

## Pd<sub>2</sub>@Sn<sub>18</sub><sup>4-</sup>: Fusion of Two Endohedral Stannaspherenes

Zhong-Ming Sun,<sup>†,‡</sup> Hai Xiao,<sup>§</sup> Jun Li,<sup>§</sup> and Lai-Sheng Wang<sup>\*,†,‡</sup>

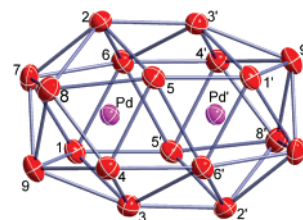
Department of Physics, Washington State University, 2710 University Drive, Richland, Washington 99354, Chemical & Materials Sciences Division, Pacific Northwest National Laboratory, MS K8-88, Post Office Box 999, Richland, Washington 99352, and Department of Chemistry & Key Laboratory of Organic Optoelectronics and Molecular Engineering of Ministry of Education, Tsinghua University, Beijing 100084, China

Received April 24, 2007; E-mail: ls.wang@pnl.gov

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<sup>1,2</sup> 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<sub>12</sub><sup>2-</sup>), named stannaspherene, was discovered serendipitously to be a highly stable icosahedral cage during gas-phase photoelectron spectroscopic experiment.<sup>3</sup> 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.<sup>4</sup> The endohedral stannaspherenes may even rival the fullerenes, which cannot trap transition-metal atoms other than the rare-earth and f-block atoms,<sup>5</sup> and be used as building blocks for novel cluster-assembled materials with tunable magnetic and electronic properties. We have found further that Pb<sub>12</sub><sup>2-</sup> (plumbaspherene)<sup>6</sup> 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<sub>12</sub><sup>+</sup> cluster has been observed as a stable gaseous species,<sup>7</sup> which can be formulated as Al<sup>3+</sup>@Pb<sub>12</sub><sup>2-</sup>. Very interestingly, Eichhorn and co-workers have synthesized a series of endohedral cage compounds, M@Pb<sub>12</sub><sup>2-</sup> (M = Ni, Pd, Pt), through chemical reactions of K<sub>4</sub>Pb<sub>9</sub> and ML<sub>4</sub> (M = Pt, Pd, L = PPh<sub>3</sub>) in ethylenediamine (ED) and crystallized them as (2,2,2-crypt)K<sup>+</sup> salts.<sup>8</sup>

We are interested in the bulk syntheses of stannaspherene (Sn<sub>12</sub><sup>2-</sup>) and plumbaspherene (Pb<sub>12</sub><sup>2-</sup>), which are expected to be stable solution species and may be crystallized with appropriate counterions, such as (2,2,2-crypt)K<sup>+</sup>. Inspired by the Eichhorn compounds,<sup>8</sup> we have started exploratory syntheses of endohedral stannaspherenes. Here we report the synthesis and structural characterization of a new Pd<sub>2</sub>@Sn<sub>18</sub><sup>4-</sup> cluster, which has been crystallized as a [(2,2,2-crypt)K]<sub>4</sub>(Pd<sub>2</sub>@Sn<sub>18</sub>)·3ED salt during our attempt to synthesize the endohedral stannaspherene Pd@Sn<sub>12</sub><sup>2-</sup>. Its structure has been determined by single-crystal X-ray diffraction, and the Pd<sub>2</sub>@Sn<sub>18</sub><sup>4-</sup> 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<sub>12</sub><sup>2-</sup>) along their C<sub>3</sub> axis by removing a Sn<sub>3</sub> triangle on each Sn<sub>12</sub> unit at the cluster-cluster joint.

The [K(2,2,2-crypt)]<sub>4</sub>(Pd<sub>2</sub>@Sn<sub>18</sub>)·3ED compound (Figure 1) was crystallized in an ED solution via the reaction of K<sub>4</sub>Sn<sub>9</sub> and Pd-



**Figure 1.** ORTEP view of the structure of Pd<sub>2</sub>@Sn<sub>18</sub><sup>4-</sup> in [K(2,2,2-crypt)]<sub>4</sub>-(Pd<sub>2</sub>@Sn<sub>18</sub>)·3ED (50% thermal ellipsoids).

[P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>]<sub>4</sub> (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<sub>2</sub>@Sn<sub>18</sub><sup>4-</sup> 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*<sub>3d</sub>. The Pd···Pd distance (3.414 Å) is beyond the range of observed single Pd–Pd bond distances (2.53–2.70 Å),<sup>9</sup> indicating nonbonding interactions or simply two isolated Pd atoms. The structure of Pd<sub>2</sub>@Sn<sub>18</sub><sup>4-</sup> is identical to that of Pd<sub>2</sub>@Ge<sub>18</sub><sup>4-</sup> reported previously by Sevov et al.<sup>10</sup> However, the Pd–Pd distance (2.831 Å) in Pd<sub>2</sub>@Ge<sub>18</sub><sup>4-</sup> indicates a weakly bonded Pd<sub>2</sub> dimer, perhaps imposed by the shorter Ge–Ge distances as suggested by Sevov et al. The Pd<sub>2</sub>@Sn<sub>18</sub><sup>4-</sup> cluster also bears some similarity to a Pt–Sn cluster (Pt<sub>2</sub>@Sn<sub>17</sub><sup>4-</sup>) recently reported by Eichhorn and co-workers.<sup>11</sup>

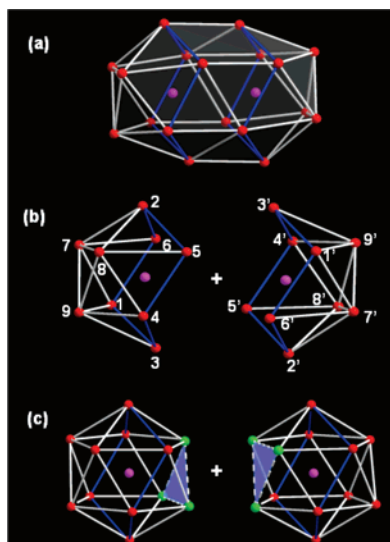
Similar to Pd<sub>2</sub>@Ge<sub>18</sub><sup>4-</sup>, which are composed of two PdGe<sub>9</sub><sup>2-</sup> units,<sup>10</sup> the Pd<sub>2</sub>@Sn<sub>18</sub><sup>4-</sup> cluster consists of two identical PdSn<sub>9</sub><sup>2-</sup> units connected by an inversion center (Figure 2). More importantly, each of the PdSn<sub>9</sub><sup>2-</sup> units is part of a Pd@Sn<sub>12</sub><sup>2-</sup> endohedral stannaspherene by removing a Sn<sub>3</sub> triangle with very little structural relaxation (Figure 2c). Thus the Pd<sub>2</sub>@Sn<sub>18</sub><sup>4-</sup> cluster can be viewed as the fusion of two endohedral stannaspherenes along their C<sub>3</sub> axis. As given in Table S2, the Pd–Sn distance is about 2.90 Å within each PdSn<sub>9</sub><sup>2-</sup> 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<sup>3</sup> 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<sub>9</sub><sup>2-</sup> 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<sub>9</sub><sup>2-</sup> 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<sub>2</sub>@Sn<sub>18</sub><sup>4-</sup> cluster, we carried out quasi-relativistic density functional calculations at the PW91/TZ2P level (see Supporting Information). We optimized the structure of Pd<sub>2</sub>@Sn<sub>18</sub><sup>4-</sup> starting from the crystallographically determined structure and also from

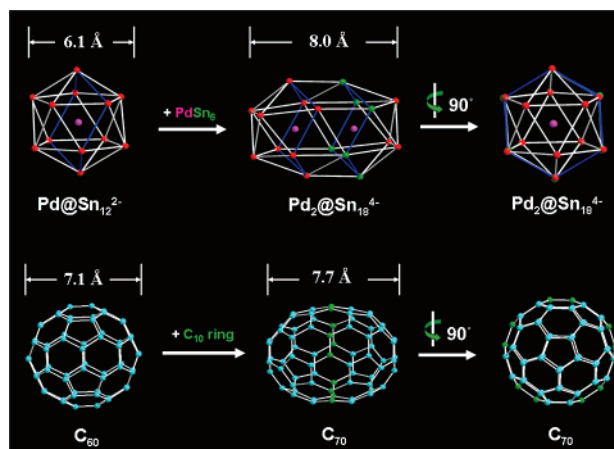
<sup>†</sup> Washington State University.

<sup>‡</sup> Pacific Northwest National Laboratory.

<sup>§</sup> Tsinghua University.



**Figure 2.** Relationship of  $\text{Pd}_2@Sn_{18}^{4-}$  and stannaspherene  $\text{Pd}@Sn_{12}^{2-}$ : (a) the  $\text{Pd}_2@Sn_{18}^{4-}$  cluster, (b) the two halves ( $\text{PdSn}_9^{2-}$ ) of  $\text{Pd}_2@Sn_{18}^{4-}$  separated along its pseudo- $C_3$  axis for clear view, (c) reconstruction of two endohedral stannaspherenes  $\text{Pd}@Sn_{12}^{2-}$  by adding a  $\text{Sn}_3$  triangle (green) to the two  $\text{PdSn}_9^{2-}$  subunits.



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

stacking two ideal  $\text{Pd}@Sn_{12}^{2-}$  endohedral stannaspherenes by removing a  $\text{Sn}_3$  triangle (i.e., from Figure 2c to 2a). Both led to the same and a more symmetric  $D_{3d}$  species for the free  $\text{Pd}_2@Sn_{18}^{4-}$  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  $\text{Sn}_{18}^{4-}$  with a large HOMO–LUMO gap of 1.44 eV (Figure S1) (compared to 1.70 eV for  $\text{Pd}@Sn_{12}^{2-}$  and 1.66 eV for  $\text{Pd}_2@Ge_{18}^{4-}$  at the same level of theory), suggesting that it is a highly electronically stable species.

Stannaspherene<sup>3</sup> 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,<sup>4</sup> analogous to endohedral fullerenes. Here we further note that the structural evolution from the nearly spherical stannaspherene to the prolate  $\text{Pd}_2@Sn_{18}^{4-}$  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  $\text{Pd}_2@Sn_{18}^{4-}$  cluster can be further extended to form carbon nanotube-like structures. Preliminary calculations suggest that insertion of up to two  $\text{PdSn}_6$  units into  $\text{Pd}_2@Sn_{18}^{4-}$  still lead to stable structures, for example, both  $\text{Pd}_3@Sn_{24}^{4-}$  and  $\text{Pd}_4@Sn_{30}^{6-}$  clusters are stable with reasonable HOMO–LUMO gaps.

Starting from the nine-atom Zintl ions  $E_9^{x-}$  ( $E = \text{Ge}, \text{Sn}, \text{Pb}$ ;  $x = 2-4$ ),<sup>12</sup> several interesting new clusters have been synthesized.<sup>8,10,11,13-15</sup> The recent synthesis of the *closo*- $\text{Pb}_{10}^{2-}$  cluster<sup>14</sup> from the  $\text{Pb}_9^{4-}$  Zintl ion suggests that the parent stannaspherene ( $\text{Sn}_{12}^{2-}$ ) and plumbaspherene ( $\text{Pb}_{12}^{2-}$ ) may also be obtained from the respective  $E_9^{x-}$  Zintl ions under appropriate reaction conditions. Indeed, the current work and the previous works<sup>8,11</sup> on  $M@Pb_{12}^{2-}$  and  $\text{Pt}_2@Pb_{17}^{4-}$ , as well as observation of other possible gaseous Cu–Sn core–shell clusters,<sup>16</sup> 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  $\text{Pd}@Sn_{12}^{2-}$  and  $\text{Pd}_2@Sn_{18}^{4-}$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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