

Pd₂@Sn₁₈⁴⁻: Fusion of Two Endohedral StannaspherenesZhong-Ming Sun,^{†,‡} Hai Xiao,[§] Jun Li,[§] and Lai-Sheng Wang^{*,†,‡}

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One of the major objectives of cluster science is to discover stable atomic clusters, which may be used as building blocks for cluster-assembled materials. The discovery and bulk synthesis of the fullerenes^{1,2} have sprouted new research disciplines in chemistry and nanoscience and precipitated intense interests to search for other similar stable clusters. However, despite major research efforts, no other analogous gas-phase clusters have been found and yielded to bulk syntheses. Recently, a 12-atom Sn cluster (Sn₁₂²⁻), named stannaspherene, was discovered serendipitously to be a highly stable icosahedral cage during gas-phase photoelectron spectroscopic experiment.³ Stannaspherene has a diameter of 6.1 Å, which is large enough to entrap a foreign atom and suggests possibilities to create endohedral stannaspherenes analogous to the endohedral fullerenes. Indeed, we have shown recently that stannaspherene can trap all transition-metal atoms, as well as f-block elements, giving rise to a whole new class of endohedral clusters.⁴ The endohedral stannaspherenes may even rival the fullerenes, which cannot trap transition-metal atoms other than the rare-earth and f-block atoms,⁵ and be used as building blocks for novel cluster-assembled materials with tunable magnetic and electronic properties. We have found further that Pb₁₂²⁻ (plumbaspherene)⁶ is also a highly stable icosahedral cage cluster in the gas phase with a diameter (6.3 Å) slightly larger than that of stannaspherene and should also be able to trap a variety of foreign atoms. Indeed, an endohedral AlPb₁₂⁺ cluster has been observed as a stable gaseous species,⁷ which can be formulated as Al³⁺@Pb₁₂²⁻. Very interestingly, Eichhorn and co-workers have synthesized a series of endohedral cage compounds, M@Pb₁₂²⁻ (M = Ni, Pd, Pt), through chemical reactions of K₄Pb₉ and ML₄ (M = Pt, Pd, L = PPh₃) in ethylenediamine (ED) and crystallized them as (2,2,2-crypt)K⁺ salts.⁸

We are interested in the bulk syntheses of stannaspherene (Sn₁₂²⁻) and plumbaspherene (Pb₁₂²⁻), which are expected to be stable solution species and may be crystallized with appropriate counterions, such as (2,2,2-crypt)K⁺. Inspired by the Eichhorn compounds,⁸ we have started exploratory syntheses of endohedral stannaspherenes. Here we report the synthesis and structural characterization of a new Pd₂@Sn₁₈⁴⁻ cluster, which has been crystallized as a [(2,2,2-crypt)K]₄(Pd₂@Sn₁₈)·3ED salt during our attempt to synthesize the endohedral stannaspherene Pd@Sn₁₂²⁻. Its structure has been determined by single-crystal X-ray diffraction, and the Pd₂@Sn₁₈⁴⁻ cluster is found to consist of 18 Sn atoms encapsulating two Pd atoms and in fact are due to the fusion of two endohedral stannaspherenes (Pd@Sn₁₂²⁻) along their C₃ axis by removing a Sn₃ triangle on each Sn₁₂ unit at the cluster-cluster joint.

The [K(2,2,2-crypt)]₄(Pd₂@Sn₁₈)·3ED compound (Figure 1) was crystallized in an ED solution via the reaction of K₄Sn₉ and Pd-

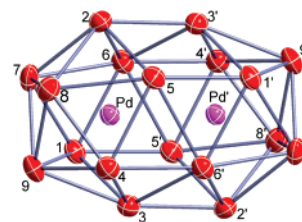


Figure 1. ORTEP view of the structure of Pd₂@Sn₁₈⁴⁻ in [K(2,2,2-crypt)]₄-(Pd₂@Sn₁₈)·3ED (50% thermal ellipsoids).

[P(C₆H₅)₃]₄ (see Supporting Information for experimental details). A summary of the crystallographic data is given in Table S1, and selected bond distances are listed in Table S2.

The Pd₂@Sn₁₈⁴⁻ anion is a *closo*-deltahedral cluster, consisting of 18 Sn atoms encapsulating two Pd atoms. It only has an inversion symmetry, but its overall prolate shape is pseudo-*D*_{3d}. The Pd···Pd distance (3.414 Å) is beyond the range of observed single Pd–Pd bond distances (2.53–2.70 Å),⁹ indicating nonbonding interactions or simply two isolated Pd atoms. The structure of Pd₂@Sn₁₈⁴⁻ is identical to that of Pd₂@Ge₁₈⁴⁻ reported previously by Sevov et al.¹⁰ However, the Pd–Pd distance (2.831 Å) in Pd₂@Ge₁₈⁴⁻ indicates a weakly bonded Pd₂ dimer, perhaps imposed by the shorter Ge–Ge distances as suggested by Sevov et al. The Pd₂@Sn₁₈⁴⁻ cluster also bears some similarity to a Pt–Sn cluster (Pt₂@Sn₁₇⁴⁻) recently reported by Eichhorn and co-workers.¹¹

Similar to Pd₂@Ge₁₈⁴⁻, which are composed of two PdGe₉²⁻ units,¹⁰ the Pd₂@Sn₁₈⁴⁻ cluster consists of two identical PdSn₉²⁻ units connected by an inversion center (Figure 2). More importantly, each of the PdSn₉²⁻ units is part of a Pd@Sn₁₂²⁻ endohedral stannaspherene by removing a Sn₃ triangle with very little structural relaxation (Figure 2c). Thus the Pd₂@Sn₁₈⁴⁻ cluster can be viewed as the fusion of two endohedral stannaspherenes along their C₃ axis. As given in Table S2, the Pd–Sn distance is about 2.90 Å within each PdSn₉²⁻ subunit, whereas the Sn–Sn distances are in the range of 3.012–3.145 Å, which are shorter than the calculated Sn–Sn distance (3.19 Å) for stannaspherene³ due to the Pd–Sn interactions. Only three Sn–Sn bonds are slightly elongated: Sn(7)–Sn(6), Sn(8)–Sn(5), and Sn(9)–Sn(3), which are probably caused by the fact that Sn(6, 5, 3) have to “reach out” to bond to the second Pd’Sn₉²⁻ subunit (Figure 2b). The six horizontal Sn–Sn bonds, such as Sn(1)–Sn(5’), Sn(2)–Sn(3’), Sn(3)–Sn(2’), Sn(4)–Sn(6’), Sn(5)–Sn(1’), and Sn(6)–Sn(4’), which bridge the two PdSn₉²⁻ units together, are relatively short and almost identical to each other (3.089–3.106 Å).

To elucidate the stability and the electronic structure of the new Pd₂@Sn₁₈⁴⁻ cluster, we carried out quasi-relativistic density functional calculations at the PW91/TZ2P level (see Supporting Information). We optimized the structure of Pd₂@Sn₁₈⁴⁻ starting from the crystallographically determined structure and also from

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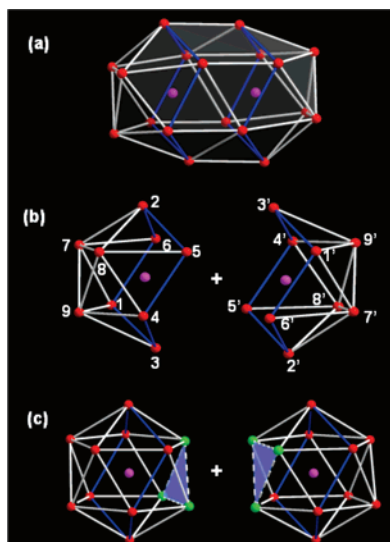


Figure 2. Relationship of $\text{Pd}_2@\text{Sn}_{18}^{4-}$ and stannaspherene $\text{Pd}@\text{Sn}_{12}^{2-}$: (a) the $\text{Pd}_2@\text{Sn}_{18}^{4-}$ cluster, (b) the two halves (PdSn_9^{2-}) of $\text{Pd}_2@\text{Sn}_{18}^{4-}$ separated along its pseudo- C_3 axis for clear view, (c) reconstruction of two endohedral stannaspherenes $\text{Pd}@\text{Sn}_{12}^{2-}$ by adding a Sn_3 triangle (green) to the two PdSn_9^{2-} subunits.

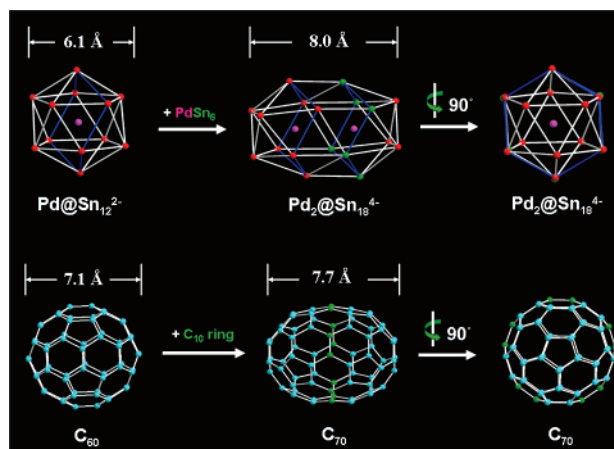


Figure 3. Comparison of the structural evolution from $\text{Pd}@\text{Sn}_{12}^{2-}$ to $\text{Pd}_2@\text{Sn}_{18}^{4-}$ to that from C_{60} to C_{70} .

stacking two ideal $\text{Pd}@\text{Sn}_{12}^{2-}$ endohedral stannaspherenes by removing a Sn_3 triangle (i.e., from Figure 2c to 2a). Both led to the same and a more symmetric D_{3d} species for the free $\text{Pd}_2@\text{Sn}_{18}^{4-}$ cluster, which is confirmed to be a minimum through vibrational frequency calculations. Molecular orbital analyses reveal that it can be viewed as two neutral Pd atoms trapped inside a polyhedral Sn_{18}^{4-} with a large HOMO–LUMO gap of 1.44 eV (Figure S1) (compared to 1.70 eV for $\text{Pd}@\text{Sn}_{12}^{2-}$ and 1.66 eV for $\text{Pd}_2@\text{Ge}_{18}^{4-}$ at the same level of theory), suggesting that it is a highly electronically stable species.

Stannaspherene³ can be viewed as an inorganic analogue of the fullerene C_{60} , and its calculated diameter (6.1 Å) is only slightly smaller than that of C_{60} (7.1 Å). It has been shown to be able to trap all transition-metal atoms including the f-block elements,⁴ analogous to endohedral fullerenes. Here we further note that the structural evolution from the nearly spherical stannaspherene to the prolate $\text{Pd}_2@\text{Sn}_{18}^{4-}$ is also reminiscent of that from C_{60} to C_{70} , as illustrated in Figure 3. Further extension of C_{70} can lead to the formation of a single wall carbon nanotube. It is interesting to

speculate if the $\text{Pd}_2@\text{Sn}_{18}^{4-}$ cluster can be further extended to form carbon nanotube-like structures. Preliminary calculations suggest that insertion of up to two PdSn_6 units into $\text{Pd}_2@\text{Sn}_{18}^{4-}$ still lead to stable structures, for example, both $\text{Pd}_3@\text{Sn}_{24}^{4-}$ and $\text{Pd}_4@\text{Sn}_{30}^{6-}$ clusters are stable with reasonable HOMO–LUMO gaps.

Starting from the nine-atom Zintl ions E_9^{x-} ($\text{E} = \text{Ge}, \text{Sn}, \text{Pb}$; $x = 2-4$),¹² several interesting new clusters have been synthesized.^{8,10,11,13-15} The recent synthesis of the *closo*- Pb_{10}^{2-} cluster¹⁴ from the Pb_9^{4-} Zintl ion suggests that the parent stannaspherene (Sn_{12}^{2-}) and plumbaspherene (Pb_{12}^{2-}) may also be obtained from the respective E_9^{x-} Zintl ions under appropriate reaction conditions. Indeed, the current work and the previous works^{8,11} on $\text{M}@\text{Pb}_{12}^{2-}$ and $\text{Pt}_2@\text{Pb}_{17}^{4-}$, as well as observation of other possible gaseous Cu–Sn core–shell clusters,¹⁶ suggest that a whole class of endohedral stannaspherenes and plumbaspherenes with various internal atoms, as well as other novel endohedral structures, may be synthesized and crystallized.

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Supporting Information Available: X-ray crystallographic file in CIF format, experimental and computational details, and MO levels of $\text{Pd}@\text{Sn}_{12}^{2-}$ and $\text{Pd}_2@\text{Sn}_{18}^{4-}$. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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