

Tuning the Electronic Structure of Atomically Precise Sn/Co/Se Nanoclusters via Redox Matching of Tin(IV) Surface Sites

Benjamin S. Mitchell, Werner Kaminsky, and Alexandra Velian*

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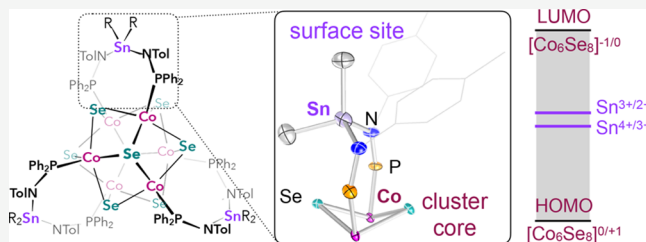
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ABSTRACT: A new strategy is reported to tailor the electronic properties of a superatomic metal chalcogenide cluster by redox matching the cluster core with surface tin(IV) sites. Two ternary clusters $(\text{SnR}_2)_3\text{Co}_6\text{Se}_8\text{L}_6$ ($\text{R} = \text{Me}, n\text{Bu}$) are synthesized by salt metathesis from the hexalithiated salt $[\text{Li}_2(\text{py})_2]_3\text{Co}_6\text{Se}_8\text{L}_6$ and R_2SnCl_2 . Cyclic and differential-pulse voltammetry studies reveal that the tristannylated clusters feature two new, near-degenerate, electronic states within the highest occupied molecular orbital–lowest unoccupied molecular orbital gap of the Co_6Se_8 core, which are attributed to the reduction of a surface tin site. Single-crystal X-ray diffraction analysis reveals that no $\text{Sn}\cdots\text{Se}$ coordination is present in the solid state. The single-crystal X-ray structure of the hexalithiated salt starting material is reported for the tetrahydrofuran (THF) adduct variant $[\text{Li}_2(\text{THF})_2]_6\text{Co}_6\text{Se}_8\text{L}_6$.

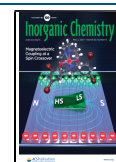


Chevrel-type molecular clusters $\text{M}_6\text{Ch}_8\text{L}_6$ ($\text{M} = \text{Cr}, \text{Co}, \text{Re}, \text{Mo}$; $\text{Ch} = \text{S}, \text{Se}, \text{Te}$; L = organic ligand) have resurfaced in recent years as potent building blocks for hierarchical nanomaterials.^{1–4} Highly symmetrical and chemically robust with rich electronic and magnetic properties, these clusters have attractive “superatomic” qualities, promising access to atomically precise materials with programmable functions. While their chemical stability enables these superatomic clusters to retain structural identity with minimal entropic changes upon assembly or redox manipulations, their large highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) gaps limit pathways to couple them and form electronic bands. Strategies to tune their electronic properties have primarily focused on the nature of the capping ligands, but these have had limited impact.^{5–7} Surface functionalization with energy-matched metals has been a successful strategy to tune the electronic structure of wide-band semiconductors.⁸ Inspired by this approach, our group previously demonstrated that the coordination of metals ($\text{M} = \text{Fe}, \text{Co}, \text{Zn}$) to the exposed chalcogens of Co_6Se_8 clusters is an effective strategy to narrow their HOMO–LUMO gaps (Figure 2b), while engendering catalytic activity^{9,10} or directing their assembly into van der Waals 2D superatomic crystals.⁴ Although the M – Se interaction is effective at stabilizing the LUMO level, the surface metals explored thus far did not introduce any new electronic states near the Co_6Se_8 -localized frontier orbitals. Upon evaluation of the reduction potentials of possible surface site metal candidates, tin stands out, with a $4+/2+$ redox couple that is energetically matched with the band gap of the Co_6Se_8 cluster, and the attractive possibility of introducing two closely spaced low-lying electronic states near the frontier orbitals.

The relative instability of the $3+$ valence state, or “valence skipping”, is a defining feature of tin chemistry that could also serve the goal of introducing multielectron states near the frontier orbitals of the Co_6Se_8 cluster. In inorganic materials (e.g., InTe , SnAs , $\text{Ag}_{1-x}\text{Sn}_{1+x}\text{Se}_2$), this advantageous local electron pairing has attracted a lot of attention because it might be responsible for superconductivity, charge-density waves, and other interesting solid-state physical phenomena.^{11–14} While the redox properties, or valence skipping, in atomically precise tin chalcogenide clusters has been largely unexplored,¹⁵ examples of mixed-valent and Sn^{3+} -containing clusters have been reported.^{16–18} Monometallic organotin complexes ($\text{Sn}^{\text{IV}}\text{R}_4\text{X}_{4-y}$; R = alkyl or aryl, X = halide) are known to undergo direduction to Sn^{2+} species via two closely spaced single-electron-transfer events, generally observed between ca. -1.1 and -1.6 V versus $\text{Fc}^{0/+}$ (Fc = ferrocene),^{19–22} which lies within the HOMO–LUMO gap of the Co_6Se_8 cluster. Interestingly, dialkyltin fragments have been used extensively in cluster chemistry as cationic linkers to polyoxometallate anions; however, their $\text{Sn}^{4+}/\text{Sn}^{2+}$ reduction could not be observed in these otherwise redox-active systems.^{23–26} Here we report that surface functionalization with dialkyltin units introduces two energy-accessible and closely spaced states within the band gap of the Co_6Se_8 cluster, demonstrating a

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new strategy to tune the electronic properties of this superatomic metal chalcogenide cluster.

Our group has introduced the $\text{Co}_6\text{Se}_8\text{L}_6$ [1-H_6 ; $\text{L}^{\text{H}} = \text{Ph}_2\text{PN}(\text{H})\text{Tol}$; Tol = 4-tolyl] cluster as an unusual metal-ligand with three coordination sites on its surface. The synthetic protocol to access trimetalated $\text{M}_3\text{Co}_6\text{Se}_8\text{L}_6$ (1-M_3) clusters relies on $[\text{Li}_2(\text{py})_2]_3\text{Co}_6\text{Se}_8\text{L}_6$ ($1\text{-}[\text{Li}_2(\text{py})_2]_3$; py = pyridine) as a starting material.⁹ Surprisingly stable to isolation and with a seemingly indefinite shelf life, this formally hexaanionic salt garnered special interest because its structure would shine light on how a single Co_6Se_8 cluster might accommodate six metals on its surface. Herein, we found that simply exchanging the pyridine for tetrahydrofuran (THF) enabled the isolation of $1\text{-}[\text{Li}_2(\text{THF})_2]_3$, which could be characterized by single-crystal X-ray diffraction (Scheme 1 and

Scheme 1. Synthesis of $1\text{-}(\text{SnR}_2)_3$ Clusters

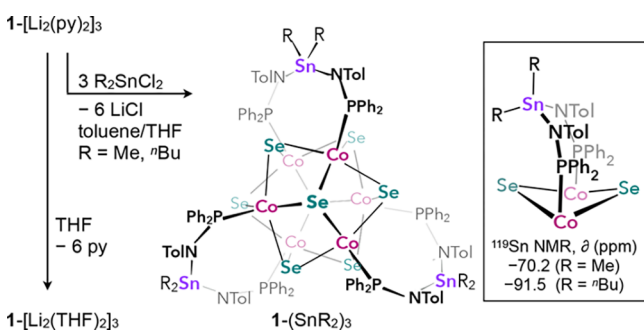


Figure 1a). Each pair of lithium ions, locked in a Li_2N_2 diamond core and anchored to the cluster via the two amides, is positioned directly above the two exposed selenium atoms, delineating a total of three $[\text{LiNPSeCo}]_2$ cages that extend the inorganic Co_6Se_8 core (Figure 1a). The multicage structure of this salt demonstrates the remarkable versatility of the $\text{Co}_6\text{Se}_8\text{L}_6$ metalloligand and raises interesting possibilities for

how it might accommodate in this fashion other, more chemically versatile, metals.

To synthesize the tritin derivatives $(\text{SnR}_2)_3\text{Co}_6\text{Se}_8\text{L}_6$ ($1\text{-}(\text{SnR}_2)_3$; R = Me or $n\text{Bu}$), $1\text{-}[\text{Li}_2(\text{py})_2]_3$ was treated with the respective R_2SnCl_2 (Scheme 1). Following a solvent workup to remove LiCl, $1\text{-}(\text{SnR}_2)_3$ was isolated pure as a dark-red solid (Me, 33%; $n\text{Bu}$, 56%). Multinuclear NMR analysis indicates that in solution $1\text{-}(\text{SnR}_2)_3$ is highly symmetrical, displaying single environments for the amidophosphines and SnR_2 . Single broad peaks are observed by ^{31}P NMR spectroscopy at +114.0 ppm ($\nu_{1/2} = 303$ Hz) and +115.3 ppm ($\nu_{1/2} = 281$ Hz) for $1\text{-}(\text{SnMe}_2)_3$ and $1\text{-}(\text{Sn}^n\text{Bu}_2)_3$, respectively, shifted downfield from +80.7 ppm for $1\text{-}[\text{Li}_2(\text{py})_2]_3$. While not discernible in $1\text{-}(\text{Sn}^n\text{Bu}_2)_3$, $^{117/119}\text{Sn}$ satellites flank the ^1H NMR methyl resonance of $1\text{-}(\text{SnMe}_2)_3$, with a coupling constant of 55 Hz.

With a wide NMR spectral window spanning from ca. +4000 to −2500 ppm, the chemical shift of the ^{119}Sn nucleus is a potent reporter on the chemical environment of the tin center.²⁸ For example, tetracoordinate tin(IV) bisamide bisalkyl complexes display ^{119}Sn chemical shifts between −10 and +60 ppm,^{29–31} while pentacoordinate tin(IV) complexes feature signals at increasingly upfield values that empirically correlate with the strength of the interaction between the tin and the fifth ligand.^{32–36} In solution, the three equivalent tin centers of $1\text{-}(\text{SnR}_2)_3$ each display a single resonance, at −70.2 ppm ($\nu_{1/2} = 191$ Hz) for the methyl derivative and at −91.5 ppm ($\nu_{1/2} = 210$ Hz) for the n -butyl derivative. While these upfield ^{119}Sn NMR chemical shifts suggest that a weak $\text{Se}\cdots\text{Sn}$ donor–acceptor interaction might transiently occur in solution, the solid-state structural data show no formal coordination of a fifth selenium ligand, as discussed below. Of all of the surface-functionalized Co_6Se_8 clusters reported thus far, including those with iron,^{9,10} cobalt,⁴ zinc,¹⁰ or lithium, $1\text{-}(\text{SnMe}_2)_3$ is the only one in which the surface metal does not coordinate to the exposed selenium, even as five- and six-coordinate organometallic tin(IV) is ubiquitous.²⁷

In contrast to the rigid and highly chelated structure of $1\text{-}[\text{Li}_2(\text{THF})_2]_3$, metalation with tin forms three flexible $\text{Sn}/\text{N}/\text{P}/\text{Co}/\text{Se}$ macrocycles with the cluster surface (Figure 1b). In the solid state, the Me_2Sn units of $1\text{-}(\text{SnMe}_2)_3$ are no longer equivalent as they appear in solution by NMR but instead are locked in asymmetric orientations. Each tin site leans toward one of the exposed selenium atoms, giving rise to one short and one long $\text{Sn}\cdots\text{Se}$ interatomic distance. The shortest $\text{Sn}\cdots\text{Se}$ contact (avg. 3.20 Å), however, remains significantly longer than 2.62 Å, the average value for a $\text{Sn}\text{—}\text{Se}$ bond in five-coordinate tin(IV) complexes.^{27,37}

Compared to iron, cobalt, or zinc, the SnMe_2 unit is bulkier, causing a notable opening of the $\text{Co}\text{—}\text{P}\text{—}\text{N}$ angles from $110.6 \pm 0.8^\circ$ in the triiron derivative to $119 \pm 2^\circ$. This distortion is accompanied by a contraction in the average $\text{P}\text{—}\text{N}$ bond distances from 1.69 to 1.55 Å. While the SnMe_2 units put strain on the organic ligands [i.e., $\text{Ph}_2\text{P}\text{—}\text{N}(\text{Tol})$], the inorganic Co_6Se_8 core remains virtually unchanged compared to 1-H_6 , forgoing the distortions previously observed upon surface metal (i.e., iron, cobalt, and zinc) coordination.^{4,9,10} Indeed, the extent of the distortions in the Co_6Se_8 cluster core is proportional to the strength of the interaction between the surface metal M and the exposed selenium. For example, zinc forms weaker bonds with selenium compared to iron, causing less distortion in the cobalt core.⁴

The stannylation is associated with a red shift in the electronic absorption spectrum of $1\text{-}(\text{SnR}_2)_3$ compared to 1-H_6

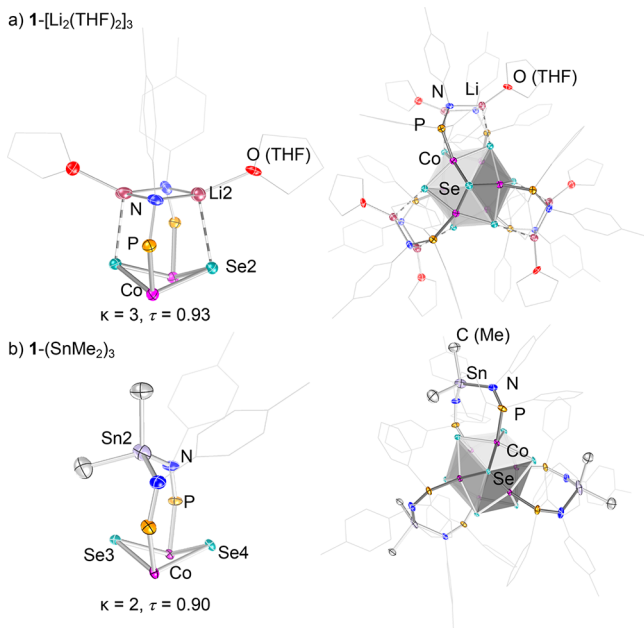


Figure 1. Solid-state structure of (a) $1\text{-}[\text{Li}_2(\text{THF})_2]_3$ and (b) $1\text{-}(\text{SnMe}_2)_3$. Hydrogen atoms, cocrystallized solvent molecules, and disorder are omitted for clarity. Thermal ellipsoids are plotted at 50%.

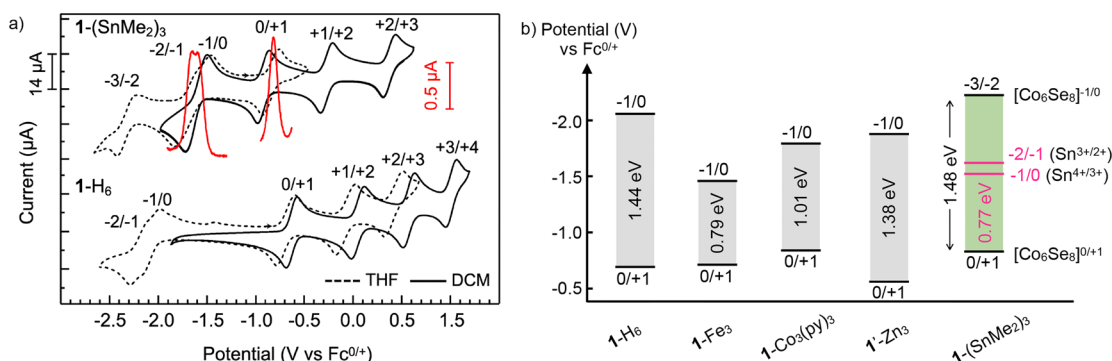


Figure 2. (a) Cyclic voltammograms of $1-(\text{SnMe}_2)_3$ and $1-\text{H}_6$ recorded in dichloromethane or THF (black), with overlaid differential-pulse voltammograms (red, in THF). (b) Relative energies of the HOMO ($0/+1$) and LUMO ($-1/0$) levels in Co_6Se_8 -based clusters: $1-\text{H}_6$; $1-\text{Fe}_3$; $1-\text{Co}_3$; $1'-\text{Zn}_3$ [$\text{Zn}_3\text{Co}_6\text{Se}_8(\text{Ph}_2\text{PN}^i\text{Pr})_6$; $i\text{Pr}$ = isopropyl], and $1-(\text{SnMe}_2)_3$, approximated from the electrochemical data. For $1-(\text{SnMe}_2)_3$, the LUMO, LUMO+1, and LUMO+2 levels are plotted.

and a new shoulder feature at ~ 680 nm ($\epsilon = 6415\text{--}6645$ $\text{M}^{-1}\text{cm}^{-1}$), possibly related to the 503 nm absorption feature in $1-\text{H}_6$ ($\epsilon = 29883$ $\text{M}^{-1}\text{cm}^{-1}$; Figures S10 and S11). These data provide a first indication that tin impacts the frontier orbital transitions, narrowing the HOMO–LUMO gap.

To further investigate how the three redox-active Sn^{4+} sites affect the electronic structure of the ternary $1-(\text{SnMe}_2)_3$ cluster, cyclic and differential-pulse voltammetry experiments were performed. Like all Co_6Se_8 -based clusters, the tritin clusters $1-(\text{SnR}_2)_3$ reveal rich redox profiles, with six single-electron redox events (Figures 2a and S12). The more electron-rich dialkyltin units shift the three cluster core-based oxidation events to more cathodic potentials by ca. 200–300 mV compared to the parent ligand (Table S1); however, they still closely resemble the electrochemical behavior of $1-\text{H}_6$ at anodic potentials.

More interestingly, the electrochemical reduction of $1-(\text{SnR}_2)_3$ proceeds markedly differently from that of the parent metalloligand $1-\text{H}_6$. The HOMO–LUMO gap, approximated electrochemically as the energy difference between the first oxidation and first reduction, contracts significantly from 1.44 eV in $1-\text{H}_6$ to 0.77 eV in $1-(\text{SnMe}_2)_3$ and 0.83 eV in $1-(\text{Sn}^n\text{Bu}_2)_3$. Compared to the other one-electron redox events, the first reduction of $1-(\text{SnR}_2)_3$ features a notably larger area size suggestive of a multielectron event. Differential-pulse voltammetry was employed to better resolve this feature and revealed two closely spaced single-electron reductions (Figures 2a and S12). Considering the data and the literature on Sn^{4+} reduction,^{19–22} we attribute the first two reductions of the $1-(\text{SnR}_2)_3$ clusters to the $\text{Sn}^{4+/3+}$ and $\text{Sn}^{3+/2+}$ couples, respectively, and only the third reduction ($-3/-2$) to $[\text{Co}_6\text{Se}_8]^{1-/0}$.

While tin introduces two new states to the ternary cluster, the lack of significant $\text{Sn}\cdots\text{Se}$ interactions is expected to result in no stabilization of the LUMO level of the Co_6Se_8 core. Indeed, although all redox events are shifted cathodically compared to those of $1-\text{H}_6$, the HOMO–LUMO gap of the Co/Se core (approximated by the energy difference between $[\text{Co}_6\text{Se}_8]^{1-/0}$ and $[\text{Co}_6\text{Se}_8]^{0/+1}$) remains almost constant upon stannylation, with values of 1.44, 1.47, and 1.51 eV for $1-\text{H}_6$, $1-(\text{SnMe}_2)_3$, and $1-(\text{Sn}^n\text{Bu}_2)_3$, respectively (Figure 2b). In contrast, the HOMO–LUMO gap in the $1-\text{M}_3$ derivatives becomes more narrow as the strength of the $\text{M}\cdots\text{Se}$ interaction increases. Notably, switching the methyl groups in $1-(\text{SnMe}_2)_3$ with the more electron-rich *n*-butyl groups has the most

pronounced effect on the first two reduction events, which shift to more reducing potentials by 60 and 110 mV, respectively, whereas the third reduction attributed to the cobalt core shifts by only 30 mV.

The metalloligand $1-\text{H}_6$ enforces a cis orientation of the alkyl groups in the R_2Sn unit, while also providing sufficient flexibility to accommodate the seesaw geometry of a putative tin(II) center formed upon reduction.^{39,40} In contrast to the ubiquitous instances where the alkyl groups are positioned trans to each other, these features of the metalloligand minimize the entropic changes expected to occur upon the reduction of tin(IV) to tin(II), positively impacting the reversibility of the process in $1-(\text{SnMe}_2)_3$.^{21,22} However, although the electrochemical direduction attributed to one of the SnMe_2 sites is surprisingly well-behaved and quasireversible (section S4.1),³⁸ the chemical reduction of $1-(\text{SnMe}_2)_3$ using decamethylcobaltocene or sodium naphthalenide has thus far been unproductive toward conclusive observation or isolation of the reduced cluster.

In conclusion, we introduced a new strategy to tune the electronic properties of a synthetically addressable cobalt chalcogenide cluster by matching the energies of surface-tethered redox-active sites. By judiciously choosing tin, a metal with an intrinsic preference for valence skipping that is redox-matched to the HOMO–LUMO gap of the cobalt cluster core, we deterministically introduce two new energetically accessible electronic states in the ternary cluster $1-(\text{SnMe}_2)_3$. The sequential direduction of $1-(\text{SnMe}_2)_3$ poses intriguing questions about the formation and electronic structure of the proposed mixed-valent $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}\text{Sn}^{\text{IV}}$ site–differentiated cluster, the further investigation of which could shine light on complex physical phenomena such as valence skipping and two-electron defects in metal chalcogenide materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00313>.

Synthetic protocols, supporting characterization, and experimental data (PDF)

Accession Codes

CCDC 2052049 and 2052050 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by

emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Alexandra Velian – Department of Chemistry, University of Washington, Seattle, Washington 98195, United States;
orcid.org/0000-0002-6782-7139; Email: avelian@uw.edu

Authors

Benjamin S. Mitchell – Department of Chemistry, University of Washington, Seattle, Washington 98195, United States
Werner Kaminsky – Department of Chemistry, University of Washington, Seattle, Washington 98195, United States;
orcid.org/0000-0002-9100-4909

Complete contact information is available at:
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Notes

The authors declare no competing financial interest.

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