

<Electronic Supporting Information>

**Photoreaction of adsorbed diiodomethane: halide effects of a series of  
neutral palladium(II) coordination cages**

Tae Hwan Noh,<sup>a</sup> Haeri Lee,<sup>a</sup> Doeon Kim,<sup>a</sup> Dohyun Moon,<sup>b</sup> Young-A Lee\*<sup>c</sup> and Ok-Sang

Jung\*<sup>a</sup>

<sup>a</sup>*Department of Chemistry, Pusan National University, Pusan 46241, Korea*

<sup>b</sup>*Beamline Department, Pohang Accelerator Laboratory/POSTECH, Pohang 37673, Korea*

<sup>c</sup>*Department of Chemistry, Chonbuk National University, Jeonju 54896, Korea*

**Refinements of structures with the SQUEEZE routine in PLATON.**

For the present  $[\text{Pd}_6\text{Cl}_{12}\text{L}_4]\cdot 6\text{Me}_2\text{SO}\cdot 5\text{H}_2\text{O}$ ,  $[\text{Pd}_6\text{Br}_{12}\text{L}_4]\cdot 7\text{Me}_2\text{SO}\cdot 4\text{H}_2\text{O}$ , and  $[\text{Pd}_6\text{I}_{12}\text{L}_4]\cdot 6\text{Me}_2\text{SO}\cdot 6\text{H}_2\text{O}$ , the solvate molecules in the voids were highly disordered and were impossible to refine using conventional discrete-atom models. Therefore, the residual electron density was treated as diffuse contributions using the SQUEEZE of the PLATON software<sup>1</sup> and located a series of voids:

For  $[\text{Pd}_6\text{Cl}_{12}\text{L}_4]\cdot 6\text{Me}_2\text{SO}\cdot 5\text{H}_2\text{O}$ ,

\_platon\_squeeze\_void\_nr  
\_platon\_squeeze\_void\_average\_x  
\_platon\_squeeze\_void\_average\_y  
\_platon\_squeeze\_void\_average\_z  
\_platon\_squeeze\_void\_volume  
\_platon\_squeeze\_void\_count\_electrons  
\_platon\_squeeze\_void\_content

1 0.011 -0.012 -0.003 30342 10926 ''

For [Pd<sub>6</sub>Br<sub>12</sub>L<sub>4</sub>] $\cdot$ 7Me<sub>2</sub>SO $\cdot$ 4H<sub>2</sub>O,

\_platon\_squeeze\_void\_nr

\_platon\_squeeze\_void\_average\_x

\_platon\_squeeze\_void\_average\_y

\_platon\_squeeze\_void\_average\_z

\_platon\_squeeze\_void\_volume

\_platon\_squeeze\_void\_count\_electrons

\_platon\_squeeze\_void\_content

1 -0.013 0.379 0.007 10105 4432 ''

For [Pd<sub>6</sub>I<sub>12</sub>L<sub>4</sub>] $\cdot$ 6Me<sub>2</sub>SO $\cdot$ 6H<sub>2</sub>O,

\_platon\_squeeze\_void\_nr

\_platon\_squeeze\_void\_average\_x

\_platon\_squeeze\_void\_average\_y

\_platon\_squeeze\_void\_average\_z

\_platon\_squeeze\_void\_volume

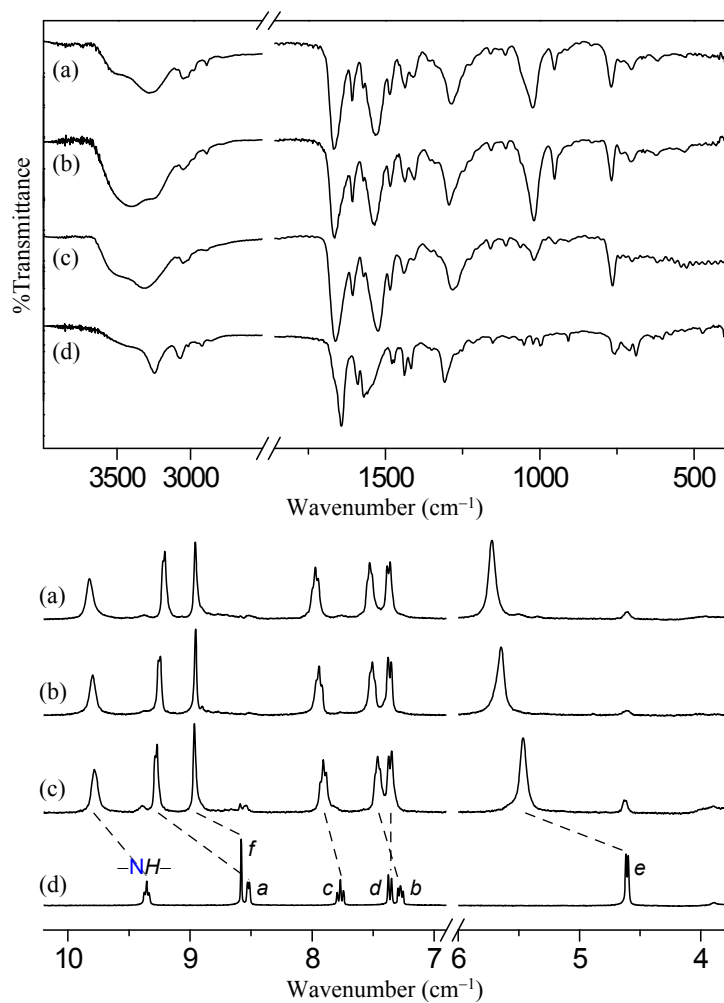
\_platon\_squeeze\_void\_count\_electrons

\_platon\_squeeze\_void\_content

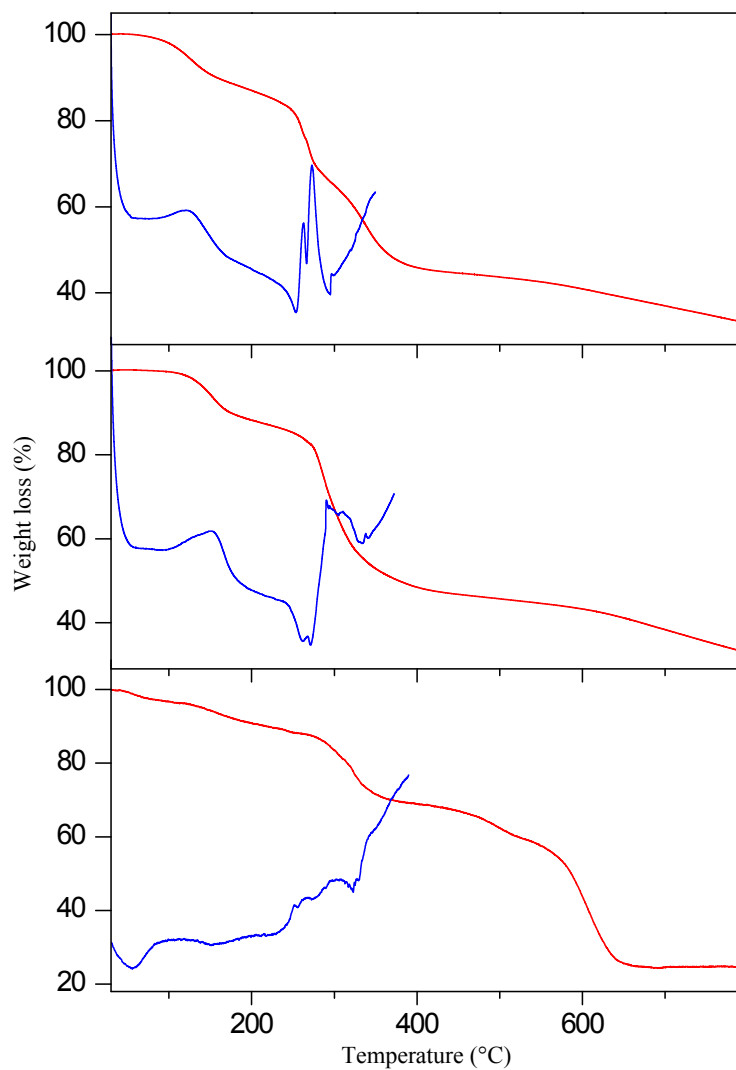
1 -0.009 0.003 0.001 9482 3145 ''

**Reference for the SQUEEZE routine in *PLATON*.**

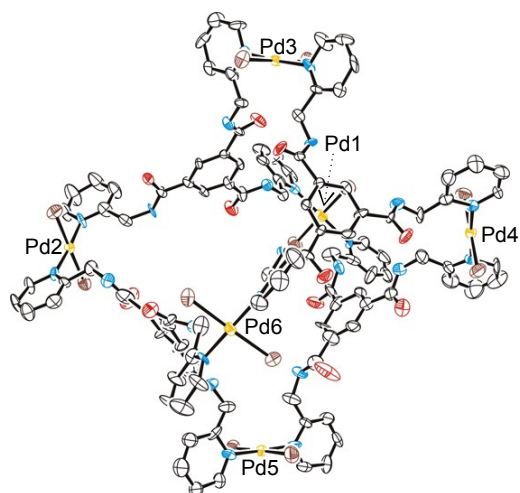
1 A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.



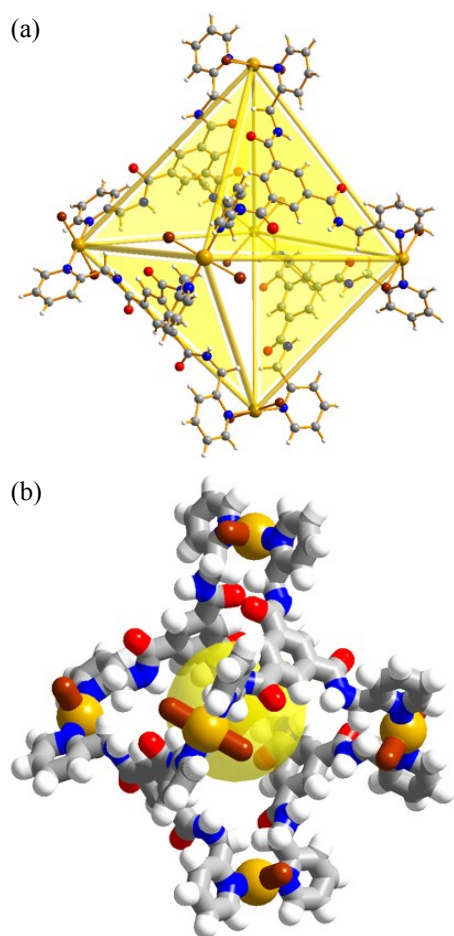
**Fig. S1** IR (top) and <sup>1</sup>H NMR (bottom, Me<sub>2</sub>SO-*d*<sub>6</sub>) spectra of [Pd<sub>6</sub>Cl<sub>12</sub>L<sub>4</sub>] (a), [Pd<sub>6</sub>Br<sub>12</sub>L<sub>4</sub>] (b), [Pd<sub>6</sub>I<sub>12</sub>L<sub>4</sub>] (c), and L (d). See Scheme 1 for the assignments in part (d).



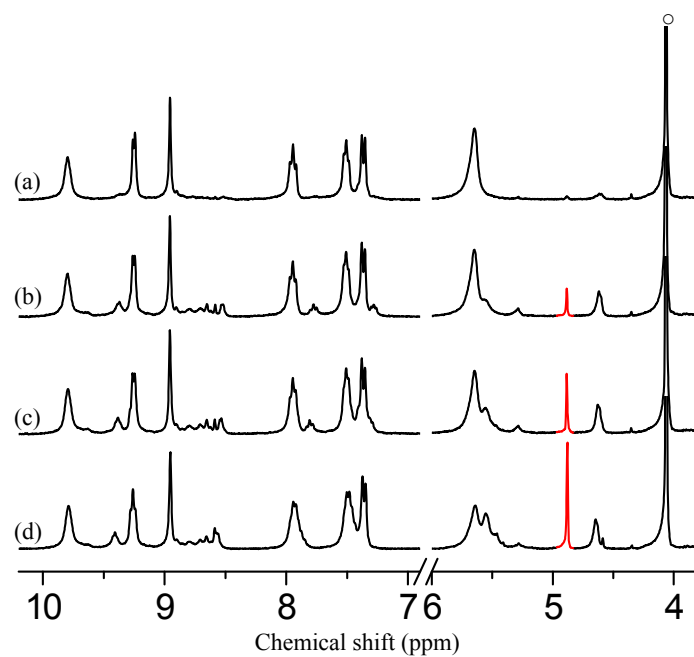
**Fig. S2** TGA (red) and DSC (blue) curves of  $[Pd_6Cl_{12}L_4]$  (top),  $[Pd_6Br_{12}L_4]$  (middle), and  $[Pd_6I_{12}L_4]$  (bottom).



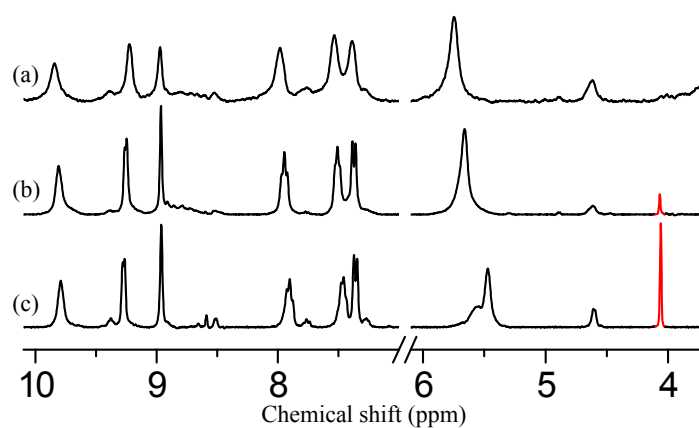
**Fig. S3** ORTEP drawing of [Pd<sub>6</sub>Br<sub>12</sub>L<sub>4</sub>] with anisotropic displacement parameters at 20% probability. Hydrogen atoms and solvate molecules were omitted for clarity.



**Fig. S4** Crystal structure of [Pd<sub>6</sub>Br<sub>12</sub>L<sub>4</sub>] showing octahedral edges (a) and inner-cavity with dummy-ball diameter of 8.3 Å (b).



**Fig. S5** <sup>1</sup>H NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>) spectra of [Pd<sub>6</sub>Br<sub>12</sub>L<sub>4</sub>] showing iodization of the coordinating bromides in the presence of CH<sub>2</sub>I<sub>2</sub> (10 *equiv.*) at room temperature in the dark for 0 d (a), 4 d (b), 9 d (c), and 22 d (d). Circle denotes the free CH<sub>2</sub>I<sub>2</sub>, and the peak at 4.88 ppm corresponds to the resulting CH<sub>2</sub>BrI.



**Fig. S6** <sup>1</sup>H NMR (Me<sub>2</sub>SO-*d*<sub>6</sub>+Me<sub>2</sub>CO-*d*<sub>6</sub>, v/v = 10 : 1) spectra showing adsorption of CH<sub>2</sub>I<sub>2</sub> into each [Pd<sub>6</sub>Cl<sub>12</sub>L<sub>4</sub>] (a), [Pd<sub>6</sub>Br<sub>12</sub>L<sub>4</sub>] (b), and [Pd<sub>6</sub>I<sub>12</sub>L<sub>4</sub>] (c) from a mixed CH<sub>2</sub>I<sub>2</sub>/diethyl ether solution. The peak at 4.06 ppm corresponds to the adsorbed CH<sub>2</sub>I<sub>2</sub>.