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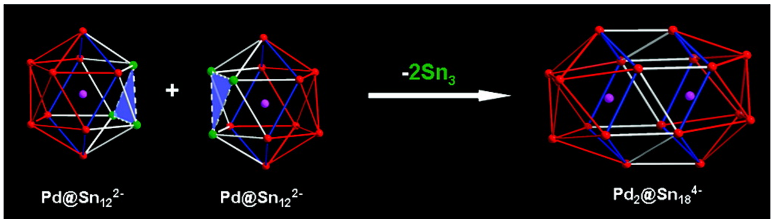
J. Am. Chem. Soc., **2007**, 129 (31), 9560-9561• DOI: 10.1021/ja0728674 • Publication Date (Web): 14 July 2007



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$Pd_2@Sn_{18}^{4-}$: Fusion of Two Endohedral Stannaspherenes

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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 (Sn_{12}^{2-}), 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 Pb_{12}^{2-} (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 $AlPb_{12}^{+}$ cluster has been observed as a stable gaseous species,[7] which can be formulated as $Al^{3+}@Pb_{12}^{2-}$. Very interestingly, Eichhorn and co-workers have synthesized a series of endohedral cage compounds, $M@Pb_{12}^{2-}$ ($M = Ni, Pd, Pt$), through chemical reactions of K_4Pb_9 and ML_4 ($M = Pt, Pd, L = PPh_3$) in ethylenediamine (ED) and crystallized them as (2,2,2-crypt)K^+ salts.[8]

We are interested in the bulk syntheses of stannaspherene (Sn_{12}^{2-}) and plumbaspherene (Pb_{12}^{2-}), 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 $Pd_2@Sn_{18}^{4-}$ cluster, which has been crystallized as a $[(2,2,2\text{-crypt})K]_4(Pd_2@Sn_{18})\cdot 3ED$ salt during our attempt to synthesize the endohedral stannaspherene $Pd@Sn_{12}^{2-}$. Its structure has been determined by single-crystal X-ray diffraction, and the $Pd_2@Sn_{18}^{4-}$ 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 ($Pd@Sn_{12}^{2-}$) along their C_3 axis by removing a Sn_3 triangle on each Sn_{12} unit at the cluster−cluster joint.

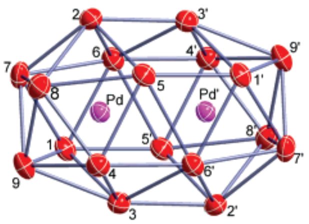

Figure 1. ORTEP view of the structure of $Pd_2@Sn_{18}^{4-}$ in $[K(2,2,2\text{-crypt})]_4(Pd_2@Sn_{18})\cdot 3ED$ (50% thermal ellipsoids).

The $[K(2,2,2\text{-crypt})]_4(Pd_2@Sn_{18})\cdot 3ED$ compound (Figure 1) was crystallized in an ED solution via the reaction of K_4Sn_9 and $Pd[P(C_6H_5)_3]_4$ (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 $Pd_2@Sn_{18}^{4-}$ 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 $Pd_2@Sn_{18}^{4-}$ is identical to that of $Pd_2@Ge_{18}^{4-}$ reported previously by Sevov et al.[10] However, the Pd−Pd distance (2.831 Å) in $Pd_2@Ge_{18}^{4-}$ indicates a weakly bonded Pd_2 dimer, perhaps imposed by the shorter Ge−Ge distances as suggested by Sevov et al. The $Pd_2@Sn_{18}^{4-}$ cluster also bears some similarity to a Pt−Sn cluster ($Pt_2@Sn_{17}^{4-}$) recently reported by Eichhorn and co-workers.[11]

Similar to $Pd_2@Ge_{18}^{4-}$, which are composed of two $PdGe_9^{2-}$ units,[10] the $Pd_2@Sn_{18}^{4-}$ cluster consists of two identical $PdSn_9^{2-}$ units connected by an inversion center (Figure 2). More importantly, each of the $PdSn_9^{2-}$ units is part of a $Pd@Sn_{12}^{2-}$ endohedral stannaspherene by removing a Sn_3 triangle with very little structural relaxation (Figure 2c). Thus the $Pd_2@Sn_{18}^{4-}$ cluster can be viewed as the fusion of two endohedral stannaspherenes along their C_3 axis. As given in Table S2, the Pd−Sn distance is about 2.90 Å within each $PdSn_9^{2-}$ 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 stannaspherene[3] 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 $Pd'Sn'_9{}^{2-}$ 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 $PdSn_9^{2-}$ 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 $Pd_2@Sn_{18}^{4-}$ cluster, we carried out quasi-relativistic density functional calculations at the PW91/TZ2P level (see Supporting Information). We optimized the structure of $Pd_2@Sn_{18}^{4-}$ starting from the crystallographically determined structure and also from

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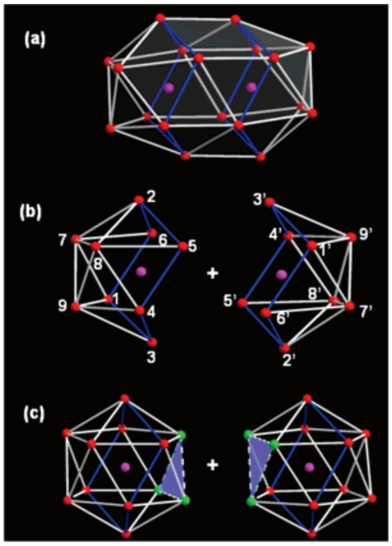

Figure 2. Relationship of $Pd_2@Sn_{18}^{4-}$ and stannaspherene $Pd@Sn_{12}^{2-}$: (a) the $Pd_2@Sn_{18}^{4-}$ cluster, (b) the two halves ($PdSn_9^{2-}$) of $Pd_2@Sn_{18}^{4-}$ separated along its pseudo-C_3 axis for clear view, (c) reconstruction of two endohedral stannaspherenes $Pd@Sn_{12}^{2-}$ by adding a Sn_3 triangle (green) to the two $PdSn_9^{2-}$ subunits.

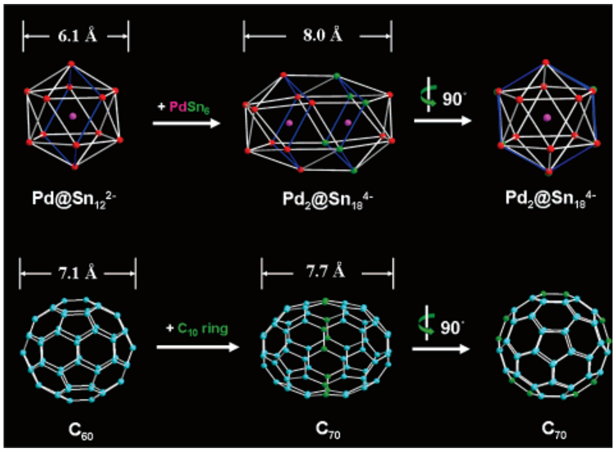

Figure 3. Comparison of the structural evolution from $Pd@Sn_{12}^{2-}$ to $Pd_2@Sn_{18}^{4-}$ to that from C_{60} to C_{70}.

stacking two ideal $Pd@Sn_{12}^{2-}$ 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 $Pd_2@Sn_{18}^{4-}$ 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 $Pd@Sn_{12}^{2-}$ and 1.66 eV for $Pd_2@Ge_{18}^{4-}$ at the same level of theory), suggesting that it is a highly electronically stable species.

Stannaspherene[3] 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 $Pd_2@Sn_{18}^{4-}$ 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 $Pd_2@Sn_{18}^{4-}$ cluster can be further extended to form carbon nanotube-like structures. Preliminary calculations suggest that insertion of up to two $PdSn_6$ units into $Pd_2@Sn_{18}^{4-}$ still lead to stable structures, for example, both $Pd_3@Sn_{24}^{4-}$ and $Pd_4@Sn_{30}^{6-}$ clusters are stable with reasonable HOMO−LUMO gaps.

Starting from the nine-atom Zintl ions E_9^{x-} (E = Ge, Sn, 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-} cluster[14] 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 $M@Pb_{12}^{2-}$ and $Pt_2@Pb_{17}^{4-}$, 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.

Acknowledgment. The experimental work was supported by the National Science Foundation (DMR-0503383) and performed at EMSL, a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at the Pacific Northwest National Laboratory, operated for DOE by Battelle. The calculations, supported by NKBRSF (2006CB 932305) and NNSFC (20525104) in China, were performed using an HP Itanium2 cluster at the National Laboratory for Information Science and Technology at Tsinghua University. We thank Dr. Mike R. Thompson for help with the X-ray diffraction measurements, and Dr. Tim L. Hubler for valuable discussions.

Supporting Information Available: X-ray crystallographic file in CIF format, experimental and computational details, and MO levels of $Pd@Sn_{12}^{2-}$ and $Pd_2@Sn_{18}^{4-}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA0728674