Building Diatomic and Triatomic Superatom Molecules

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Supporting Information

ABSTRACT: In this study, we have developed a method to create Co₆Se₈ superatoms in which we program the metal–ligand bonds. We exclusively form the Co₆Se₈ core under simple reaction conditions with a facile separation of products that contain differential substitution of the core. The combination of Co₆(CO)₈ and PR₃ with excess Se gives the differentially and directionally substituted superatoms, Co₆Se₈(CO)ₓ(PR₃)₁⁻ₓ. The CO groups on the superatom can be exchanged quantitatively with phosphines and isonitriles. Substitution of the CO allows us to manipulate the type and length of chemical bridge between two redox-active superatomic centers in order to modulate intersuperatomic coupling. Linking two superatoms together allows us to form the simplest superatom molecule: a diatomic molecule. We extend the superatom molecule concept to link three superatoms together in a linear arrangement to form acyclic triatomic molecules. These superatom molecules have a rich electrochemical profile and chart a clear path to a whole family of superatom molecules with new and unusual collective properties.

KEYWORDS: Superatoms, nanoscale atoms, superatom molecules, nanoscale building blocks

In this study, we create the superatomic¹⁻⁴ version of the simplest molecules, diatomic and linear triatomic molecules. The constituent superatoms are atomically defined clusters of metal chalcogenides that are capped with passivating two-electron ligands. The key to being able to discretely link these superatoms into superatom molecules (SMs) was to control the reaction chemistry of the capping ligands and to thereby program the intersuperatom bonding. Having control over the geometry, distance, and linker between the superatoms is crucial to further the understanding of how to promote electronic and magnetic coupling within SMs. Previous studies on colloidal semiconductors have gone to great lengths to link electronic and magnetic nano-objects allows collective properties to emerge. The study here provides a means to synthesize ~1 nm superatoms and to couple them together into molecular form with atomic precision and having a well-defined surface definition/bonding.

Prior studies on superatoms have focused on the “outersphere” reaction chemistry of cobalt chalcogenide clusters and created solid-state materials via either the transfer of electrons from the cluster to acceptors such as fullerenes¹²⁻¹⁴ or the molecular recognition of fullerenes by fluxional phenanthrene ligands (Figure 1a).¹⁵ In these cases, the essential structure of neither the inorganic core of the superatoms nor the ligand shell changes. As such, these superatoms in this context form extended solid-state materials with tunable properties. Those approaches have relied on self-assembly and shape complementarity; here we describe reactions of the superatoms in which we manipulate the metal–ligand bonds by intentionally including labile surface-ligands. We prepare a series of superatoms, Co₆Se₈(CO)ₓ(PR₃)₁⁻ₓ (x = 1–5, R = Et, Ph) and show that they are stereochemically robust. These new superatoms undergo CO-displacement reactions with neutral two-electron donors (phosphines and isocyanides) and these reactions depend on the ligand arrangements of the initial superatoms. These “inner-sphere” reactions allow us to form diatomic and linear triatomic SMs (Figure 1b).

Superatoms having neutral cores capped with phosphate ligands are typically synthesized so that each ligand coordinates to a metal atom to form, for example, MₓEₓ(PR₃)₅ structures (M = Cr, Co, Mo, Rh; E = S, Se, Te).¹⁶⁻²⁰ Substitution reactions of these phosphines are difficult because the M–P bonds tend to display low chemical reactivity at moderate temperatures and indiscriminate reactions at higher temperatures; the latter thermal reactions typically yield solid-state products.²¹,²² Moreover, the differentiation of one of the phosphines from another in a symmetrically substituted metal chalcogenide cluster is a vexing challenge.

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Here we sought a bottom-up approach to SMs by developing simple solution-phase chemistry to synthesize electrically neutral and directionally substituted superatoms in one step. We were inspired by the rich reaction chemistry developed for Re₆Se₈L₆ clusters.²³−²⁹ Our important finding is a simple and mild synthesis of heteroleptic Co₆Se₈ superatoms. The subsequent separation of different regioisomers is facile and efficient. We further demonstrate that the reaction chemistry of trans- and cis-dicarbonylated superatoms offers a clear path to linear, bent, cyclic, and oligomeric SMs.

Our synthesis of differentially substituted Co₆Se₈ superatoms refines previous methods:³⁰−³² the combination of Co₂(CO)₈ and PR₃ with a significant excess of Se produces the family of substituted superatoms, Co₆Se₈(CO)x(PR₃)₆−x. We require some amount of phosphine to passivate the Co₆Se₈ core, but the stoichiometric excess of Se effectively decreases the amount of phosphine available to displace the carbonyl groups and thus modulates x. While mixtures of the carbonylated superatoms are produced regardless of the initial reagent ratios, the PR₃/Se stoichiometry governs the average value of x. We separated particular superatoms using conventional silica gel chromatography, relying on the distinct and diagnostic ¹H NMR for each of the ligand substitution patterns around the Co₆Se₈ core (detailed in the Supporting Information).

We focus on three basic Co₆Se₈ superatom building blocks: two with two CO groups in either a cis or trans arrangement and the monocarbonylated superatom, (Figure 2) because they constitute fundamental blocks with which to build diatomic and triatomic SMs as well as one- and two-dimensional materials. The Co₆Se₈ superatom core is built from a slightly distorted octahedron of six cobalt atoms each face of which is capped by a selenium atom. The superatomic cores of Co₆Se₈(CO)x(PR₃)₆−x are isostructural and they show no clear systematic trend in the Co-Co, Co-Se, or Co-P distances (Table S1).

By modifying the reaction and purification conditions, we also isolate and crystallographically characterize both mer- and fac-Co₆Se₈(CO)₃(PhP₃)₃, cis- and trans-Co₆Se₈(CO)₃(PhP₃)₃.

Figure 1. (a) Previously studied outer-sphere reactions of Co₆Se₈(PR₃)₆ superatoms. (b) We study here the inner-sphere reactions of Co₆Se₈(CO)x(PR₃)₆−x.

Scheme 1. Mono- and Disubstitution of trans-Co₆Se₈(CO)₂(PEt₃)₄

The formation of products can be controlled by the stoichiometry of the ligand.
Co₆Se₈(CO)₃(PPh₃)₃, and Co₆Se₈(CO)₅(PPh₃) (Figure S1). We also extended these reactions to tellurium: the same reaction conditions yield a distribution of Co₆Te₈(CO)ₓ(PET₃)₆−x (Figure S2). The tellurium-containing superatoms are more difficult to chromatograph due to their greater sensitivity to ambient conditions.

The CO ligands are chemically active and the substitution reaction is induced photochemically. This behavior is similar to that of metal carbonyl complexes undergoing dissociation and substitution of CO ligands upon photolysis. Scheme 1 shows the substitution reactions in which two electron donors such as phosphines and isocyanides replace the CO of the trans-CO superatom. Room temperature irradiation of a THF solution of the superatom with a 200−400 nm broadband lamp allows a selective substitution of CO groups. When we irradiate a solution of trans-Co₆Se₈(CO)₂(PEt₃)₄ containing two equivalents (per superatom) of the incoming electron donor ligand, we obtain the product in quantitative yields. When we treat the same superatom with less than 2 stoichiometric equivalents of the ligand, we obtain a mixture of the monosubstituted and disubstituted products (Scheme 1).

There are two important findings in these reactions. (1) The stereochemistry of either the cis- or trans- arrangement of the CO groups is maintained in these reactions. The implication is that the phosphine ligands are not fluxional during this process. (2) The reactions only substitute the CO groups, not the phosphines. These two findings demonstrate that selective chemistry is possible to build up SMs and one-, two-, and higher-dimensional materials with either of the CO-substituted superatoms.

We create the simplest SMs, diatomic and acyclic triatomic SMs, by replacing the CO group with chemical bridges. Appropriate ditopic ligands link two redox-active superatomic centers, and varying these ligands modulates intersuperatomic coupling. The linking chemistry of the cis- and trans-dicarbonylated superatoms is similar; in making the SMs, we focus only on the chemical reactions of trans-Co₆Se₈(CO)₂(PEt₃)₄ isomer. In the SM aufbau, the trans-Co₆Se₈(CO)₂(PEt₃)₄ is a link and Co₆Se₈(CO)(PEt₃)₅ is a cap. We chose 1,4-phenylene diisocyanide (CNC₆H₄NC), a rigid linear linker.

From the building blocks trans-Co₆Se₈(CNC₆H₄NC)₂(PEt₃)₄, 1,4-phenylene diisocyanide, and Co₆Se₈(CO)(PEt₃)₅, we synthesized a diatomic SM Co₁₂Se₁₆(PEt₃)₁₀(CNC₆H₄NC) and linear triatomic SM Co₁₈Se₂₄(PEt₃)₁₄(CNC₆H₄NC)₂ (Figure 1b). We prepare the superatom in Figure 3a in quantitative yields from the photolysis of trans-Co₆Se₈(CO)₂(PEt₃)₄ in the presence of excess 1,4-phenylene diisocyanide. We can form cis-Co₆Se₈(CNC₆H₄NC)₂(PEt₃)₄ similarly from its cis-CO precursor (Figure 3b). ¹H NMR confirms formation of the diatomic SM and the linear triatomic SM (Figures S4 and S5).

Figure 3c displays the crystal structure of the diatomic SM in its doubly oxidized form [Co₁₂Se₁₆(PEt₃)₁₀(CNC₆H₄NC)]²⁺[PF₆]₂. We isolate this by treating two equivalents of the oxidized superatom [Co₆Se₈(CO)(PEt₃)₅][PF₆] with one equivalent of linker (see Supporting Information for details). The diatomic SM is symmetrical about the linker with crystallographically equivalent Co₆Se₈ superatomic cores. Figure S6 displays the UV−vis spectrum for the monomeric superatom (trans-Co₆Se₈(CNC₆H₄NC)₂(PEt₃)₄), the diatomic
SM, and triatomic SM. Each of the spectra has a long tail that extends into the near-IR.

We used electrochemical methods to investigate electronic coupling between the cores of the diatomic and linear triatomic SMs. In order to understand how the electronic properties of isocyanide-bridged superatom oligomers compare to those of a single Co$_6$Se$_8$ core, we prepared two monomers as points of reference: mono- and di-substituted superatoms with 2,6-dimethylphenyl isocyanide (See Supporting Information for synthetic details). The isocyanide-substituted superatoms behave similarly to their CO-substituted analogues (Figure S7); the strong pi-acceptor ligands bonded to the Co$_6$Se$_8$ core make it less electron rich than the parent Co$_6$Se$_8$(PET$_3$)$_6$ (Table S2). The cyclic voltammograms of both species are shown in Figure 4a and as expected, the $E_p$ values (i.e., the peak value of the potential) of each superatom differ and are dependent upon the ligand environment.

The electrochemistry of the diatomic SM and the linear triatomic SM is rich in information. While the neutral diatomic SM exhibits three reversible oxidation peaks (Figure 4b), the neutral triatomic SM exhibits discernible electrochemical splitting (Figure 4c). This splitting is even more pronounced when the voltammogram is taken in nitrobenzene (Figure 4d), a solvent with a much higher dielectric constant, known to better stabilize charged species ($\epsilon_{\text{THF}} = 7.58$ vs $\epsilon_{\text{nitrobenzene}} = 34.82$). We determined that each of the three reversible oxidation peaks in the CV of the neutral diatomic SM (Figure 4b) corresponds to a two-electron event as follows: under the same conditions we measured the open circuit potential of the diatomic SM dication as $-0.671$ V versus the ferrocene/ferrocenium redox couple. This potential corresponds to the species formed after the first oxidation event (at $E_{1/2} \sim -0.8$ V in Figure 4c) in the trimer as the 0 to +3 transition. We therefore attribute the pronounced splitting behavior of the linear triatomic SM to the existence of two types of superatoms, bridging and terminal, whose redox potentials differ. The smooth redox peaks of the dimer arise because each is a terminal unit oxidized at the same potential.

Magnetic susceptibility measurements of the oxidized superatom [Co$_6$Se$_8$(CO)(PET$_3$)$_5$][PF$_6$], as well as the doubly oxidized diatomic SM [Co$_{12}$Se$_{16}$(PET$_3$)$_{10}$(CNC$_6$H$_4$NC)]$_2$[PF$_6$]$_2$ elucidate their open-shell characteristics (Figure S8). Specifically, [Co$_6$Se$_8$(CO)(PET$_3$)$_5$][PF$_6$] shows a temperature-independent magnetic susceptibility ($X_M$) with $X_M = 0.45$ cm$^3$K/mol at $T = 3$ K, suggesting that the core contains one unpaired electron with a $g$-factor greater than 2 (spin-only value $S = 1/2$ of an unpaired electron is 0.375 cm$^3$K/mol for $g = 2$). The doubly oxidized diatomic SM has $X_M = 0.91$ cm$^3$K/mol at $T = 3$ K. This result suggests that the diatomic SM contains two noninteracting spins, each having $X_M$ of the monomeric species.

In summary, we have found a simple method to synthesize and isolate Co$_6$Se$_8$ superatoms that are substituted with both phosphine and carbonyl ligands. The CO ligands can be replaced with two electron donors such as phosphines and isocyanides. From the trans-CO superatom and monocarbonylated superatom we can create diatomic SMs and linear triatomic SMs that are linked together with diisocyanides. Forming these new SMs is an important step toward studying SMs in single molecule and materials applications. The method described here gives access to the vast number of magnetic and electroactive superatoms whose intersuperatom coupling can be easily varied by changing the linker. For example, we are exploring mixed Se/Te systems, which we can access by covalently linking Co$_6$Se$_8$ and Co$_6$Te$_8$ carbonylated super-
tomato. The hetero diatomic superatoms offer a unique opportunity to study the magnetic coupling between two spins as the linker is modified. Moreover, the reaction of the trans-CO superatom and a ditopic linker would give rise to oligomeric SM chains.

**REFERENCES**


(34) We treat the starting material with an excess of the linker (5 equivalents) to prevent undesired oligomerization and subsequently remove the leftover linker by trituration.
