkkinen, H.; Bürgi, T.;
Barrabés, N. *Nanoscale* 2015, *7*, 17012–17019.

(18) Negishi, Y.; Kurashige, W.; Niihori, Y.; Iwasa, T.; Nobusada, K. *Phys. Chem. Chem. Phys.* 2010, *12*, 6219–6225.

(19) Zhu, M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. J. Am. Chem. Soc. 2008, 130, 5883–5885.

(20) Dainese, T.; Antonello, S.; Gascón, J. A.; Pan, F.; Perera, N. V.; Ruzzi, M.; Venzo, A.;
Zoleo, A.; Rissanen, K.; Maran, F. *ACS Nano* 2014, *8*, 3904–3912.

(21) Zhu, M.; Eckenhoff, W. T.; Pintauer, T.; Jin, R. J. Phys. Chem. C 2008, 112, 14221–14224.

(22) Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. J. Am. Chem. Soc.
2008, 130, 3754–3755.

(23) Ni, T. W.; Tofanelli, M. A.; Phillips, B. D.; Ackerson, C. J. Inorg. Chem. 2014, 53, 6500–6502.

(24) Fields-Zinna, C. A.; Crowe, M. C.; Dass, A.; Weaver, J. E. F.; Murray, R. W. *Langmuir*2009, 25, 7704–7710.

- (25) Lopez-Acevedo, O.; Akola, J.; Whetten, R. L.; Gronbeck, H.; Hakkinen, H. J. Phys. Chem. C 2009, 113, 5035–5038.
- (26) Tofanelli, M. A.; Salorinne, K.; Ni, T. W.; Malola, S.; Newell, B. S.; Phillips, B.; Häkkinen, H.; Ackerson, C. J. Chem. Sci. 2015, 7, 1882-1890.
- (27) Zabrodsky, H.; Peleg, S.; Avnir, D. J. Am. Chem. Soc. 1992, 114, 7843-7851.
- (28) Negishi, Y.; Kurashige, W.; Niihori, Y.; Iwasa, T.; Nobusada, K. *Phys. Chem. Chem. Phys.* 2010, *12*, 6219–6225.
- (29) Yan, J.; Su, H.; Yang, H.; Malola, S.; Lin, S.; Häkkinen, H.; Zheng, N. J. Am. Chem. Soc.
 2015, 137, 11880–11883.

Chapter 5

Relaxation of Metallic Au₁₄₄(SR)₆₀ Nanoclusters^{*}

5.1 Synopsis

Electronic energy relaxation of $Au_{144}(SR)_{60}^{q}$ ligand-protected nanoclusters, where $SR = SC_6H_{13}$ and q = -1, 0, +1, and +2, was examined using femtosecond time-resolved transient absorption spectroscopy. The observed differential transient spectra contained three distinct components: (1) transient bleaches at 525 and 600 nm, (2) broad visible excited-state absorption (ESA), and (3) stimulated emission (SE) at 670 nm. The bleach recovery kinetics depended upon the excitation pulse energy and were thus attributed to electron–phonon coupling typical of metallic nanostructures. The prominent bleach at 525 nm was assigned to a core-localized plasmon resonance (CLPR). ESA decay kinetics were oxidation-state dependent and could be described using a metal-sphere charging model. The dynamics, emission energy, and intensity of the SE peak exhibited dielectric-dependent responses indicative of Superatom charge transfer states. On the basis of these data, the $Au_{144}(SR)_{60}$ system is the smallest-known nanocluster to exhibit quantifiable electron dynamics and optical properties characteristic of metals.

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5.2 Introduction

Metallic nanostructures represent a promising class of nanomaterials for catalysis, medical diagnostics, therapeutics, and the utilization of electromagnetic energy.^{1,-6} Many of these opportunities depend on the unique optical and electronic properties exhibited by metals confined to nanoscale dimensions. For colloidal nanoparticles, these properties change dramatically over the nanometer length scale, evolving from subnanometer, quantum-confined nanoclusters with discrete electronic orbitals and HOMO-LUMO energy gaps to the collective properties of plasmon-supporting nanoparticles (>2 nm). Although significant progress has been made using Superatom models to describe the electronic structure of smaller nanoclusters,⁷⁻¹⁵, and classical approaches accurately account for the optical and electronic characteristics of larger nanoparticles,^{16,17} the properties-including the onset of metallic behavior-of intermediate (~1.5 nm) nanometals are poorly understood. Monolayer-protected gold nanoclusters (MPCs) are an emerging class of nanomaterials, which can be examined in an attempt to bridge the gap in understanding the evolution from molecular to bulk metal behavior. Much like gas-phase clusters, specific "magic" sizes of MPCs can be isolated based on a combination of electronic and geometric shell closings.^{7-15, 18-20} Moreover, synthetic and electrochemical methods exist for tailoring the optical, electronic, and capacitive properties of these materials.^{3, 18, 21-25}

The Au₁₄₄(SR)₆₀ MPC, where SR is SC₆H₁₃, nanocluster is especially well-suited for studying the properties of 1–2 nm nanometals. Widely accepted DFT models that are consistent with structural data posit a core–shell structure that contains a polyhedral 114-atom gold core, which is protected by 30 RS-Au-RS "staple" moieties in the outer shell.^{18, 26} The core has three concentric shells of 12, (42), and 60 symmetrically equivalent atoms, yielding a total core diameter of 1.5 nm, with a total inorganic diameter of 1.8 nm including the RS-Au-RS units.^{18, 27}

The first evidence of the metal-like behavior for Au₁₄₄ was obtained from electrochemical and tunneling microscopy measurements that indicated that these nanoclusters could accommodate classical double-layer charging,²¹ with up to 15 discrete charge states resolvable for this MPC.²⁸ These results are supported by recent infrared absorption measurements and electronic-structure calculations that suggest Au₁₄₄ nanoclusters are gapless.²⁵ A 20-meV energy gap was detected in the HOMO–LUMO energy region, but this effect arose from spectroscopic selection rules.²⁵ Simulated optical spectra for Au₁₄₄(SH)₆₀ included two peaks at 540 and 600 nm, for which the electron densities are localized to the 114-atom core.^{18, 19} Taken together, these results suggest Au₁₄₄(SR)₆₀ is an ideal prototype for studying the onset of *metallic* electronic relaxation and optical properties, including emergent plasmon phenomena.

Femtosecond time-resolved differential extinction spectroscopy is a reliable experimental diagnostic for quantifying the optical and electronic properties of metal nanostructures.³⁰⁻⁴¹ Excitation of metals by short-pulse lasers generates a nonequilibrium electron gas, which subsequently cools through coupling with the phonon bath of the metal lattice over a picosecond time scale.²⁹ Formation of the hot electron gas results in a transient bleach in the differential extinction spectra at the plasmon resonance wavelength of the nanoparticle. The dynamics of the approximately picosecond electron–phonon equilibration can be recorded by monitoring the time-dependent recovery of the plasmon bleach. For metals, these electron cooling rates depend directly on the excitation pulse energy.³⁰

Here, we present the results of a study of femtosecond time-resolved transient extinction measurements of Au₁₄₄(SC₆H₁₃)₆₀ manipulated by bulk electrolysis into 4 different oxidation states, q (q = -1, 0, +1, +2). We provide the first direct experimental evidence of MPCs displaying electronic energy relaxation characteristic of metallic nanostructures, with a

quantifiable electron-phonon coupling constant. Also, transient difference spectra included discrete peaks at visible wavelengths, consistent with a collective resonance of the free electrons, which we described as a core-localized plasmon resonance (CLPR). Although significant contributions from Superatom orbitals were required to account fully for the observed relaxation dynamics, the 144-gold-atom nanocluster is, to date, the smallest cluster known to exhibit metallic electronic-energy relaxation dynamics and optical properties.

5.3 Results and Discussion

For all time- and wavelength-resolved transient extinction measurements, Au₁₄₄(SR)₆₀ nanoclusters were excited using the 400-nm second harmonic of an amplified Ti:sapphire laser, and the time domain relaxation dynamics were recorded using a temporally delayed broadbandwidth visible continuum pulse. The experimental setup has been described previoulsy;⁴² pertinent details are provided as Supporting Information. The 400-nm excitation was resonant with multiple nanocluster states that included contributions from the ligand shell and the gold interband transition.¹⁸ Figure 5.1 portrays typical transient differential extinction spectra for nanoclusters in the q = -1 (a), 0 (b), +1 (c), and +2 (d) oxidation states recorded at a pump–probe time delay of 0.8 ps. For all oxidation states, the transient spectra included three distinct components: (i) ground-state bleach at short wavelengths, (ii) broad excited-state absorption (ESA) that spanned most of the visible spectrum, and (iii) transient induced transparency at 670 nm, which we attributed to stimulated emission. Analysis of the time-domain response was complicated by the spectral overlap of the three components described above, which resulted primarily from the broad ESA peak. Although the general features of the transient spectra were consistent for all four oxidation states, the magnitude of the stimulated emission decreased with increasing oxidation state.



Figure 5.1. Differential transient extinction spectra obtained for Au₁₄₄(SR)₆₀ MPCs in the (a) q = -1, (b) q = 0, (c) q = +1, and (d) q = +2 oxidations states. Transient spectra were recorded at a pump–probe time delay of 0.8 ps, following excitation by 90-fs pulses of 400-nm light.

To study the dynamics of electronic relaxation, the transient data were analyzed using global analysis and singular value decomposition methods.⁴³ In this way, the contribution of each component to the time-dependent decay of the transient data could be resolved. Figure 5.2 portrays the results from global analysis. For the q = 0 and -1 oxidation states, the best result included three components, which distinguished ground-state bleaching, excited-state absorption and stimulated emission. The stimulated emission component is amplified in the inset of Figure 5.2a. In contrast, only two components were included in the global analysis results for the q = +1

and +2 oxidation states (Figure 5.2b), which corresponded to ground-state bleaching and excitedstate absorption. This result was not surprising based on the relatively weak stimulated emission observed for nanoclusters in positive oxidation states. Temporal analysis of the three components yielded characteristic time constants of (i) ~1 ps, (ii) ~3 ps, and (iii) ~20 ps. These three components, which provided direct experimental evidence for metallic electron energy relaxation, as well as relaxation via Superatom states, will be discussed separately.



Figure 5.2. (a) Global analysis results obtained from the differential transient extinction spectra typical for $Au_{144}(SR)_{60}$ MPCs in the q = -1 and q = 0. The spectra included three distinct components. (b) Global analysis results obtained from the differential transient extinction spectra typical for $Au_{144}(SR)_{60}$ MPCs in the q = +1, and q = +2 oxidations states. The spectra included two distinguishable components.

Component 1: Ground-State Bleaching

Component one contributes negative amplitude to the transient difference spectra with an onset of approximately 630 nm, reminiscent of the well-known LSPR bleach exhibited by larger colloidal gold nanoparticles. This bleach component contributed two peaks with maxima at 525 and 600 nm, consistent with electronic structure calculations.¹⁸ The intensity of the 600-nm component was most significant for nanoclusters with q = 0, -1. To determine the nature of electronic energy relaxation in the Au₁₄₄ nanoclusters, the time dependence of the component-1 bleach recovery was monitored. Time-domain data obtained after electronic excitation of the Au₁₄₄(0) nanocluster using a range of excitation pulse energies are shown in Figure 5.3a. These time-dependent traces were generated using the magnitude of the 525-nm transient bleach signal as a function of time after nanocluster excitation. For this sample, the pump laser power was varied from 300 to 800 nJ per pulse, with larger pulse energies resulting in longer relaxation times. The experimental time-domain data were fit using an exponential decay function. The instrument response function was deconvoluted to the Gaussian pump and probe laser pulses using a program written in house that relies on an iterative least-squares approach.⁴²



Figure 5.3. (a) Bleach recovery kinetics observed for the 525-nm bleach component (for the neutral species) for a series of laser excitation pulse energies. The data were fit to an exponential decay function. Longer relaxation time constants were obtained for higher laser pulse energies. (b) Relaxation time constants determined for the 525-nm (component 1) bleach recovery when different laser excitation pulse energies were used to excite the sample. The two-temperature model was used to determine the nanocluster room-temperature electron–phonon coupling time constant from the *y*-intercept of the linear fit. Data obtained from Au₁₄₄(SR)₆₀ nanoclusters provided good agreement with data for citrate-stabilized solid gold nanospheres (inset, panel b).

To examine more carefully the excitation pulse energy dependence of the data in Figure 5.3a, the resulting time constants were plotted as a function of laser pulse energy in Figure 5.3b. Although Figure 5.3b portrays only the data obtained for the neutral Au₁₄₄(SR)₆₀ system, the relaxation time constants for all four nanocluster oxidation states were linearly dependent on excitation pulse energy; the complete data set is provided as Supporting Information. Linear power-dependent data are a characteristic feature of electron cooling in metallic nanostructures and are accurately described using the two-temperature model.^{44, 45} The use of pulsed lasers to excite metals results in the formation of a nonequilibrium electron gas. In the two-temperature model, the electron gas and the metal lattice are treated as two coupled subsystems at different temperatures; upon impulsive excitation, the temperature of the electron gas is determined by the laser pulse energy, whereas the lattice remains at room temperature. The extent of electron–phonon coupling determines the rate of energy flow from the electron gas to the lattice. The two temperature model can be described using eqs 1 and 2:^{44, 45}

$$C_{\rm l}(\delta T_{\rm l}/\delta t) = G(T_{\rm e} - T_{\rm l})$$
eq 1

$$C_{\rm e}(T_{\rm e}) = \gamma T_{\rm e}$$
 eq 2

where T_e and T_1 are the respective temperatures of the electron gas and the lattice, and C_e and C_1 are the electron and lattice heat capacities. The coupling of T_e and T_1 is quantified by the electron–phonon coupling constant, *G*. The linear dependence of the relaxation time constant on the excitation pulse energy results from the direct dependence of C_e on T_e , as shown in eq 2 where $\gamma = 66 \text{ Jm}^{-3} \text{ K}^{-2}$ for gold.³⁰

Hence, the pulse-energy dependence of the relaxation time constants could be used to quantify the electron–phonon coupling constants observed for the Au₁₄₄ nanoclusters. First, the
room-temperature electron–phonon coupling time constant was determined for the Au_{144} nanoclusters by applying a linear fit to the data in Figure 5.3b and extrapolating to zero laser pulse energy. The room-temperature time constant obtained in this manner was then converted to the nanocluster electron–phonon coupling constant using eq 3:³⁰

$$\tau_0 = \gamma T_0 / G \qquad \text{eq. 3}$$

Analysis of all four nanoclusters yielded an average electron-phonon coupling constant of $G = (1.68 \pm 0.15) \times 10^{16}$ W m³⁻ K⁻¹. This value agreed well with the reported value of ~2 × 10¹⁶ W m³⁻ K⁻¹ for larger citrate-stabilized gold nanoparticles;³⁰ using the same laser system as in the current study, we recently obtained $G = 1.85 \times 10^{16}$ W m³⁻ K⁻¹ for solid gold nanospheres ranging from 20 to 83 nm in diameter.⁴² Therefore, the bleach-recovery results for Au₁₄₄(SR)₆₀ nanoclusters agreed well with electron-lattice equilibration, which we attribute to interband excitation of the 114-atom gold core of the nanocluster. The small differences in the G values of the nanoclusters and nanoparticles could arise from the dispersing medium and capping ligands; the nanoclusters are stabilized by thiols whereas the large nanoparticles are capped using citrate. Taken together, the transient bleach at 525 nm and the electron cooling dynamics suggested that the Au₁₄₄ nanoclusters exhibited properties characteristic of larger plasmonic noble metal nanoparticles. Although transient extinction measurements have been performed on other ligandprotected gold nanoclusters,⁴⁶⁻⁵⁰ these data provide the first experimental evidence of quantifiable electron-phonon coupling that is characteristic of a metal nanostructure. Previous experiments carried out on Au₅₅ revealed a rapid energy relaxation process occurring on a

picosecond time scale, but an electron–phonon coupling constant could not be determined for those clusters.³⁴

The electronic relaxation dynamics of the Au₁₄₄ nanoclusters were consistent with electronic structure calculations²⁵ as well as electrochemical measurements²¹ that predict a vanishing energy gap separating the HOMO and LUMO levels and the onset of metallic behavior. The gap closing also results in a high density of states in the HOMO-LUMO region, leading to efficient electrical charging.²¹ The capacitive properties of Au₁₄₄(SR)₆₀ nanoclusters can be described using a metallic-sphere model. Nonlinear absorption measurements provide further evidence of metallic behavior for Au₁₄₄(SR)₆₀ nanoclusters.⁵¹ Recent electronic structure calculations indicate that optical excitation of Au₁₄₄(SR)₆₀ nanoclusters results in a collective resonance that is localized to the nanocluster core.²⁹ This collective resonance likely gives rise to the transient bleach observed at 525 nm in the differential extinction spectra following 400-nm excitation of the Au₁₄₄(SR)₆₀ interband transition. Because this resonance is confined to the interior core of the core-shell nanoparticle, we distinguish it from the localized surface plasmon resonances (LSPR) of colloidal nanoparticles by calling it a core-localized plasmon resonance (CLPR). To our knowledge, these transient data provide the first experimental observation of a prominent CLPR transition. Moreover, the 144-atom nanocluster is the smallest gold system for which a plasmon resonance has been verified and characteristic metallic electron cooling has been quantified.

Component 2: Excited-State Absorption

Further direct evidence of the metallic behavior of Au_{144} nanoclusters was obtained from the oxidation state-dependent kinetics of component two (excited state absorption). In addition to

exciting the interband transition, the 400-nm pump pulse is also resonant with excited states that include mixed contributions from Au(sp) and ligand orbitals.^{18, 25} For smaller nanoclusters, these Superatom states relax by rapid internal conversion to the HOMO level and subsequent charge transfer to states localized on the "RS-Au-RS" staple unit (outer shell).^{46, 47} For the metallic Au₁₄₄(SR)₆₀, the HOMO consists of a manifold of electronic states, which account for the capacitive properties of the nanocluster. Consistent with the behavior of metal spheres, charging of Au₁₄₄(SR)₆₀ nanoclusters induces small energy gaps that separate the states located near the HOMO.^{18, 21} In order to study the oxidation-state dependence of states near the HOMO, we analyzed the relaxation time constant of component 2, which reports on electron thermalization near the HOMO. The time-dependent magnitudes of the difference absorption signal obtained for nanoclusters in q = 0 and q = +2 oxidation states are compared in the log-linear plot in Figure 5.4a. The q = +2 nanocluster clearly exhibited a longer relaxation time constant than the neutral species. The component-2 time constants obtained for all four nanoclusters are summarized in Table 1 and Figure 5.4b. The best fit to the data in Figure 5.4b indicated that the component-2 relaxation time constant exhibited a quadratic dependence on the oxidation state of the nanocluster, with more oxidized clusters displaying longer time constants.



Figure 5.4. (a) Comparison of the component 2 principle kinetics obtained for $Au_{144}(SR)_{60}$ in the q = 0 (blue) and q = +2 (red) oxidation states. The black lines represent fits to the data obtained using an exponential decay function. The time-dependent data clearly reflected slower relaxation rates for the nanocluster with a higher oxidation state. (b) Component 2 (C_2) relaxation time constant plotted as a function of nanocluster oxidation state. The red line portrays the quadratic fit that was applied to the data. The average and standard deviation was obtained from statistical analysis of the results from several experiments.

cluster	t_2 (ps)
$Au_{144}(SR)_{60}^{-1}$	2.68 ± 0.20
$Au_{144}(SR)_{60}^{0}$	2.74 ± 0.06
$Au_{144}(SR)_{60}^{+1}$	3.13 ± 0.27
$Au_{144}(SR)_{60}^{+2}$	3.55 ± 0.18

Table 5.1. Summary of Component 2 Fitting Results

The quadratic dependence noted in the data in Figure 5.4b can be explained by considering the charging behavior of metal spheres. In this model, the energy required to add a charge to a metallic sphere increases quadratically with charge state $[E(Q) \propto Q^2/2C]$, where *C* is capacitance].²¹ Indeed, electronic structure calculations for the Au₁₄₄ nanoclusters examined here reveal an energy gap that increases quadratically with increasing charge state.¹⁸ Therefore, the oxidation-state dependence of the data in Figure 5.4b clearly reflected charging effects of the metallic nanoclusters. The time required for an electron to relax from a higher- to a lower-energy state depends upon the size of the energy gap separating the two states; relaxation is fastest for the smallest gap and occurs more slowly for larger gaps.¹⁸ Considering electronic relaxation through the manifold of states near the HOMO level, the larger time constants obtained for higher charge states of the Au₁₄₄ nanocluster resulted from the larger energy gap separating the states in this region.

Taken together, the excitation-pulse-energy-dependent electron–phonon equilibration (component 1) and electron thermalization (component 2) provided strong, direct evidence of the metallic properties of the Au₁₄₄ nanocluster. To our knowledge, this study, which combined ultrafast laser spectroscopy with controlled electrochemical preparation of nanocluster charge states, provides the first experimental evidence of metallic electron relaxation dynamics for ultrasmall, ligand-protected nanoclusters.

Component 3: Stimulated Emission

The third component of the transient spectra resulted from transient induced transparency at 670 nm, which we attributed to stimulated emission. The magnitude of the component 3 signal increased concomitantly with the probe energy, and the peak energy, amplitude, and width all exhibited time-dependent behaviors. These factors implied that the spectral feature at 670 nm resulted from stimulated emission rather than saturated ground-state absorption.⁵³ As portraved by the transient spectra in Figure 5.1, the relative contribution from stimulated emission was largest for the q = 0, -1 nanoclusters, whereas only small contributions were observed for the cationic species. Stimulated emission is often observed in transient extinction spectra of organometallic compounds, and it originates from charge-transfer states.⁵⁴ Ligand-to-metal charge transfer processes have been invoked to account for NIR photoluminescence of smaller (Au₂₅) nanoclusters.⁵⁵ Nanocluster-to-ligand-shell charge transfer has also been used to reconcile picosecond relaxation dynamics of Au₂₅.⁴⁶ However, for Au₁₄₄, electronic energy relaxation proceeds by rapid thermalization of a manifold of states with an electron gap of approximately 20 meV. On the basis of energy conserving arguments, this relaxation process should preclude electron transfer from the nanocluster to the ligand shell. One possible explanation to account for component three dynamics is that the time-dependent stimulated emission signal tracks electronic energy relaxation of charge-transfer Superatomic orbitals with significant ligand character that are excited independently of the nanocluster core. On the basis of electronic structure calculations, 400-nm pumping of Au₁₄₄(SR)₆₀ excites both the interband transition and ligand states.²⁵

To examine whether component three resulted from stimulated emission mediated by charge-transfer Superatom states, we analyzed the integrated intensities (Figure 5.5a; blue) and

emission energy (Figure 5.5a; red) of the stimulated-emission signal component in a series of solvents with dielectric constants ranging from 2.4 to 9.1. The data in Figure 5.5a were generated by analyzing the stimulated-emission peak for the neutral nanocluster obtained at a pump-probe time delay of 1 ps. Upon increasing the solvent dielectric constant from 2.4 to 9.1, we observed an increase in stimulated emission intensity. This observation was consistent with expectations because the larger dielectric constant stabilized the charge-transfer state, yielding greater stimulated-emission intensity. The shift to lower energies with increasing dielectric constant was also expected because of charge-transfer stabilization. In fact, the temporal response provided evidence that the charge-transfer states relaxed into a lower-energy stabilized-charge-transfer state (Figure 5.5b). As the time-dependent stimulated emission data in Figure 5.5b illustrate, the magnitude of the induced transparency increased exponentially during the first few picoseconds and then subsequently decayed with an apparent time constant of 18 ± 2 ps (neutral Au₁₄₄(SR)₆₀) dispersed in toluene; blue data). Upon increasing the solvent polarity (THF; $\varepsilon = 7.5$),⁵⁶ the relaxation time constant decreased to 8 ± 2 ps. These data indicated that relaxation from an initial charge-transfer state into a stabilized configuration was facilitated when the nanoclusters were dispersed in solvents with large dielectric constants. We also analyzed the time-dependent stimulated-emission energy and bandwidth (Figure S9). As expected, the bandwidth increased at longer pump-probe time delays owing to thermalization processes.



Figure 5.5. Component 3 (stimulated emission) solvent dependence obtained for the neutral $Au_{144}(SR)_{60}$ nanocluster. (a) Integrated intensity (blue) and emission energy (red) of the stimulated emission peak plotted versus solvent dielectric constant. All data were obtained from analysis of the stimulated emission peak recorded at a pump–probe delay of 1 ps, following excitation using 400-nm light. The average and standard deviations for the integrated intensities and emission energies were obtained from statistical analysis of the results from several experiments. (b) Normalized, and inverted, time-dependent amplitude of the stimulated emission signal (blue, toluene; red, tetrahydrofuran). The black line represents a fit using a biexponential function that included an initial growth and subsequent decay components. The energy, intensity and time-dependence of the stimulated emission peaks were all sensitive to the dispersing solvent.

Electronic energy relaxation of $Au_{144}(SR)_{60}$ nanoclusters proceeds via several mechanisms. Systematic analysis of the multicomponent transient extinction spectra allowed for elucidation of these processes. Two of these components (C_1 and C_2) exhibited the characteristic features of electronic energy relaxation for metal nanostructures, thereby providing direct evidence of the metallic behavior of the ligand-protected Au_{144} system. However, analysis of component 3, which showed signatures of charge-transfer states, suggested that Superatom concepts are still needed for providing a complete description of the electron dynamics of monolayer-protected nanoclusters with diameters of approximately 1.8 nm.

5.4 Conclusion

We have presented the first systematic study of electronic energy relaxation of Au₁₄₄(SR)₆₀ nanoclusters using a comprehensive range of oxidation states. Our ultrafast transient extinction data showed direct evidence of the metallic properties of this nanocluster. To our knowledge, the Au₁₄₄(SR)₆₀ species is the smallest gold nanoparticle to exhibit quantifiable metallic behavior. The transient-difference spectra obtained for Au₁₄₄(SR)₆₀ also provided compelling experimental evidence for collective optical excitations that localize electron density to the interior core of the nanocluster. We designate these optical transitions as core-localized plasmon resonances. The potential impacts of metal nanostructure optical, thermal, and electrical properties are far reaching, with applications including applied spectroscopy, solar-to-electric energy conversion, medical imaging and therapeutics, and nonlinear optical technologies based on negative index metamaterials. Clearly, gold nanoparticles with diameters of approximately 1.8 nm are important nanomaterials for developing a predictive understanding of the transition from molecular to bulk-like properties.

References

(1)	Valden, M.; Lai, X.; Goodman, D. W. Science 1998, 281, 1647-1650
(2)	Hirsch, L. R.; Stafford, R. J.; Bankson, J. A.; Sershen, S. R.; Rivera, B.; Price, R. E.;
Hazle	J. D.; Halas, N. J.; West, J. L. Proc. Natl. Acad. Sci. U.S.A. 2003, 100, 13540-13554
(3)	McCoy, R. S.; Choi, S.; Collins, G.; Ackerson, B. J.; Ackerson, C. J. ACS Nano 2013, 7,
2610–	2616
(4)	Knappenberger, K. L., Jr.; Dowgiallo, A. M.; Chandra, M.; Jarrett, J. W. J. Phys. Chem.
Lett. 2013, 4, 1109–1119	
(5)	Daniel, MC.; Astruc, D. Chem. Rev. 2004, 104, 293-346
(6)	Sardar, R.; Funston, A.; Mulvaney, P.; Murray, R. Langmuir 2009, 24, 13840-13851
(7)	Aikens, C. M. J. Phys. Chem. Lett. 2010, 1, 2594–2599
(8)	Jin, R. <i>Nanoscale</i> 2010 , <i>2</i> , 343–362
(9)	Price, R. C.; Whetten, R. L. J. Am. Chem. Soc. 2005, 127, 13750-13751
(10)	Aikens, C. M. J. Phys. Chem. Lett. 2011, 2, 99-104
(11)	Wyrwas, R. B.; Alvarez, M. M.; Khoury, J. T.; Price, R. C.; Schaaff, T. G.; Whetten, R.
L. <i>Eur</i>	: Phys. J. D 2007 , 43, 91–95
(12)	Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.;
Whetten, R. L.; Gronbeck, H.; Hakkinen, H. Proc. Natl. Acad. Sci. U.S.A. 2008, 105, 9157-	
9162	
(13)	Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. J. Am. Chem. Soc.
2008,	130, 3754– 3755

- (14) Zhu, M.; Aikens, C. M.; Hollander, F.; Schatz, G.; Jin, R. J. Am. Chem. Soc. 2008, 130, 5883–5885
- (15) Tofanelli, M. A.; Ackerson, C. J. Am. Chem. Soc. 2012, 134, 16937-16940
- (16) Mie, G. Ann. Phys. 1908, 330, 377–445

(17) Kreibig, U.; Vollmer, M. Optical Properties of Metal Clusters; Springer: Berlin-Heidelberg, **1995**.

- (18) Lopez-Acevedo, O.; Akola, J.; Whetten, R. L.; Grönbeck, H.; Häkkinen, H. J. Phys. Chem. C 2009, 113, 5035–5038
- (19) Dass, A. J. Am. Chem. Soc. 2011, 133, 19259–19261
- (20) Knoppe, S.; Boudon, J.; Dolamic, I.; Dass, A.; Burgi, T. *Anal. Chem.* 2011, *83*, 5056–5061
- (21) Ingram, R. S.; Hostetler, M. J.; Murray, R. W.; Schaaff, T. G.; Khoury, J. T.; Whetten, R.
- L.; Bigioni, T. P.; Guthrie, D. K.; First, P. N. J. Am. Chem. Soc. 1997, 119, 9279-9280
- (22) Chaki, N. K.; Negishi, Y.; Tsunoyama, H.; Shichibu, Y.; Tsukuda, T. J. Am. Chem. Soc.
 2008, 130, 8608–8610
- (23) Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. Science
 2007, 318, 430–433
- (24) Parker, J. F.; Fields-Zinna, C. A.; Murray, R. W. Acc. Chem. Res. 2010, 43, 1289–1296
- (25) Koivisto, J.; Malola, S.; Kumara, C.; Dass, A.; Hakkinan, H.; Pettersson, M. J. Phys. Chem. Lett. 2012, 3, 3076–3080
- (26) Wong, O. A.; Heinecke, C. L.; Simone, A. R.; Whetten, R. L.; Ackerson, C. J. *Nanoscale*2012, 4, 4099–4102

- Bahena, D.; Bhattarai, N.; Santiago, U.; Tlahuice, A.; Ponce, A.; Bach, S. B.; Yoon, B.;
 Whetten, R. L.; Landman, U.; Jose-Yacaman, M. J. Phys. Chem. Lett. 2013, 4, 975–981
- (28) (a) Hicks, J. F.; Miles, D. T.; Murray, R. W. J. Am. Chem. Soc. 2002, 124, 13322-13328
- (b) Quinn, B. M.; Liljeroth, P.; Ruiz, V.; Laaksonen, T.; Kontturi, K. J. Am. Chem. Soc. 2003, 125, 6644–6645
- (28) Malola, S.; Lehtovara, L.; Enkovaara, J.; Hakkinan, H. ACS Nano 2013, 125, 6644-6645
- (30) Hartland, G. V. Phys. Chem. Chem. Phys. 2004, 6, 5263-5274
- (31) Voisin, C.; Del Fatti, N.; Christofilos, D.; Vallee, F. J. Phys. Chem. B 2001, 105, 2264–
 2280
- (32) Pelton, M.; Sader, J. E.; Burgin, J.; Liu, M. Z.; Guyot-Sionnest, P.; Gosztola, D. Nat. Nanotechnol. 2009, 4, 492–495
- (33) Voisin, C.; Del Fatti, N.; Christofilos, D.; Vallee, F. Appl. Surf. Sci. 2000, 164, 131–139
- (34) Smith, B. A.; Zhang, J. Z.; Giebel, U.; Schmid, G. Chem. Phys. Lett. 1997, 270, 139-144
- (35) Link, S.; El-Sayed, M. A. J. Phys. Chem. B 1999, 103, 8410-8426
- (36) Hartland, G. V. J. Chem. Phys. 2002, 116, 8048-8055
- (37) Averitt, R. D.; Westcott, S. L.; Halas, N. J. Phys. Rev. B 1998, 58, R10203-10206
- (38) Dowgiallo, A. M.; Knappenberger, K. L., Jr. J. Am. Chem. Soc. 2012, 134, 19393–19400
- (39) Grant, C. D.; Schwartzberg, A. M.; Yang, Y.; Chen, S.; Zhang, J. Z. Chem. Phys. Lett.
 2004, 383, 31–34
- (40) Guillon, C.; Langot, P.; Del Fatti, N.; Vallee, F.; Kirakosyan, A. S.; Shahbazyan, T. V.;
 Cardinal, T.; Treguer, M. *Nano Lett.* 2007, *7*, 138–142
- (41) Dowgiallo, A. M.; Schwartzberg, A. M.; Knappenberger, K. L., Jr. *Nano Lett.* 2011, *11*, 3258–3262

- (42) Dowgiallo, A. M.; Knappenberger, K. L., Jr. *Phys. Chem. Chem. Phys.* 2011, *13*, 21585–21592
- (43) Van Stokkum, I. H. M.; Larsen, D. S.; Van Grondelle, R. *Biochim. Biophys. Acta, Bioenerg.* 2004, 87, 1858–1872
- (44) Kaganov, M. I.; Lifshitz, I. M.; Tanatarov, L. V. Sov. Phys.-JETP 1957, 4, 173
- (45) Fujimoto, J. G.; Ippen, E. P.; Bloemberger, N. Phys. Rev. Lett. 1984, 53, 1837-1840
- (46) Miller, S. A.; Fields-Zinna, C. A.; Murray, R. W.; Moran, A. M. J. Phys. Chem. Lett.
 2010, 1, 1383–1387
- (47) Devadas, M. S.; Kim, J.; Sinn, E.; Lee, D.; Goodson, T. G.; Ramakrishna, G. J. Phys. *Chem. C* 2010, 114, 22417–22423
- (48) Qian, H.; Sfeir, M. Y.; Jin, R. J. Phys. Chem. C 2010, 114, 19935–19940
- (49) Green, T. G.; Knappenberger, K. L., Jr. Nanoscale 2012, 4, 4111-4118
- (50) Yau, S. H.; Varnavski, O.; Goodson, T. Acc. Chem. Res. 2013, 46, 1506-1516
- (51) Philip, R.; Chantharasupawong, P.; Qian, H.; Jin, R.; Thomas, J. *Nano Lett.* **2012**, *12*, 4661–4667
- (52) Englman, R.; Jortner, J. Mol. Phys. 1970, 18, 145–164
- (53) Bingemann, D.; Ernsting, N. P. J. Chem. Phys. 1995, 102, 2691–2700
- (54) Leung, M. H. M.; Pham, D. T.; Lincoln, S. F.; Kee, T. W. Phys. Chem. Chem. Phys.
 2012, 14, 13580–13587
- (55) Wu, Z.; Jin, R. Nano Lett. 2010, 10, 2568–2573
- (56) CRC Handbook of Chemistry and Physics, 92nd ed.; CRC Press: Boca Raton, FL, 2011–
 2012; pp 6–242.

Chapter 6

Polymorphism in magic-sized Au₁₄₄(SR)₆₀ clusters^{*}

6.1 Synopsis

Ultra-small, magic-sized metal nanoclusters represent an important new class of materials with properties between molecules and particles. However, their small size challenges the conventional methods for structure characterization. Here we present the structure of ultra-stable Au₁₄₄(SR)₆₀ magic-sized nanoclusters obtained from atomic pair distribution function analysis of X-ray powder diffraction data. The study reveals structural polymorphism in these archetypal nanoclusters. In addition to confirming the theoretically predicted icosahedral-cored cluster, we also find samples with a truncated decahedral core structure, with some samples exhibiting a coexistence of both cluster structures. Although the clusters are monodisperse in size, structural diversity is apparent. The discovery of polymorphism may open up a new dimension in nanoscale engineering.

6.2 Introduction

The promise of nanotechnology, to engineer materials at the nanoscale with improved properties, is predicated on the idea that material structure and properties are fundamentally modified on this scale. Gold clusters are prototypical inorganic materials that exemplify this¹⁻⁸.

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In addition to being technologically important in their own right⁹, they are a model system for studying this paradigm, as they form ultra-stable 'magic number' molecule-like clusters of different sizes^{10,11}. A major challenge, in the majority of cases where the clusters cannot be crystallized, is to determine their structure. We overcome this 'nanostructure problem'¹² by using atomic pair distribution function (PDF) analysis of X-ray diffraction (XRD) data to study the structure of $Au_{144}(SR)_{60}$ (where R is the organic part of the thiol), one of the largest of the ultra-stable magic-sized clusters with known composition^{13,14}. The PDF data successfully yield the core structure, with the surprising result that these clusters exhibit polymorphism. In very recent studies, single crystal structure determination illustrated that the much smaller $Au_{38}(SR)_{24}$ interconverts reversibly between two forms, depending on temperature¹⁵. Here we use PDF to show that polymorphism exists also in the large $Au_{144}(SR)_{60}$ cluster, representing the size regime in the transition between clusters forming non-bulk geometric structures and bulk face-centred cubic (fcc) nanoparticles⁸. The discovery of polymorphism brings an additional dimension to the phase space for nanoscale engineering.

The Au₁₄₄(SR)₆₀ structure has already been subject to many studies. Initially described as a ubiquitous 29-kDa core-mass compound^{14,16,17}, more recently the composition was determined by mass spectrometry as Au₁₄₄(SR)₆₀ (refs 18, 19). Lopez-Acevedo *et al.*²⁰ developed a detailed structural model, tested by density functional theory (DFT), where the cluster consists of an icosahedral gold core surrounded by a gold/thiol surface layer. NMR (nuclear magnetic resonance) studies later suggested that all ligands are in symmetry equivalent positions²¹. Scanning transmission electron microscopy (STEM) studies by Bahena *et al.*²² were consistent with the icosahedral core and by introducing the NMR symmetry requirement in theoretical calculations they proposed a symmetrized structure model featuring an equivalent ligand arrangement²². This model consists of a gold core of 54 atoms arranged as two Mackay icosahedral shells (Figure 6.1a), whereas a 60-atom layer covers the 55-site inner core in an 'anti-Mackay' manner (Figure 6.1b). The surface of the cluster structures consist of -SR-Au-SR-type structures (Figure 6.1d), referred to as 'staples'²³, and in combination this gives the full proposed structure as illustrated in Figure 6.1c. The structure is closely related to that of $Pd_{145}(CO)(PEt_3)$ determined by single-crystal XRD²⁴.

In this study, we apply atomic PDF analysis to Au₁₄₄(SR)₆₀. PDF analysis has become widely used for nanostructure analysis²⁵⁻²⁹ and is a potential tool for nanostructure solution³⁰⁻³². In recent times, PDF has also been applied to the fingerprinting of gold nanocluster structure^{33,34}. PDF goes beyond conventional X-ray powder diffraction, which typically covers only a narrow



Figure 6.1. a) Fifty-four atom gold core consisting of two Mackay icosahedron shells. (b) The icosahedral gold core (pink) is covered by 60 gold atoms (yellow) making up the grand core. (c) Total structure, where the grand core is covered in 'staples'—green atoms represent sulfur, whereas blue atoms represent gold in the staple structure. The organic carbon chains have been left out for clarity. (d) Illustration of staple structure on gold surface. (e) Thiolate ligands used in the study. From left: *p*-MBA, PET, SC4, SC6 and SC12.

range of reciprocal space³⁵ and neglects diffuse scattering. The total scattering approach contains significantly more structural information, allowing a quantitative assessment of the structure that is impossible with conventional data from such small particles. We apply PDF nanostructure analysis to Au₁₄₄(SR)₆₀ clusters prepared with different ligands (Figure 6.1e): phenylethane thiol (PET), *para*-mercaptobenzoic acid (*p*-MBA), butane thiol (SC4), hexanethiol (SC6) and dodecanethiol (SC12). Sample homogeneity is characterized by electrospray ionization–mass spectrometry (ESI–MS) and electrochemical methods. The approach results in full quantitative refinements of the structure of the gold core, with a semi-quantitative assessment of the surface structure. Surprisingly, we find two distinct structural forms for this cluster's core, one based on icosahedra seen in smaller clusters, proposed earlier for this 144 gold atom cluster²⁰⁻²², and one based on close packed decahedra that resemble larger gold clusters and bulk gold. The discovery of polymorphism in gold nanoclusters opens up a new dimension in nanoparticle engineering, presenting the possibility of engineering nanoparticle structure, as well as size and morphology.

6.3 Results and discussion

We first investigate the sample prepared with SC6 ligands. ESI–MS data (see Figure S10 and Table S5) confirmed homogeneity of this sample, with at least 90% of the sample being Au₁₄₄(SC6)₆₀ and a small byproduct (<10%) with ESI–MS peaks, which can be assigned to Au₁₃₇(SR)₅₆ (ref. 36). Previously in the literature, this impurity signal has been assigned to Au₁₄₄(SR)₆₀ fragments^{37,38}. No other cluster sizes, such as Au₁₃₀(SR)₅₀ or Au₁₃₃(SR)₅₂ were detected. The low *Q* scattering signal (where $Q=4\pi\sin(\theta)/\lambda$ is the magnitude of the scattering vector), corresponding to conventional XRD data, the total scattering structure function *F(Q)* and the PDF, *G(r)*, from this sample at 100 K are shown in Figure 6.2. Owing to the small size of the

gold clusters, only very broad scattering peaks are present in the low Q signal (Figure 6.2a), resulting in too little information to attempt a total structure solution by crystallographic means. In the total scattering structure function F(Q) (Figure 6.2b) we see that the diffuse scattering extends over a wide range of reciprocal space containing scattering features with rich information that cannot be resolved when just the low Q conventional XRD data are used. The PDF, plotted in blue in Figure 6.2c, is the Fourier transform of the data in Figure 6.2b. This realspace function contains peaks at distances separating pairs of atoms in the structure. The observation of sharp peaks in real-space indicates that the gold clusters have a well-defined structure. The peaks in G(r) disappear above 12.5 Å, which puts a lower bound on the diameter of the gold core of the clusters. The first large peak at ca. 2.9 Å is the nearest-neighbour goldgold distance, r_{nn} , and is sharp. The strength and sharpness of the low r peaks suggests a high multiplicity for these distances, indicating a rather well-packed structure. In Figure 6.2c, we also show the experimental PDFs from the Au_{144} (PET)₆₀ sample plotted in green. The similarity of the PDFs from Au₁₄₄(SC6)₆₀ and Au₁₄₄(PET)₆₀ indicates that these clusters have identical core structures and also establishes the reproducibility of the PDF measurements.



Figure 6.2. Collected scattering data for $Au_{144}(SR)_{60}$ clusters. (a) Low *Q* scattering data, corresponding to the conventional XRD signal for the $Au_{144}(SC6)_{60}$ sample. (b) Total scattering structure function F(Q) for $Au_{144}(SC6)_{60}$. (c) PDFs obtained from $Au_{144}(SC6)_{60}$, $Au_{144}(PET)_{60}$ and $Au_{144}(p-MBA)_{60}$.

The red line in Figure 6.2c shows the PDF from $Au_{144}(p-MBA)_{60}$. There is a remarkable difference between this PDF and those of $Au_{144}(SC6)_{60}$ and $Au_{144}(PET)$. These clusters have the same size, as evident from the disappearance of sharp features in the PDF, by the characteristic, well-defined differential pulse voltammetry and from mobility in polyacrylamide gel electrophoresis consistent with $Au_{144}(SR)_{60}$. Both the SC6, PET- and *p*-MBA-protected preparations, formed the poorly diffracting hexagonal plate crystals previously observed for these compounds^{39,40}. The sharp PDF peaks indicate that the $Au_{144}(p-MBA)_{60}$ clusters also have a well-defined ordered structure. However, their structure is remarkably different from that of the SC6- and PET-terminated clusters: the $Au_{144}(SR)_{60}$ clusters are exhibiting polymorphism. We now explore quantitatively the two structural polymorphs, Form I and Form II, of these clusters.

Form I

We begin by calculating PDFs from candidate structures suggested in the literature to compare with the data. The relative atomic positions are highly constrained in the modeling with only five parameters allowed to vary: a scale factor accounting for the overall PDF intensity, a uniform cluster expansion factor that allows the cluster structure to contract or expand, two isotropic atomic displacement parameter applied separately to the core and surface atoms, as well as a parameter accounting for correlated atomic motion⁴¹. Therefore, good fits to the data are a strong indicator that the model has captured the correct geometry of the core. To simplify the models, only the Au and S atoms were included in the refinements, as the scattering signal from the organic ligands is negligible (see Supplementary note 3) . Figure 6.3a shows the calculated PDF from the model suggested by Bahena *et al.*²², fitted to the SC6 data²⁰. The result of a refinement to the same data, but using the structure reported by Lopez-Acevedo *et al.*²⁰ is shown

in Figure S11. Both models describe the main features of the PDF of the $Au_{144}(SC6)_{60}$ nanoclusters very well, with the Bahena structure giving a slightly better fit to the PDF with agreement factor R_W =16.3%. This confirms the proposed structures of previous theoretical and STEM studies^{21,22}.

Similar fits to the Au₁₄₄(PET)₆₀ sample are given in Figure S12 and Table S6, also showing good agreement with the icosahedral model (R_W =15.8%). Furthermore, a direct comparison of the experimental data from the PET and SC6 data show that the two samples give rise to practically identical PDFs as illustrated in Figure S13, where the difference curve between the two PDFs is essentially a flat line. Interestingly, the ESI–MS data indicated ~16% Au₁₃₇(SR)₅₆ in the PET sample, that is, a higher fraction than seen in the SC6 sample. The flat difference curve between the two PDFs would not be expected if the byproduct signal in ESI– MS is coming from a different cluster, that is, Au₁₃₇(SR)₅₆. Thus, the PDFs either indicate that the byproduct signal is coming from fragments of Au₁₄₄(SR)₆₀ created during the ESI–MS measurement, or that the core structure of Au₁₃₇(SR)₅₆ is indistinguishable to that of Au₁₄₄(SR)₆₀ Form I. As we see later, the PDF is quite sensitive to small changes in core structure and, although the latter scenario cannot be ruled out, the former is more probable, indicating that our samples are pure Au₁₄₄(SR)₆₀. If the latter scenario is correct, it establishes that the core of Au₁₃₇(SR)₅₆ is highly similar to that of Au₁₄₄(SR)₆₀.

The data shown in Figure 6.2 are obtained at 100 K. Scattering data from $Au_{144}(PET)_{60}$ were also taken at 300 K, showing no structural changes between the two temperatures (Figure S14). Furthermore, we measured data using three different X-ray energies, ranging from 39 to 87 keV, and all PDFs (Figure S14) showed the same structure.



Figure 6.3. Fits to experimental PDFs. (a) Fit of Bahena model to $Au_{144}(SC6)_{60}$ data. (b) Fit of icosahedral model to $Au_{144}(p-MBA)_{60}$ data. (c) Fit of fcc/hcp model to $Au_{144}(p-MBA)_{60}$ data. (d) Fit of 114 atom decahedral model to $Au_{144}(p-MBA)_{60}$ data. (e) Fit of decahedral model with staples to $Au_{144}(p-MBA)_{60}$ data.

Form II

We now turn to the structure of the Au₁₄₄(*p*-MBA)₆₀ cluster, which has the very different PDF evident in Figure 6.2c. The homogeneity of this cluster sample was characterized by electrochemical measurements. Total scattering data were measured from samples of Au₁₄₄(*p*-MBA)₆₀ from two different synthesis batches and as shown in Figure S15 the two PDFs are completely reproduced with a small difference residuum of R_W =7.8%, illustrating reproducibility of the synthesis and reliability of the measurements. We first attempt to use the Form I icosahedral structural model to establish whether this can be made to fit the different PDF by adjusting the refinement parameters. However, the model gives a very poor fit with a large difference between the calculated and measured PDF, and poor fit residuum of R_W =36.0% as shown in Figure 6.3b. To further confirm that the sample does not simply contain stable clusters of a different size, for example, Au₁₀₂(SR)₄₄ (ref. 3), Au₁₃₀(SR)₅₀ (ref. 42) or Au₁₃₃(SR)₅₂ (ref. 43), we fitted known structural models for these clusters to the *p*-MBA data. In all cases, the models gave very poor agreements with the data (fits shown in Figures S16-19), confirming that the samples are not made up of other stable cluster sizes.

Therefore, other models for the $Au_{144}(SR)_{60}$ gold cluster were explored. Initially, we considered only the positions of the 144 gold atoms and ignored the ligands in the model. We based this on the dominating scattering power of gold compared with the thiolates. First, a series of close-packed core models were constructed, closely related to bulk fcc gold. These included a 147-atom cuboctahedron, as well as clusters formed by cutting a sphere of ~144 atoms from fcc and hexagonal close-packed (hcp) lattices. The next attempted model was a two-phase fit of the PDFs from cutouts from fcc and hcp, which has been used as a proxy model in PDF modelling for close-packed structures that contain stacking faults²⁷. A summary of these simulations is

given in Table S7. None of the fcc- or hcp-based clusters produced completely convincing fits to the observed PDF. However, the fits were significantly better than for the Bahena model, especially for the fcc/hcp mixture as shown in Figure 6.3c. The PDF agreement of the fcc/hcp model was remarkably improved after allowing for a separate expansion ratio for the atoms in the outermost shell, giving $R_{\rm W}=16.3\%$, a step which was motivated by allowing for a possible surface relaxation. This improved the refinement by fitting the asymmetry in the first Au–Au peak. However, the results indicated that the bond lengths between the atoms in the surface were contracted compared with the bonds in the core and the atomic displacement parameters were excessively large over 0.03 Å^2 for the core atoms, suggesting the existence of some atomic relaxations that are not part of these simple models. Furthermore, this model contains 141 atoms in the fcc phase and 147 atoms in the hcp phase. We seek a model that can also explain the high stability of the Au core with 144 atoms, whereas spherical chunks of close-packed bulk material would not have special stability. Nonetheless, the fitting results establish that the structure of $Au_{144}(SR)_{60}$ is much closer to a three-dimensional close-packed structure than the icosahedral, DFT-derived models.

Our search for close-packed structures that have special atom counts led us to explore a series of Marks decahedral structures that are constructed by introducing twin boundaries along the *(110)* planes of the fcc lattice^{44,45}. Closed shell, truncated decahedra can be constructed with a large range of discrete number of atoms, including 144, that is, the exact number of gold atoms in the cluster. This structure and the fit to the experimental PDF are shown in Figure S19, where excellent fits are seen. However, as described above, thiolate ligands are known to create –SR-Au-SR– or –SR-Au-SR– 'staples' on gold surfaces^{23,46}. The short staple, that is, –SR-Au-SR– is mainly seen on larger clusters, where the curvature is small, as would be the case in the

 ~ 2 nm Au₁₄₄(SR)₆₀ structure, and Au₁₄₄(SR)₆₀ may thus better be represented as Au₁₁₄[(SR)-Au-(SR)]₃₀. This pointed us towards a smaller ino decahedral structure as the core of the cluster, as illustrated in Figure 6.4a,b. The cluster shown has exactly 114 gold atoms, leaving 30 gold atoms for the staples as required by the putative stoichiometry. The fit of this cluster to the data is shown in Figure 6.3d and, as illustrated, the model very well describes the experimental PDF. All distinct sharp peaks up to 8 Å are reproduced and the fit remains very close even at higher *r*-values where the features are broader and less resolved. In studies of smaller clusters, it has been shown that although the core of the cluster is decahedral, a shell of gold atoms may be seen between the core structure and the staple layer³. Therefore, we tried stripping down the decahedral structure to a yet smaller core and reattaching the atoms as 'caps' on the remaining structure³. However, interestingly, any modification to the 114 atom decahedral core highly deteriorated the PDF fit, making lower symmetry structures unlikely. This makes us confident in a core structure based on the 114 atom decahedron, closely related to the ino decahedron described by Cleveland *et al.*¹⁷

Various configurations of the staples on the 114-atom decahedral structure cluster were then considered, where one example is presented in Figure 6.4c and other selected models are shown in Figure S19. Staples were placed on the (*111*) surfaces as previously seen²³; however, to accommodate all ligands to the structure in a physically sensible manner, staples were also attached to the (*100*) surfaces, although this motif has not yet been reported. Several different models were constructed, which all give comparably good fits to the data with R_W values of *ca*. 15–18%, with one example shown in Figure 6.3e, where the presence of staples fit to the shoulder of the nearest neighbor Au–Au peak. The PDF refinements were somewhat sensitive to the staple attachment, as subtle differences between the features in the fitted PDF can be observed. However, based on PDF data alone we cannot determine the exact ligand arrangement and further studies combining total scattering with techniques sensitive to the ligand attachment are needed to determine the surface structure with full confidence.

Nevertheless, the PDF analysis clearly shows that the $Au_{144}(p-MBA)_{60}$ core takes a decahedral structure, unlike the $Au_{144}(SC6)_{60}$ and $Au_{144}(PET)_{60}$ samples described above. We call this second stable structure for $Au_{144}(SR)_{60}$ Form II. The decahedral structure fits well in the thiol stabilized gold cluster structure series. From single-crystal XRD of smaller clusters, a strong effect of ligand on internal structure and allowed nuclearity can be inferred, with close-packed and icosahedral structures both observed. For instance, $Au_{25}(PET)_{18}$ (ref. 47), $Au_{38}(PET)_{24}$ (ref. 48) and $Au_{133}(SPh-tBu)_{52}$ (ref. 43) have been determined to have icosahedral cores. This is in contrast to $Au_{18}(SC_6H_{11})_{14}$ (ref. 49), $Au_{36}(SPh-tBu)_{24}$ (ref. 50) and $Au_{102}(p-MBA)_{44}$ (ref. 3), which have close-packed cores. A cuboctahedron-like structure (which also has closed-packed motifs) was seen for the $Au_{68}(p-MBA)_{32}$ cluster by advanced single-particle



Figure 6.4. 114-Atom and 144-atom ino decahedron cluster. (a) Side view. (b) Top view. (c) Decorated with 60 (SR-Au-SR) staples. Pink spheres show gold atoms in the cluster core, whereas blue spheres show gold in the staple structure. Sulfur is shown in yellow. The organic chains have been left out for clarity.

electron microscopy methods⁵¹. It has furthermore been shown that substituting Au by Ag in ligand-free clusters containing *ca.* 312 metal atoms changes the structure from fcc to icosahedral⁵².

Form I and II coexistence

We next attempted to find a trend in ligand type for stabilizing the different structural forms and tested the effects of using linear thiol ligands of different length, namely SC4 and SC12, which we compare with the SC6 and PET samples. The PDF data for SC4, SC12 and PET are shown in Figure 6.5a–c along with fits using the Form I model. The refined parameters are given in Table S8, where the data from the hexane thiolated sample (SC6) and PET samples show good agreement with the icosahedral Form I model, and the SC4 and SC12 samples give much larger residuum values of 17.9% and 18.6%, respectively. Interestingly, the disagreement between data and model is particularly large around r=5 Å, which is exactly the position for one of the most dominating peaks in the decahedral PDF. ESI–MS data from both the SC4 and SC12 samples showed Au₁₄₄(SR)₆₀, as well as impurity peaks corresponding to Au₁₃₇(SR)₅₆ in quantities comparable to the PET-protected samples. No other clusters were seen. As the presence of Au₁₃₇(SR)₅₆ in the ESI–MS data did not affect the PDF fits to the PET-protected sample and as no other clusters are identified by ESI–MS, we can rule out that the disagreement is due to the presence of other cluster sizes.



Figure 6.5. Fits of the Bahena model to experimental data. (a) Fit to $Au_{144}(SC4)_{60}$ data, (b) to $Au_{144}(SC12)_{60}$ data and (c) to $Au_{144}(PET)_{60}$ data. (d) Data for the $Au_{144}(PET)_{60}$ and $Au_{144}(SC12)_{60}$; the difference between them and the calculated PDF from the 114-atom decahedron model. The difference curve has been doubled in scale for clarity.

In Figure 6.5d, the experimentally derived PET PDF (in Form I) has been subtracted from the SC12 calculated PDF and the difference curve is plotted below. Close inspection indicates that it strongly resembles the PDF of the Form II decahedral core structure, as seen when comparing with the calculated PDF from the 114-atom decahedron plotted along with the data. The difference curve has exactly the same features as seen from the decahedron phase, showing that the sample contains clusters of two distinct structures: Form I and Form II. Similar results are seen for the SC4 sample as illustrated in Figure S21. Two-phase fits showed that the SC4 sample contains 12% decahedral clusters (88% icosahedral clusters), whereas the SC12 sample has 14% decahedral clusters, as listed in Table S9 and illustrated in Figure S22. When including the decahedral phase in the fit, the resulting R-values are reduced to *ca*. 16%. The results unambiguously show that two polymorphs of the Au₁₄₄(SR)₆₀ cluster are present.

6.4 Conclusion

The question remains which factors affect the polymorph. Previous studies of gold clusters have indicated that ligand length may influence the structure of the gold core¹⁴. Our total scattering data cannot confirm this trend, as both the longest (SC12) and shortest (SC4) linear ligand give mainly icosahedral clusters, with a smaller fraction of decahedral clusters present in each sample. The fact that we see both the icosahedral and decahedral clusters in samples made with the same ligands illustrate that the structural diversity is not a simple effect of the ligand chain length, bulkiness or bonding strength. It is a clear indication that the two structures are very close in energy. As discussed above, Wong *et al.*²¹ reported ¹H-NMR studies of Au₁₄₄(*p*-MBA)₆₀ clusters, which showed only one doublet in the aromatic region of the spectrum, suggesting that all ligands are in symmetry equivalent positions. Interestingly, ¹³C-NMR studies

on 29 kDa gold clusters have shown that the NMR signal is highly dependent on the charge state of the nanocluster. The simple NMR signal indicating symmetry equivalent ligands was seen only when the clusters were in charge state +3, whereas other signals were seen at lower charge states⁵³. In recent work, Tlahuice-Floret et al.⁵⁴ used DFT to study the effect of charge state on structure of the gold subhalide Au₁₄₄Cl₆₀, which is isoelectronic with Au₁₄₄(SR)₆₀. It was shown that a fully symmetric icosahedral structure is stable at charge states +2 and +4, but not at neutrality. Furthermore, other studies have experimentally illustrated charge-dependent thermal stability of Au₁₄₄(SC₆H₁₃)⁵⁵. All our data have been measured in the uncharged state and, therefore, we cannot comment on a charge-dependent structure in $Au_{144}(p-MBA)$. However, when considering our new PDF data, applicable for detailed nanostructure analysis, along with the previously published powder x-Ray diffraction (PXRD), STEM and NMR data, this again points to a scenario where the icosahedral core structure and decahedral structure both exist with very similar energies. Small differences in the electronic state of the cluster from, for example, charge or ligand binding, could lead to different structures and, possibly, even switching between the different structural forms.

As noted above, the full staple arrangement on the decahedral clusters cannot be deduced from the PDFs and X-ray scattering data must be combined with techniques sensitive to the organic ligands to establish the total structure. If considering also the experimental PDFs from the icosahedral structures (that is, with SC6 and PET ligands), we note that neither the Bahena *et al.*²² or Lopez-Acevedo *et al.*²⁰ models fully capture the details in the PDFs, for example, in the peaks between 4 and 5 Å in Figure 6.3a. Some structural details exist, which are not present in the established models. Therefore, further studies of the structure are needed, where scattering is combined with theory⁵⁴ and spectroscopy⁵⁶, to establish the total structure.

The polymorphism seen in our data suggests many new studies of gold nanoclusters. The close energies between different cluster structures may not be limited to the Au₁₄₄(SR)₆₀ cluster family, but exist in a larger size range and in different materials systems. The presence of polymorphism challenges some of the characterization methods that are used for structure solution. For example, when applying single-crystal XRD, the crystallization process works as a structural sieve that will favour only one cluster polymorph over others that may be present in suspension, resulting in an incomplete picture. As we show, PDF will see the average sample and any structural heterogeneity will be observed in the data. Compared with electron beams used for STEM studies, X-rays are much less perturbing of the system and any structural changes due to beam irradiation are therefore less probable. Furthermore, PDF allows to distinguish between seemingly similar clusters, that is, Au₁₃₀(SR)₅₀, Au₁₃₃(SR)₅₂ and the two forms of Au₁₄₄(SR)₆₀.

In summary, we have shown by means of total scattering PDF analysis on wellcharacterized samples of $Au_{144}(SR)_{60}$ that the clusters can take two distinct structures: a truncated decahedron structure (Form II) and the previously proposed icosahedral structure (Form I). The two structures have been isolated in samples with *p*-MBA and SC6 ligands, respectively, but in samples with SC4 and SC12, the two structures are seen to coexist, indicating that the energy of the two structures are very close to each other. In recent times, several new metal clusters have been isolated in the size range from 50 to 300 atoms^{57,58}. The structures of many of these clusters remain undetermined, owing to difficulties in crystallizing the clusters into a large, single crystal suitable for structure determination. We believe that PDF will be an excellent tool for these studies and, when combined with spectroscopic methods, will be able to provide full structure solutions to many new nanomaterials.

6.5 Methods

Total scattering data were acquired during three different beamtimes at three different facilities. For all samples, the cluster powders were loaded in Kapton tubes with inner diameter of 1 mm. Data for both samples of the $Au_{144}(p-MBA)_{60}$ cluster was obtained at ID11 at the European Synchrotron Radiation Facility with an X-ray wavelength of 0.1774 Å at 100 K. For the $Au_{144}(PET)_{60}$, $Au_{144}(SC6)_{60}$, $Au_{144}(SC4)_{60}$ and $Au_{144}(SC12)_{60}$ clusters, data were measured at beamline 11-ID-B at the Advanced Photon Source, at Argonne National Laboratory. Here, data were measured at 100 and 300 K with X-ray wavelength 0.143 Å. Additional data sets for the $Au_{144}(PET)_{60}$ were furthermore measured at the X7B beamline at room temperature with X-ray wavelength of 0.319 Å, as well as at the X17A beamline, X-ray wavelength 0.186 Å at 100 and 300 K, both at the National synchrotron light source facility at Brookhaven National Laboratory.

The experimental powder diffraction patterns were integrated using the programme $Fit2D^{60}$ and Fourier transformed to obtain the PDF using the programme $PDFgetX3^{61}$. Modeling was done using *DiffPy-CMI*.

References

Brust, M.; Fink, J.; Bethell, D.; Schiffrin, D. J.; Kiely, C. J. Chem. Soc., Chem. Commun.
 1995, 1655-1656.

(2) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. J. Chem. Soc., Chem. Commun. 1994, 801-802.

Maier, S. A.; Brongersma, M. L.; Kik, P. G.; Meltzer, S.; Requicha, A. A. G.; Atwater,
H. A. *Adv. Mater.* 2001, *13*, 1501-1505.

(4) Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.; Bushnell, D. A.; Kornberg, R. D. Science
2007, 318, 430-433.

Walter, M.; Akola, J.; Lopez-Acevedo, O.; Jadzinsky, P. D.; Calero, G.; Ackerson, C. J.;
Whetten, R. L.; Gronbeck, H.; Hakkinen, H. *Proc. Natl. Acad. Sci. U.S.A.* 2008, *105*, 9157-9162.

(6) Zhu, M.; Aikens, C. M.; Hollander, F. J.; Schatz, G. C.; Jin, R. J. Am. Chem. Soc. 2008, 130, 5883-5889.

Weissker, H. C.; Escobar, H. B.; Thanthirige, V. D.; Kwak, K.; Lee, D.; Ramakrishna,
G.; Whetten, R. L.; Lopez-Lozano, X. *Nat. Commun.* 2014, *5*, 3785.

(8) Philip, R.; Chantharasupawong, P.; Qian, H. F.; Jin, R. C.; Thomas, J. *Nano Lett.* 2012, *12*, 4661-4667.

Negishi, Y.; Nakazaki, T.; Malola, S.; Takano, S.; Niihori, Y.; Kurashige, W.; Yamazoe,
S.; Tsukuda, T.; Häkkinen, H. J. Am. Chem. Soc. 2014, 137, 1206–1212

Mandal, S.; Bakeine, G. J.; Krol, S.; Ferrari, C.; Clerici, A. M.; Zonta, C.; Cansolino, L.;
Ballarini, F.; Bortolussi, S.; Stella, S.; Protti, N.; Bruschi, P.; Altieri, S. *Appl. Radiat. Isot.* 2011, 69, 1692-1697.

- (11) Daniel, M. C.; Astruc, D. Chem. Rev. 2004, 104, 293-346.
- (12) Pasquato, L.; Pengo, P.; Scrimin, P. J. Mater. Chem. 2004, 14, 3481-3487.
- (13) Jin, R. C. Nanoscale **2010**, *2*, 343-362.
- (14) Qian, H. F.; Zhu, M. Z.; Wu, Z. K.; Jin, R. C. Acc. Chem. Res. 2012, 45, 1470-1479.
- (15) Billinge, S. J. L.; Levin, I. Science 2007, 316, 1698-1698.
- (16) Whetten, R. L.; Khoury, J. T.; Alvarez, M. M.; Murthy, S.; Vezmar, I.; Wang, Z. L.; Stephens, P. W.; Cleveland, C. L.; Luedtke, W. D.; Landman, U. *Adv. Mater.* **1996**, *8*, 428-433.
- (17) Schaaff, T. G.; Shafigullin, M. N.; Khoury, J. T.; Vezmar, I.; Whetten, R. L. J. Phys. Chem. B 2001, 105, 8785-8796.
- (18) Alvarez, M. M.; Khoury, J. T.; Schaaff, T. G.; Shafigullin, M.; Vezmar, I.; Whetten, R.
 L. *Chem. Phys. Lett.* **1997**, *266*, 91-98.
- (19) Chaki, N. K.; Negishi, Y.; Tsunoyama, H.; Shichibu, Y.; Tsukuda, T. J. Am. Chem. Soc.
 2008, 130, 8608-8612.
- (20) Qian, H. F.; Jin, R. C. Nano Lett. 2009, 9, 4083-4087.
- (21) Lopez-Acevedo, O.; Akola, J.; Whetten, R. L.; Gronbeck, H.; Hakkinen, H. J. Phys. Chem. C 2009, 113, 5035-5038.
- (22) Wong, O. A.; Heinecke, C. L.; Simone, A. R.; Whetten, R. L.; Ackerson, C. J. *Nanoscale*2012, *4*, 4099-4102.
- (23) Bahena, D.; Bhattarai, N.; Santiago, U.; Tlahuice, A.; Ponce, A.; Bach, S. B. H.; Yoon,
- B.; Whetten, R. L.; Landman, U.; Jose-Yacaman, M. J. Phys. Chem. Lett. 2013, 4, 975-981.
- (24) Hakkinen, H. Nat. Chem. 2012, 4, 443-455.
- (25) Billinge, S. J. L.; Kanatzidis, M. G. Chem. Commun. 2004, 7, 749-760.
- (26) Billinge, S. J. L. J. Solid State Chem. 2008, 181, 1695-1700.

- (27) Young, C. A.; Goodwin, A. L. J. Mater. Chem. 2011, 21, 6464-6476.
- (28) Yang, X. H.; Masadeh, A. S.; McBride, J. R.; Bozin, E. S.; Rosenthal, S. J.; Billinge, S. J.
 L. Phys. Chem. Chem. Phys. 2013, 15, 8480-8486.
- (29) Neder, R. B.; Korsunskiy, V. I. J. Phys.: Condens. Matter 2005, 17, S125-S134.
- (30) Newton, M. A.; Chapman, K. W.; Thompsett, D.; Chupas, P. J. J. Am. Chem. Soc. 2012, 134, 5036-5039.
- (31) Page, K.; Hood, T. C.; Proffen, T.; Neder, R. B. J. Appl. Crystallogr. 2011, 44, 327-336.
- (32) Juhas, P.; Cherba, D. M.; Duxbury, P. M.; Punch, W. F.; Billinge, S. J. L. *Nature* 2006, 440, 655-658.
- (33) Cliffe, M. J.; Dove, M. T.; Drabold, D. A.; Goodwin, A. L. Phys. Rev. Lett. 2010, 104.
- (34) Billinge, S. J. L.; Dykhne, T.; Juhas, P.; Bozin, E.; Taylor, R.; Florence, A. J.; Shankland,K. *Crystengcomm* 2010, *12*, 1366-1368.
- (35) Ackerson, C. J.; Jadzinsky, P. D.; Sexton, J. Z.; Bushnell, D. A.; Kornberg, R. D. *Bioconjugate Chem.* 2010, *21*, 214-218.
- (36) Koivisto, J.; Salorinne, K.; Mustalahti, S.; Lahtinen, T.; Malola, S.; Hakkinen, H.; Pettersson, M. J. Phys. Chem. Lett. 2014, 5, 387-392.
- (37) Jeong, I. K.; Proffen, T.; Mohiuddin-Jacobs, F.; Billinge, S. J. L. J. Phys. Chem. A 1999, 103, 921-924.
- (38) Marks, L. D. *Philosophical Magazine a-Physics of Condensed Matter Structure Defects and Mechanical Properties* **1984**, *49*, 81-93.
- (39) Marks, L. D. Rep. Prog. Phys. 1994, 57, 603-649.
- (40) Jiang, D. E.; Tiago, M. L.; Luo, W. D.; Dai, S. J. Am. Chem. Soc. 2008, 130, 2777-2784.

(41) Heaven, M. W.; Dass, A.; White, P. S.; Holt, K. M.; Murray, R. W. J. Am. Chem. Soc.
2008, 130, 3754-3762.

(42) Qian, H. F.; Eckenhoff, W. T.; Zhu, Y.; Pintauer, T.; Jin, R. C. J. Am. Chem. Soc. 2010, 132, 8280-8284.

(43) Dass, A.; Theivendran, S.; Nimmala, P. R.; Kumara, C.; Jupally, V. R.; Fortunelli, A.;
Sementa, L.; Barcaro, G.; Zuo, X. B.; Noll, B. C. J. Am. Chem. Soc. 2015, 137, 4610-4613.

(44) Das, A.; Liu, C.; Byun, H. Y.; Nobusada, K.; Zhao, S.; Rosi, N.; Jin, R. C. Angew. Chem. *Int. Ed.* 2015, 54, 3140-3144.

(45) Das, A.; Liu, C.; Zeng, C. J.; Li, G.; Li, T.; Rosi, N. L.; Jin, R. C. J. Phys. Chem. A 2014, 118, 8264-8269.

(46) Azubel, M.; Koivisto, J.; Malola, S.; Bushnell, D.; Hura, G. L.; Koh, A. L.; Tsunoyama,

H.; Tsukuda, T.; Pettersson, M.; Hakkinen, H.; Kornberg, R. D. Science 2014, 345, 909-912.

(47) Cleveland, C. L.; Landman, U.; Schaaff, T. G.; Shafigullin, M. N.; Stephens, P. W.;Whetten, R. L. *Phys. Rev. Lett.* **1997**, *79*, 1873-1876.

- (48) Song, Y.; Harper, A. S.; Murray, R. W. Langmuir 2005, 21, 5492-5500.
- (49) Wang, Z. W.; Palmer, R. E. Phys. Rev. Lett. 2012, 108, 245502.
- (50) Wells, D. M.; Rossi, G.; Ferrando, R.; Palmer, R. E. *Nanoscale* **2015**, *7*, 6498-6503.
- (51) Li, G.; Zeng, C. J.; Jin, R. C. J. Am. Chem. Soc. 2014, 136, 3673-3679.
- (52) Nimmala, P. R.; Yoon, B.; Whetten, R. L.; Landman, U.; Dass, A. J. Phys. Chem. A
 2013, 117, 504-517.
- (53) Qian, H. F.; Jin, R. C. Chem. Mater. 2011, 23, 2209-2217.

(54) Hammersley, A. P.; Svensson, S. O.; Hanfland, M.; Fitch, A. N.; Hausermann, D. *High Pressure Res.* **1996**, *14*, 235-248.
(55) Juhas, P.; Davis, T.; Farrow, C. L.; Billinge, S. J. L. J. Appl. Crystallogr. 2013, 46, 560-566.

Chapter 7

Summary

Gold thiolate MPCs are very stable and can be isolated in a wide range of sizes making them an instrumental tool for studying metal clusters from molecular to bulk material. For very small gold MPCs the properties can be well described through molecular orbital theory, while for much larger clusters can be understood by band theory. However medium sized gold clusters $(13 \le x \le 144)$ cannot be easily explained through either molecular or bulk models.

In order to understand the properties of medium sized gold MPCs superatom theory has been applied. For a gold cluster in this size range the valence electrons of each metal atom are donated to the superatomic orbitals, and this gives rise to the properties of the cluster. Oxidation or reduction of a metal cluster will cause large shifts in the physiochemical properties that can be understood through changes to the superatomic valence. In addition it is shown that gold thiolate clusters can by produced with single metal atom substitution. It is shown that the properties of the bi-metallic clusters mimic the properties of monometallic clusters when identical superatomic valences are achieved. This indicates that the properties described by the superatom model are largely dependent on the superatomic orbitals, with smaller variations arising due to the nature of the metal or the protecting ligand shell.

Furthermore superatom theory works well to understand the transition from molecular to bulk metal clusters. For small metal clusters the properties are heavily dependent on the superatomic valence, thus removal or addition of an electron has a large effect on the physiochemical properties. This is due to the large energy spacing between superatomic orbitals, which gives rise to more molecular-like behavior. For larger metal clusters the effects of the

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superatomic valence are less apparent, because there exist much smaller spacing between energy levels of the superatomic orbitals. The closely spaced energy levels allow for the emergence of bulk behaviors, such as a plasmon resonance. However since these clusters are quantized and the properties significantly deviate away from typical bulk behavior and in order to rationalize all of the observed properties superatom theory must be applied.

The research performed herein shows that superatom theory can be used to describe the properties of gold thiolate MPCs and that the superatom model likely could be applied to other ligated metal clusters that lie between molecular and bulk material.

SUPPLEMENTAL INFORMATION



Figure S1. The decay of the UV/Vis spectrum over time for $Au_{25}(SC_6)_{18}^+$.



Figure S2. The effect of electrolyte on thermal stability. Square points show average thermal decomposition temperature acquired in DSC runs after bulk electrolysis with TBAPF6 electrolyte. Diamond shaped points show the same for DSC runs performed after bulk electrolysis in either TMAPF6 or TEABF4, which appeared to give indistinguishable results. The effect of electrolyte is minor compared to changing the charge state and only observed in the Au25(SR)18 system for the -1 charge state. Each series is offset + or -0.1 from the actual integer charge value for the purpose of clarity.

		Au ₂₅ (PET) ₁₈ ⁻¹	Au ₂₅ (PET) ₁₈ 0	Au ₂₅ (PET) ₁₈ +1
Shell I				
	Average edge bond length	2.92	2.94	2.94
	Variation in edge length	0.3	0.4	0.7
	Standard deviation	0.08	0.11	0.18
bond I-II				
	Average	2.40	2.40	2.38
	Biggest variation in bond length	0	0	0.2
	Standard deviation	0	0	0.06
II-III bor	nd length			
	Average bond length	2.30	2.30	2.30
	Standard deviation	0	0	0
III-IV bond length				
	Average bond length	2.30	2.30	2.30

Table S1. Average bond lengths (Angstroms) and standard deviations.

 Table S2. Average dihedral angles for shells II-IV with respect to shell I.

	Au ₂₅ (PET) ₁₈ ⁻¹	Au ₂₅ (PET) ₁₈ 0	Au ₂₅ (PET) ₁₈ ⁺¹
S-I	15.28	22.14	26.36
Au-II	2.74	3.73	7.3
S-III	3.94	0.38	5.07

	Table S3.	UV/Vis	data	of Au ₂₅ ($PET)_{18}^{-1,0+1}$
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	Au ₂₅ (PET) ₁₈ ⁻¹	Au ₂₅ (PET) ₁₈ 0	Au ₂₅ (PET) ₁₈ +1	
core	685 nm	693 nm	660 nm	
homo-lumo+1	450 nm	463 nm	477 nm	
ligand to D	ligand to D 402 nm		393 nm	
core	1.81 eV	1.78 eV	1.88 eV	
homo-lumo+1 2.76 eV		2.68 eV	2.58 eV	
ligand to D 3.08 eV		3.08 eV	3.15 eV	



Figure S3. Calculated absorption spectrum of $Au_{25}(PET)_{18}^{q}$ with q = -1, 0, 1, 2. The spectrum is offset for clarity.

Atomic layer	N	Au ₂₅ (PET) ₁₈ -1	$Au_{25}(PET)_{18}^{0}$	Au ₂₅ (PET) ₁₈ ⁺¹
1. Au-atoms of the core	13	0.29	0.48	0.63
2. Au-atoms of the units	12	1.12	1.15	1.40
3. PET-groups	18	-2.42	-1.65	-1.06

Table S4. Bader Charge analysis of $Au_{25}(PET)^{-1,0+1}$.



Figure S4. Crystallographically Independent semirings, units 1, 2 and 3, showing the gauche (g) and anti (a) torsion angles of the 9 crystallographically independent PET ligands (see Table 1 for color code).



Figure S5. Cluster viewed from 3 different intersections of the units 1, 2 and 3.



Scheme S1. Anti and gauche conformations of PET ligands.



Figure S6. Packing diagrams viewed from top, front and side views highlighting the intercluster interaction themes 1 (red), 2 (blue) and 3 (magenta) between the PET ligands of the neighboring $Au_{25}(PET)_{18}^{+1}$ clusters, counter anion PF_6^- and solvent DCM molecules in the crystal lattice.



Figure S7. Shown above is the "negative" electron density when trying to place gold as the center atom.



Figure S8. The UV/Vis absorption spectrum of PdAu₂₄.



Figure S9. (a)Time-dependent stimulated emission energy obtained using three different laser pulse energies, black: 800 nJ, red: 600nJ, blue: 400nJ. (b) Time-dependent stimulated emission bandwidth under 400 nJ excitation laser pulse.



Figure S10. ESI-MS Spectra for Au_{144} products. Peak assignments are given in Supplementary Table 5.

Peak index	Assignment	Calculated Mass	Observed Mass
1	Au ₁₃₇ (SC ₄ H ₉) ₅₆ ⁴⁺	7993	7994
2	$Au_{144}(SC_4H_9)_{60}^{4+}$	8427	8429
3	Au ₁₃₇ (SC ₄ H ₉) ₅₅ ³⁺ KNaH	10651	10651
4	Au ₁₄₄ (SC ₄ H ₉) ₅₉ ³⁺ KNaH	11236	11227
5	$Au_{144}(SC_4H_9)_{60}^{3+}K_2Cs$	11306	11304
6	$Au_{137}(SC_6H_{11})_{55}^{3+}KNa_2$	11173	11173
7	$Au_{144}(SC_6H_{11})_{60}^{3+}KNa_2$	11785	11787
8	Au ₁₄₄ (PET) ₆₀ ³⁺	9147	9144
9	Au ₁₃₇ (PET) ₅₅ ³⁺ K ₂ Na	11545	11545
10	Au ₁₄₄ (PET) ₆₀ ³⁺ K ₂ Na	12187	12185
11	Au ₁₃₇ (SC ₁₂ H ₂₅) ₅₅ ³⁺ CsNaH	12740	12739
12	$Au_{144}(SC_{12}H_{25})_{59}^{3+}SK_3$	13465	13464
13	$Au_{144}(SC_{12}H_{25})_{60}^{3+}CsNaK$	13543	13543
14	No isotope pattern		

Table S5. Assignment of major peaks in ESI-MS spectra



Figure S11. Fits of the Lopez - Acevedo model to the SC6 data



Figure S12. Fits of the Bahena (A) and Lopez-Acevedo(B) model to the PET data.

	Bahena	Lopez-Acevedo
$R_w(\%)$	15.0	15.8
$U_{\rm core}$ (Å ²)	0.006(4)	0.004(3)
$U_{ m shell}$ (Å ²)	0.02(1)	0.02(1)
$\delta_2(\text{\AA})$	5(1)	6(2)
3	0.013(2)	0.015(2)

Table S6. Results from the Bahena and Lopez-Acevedo models fitted to the Au₁₄₄(PET)₆₀ data.



Figure S13. Difference between the experimental PDFs obtained for PET and SC6 protected samples.



Figure S14. Data for the $Au_{144}(PET)_{60}$ sample collected at 100K and 300K, and 39 keV, 66 keV and 87 keV. The structural features are the same for all data sets; the only differences between the PDFs are from increased r-resolution with higher beam energy (allowing higher accessible Qmax) and peak sharpening at low temperatures.



Figure S15. X-ray PDFs measured from 2 batches of $Au_{144}(p-MBA)_{60}$. Sample I in blue, sample II in red. (a) Raw total scattering data. (b) Reduced scattering structure function F(Q) and (c) the corresponding PDFs G(r). The difference between the PDFs plotted in green yields residuum $R_w = 7.8\%$.



Figure S16. Fit of the $Au_{102}SR_{44}$ structure to the pMBA data. R_w = 25%.



Figure S17. Fit of the $Au_{130}SR_{50}$ structure to the pMBA data. $R_W = 22\%$.



Figure S18. Fit of the $Au_{133}SR_{52}$ structure to the pMBA data. $R_W = 32\%$.

Model	R _w	$U_{\rm iso,c}({\rm \AA}^2)$	$U_{\rm iso,s}({\rm \AA}^2)$	$\delta_2(\text{\AA})$	¶3	BPA
Lopez-Acevedo	0.361	0.038(6)	0.025(9)	7.85(4)	0.0171(9)	-
Bahena	0.353	0.021(2)	0.060(8)	7.42(7)	0.0153(9)	-
Au ₁₄₇ icosahedron	0.307	0.029(3)	0.021(3)	7.1(1)	-0.0019(9)	2.531
Au ₁₄₇ cuboctahedron	0.245	0.0130(9)	0.14(1)	6.3(1)	-0.0019(9)	3.020
$Au_{147} hcp$	0.259	0.012(1)	0.042(8)	5.3(2)	-0.0063(7)	2.939
Au_{141} fcc	0.223	0.020(1)	0.29(7)	6.3(1)	-0.0090(7)	3.149
$Au_{141} fcc + Au_{147}$	0.184	0.0129(3)	0.09(2)	5.5(2)	-0.0075(7)	3.033
hcp*						
$Au_{141} fcc + Au_{147}$	0.163	0.031(3)	0.006(1)	6.8(2)	-0.029(2),	3.033
<i>hcp</i> * [§]					-0.0070(8)	
Au ₁₄₄ MD6441 [§]	0.158	0.011(3)	0.0025(3)	5.0(5)	-0.018(2)	2.861
					0.002(1)	
Au ₁₁₄ MD6341 [§]	0.163	0.010(2)	0.0022(5)	4.7(6)	0.00723(6	3.175
)	
					0.00740(7	
)	

 Table S7. Results from fits to the Au144(p-MBA)60 data.

[¶] The expansion coefficient ε was obtained from the ratio of the mean bond length to the bond length in bulk gold standard.

* The expansion coefficients in both phases were tied to the same value in the refinement as were the ADPs of their core and shell atoms. The refined hcp fraction was 55(3)% for both fit protocols.

[§] Fitted with separate expansion coefficients for core and shell atoms listed as (ε_c , ε_s) See supplementary note 4 for a description of BPA.



Figure S19. Left: Top and side view of the MD6441 model, with exactly 144 gold atoms. Right: Fit of the MD6441 model to the $Au_{144}(p-MBA)_{60}$. The data are shown in blue, the model in red, and the difference curve in green.



Figure S20. Fits and structures of staple-covered MD6341. In the structural model, the MD6341 core is shown with pink atoms, while the gold bound in the staple is shown in blue. Yellow spheres show sulfur. The R_w values for each fit are given in the figure.

Sample	R _w	$U_{\rm iso,c}$ (Å ²)	$U_{\rm iso,s}$ (Å ²)	δ ₂ (Å)	Expansion
					rate
SC4	17.9%	0.007(5)	0.02(5)	6(2)	0.012(1)
SC6	16.3%	0.007(4)	0.02(2)	5(1)	0.011(1)
SC12	18.6%	0.008(5)	0.03(1)	6(1)	0.012(1)

Table S8. Fits of the Bahena model to data from Au144(SC4)60, Au144(SC6)60 and Au144(SC12)60.



Figure S21. Data for the $Au_{144}(PET)_{60}$ and $Au_{144}(SC4)_{60}$; the difference between them and the calculated PDF from the 114-atom MD model. The difference curve has been doubled in intensity for clarity.

Table S9. Two phase fits to data from Au144(SC4)60, Au144(SC6)60 and Au144(SC12)60. For all the two-phase refinements, the U-values (for core and shell) were constrained to take the same values for both the decahedral and icosahedral model. The δ 2 value was also constrained to one value for the two phases. The fits for SC4 and SC12 are shown in Supplementary Figure 22.

Sample	R_w	$U_{iso,c}(A^2)$	U _{iso,s}	δ_2	Phase	Expansion,	Expansion,
			(Å ²)	(Å)	fraction,	icosahedron	decahedron
					decahedra		
SC4	15.7%	0.006(6)	0.02(2)	6(2)	12%	0.062(3)	-0.02(1)
SC6	15.8%	0.006(5)	0.02(2)	5(2)	1%	0.057(2)	0.04(1)
SC12	16.4%	0.007(6)	0.03(1)	6(2)	14%	0.061(3)	-0.02(1)



Figure S22. Two-phase fits for $Au_{144}(SC4)_{60}$ and $Au_{144}(SC12)_{60}$ data, illustrating the presence of both icosahedral and decahedra.



Figure S23. DPV of Au₁₄₄(SC4)₆₀ starting run from negative to positive potentials.



Figure S24. DPV of Au₁₄₄(SC6)₆₀ starting run from negative to positive potentials.



Figure S25. DPV of Au₁₄₄(PET)₆₀ starting run from negative to positive potentials.