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Crystal Structure of the PdAu₂₄(SR)₁₈⁰ Superatom

Marcus A. Tofanelli, Thomas W. Ni, Billy D. Phillips, and Christopher J. Ackerson

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523, United States

Christopher J. Ackerson: ackerson@colostate.edu

Abstract

The single-crystal x-ray structure of Pd doped Au₂₅(SR)₁₈ was solved. The crystal structure reveals that in PdAu₂₄(SR)₁₈, the Pd atom is localized only to the centroid of the Au₂₅(SR)₁₈ cluster. This single crystal x-ray structure shows that PdAu₂₄(SR)₁₈⁰ is well conceptualized with superatom theory. The PdAu₂₄(SR)₁₈⁰ charge state is structurally isoelectronic with Au₂₅(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 Au₂₅(SR)₁₈.

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 magnetism³ 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 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 of 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, and Ag_xAu_{25-x}(SR)₁₈, and Pd_xAu_{144-x}(SR)₆₀ clusters.⁸⁻¹⁰ 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)₆₀.¹¹⁻¹⁵ In the case of coinage metals (Cu, Ag, Au) each metal is now understood to donate one electron (i.e., the 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

Correspondence to: Christopher J. Ackerson, ackerson@colostate.edu.

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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 $\text{Au}_{25}(\text{SR})_{18}$ 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; (3) in the semiring (i.e., replacing an Au atom in the SR-Au(I)-SR-Au(I)-SR structure). In the case of $\text{PdAu}_{24}(\text{SR})_{18}$, DFT and EXAFS studies place the dopant atom at the centroid position for $\text{Au}_{24}\text{X}(\text{SR})_{18}$ clusters where X is Pt or Pd.^{14,16} However, the position of Pd in the $\text{Pd}_2\text{Au}_{36}(\text{SR})_{24}$ structure is not speculated as found at the centroid positions of each fused bi-icosahedra.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.

Here we present the single crystal x-ray structure of $\text{PdAu}_{24}(\text{SR})_{18}$, 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 $1\text{S}^21\text{P}^4$ superatom configuration, suggesting that the Pd heteroatom donates no electrons to the superatom electronic structure.

We synthesized $\text{PdAu}_{24}(\text{PET})_{18}$ (PET = phenylethanethiol) by methods adopted from Negishi.¹⁸ The $\text{PdAu}_{24}(\text{PET})_{18}$ compound was crystallized as discussed in the SI. Crystal diffraction data was collected on Advanced Light Source Beamline 4.2.2; Synchrotron flux was required for timely collection of data especially at higher angle diffraction. $\text{PdAu}_{24}(\text{PET})_{18}^0$ forms a triclinic lattice in the space group $\text{P}\bar{1}$, as observed for every other crystallographically resolved $\text{Au}_{25}(\text{SR})_{18}$ cluster structure.¹⁹⁻²³ The crystal structure was solved in SHELXTL. The single crystal x-ray structure of $\text{PdAu}_{24}(\text{PET})_{18}$ is shown in Figure 1, left panel. The structure reveals identical connectivity to the other $\text{Au}_{25}(\text{SR})_{18}$ crystal structures so far reported, with a filled 13-atom icosahedral core protected by 6 SR-Au-SR-Au-SR semirings.¹⁹⁻²³ 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 S1) 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 $\text{PdAu}_{24}(\text{PET})_{18}$ cluster is isoelectronic with the $\text{Au}_{25}(\text{SR})_{18}$ cluster. Electrochemically, $\text{PdAu}_{24}(\text{PET})_{18}$ and $\text{Au}_{25}(\text{PET})_{18}$ 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 $\text{PdAu}_{24}(\text{PET})_{18}$ compared to $\text{Au}_{25}(\text{PET})_{18}$ (Figure 2)²⁴ Likewise, the linear absorption spectra of $\text{PdAu}_{24}(\text{PET})_{18}^0$ are similar to $\text{Au}_{25}(\text{PET})_{18}^0$; each compound has a broad band peak centered at 650 nm and 688 nm with a sharp feature at 380 nm and 400 nm for $\text{PdAu}_{24}(\text{PET})_{18}^0$ and $\text{Au}_{25}(\text{PET})_{18}^0$, 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 Au₂₅(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 the substantially shifted electrochemical response.²⁵

Despite the similarities, it is obscure which oxidation state of Au₂₅(PET)₁₈ is formally isoelectronic with PdAu₂₄(PET)₁₈⁰. In general only the s and p electrons of a metal are donated to the superatom. With an electron configuration of 5s⁰ 4d¹⁰, it is expected that Pd makes no contribution to the superatom electron count. Thus, PdAu₂₄(PET)₁₈⁰ is expected to be “superatom-isoelectronic” with Au₂₅(PET)₁₈⁺.

Assuming this, each event in the square wave voltammogram of PdAu₂₄(SR)₁₈ can be assigned with the superatomic configuration shown in Figure 2. The resting potential of the PdAu₂₄(PET)₁₈⁰ used in formation of single-crystals is at 50 mV vs SCE suggesting a 1S²1P⁴ 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 Au₂₅(SR)₁₈^{-1/0/+1}.²⁶

Indeed, analysis of the central icosahedron of PdAu₂₄(SR)₁₈ reveals that the structure is distorted away from idealized icosahedral symmetry with remarkable similarity to the distortion observed previously in the Au₂₅(SR)₁₈¹⁺ (1S²1P⁴) superatom. In the 1S² 1P⁴ superatom structure of Au₂₅(SR)₁₈¹⁺, bond lengths in the icosahedral core varied from 2.7 to 3.3 Å, whereas for the 1S²1P⁶ configuration, bond lengths vary only from 2.8 Å to 3.0 Å. The variability in bond lengths observed in PdAu₂₄(SR)₁₈⁰ span an identical range to those of Au₂₅(SR)₁₈¹⁺. 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 Au₂₅(SR)₁₈^{-1/0/+1} are 0.67, 0.201 and 0.524. The CSM value for the corresponding structure in PdAu₂₄(SR)₁₈⁰ is 0.350, falling between the values previously observed for the neutral and cationic Au₂₅(SR)₁₈ species.

We observe that the Pd-Au bond lengths in this structure are shorter than Au-Au bond lengths. Overall, this appears to result in a contraction around the Pd centroid with resulting shortening of the gold-gold bonds of the PdAu₂₄(SR)₁₈ icosahedron by an average of 0.04 Å. Thus, the higher stability of PdAu₂₄(PET)₁₈⁰ compared to Au₂₅(SR)₁₈ suggested by previous results may be attributed to an overall stronger bonding in the inorganic core.^{2,28}

We isolated the PdAu₂₄(PET)₁₈ as the neutral (1S²1P⁴) compound without taking any measures to preserve the oxidation state of the cluster. We suggest that the as-synthesized PdAu₂₄(PET)₁₈ is in the -2 charge state (1S²1P⁶, presumably more stable). We suggest that, similar to Au₂₅(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 PdAu₂₄(PET)₁₈ compared to Au₂₅(PET)₁₈, oxidation in the presence of atmospheric oxygen is expected to be more facile.

Herein we report the crystal structure of PdAu₂₄(PET)₁₈⁰ revealing that Pd is localized to the cluster core, which retains the same atomic connectivity and nearly identical geometry to Au₂₅(PET)₁₈^{-0,+} clusters. The Pd dopant results in shorter bonds in the 13-atom core and a blue-shift in the UV/Vis spectrum. Overall we suggest that PdAu₂₄(PET)₁₈, like Au₂₅(SR)₁₈ is well predicted by a spherical superatom model.

During revision of this manuscript we became aware of a similar report of structures of doped XAg₂₄(SR)₁₈ clusters, where X is Pt or Pd.²⁹ Notably these authors arrive at the same conclusion regarding the contribution of Pt or Pd to the superatom electron count.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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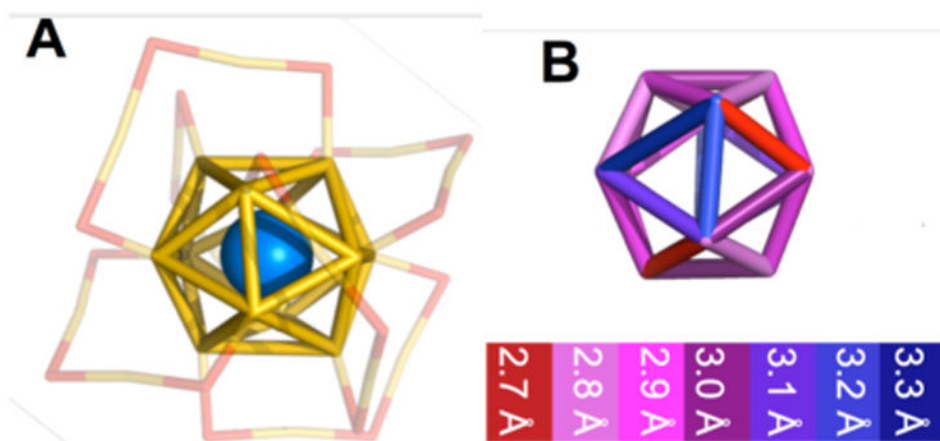


Figure 1. Shown in A is the crystal structure of PdAu₂₄(PET)₁₈ with gold in yellow, thiol in red and palladium in blue. The carbon chains have been removed for clarity. Panel 1B is illustrates bond lengths of the gold icosahedron.

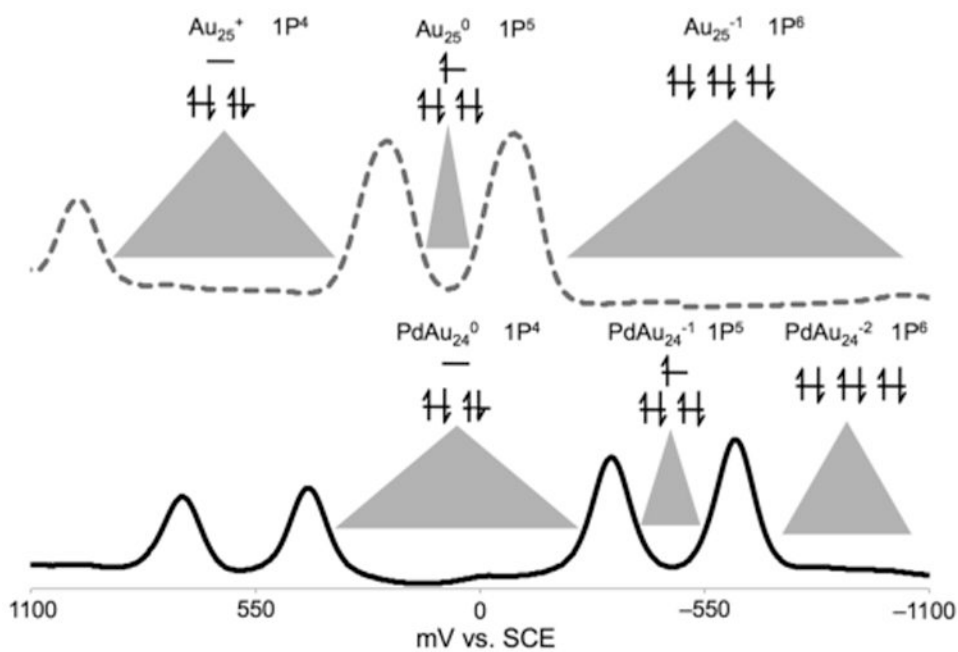


Figure 2. Shown above are the square wave voltammograms of $\text{PdAu}_{24}(\text{PET})_{18}$ and $\text{Au}_{25}(\text{PET})_{18}$. The current axis is offset and normalized for comparison.