Endohedral Tin Cages

Endohedral Stannaspherenes M@Sn₁₂ : A Rich Class of Stable Molecular Cage Clusters

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Since the discovery and bulk synthesis of fullerenes[1,2] there have been great expectations in cluster science to uncover other stable atomic clusters that may be used as building blocks for cluster-assembled nanomaterials. The heavy congeners of carbon in Group 14 were not known to form fullerene-like empty cage structures until very recently, when it was discovered serendipitously that a 12-atom Sn cluster forms a highly stable empty cage (Sn₁₂²⁻, stannaspherene)[3] with a large inner diameter (6.1 Å) that is only slightly smaller than that of C₆₀. Although polyhedral cages are common in inorganic compounds[4,5] empty cage clusters with large internal volumes are rare.[6,7] Stannaspherene can be viewed as a real inorganic analogue of the fullerenes because of its spherical σ bonding,[3] which is similar to that in the B₁₂H₁₂²⁻ cage molecule.[8,9] Several metal-encapsulated cage clusters of heavy Group 14 elements are known,[10–22] but the metal encapsulation was thought to be essential to stabilize the cage structure. Here, we report that stannaspherene can trap an atom from any of the transition metals or the f-block elements to form a large class of new endohedral cage clusters. We have produced a set of M@Sn₁₂ cages (M = Ti, V, Cr, Fe, Co, Ni, Cu, Y, Nb, Gd, Hf, Ta, Pt, Au) by laser vaporization and characterized them by photoelectron spectroscopy. Both experimental and theoretical evidence shows that these clusters have perfect or pseudo-icosahedral symmetry, with the central atom inducing very little distortion in the Sn₁₂⁻ cage. Since the central atom in M@Sn₁₂⁻ maintains its quasi-atomic nature, as in the endohedral fullerenes[23,24] the clusters are a rich class of potential building blocks for new materials with tunable electronic, magnetic, or chemical properties.

The experiment was carried out on a magnetic-bottle photoelectron spectroscopy apparatus equipped with a laser vaporization cluster source (see Experimental Section).[25] Figure 1 shows the 193-nm photoelectron spectra of Sn₁₂⁻ doped with 3d transition metals and selected 4d and 5d dopants. (More spectra with other dopants, including rare-earth elements, are given in the Supporting Information.) All spectra are well resolved and show numerous distinct electronic transitions. In general, the spectra of M@Sn₁₂⁻ become more complicated as one moves from Cu to the left of the transition series due to the open d shell and the relative orbital-energy variation of the 3d electrons, which are core-like in Cu but become frontier levels in the early transition metals. Remarkably, there is a characteristic doublet feature near 5 eV (labeled g₀ in Figure 1), which is present in all spectra, with little variation between the different M@Sn₁₂⁻ species.
Our previous study has shown that the stannaspherene Sn$_{12}^-$ possesses an inner diameter of 6.1 Å, which is large enough to trap any transition metal, f-block element, or certain main-group elements. The doublet feature near 5 eV in all M@Sn$_{12}^-$ clusters bears considerable resemblance to similar spectral features primarily derived from the on-sphere g, o orbitals in stannaspherene (Figure 3), which suggests that all M@Sn$_{12}^-$ clusters possess similar structures and that the Sn$_{12}$ cage is intact in M@Sn$_{12}^-$. Cu@Sn$_{12}^-$ is a perfect icosahedral cluster (I$_h$; Figure 2) with a Sn–Sn distance (3.21 Å) very close to that in stannaspherene (3.19 Å), which suggests only moderate interactions between the central Cu atom and the Sn$_{12}$ cage. The Cu–Sn distance (3.05 Å) in Cu@Sn$_{12}^-$ is considerably longer than the Cu–Sn distance (2.6 Å) in diatomic CuSn$_2$ which is consistent with relatively weak covalent interactions between Cu and the Sn$_{12}$ cage in Cu@Sn$_{12}^-$. In fact, Cu@Sn$_{12}^-$ can be described as a Cu$^+$ ion trapped inside stannaspherene ([Cu@Sn$_{12}^-$]), similar to the charge-transfer complexes formed in endohedral fullerences.$^{[23,24,27]}

Figure 3 compares the scalar-relativistic (SR) and spin–orbit (SO)-coupled energy levels of the valence molecular orbitals (MO) of Cu@Sn$_{12}^-$ and those of stannaspherene. As we showed previously, stannaspherene is bonded by the Sn 5p electrons only, which transform into h$_g$, t$_{1u}$, g$_u$, and a$_g$ valence MOs (Figure 3), whereas the Sn 5s electrons are mainly nonbonding lone pairs. Upon insertion of Cu$^+$ into Sn$_{12}^-$, the radial bonding MOs (a$_g$ and t$_{1u}$) are stabilized because they are symmetry-allowed to interact with the d orbitals of the dopant, whereas the purely tangential g$_u$ MO is not affected at all because of symmetry restrictions. The h$_g$ highest occupied molecular orbital (HOMO), which has a small amount of mixing from the radial orbitals, is slightly destabilized. The filled 3d$^9$ shell of the Cu$^+$ ion transforms into an h$_g$ orbital in Cu@Sn$_{12}^-$ whilst maintaining its fivefold degeneracy. When SO coupling is taken into account, each degenerate orbital is split into two levels. The SO coupling in the corresponding MOs in Cu@Sn$_{12}^-$ and Sn$_{12}^-$ is very similar (Figure 3). The SO-split MO pattern of Cu@Sn$_{12}^-$ is in excellent agreement with the observed spectral pattern, as can be seen in the spectrum of Cu@Sn$_{12}^-$ (Figure 1). The Cu 3d levels and the a$_g$ orbitals have too high binding energies to be ionized at the photon energy used. The SO splittings in the h$_g$ HOMO and the g$_u$ orbitals are large enough to be clearly resolved experimentally.

The spectrum of Au@Sn$_{12}^-$ is almost identical to that of Cu@Sn$_{12}^-$ except that the SO splitting in the t$_{1u}$ orbital is enhanced in Au@Sn$_{12}^-$, which is also borne out by our calculations, thus confirming the endohedral nature of Au@Sn$_{12}^-$. The first adiabatic detachment energy (ADE) and vertical detachment energy (VDE) of Cu@Sn$_{12}^-$ and Au@Sn$_{12}^-$ are identical within our experimental uncertainties (see Supporting Information).

Although the Cu@Sn$_{12}^-$ cluster has perfect icosahedral symmetry, our calculations show that the other endohedral M@Sn$_{12}^-$ clusters with open d shells on the central dopant, except Cr@Sn$_{12}^-$ (see Supporting Information), have slightly distorted structures, owing to the Jahn–Teller effect. However, these structural distortions are very small and the actual cage structures of all M@Sn$_{12}^-$ clusters are very close to the ideal I$_h$ symmetry. The nearly identical doublet features near 5 eV in all spectra of the M@Sn$_{12}^-$ clusters are due to the same g$_u$ orbitals (Figure 1), which are purely on-sphere o orbitals (Figure 3) and are not expected to be affected by the central atom. This spectral characteristic provides a fingerprint for the endohedral cage structures for all M@Sn$_{12}^-$ clusters and reflects the robustness of the stannaspherene cage. The more complicated spectral features in the lower binding energy
range in the M@Sn_{12}^{-} clusters with open d shells are as expected.

For the late transition metal dopants (M = Ni, Fe, Co), our calculations show that the 3d electrons are still significantly lower in energy and cannot be detached at 193 nm. The extra spectral features in Co@Sn_{12}^{-} and Fe@Sn_{12}^{-} are likely due to spin polarization of the h_{c} HOMO and the t_{uu} orbitals. For the early transition metal dopants (Cr, V, Ti), the 3d electrons have similar binding energies to the Sn-derived frontier h_{c} and t_{uu} orbitals, which results in much more complex spectral patterns due to direct detachment from the 3d valence levels in the low binding energy region (Figure 1).

The 4d and 5d dopants behave similarly to the 3d dopants, which results in similar photoelectron spectra for the corresponding endohedral stannaspheres. Our photoelectron spectra suggest that the rare-earth atoms also form endohedral stannaspheres, as indicated by the g_{e} doublet spectral fingerprint in the spectra of Y@Sn_{12}^{-} and Gd@Sn_{12}^{-} (see Supporting Information) and confirmed subsequently by theoretical calculations.

All M@Sn_{12}^{-} anions can be described as [M^{+}@Sn_{12}^{-}], whereas the neutral endohedral stannaspheres M@Sn_{12} can be described as [M^{2+}@Sn_{12}]. For the 3d dopants, all endohedral stannaspheres are magnetic with high spins resulting from the 3d-electron configurations of the transition metal atoms. Thus, a new class of cage clusters with tunable magnetic and optical properties is accessible. In contrast to the encapsulated Si or Ge clusters, where the dopants are critical to stabilize the cage structures, the stability of M@Sn_{12} derives from the intrinsic stability of stannasphere itself, much like the endohedral fullerences. Our study indicates that all transition metal or f-block atoms can be trapped inside stannasphere. This is an important advantage with respect to the endohedral fullerences, which can only trap alkali, alkaline earth, or rare-earth atoms; the chemically more interesting transition metal atoms do not form endohedral fullerences.

Ni- or Pt-encapsulated Pb_{12} icosahedral clusters similar to Ni@Sn_{12}^{-} or Pt@Sn_{12}^{-} have been synthesized in solution and characterized in the bulk. Even though the doped Ni or Pt atom was thought to be essential for the cage compounds, we have evidence that Pb_{12}^{2-} is also a highly stable empty cage cluster (plumbaspherenne) similar to Sn_{12}^{-}, both of which are isoelectronic with the well-known borane cage molecule B_{12}H_{12}^{2-}. Hence, the previously observed Pt@Pb_{12}^{2-} and Ni@Pb_{12}^{2-} anions, as well as the Al@Pb_{12}^{2-} cation ([Al^{3+}@Pb_{12}^{2-}]), should belong to a whole family of endohedral plumbaspherenne that are similar to the endohedral stannaspheres. Icosahedral M@Au_{12}^-type cage clusters have also been predicted and observed experimentally. However, similar to the metal-encapsulated Si or Ge clusters, the dopant is critical for the cage structure of M@Au_{12} because Au_{12} does not possess a cage structure. If flexible, bulk synthetic methods can be found for this vast number of endohedral stannaspheres, it may be possible to create novel cluster-assembled materials with continuously tunable electronic, magnetic, or optical properties across the entire transition series or the f block.

**Experimental Section**

Cluster generation, mass selection, and photoelectron spectroscopy: All experiments were carried out on a magnetic-bottle photoelectron spectroscopy apparatus equipped with a laser vaporization cluster source, details of which have been described previously. The targets were prepared by pressing a mixed powder of tin with the desired dopant (M = Ti, V, Cr, Fe, Co, Ni, Cu, Y, Nb, Gd, Hf, Ta, Pt, Au). The pressed Sn/M disk target was vaporized by the second harmonic output (532 nm) of a Nd:YAG laser. The laser-induced plasma was entrained in a high pressure helium carrier gas in which the vaporized Sn and M atoms nucleate to form pure Sn clusters and Sn clusters doped with the desired impurity atom. It was important to adjust the M/Sn ratio in the target so that only one or two dopant atoms were incorporated into the Sn clusters. We found that targets prepared with less than 10% dopant by atom yielded mainly clusters with only one dopant atom (M(Sn), along with pure Sn_{n} clusters.

Negatively charged clusters from the laser vaporization source were extracted from the cluster beam and subjected to a time-of-flight mass analysis. The clusters of interest (M(Sn)) were mass-selected and decelerated before crossing with a laser beam for photodetachment. Photoemitted electrons were analyzed by a magnetic-bottle time-of-flight electron analyzer calibrated against the known spectrum of Pt. The electron energy resolution of the magnetic-bottle spectrometer was ∆E/E ≈ 2.5% (i.e., 25 meV) for 1 eV electrons. Because of the broad isotopic distribution of Sn, the mass gate was carefully set to minimize contamination of the selected M(Sn) peaks from pure Sn_{n} clusters. Negligible contamination was achieved for all PES spectra reported in the current work.

Calculations: All structures were optimized using density functional theory at the B3LYP level, and frequency calculations were performed to confirm that the calculated structures were minima. The Stuttgart small-core relativistic effective core potentials and basis sets were used to describe Sn, Ti, V, Cr, Fe, Co, Ni, Cu, and K, with polarization and diffuse functions added for Sn (ζ(d) = 0.183, ζ(p) = 0.0231). The calculations were accomplished using the NWChem 4.7 program. Because of the importance of spin–orbit coupling effects in the Sn clusters, we also performed two-component relativistic DFT calculations using the zero-order regular approximation (ZORA) implemented in the Amsterdam Density Functional (ADF) code.

These calculations used the PW91 exchange-correlation functional and the TZ2P Slater basis sets with the frozen-core approximation. The electron detachment spectra (see Supporting Information) were simulated by fitting the calculated spin–orbit energies with Gaussian functions, and the intensities were not explicitly computed.

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[28] The M@Sn$_{12}$ endohedral clusters with open d shells may be more reactive and may exist in different charge states if synthesized in bulk.


