Supporting Information

$\text{Pd}_2@ \text{Sn}_{18}^{4-}$: Fusion of Two Endohedral Stannaspherenes

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Experimental and Theoretical Methods

Synthesis of $[\text{K}(2,2,2\text{-crypt})]_4(\text{Pd}_2@ \text{Sn}_{18}) \cdot 3\text{ED}$. All manipulations were carried out under an inert atmosphere using standard Schlenk-line and glovebox techniques. The K_4Sn_9 precursor was synthesized from a stoichiometric mixture of the elements of K and Sn sealed in a Ta tube, which was heated to 900 °C for 8 hours in a quartz tube furnace under argon flow. Ethylenediamine (ED) (99+%, Acros) was commercially purchased and distilled over CaH_2 (Aldrich), collected and freshly used. 2,2,2-crypt (Acros, 98%) and $\text{Pd}(\text{PPh}_3)_4$ (Alfa-Aesar, 99%) were used as received after being dried under vacuum. A mixture of K_4Sn_9 (123 mg, 0.10 mmol) and 2,2,2-crypt (157 mg, 0.40 mmol) was dissolved in ED (3 ml) in a 7-ml vial (No. 1) inside a N_2 -filled glovebox and stirred for 10 minutes, resulting in a red-brown solution. $\text{Pd}(\text{PPh}_3)_4$ (116 mg, 0.10 mmol) was dissolved in toluene (2 ml) in vial 2 (gently heated to accelerate desolution), yielding a yellow solution. The solution of vial 2 was added dropwise to vial 1 and the mixture was stirred for 3 hours. The resulting red-brown solution was filtered by tightly packed glass wool and layered with toluene; dark brown brick-like crystals mixed with some amorphous powder were observed on the vial wall after several days. The yield is approximately 10% (20 mg). EDX measurements on several crystals indicated the presence of K, Sn, and Pd, but the atomic ratio could not be quantitatively determined due to the energy overlap between Sn and Pd. The amorphous powder was confirmed as elemental Sn, which might be resulted from the decomposition of Sn_9^{4-} . Single-crystal X-ray diffraction indicated that small amounts of side compounds, $[\text{K}-(2,2,2\text{-crypt})]_3\text{KSn}_9$ (red-brown rhombohedrons)¹ and $[\text{K}-(2,2,2\text{-crypt})]_3\text{Sn}_9 \cdot 1.5\text{ED}$ (brown plates),² were also isolated in the synthesis.

Single-Crystal X-Ray Diffraction Characterization. Data sets were collected on a Bruker Proteum diffractometer with a CCD area detector at 180 K with $\text{Cu K}\alpha$ radiation. Crystals (sizes around $0.20 \times 0.04 \times 0.04 \text{ mm}^3$) were selected under high vacuum grease, mounted on a crystal loop, and positioned in a cold N_2 stream in the diffractometer. The structure was solved and refined (on F^2) using the SHELXL-97 package. Crystal data: triclinic, *P*-1 (No. 2), $a = 14.913(3) \text{ \AA}$, $b = 15.930(3) \text{ \AA}$, $c = 16.270(3) \text{ \AA}$, $\alpha = 115.71(3)^\circ$, $\beta = 98.62(3)^\circ$, $\gamma = 100.53(3)^\circ$, $V = 3307.3(1) \text{ \AA}^3$, $Z = 1$, $\rho_{\text{calcd}} = 2.105 \text{ g.cm}^{-3}$, $\mu (\text{Cu K}\alpha) = 30.225 \text{ mm}^{-1}$, $\text{GOF} (F^2) = 1.027$. Of 10,371 total reflections collected, 3,605 were unique ($R_{\text{int}} = 0.0709$). $R1$ ($wR2$) = 0.0499(0.1204) for 621 parameters and 2,803 reflections ($I > 2\sigma(I)$), and $R1 = 0.0690$, $wR2 = 0.1322$ for all 3,605 reflections.

Theoretical Calculations. Quasi-relativistic density functional calculations were performed on the gas-phase $\text{Pd}_2@ \text{Sn}_{18}^{4-}$ cluster, endohedral $\text{Pd}@ \text{Sn}_{12}^{n-}$ ($n = 1, 2$), and the exohedral isomers. We used generalized gradient approach of Perdew-Wang 1991 (PW91) with uncontracted Slater basis sets with quality of triple-zeta plus two polarization functions (TZ2P).^{3,4} The frozen core approximation was applied to the $[1s^2-4p^6]$ and $[1s^2-3d^{10}]$ atomic cores of Sn and

Pd, with the rest of the electrons explicitly treated variationally.⁵ The zero-order-regular approximation (ZORA) was used to account for the scalar and spin-orbit coupling relativistic effects.⁶ The geometries were fully optimized with inclusion of the scalar relativistic effects and single-point calculations were performed with inclusion of the spin-orbit coupling effects. Vibrational frequency calculations were accomplished to verify the nature of the species on the potential energy surfaces. These calculations were carried out using the Amsterdam Density Functional program (ADF 2006.01).⁷ Further calculations were also performed using the hybrid B3LYP functional as implemented in NWChem program.^{8,9} The Gaussian basis sets and energy-consistent pseudopotentials used were the same as described previously.¹⁰ The calculations using the two theoretical approaches yield similar results and both confirm the electronic stability of the endohedral tin clusters.

References

1. Burns, R. C.; Corbett, J. D. *Inorg. Chem* **1985**, *24*, 1489.
2. Critchlow, S. C.; Corbett, J. D. *J. Am. Chem. Soc.* **1983**, *105*, 5715.
3. Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.
4. van Lenthe, E.; Baerends, E. J. *J. Comp. Chem.* **2003**, *24*, 1142.
5. Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 42.
6. van Lenthe, E.; Baerends, E. J.; J. G. Snijders, J. G. *J. Chem. Phys.* **1993**, *99*, 4597.
7. ADF 2006.01, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands (<http://www.scm.com>). (a) te Velde, G.; Bickelhaupt, F. M.; van Gisbergen, S. J. A.; Fonseca Guerra, C.; Baerends, E. J.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931. (b) Fonseca Guerra, C.; Snijders, J. G.; te Velde, G.; Baerends, E. *J. Theor. Chem. Acc.* **1998**, *99*, 391.
8. T. P. Straatsma, E. Apra, T. L. Windus, M. Dupuis, E. J. Bylaska, W. de Jong, S. Hirata, D. M. A. Smith, M. T. Hackler, L. Pollack, R. J. Harrison, J. Nieplocha, V. Tipparaju, M. Krishnan, E. Brown, G. Cisneros, G. I. Fann, H. Fruchtl, J. Garza, K. Hirao, R. Kendall, J. A. Nichols, K. Tsemekhman, M. Valiev, K. Wolinski, J. Anchell, D. Bernholdt, P. Borowski, T. Clark, D. Clerc, H. Dachsel, M. Deegan, K. Dylla, D. Elwood, E. Glendening, M. Gutowski, A. Hess, J. Jaffe, B. Johnson, J. Ju, R. Kobayashi, R. Kutteh, Z. Lin, R. Littlefield, X. Long, B. Meng, T. Nakajima, S. Niu, M. Rosing, G. Sandrone, M. Stave, H. Taylor, G. Thomas, J. van Lenthe, A. Wong, and Z. Zhang, *NWChem, A Computational Chemistry Package for Parallel Computers*, Version 4.5 (2003), Pacific Northwest National Laboratory, Richland, Washington 99352-0999, USA.
9. (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.
10. Cui, L. F.; Huang, X.; Wang, L. M.; Li, J.; Wang, L. S. *Angew. Chem. Int. Ed.* **2007**, *46*, 742.

Table S1. Summary of cell parameters, data collection and structural refinements.

empirical formula	C ₇₈ H ₁₆₈ K ₄ N ₁₄ O ₂₄ Pd ₂ Sn ₁₈
fw	4191.88
space group	Triclinic, P- <i>I</i> (No. 2)
<i>a</i> /Å	14.913(3)
<i>b</i> /Å	15.930(3)
<i>c</i> /Å	16.270(3)
α , deg	115.71(3)
β , deg	98.62(3)
γ , deg	100.53(3)
<i>V</i> , Å ³	3307.3(1)
<i>Z</i>	1
<i>D</i> _{calcd} , g.cm ⁻³	2.105
temp, K	180(2)
λ (Å)	Cu K α , 1.54178
μ , mm ⁻¹	30.225
F(000)	1994
<i>hkl</i> ranges	± 12 , (-13, 11), (-11, 13)
Reflections collected /unique	10371/3605 (<i>R</i> _{int} = 0.0709)
GOF on <i>F</i> ²	1.027
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.0499/0.1204
<i>R</i> 1, <i>wR</i> 2(all data)	0.0690/0.1322
Largest diff. peak and hole (e. Å ⁻³)	1.059 and -0.781

$$R1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR2 = \{ \sum w[(F_o)^2 - (F_c)^2]^2 / \sum w[(F_o)^2]^2 \}^{1/2}$$

Table S2. Selected bond lengths (Å) for $[\text{Pd}_2@\text{Sn}_{18}]^{4-}$ in the compound $[\text{K}@2,2,2\text{-crypt}]_4[\text{Pd}_2@\text{Sn}_{18}]\cdot 3\text{ED}$ according to the atom labels in Figure 1.

Pd...Pd'	3.414(4)		
Pd-Sn(1)	2.895(3)	Pd-Sn(6)	2.882(2)
Pd-Sn(2)	2.917(3)	Pd-Sn(7)	2.896(3)
Pd-Sn(3)	2.908(3)	Pd-Sn(8)	2.885(3)
Pd-Sn(4)	2.857(2)	Pd-Sn(9)	2.904(3)
Pd-Sn(5)	2.900(3)		
Sn(1)-Sn(5')	3.106(3)	Sn(3)-Sn(5')	3.426(5)
Sn(2)-Sn(3')	3.096(3)	Sn(3)-Sn(6')	3.239(3)
Sn(3)-Sn(2')	3.096(3)	Sn(5)-Sn(3')	3.426(5)
Sn(4)-Sn(6')	3.089(3)	Sn(5)-Sn(6')	3.272(4)
Sn(5)-Sn(1')	3.106(3)	Sn(6)-Sn(3')	3.239(3)
Sn(6)-Sn(4')	3.089(3)	Sn(6)-Sn(5')	3.272(4)
Sn(1)-Sn(3)	3.044(3)	Sn(1)-Sn(6)	3.143(3)
Sn(1)-Sn(9)	3.054(3)	Sn(1)-Sn(7)	3.076(3)
Sn(2)-Sn(6)	3.067(3)	Sn(2)-Sn(5)	3.070(3)
Sn(2)-Sn(7)	3.090(3)	Sn(2)-Sn(8)	3.102(3)
Sn(3)-Sn(4)	3.145(3)	Sn(3)-Sn(9)	3.270(3)
Sn(4)-Sn(8)	3.071(3)	Sn(4)-Sn(9)	3.081(3)
Sn(4)-Sn(5)	3.133(3)	Sn(5)-Sn(8)	3.303(3)
Sn(6)-Sn(7)	3.268(3)	Sn(7)-Sn(8)	3.012(3)
Sn(7)-Sn(9)	3.050(3)	Sn(8)-Sn(9)	3.032(3)

Figure S1. Scalar-relativistic molecular orbital levels of Pd@Sn_{12}^{2-} (I_h) and $\text{Pd}_2\text{@Sn}_{18}^{4-}$ (D_{3d}). The orbital energies of the Sn and Pd atoms and the Pd@Sn_{12}^{2-} dianion are shifted up to match those of the $\text{Pd}_2\text{@Sn}_{18}^{4-}$ tetraanion. Note the large HOMO-LUMO gaps for both clusters.