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Motion of an Isolated Water Molecule within a Flexible Coordination Cage: Structural Properties and Catalytic Effects of Ionic Palladium(II) Complexes

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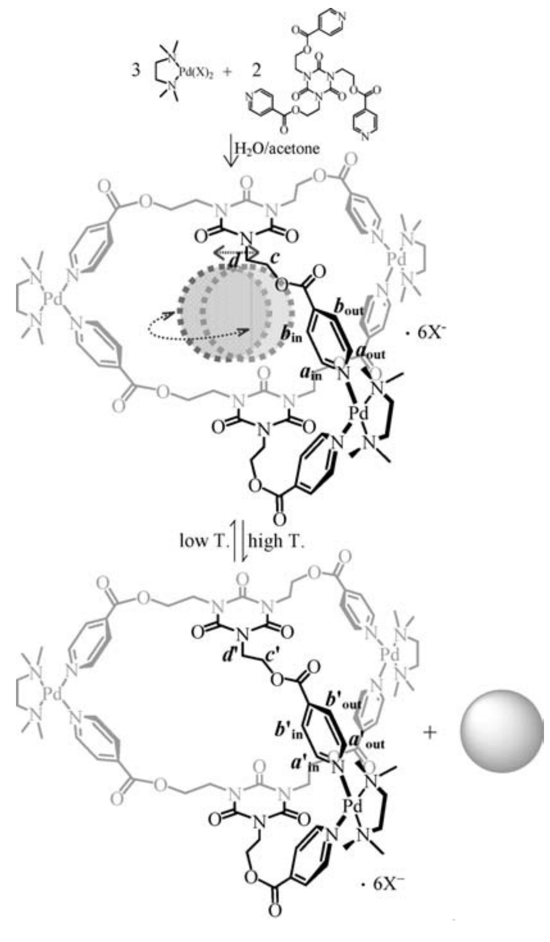
ABSTRACT: The unique cage complexes $[[(\mathrm{Me_4en})\mathrm{Pd}]_3(\mathrm{L})_2](\mathrm{X})_6$ (L = 1,3,5-tris(isonicotinoyloxyethyl)cyanurate; $\mathrm{X^-} = \mathrm{BF_4^-}$, $\mathrm{ClO_4^-}$) were constructed. A single water molecule in a skeletal cage was reversibly associated and dissociated via a combination of the adequate space, polar environment, and conformational flexibility of the cage. In Suzuki−Miyaura C−C cross-coupling reactions, the cage complex showed significant catalytic activity along with the effects of the isolated single water molecule.

A single water molecule within an isolated space is a hot research topic in molecular science, owing to potential applications to delicate functions such as proton transfer, tautomerism, recognition, and biological systems.[1−3] Studies on discrete hydrogen-bond tetramer, pentamer, hexamer, octamer, and decamer water clusters within various crystalline hosts have been conducted,[4−8] but reports on the existence of a single water molecule within a special space are rare, except those of Huc et al. on isolated water molecules within helical folded aromatic oligoamides.[2,9] Coordination cages that reversibly encapsulate guest molecules have been employed to task-specific spaces for guest binding, recognition, dynamic materials, delivery, storage, and catalysis.[10−14] The essential elements for coordination-driven self-assembled cages are rigid multitopic ligands and angular units of metal ions.[10,13] Some rigid organic tripodal linkers have been applied for manipulation of the shape and symmetry of cage assemblies,[15,16] but there has been little corresponding research on the dynamic system.[17] In this context, in order to validate the concept and confirm the behavior of a single water molecule within an isolated flexible cage, we report both a $[\mathrm{Pd_3L_2}]^{6+}$ (Pd = $(\mathrm{Me_4en})\mathrm{Pd^{II}}$) cage constructed with cis-protected ditopic $(\mathrm{Me_4en})\mathrm{Pd^{II}}$ by means of a new C_3-symmetric flexible triangular ligand and the motional behavior of a single water molecule within it. The dual properties of the liberal/restrictive aspects of the single water molecule together with its catalytic activity were explored. Certainly, some palladium(II) complexes have been known to be very good catalysts for various organic reactions.[18]

Reactions of $(\mathrm{Me_4en})\mathrm{PdX_2}$ ($\mathrm{X^-} = \mathrm{BF_4^-}$, $\mathrm{ClO_4^-}$) with 1,3,5-tris(isonicotinoyloxyethyl)cyanurate (L) were achieved in a mixture of water and acetone for 2 h, after which slow evaporation of the resulting solution produced high-yield hexagonal-prismatic single crystals suitable for X-ray crystallographic analysis (Scheme 1).[19] The construction of the skeletal structure was not significantly affected by changes to the mole ratio, solvents, counteranions, or concentration, indicating a favorable species of product. The $[\mathrm{Pd_3L_2}]^{6+}$ cage compound was shown to be insoluble in common organic solvents such as acetone, chloroform, and tetrahydrofuran but soluble in acetonitrile, dimethyl sulfoxide, and *N*,*N*-dimethylformamide. The $[\mathrm{Pd_3L_2}]^{6+}$ cage compound was retained in solution for several days but dissociated in methanol or ethanol.

Scheme 1. Formation and Dynamic Behavior of $[\mathrm{Pd_3L_2}]^{6+}$ Cage[a]



[a] The sphere denotes a water molecule. $\mathrm{X^-} = \mathrm{BF_4^-}$, $\mathrm{ClO_4^-}$.

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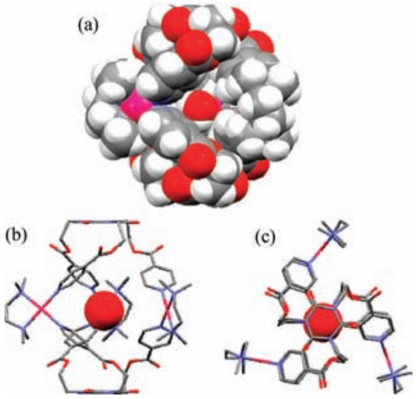


Figure 1. Space-filling side view (a), stick side view (b), and stick top view (c) of $H_2O@[Pd_3L_2](BF_4)_6$. The anions, solvated acetone, and hydrogen atoms (b, c) are omitted for clarity.

For example, the skeletal structure was completely dissociated within 60 h in a mixture of CD_3CN and CD_3OD (3/2 v/v) and in a mixture of CD_3CN and ethanol-d_6 (3/2 v/v) at room temperature but was retained for several days in a mixture of CD_3CN and D_2O.

With regard to the tetrafluoroborate crystal, an elegant $[Pd_3L_2]^{6+}$ cage structure, depicted in Figure 1, was demonstrated. Specifically, the C_3-symmetric L connects to three cis-protected (Me_4en)-Pd(II) ions in a pinwheel fashion, forming a truncated trigonal-bipyramidal cage with a C_{3h} symmetry point group. Each L occupies a pyramid, and three Pd(II) ions lie in equatorial positions. The local geometry around the Pd(II) ion approximates to a typical square-planar arrangement (N−Pd−N for Me_4en = 86.7(3)°; N−Pd−N for Py = 87.0(2)°) with four nitrogen atoms (Me_4en, Pd−N = 2.028(5) and 2.036(5) Å; Py ligands, Pd−N = 2.051(7) and 2.076(9) Å). The distance between the two cyanuric planes of the cage is 13.15(2) Å, and the Pd···Pd separation in the equatorial position is 9.738(1) Å. Thus, the cage has an elliptical cavity of approximately 10.0 × 5.0 Å diameter and the same three entrances of 3.5 Å diameter. The most prominent feature is the single, disordered water molecule nestled into the cavity. Of course, there is no significant interaction between the single water molecule and the cage skeleton in the solid state. Thus, the product can be described as $H_2O@[Pd_3L_2](BF_4)_6 \cdot 3Me_2CO$. The FAB-mass data (matrix 3-nitrobenzyl alcohol) for $H_2O@[Pd_3L_2](BF_4)_6$ did not show a mass peak corresponding to the cage containing the encapsulated single water molecule but instead showed the mass peak corresponding to $[[Pd_3L_2](BF_4)_6 - BF_4]^+$ (obsd 2253.45; calcd 2253) (Supporting Information). The structure of the ClO_4^- product is very similar to that of the BF_4^- product, except for another solvate water molecule, $H_2O@[Pd_3L_2](ClO_4)_6 \cdot 3Me_2CO \cdot H_2O$. The IR spectra and elemental analyses, in fact, were consistent with the proposed cage structure (Supporting Information).

For $H_2O@[Pd_3L_2](BF_4)_6$, the thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) results were traced as shown in Figure 2. The cage skeleton was stable up to 241 °C but, in the 241−372 °C temperature range, decomposed into palladium oxide and trace tar. The DSC plot shows a signal corresponding to the loss of the single water molecule, which evaporated in the 45−104 °C temperature range. This evaporation is an endothermic process (15.9 kcal/mol), the energy of which is comparable to that of an organic supramolecule.[3] The −OH band at 3628 cm^{-1} (in a Nujol mull), unlike the general hydrogen-bonded −OH frequency range (3400−3200 cm^{-1}),[20] revealed a "free" −OH group: that is, the presence of an isolated single water molecule. The isolated water molecule was smoothly evaporated from the cage in vacuo at ambient temperature and was reincorporated into the cavity by exposure to air. To test this finding, the cage product was monitored by way of the characteristic −OH stretching band at 3628 cm^{-1}. After the sample was evacuated, the intense −OH band was observed to gradually disappear. With the evacuated sample standing for 1 day in air, the −OH band again returned to its original intensity (Figure 2). The other peaks of the spectrum remained virtually unchanged, indicating that the skeletal structure remained unchanged in the solid state (Supporting Information).

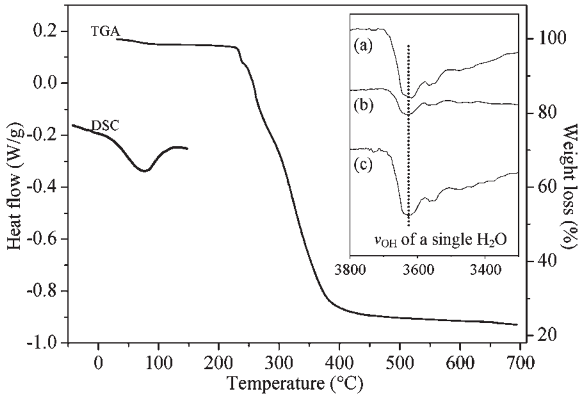


Figure 2. TGA and DSC curves of $[[(Me_4en)Pd]_3(L)_2](BF_4)_6$. Inset: ν(OH) IR spectra (Nujol mull) before (a) and after (b) dryness in vacuo and on exposure to air (c).

The behavior of a single water molecule within the cage in acetonitrile was studied using temperature-dependent ^1H NMR spectra (Figure 3). The spectrum at room temperature shows that the resonances at 9.07, 7.95, 4.48, and 4.30 ppm from L, along with the peaks at 3.02 and 2.62 ppm from the Me_4en moiety, are relatively broad. After the sample was cooled to −10 °C, the resonance signals at 9.07, 3.02, and 2.62 ppm separated into two conformer signals that could be assigned as outside and inside Py-H (outside and inside Me_4en in Figure 3b). Further cooling (to −30 °C) of the sample resulted in satellite signals, indicating that the $[Pd_3L_2]^{6+}$ (main peaks) and $H_2O@[Pd_3L_2]^{6+}$ (satellite peaks) species were equilibrated in solution.[9] The singlet at 2.78 ppm was assigned, with the aid of the ^1H NMR spectra via addition of D_2O, as a single water molecule within the cage (Supporting Information). That is, the intensity of the signal at 2.78 ppm decreased with the addition of D_2O.[9] The signal was clearly discerned from the resonance of water in acetonitrile solvent (2.14 ppm, Supporting Information). The signal broadened as the temperature continued to drop, indicating that the motion of the single water molecule is restricted at low temperature.

The reversible adsorption and desorption of the guest single water molecule suggests a lack of strong interaction between it and the cage (Supporting Information). The kinetics of such a process should fundamentally differ from the adsorption and desorption of a water molecule via general hydrogen bonding. Both adequate space and the polar environment inside the cavity seem together to play a crucial role in the duality of the single water molecule's combined liberal and restrictive aspects. The cavity provides a nice symmetric environment for a single water molecule, owing presumably to the presence of a tridentate

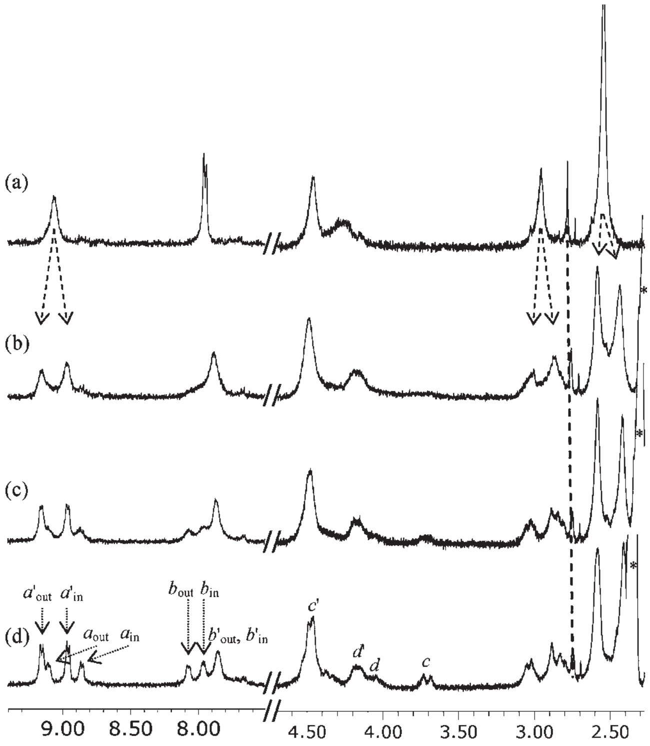
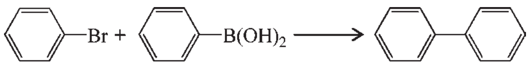


Figure 3. Temperature-dependent ^1H NMR (300 MHz) spectra of $H_2O@[Pd_3L_2]^{6+}$ at room temperature (a), −10 °C (b), −20 °C (c), and −30 °C (d). See Scheme 1 for the assignments in part d. The peak at 2.78 ppm designated by the dashed line indicates the encapsulated water molecule; the asterisk indicates the resonance of water in CD_3CN. The peaks at 2.95 and 2.54 ppm in part a indicate the resonances of Me_4en.

ligand with many functional groups, including three amides, three esters and six N donors. However, the presence of a single water molecule via rigid interactions within a symmetric cage is not to be expected, in contrast with a rigid water molecule within an asymmetric crownophane.[3] This fact is consistent with the disorder of hydrogen atoms in X-ray crystallography, implying the dynamic nature of the behavior of the single water molecule within the cage. The symmetric and somewhat large cavity is an obstacle to directional rigid interaction between a single water molecule and the inside of the cage. The broad −OH stretching frequency also suggests that behavior (Figure 2). The general "free" −OH stretching frequency appeared in the range of 3650−3600 cm^{-1} as a sharp band.[20] The single water molecule can freely move around within a cage consisting of six pinwheel pyridyl groups and can be released from the cavity through the 3.5 Å pinholes via the temperature-dependent rotation of the pyridyl groups.

In order to test the catalytic effects of the palladium(II) cage complex, typical C−C Suzuki−Miyaura cross-couplings were preliminarily achieved without phosphine or any other additive, as shown in Table 1. The reactions were carried out in anhydrous *N*,*N*-dimethylformamide, as the solvent, and in K_2CO_3 as the selected base. The yields, the averages of two runs, were determined on the basis of the residual bromobenzene. In order to gauge the effect of the encapsulated water molecule, the catalysis of $H_2O@[Pd_3L_2]^{6+}$ was compared with that of $[Pd_3L_2]^{6+}$, the former showing a better result than the latter. The isolated water molecule increased the yields significantly, which is consistent with the water-assistant effects of the Suzuki−Miyaura C−C cross-coupling reactions.[21] Of course, the catalytic reaction was better with a high catalyst content and a high temperature. The detailed catalytic reactions are underway.

Table 1. Suzuki−Miyaura Coupling Reactions Catalyzed by $H_2O@[Pd_3L_2](BF_4)_6$ and $[Pd_3L_2](BF_4)_6$ in *N*,*N*-Dimethylformamide with K_2CO_3 as Base



entry	cat. contents (mol %)	temp (°C)	time (h)	yield (%) *a*	yield (%) *b*
1	0.01	200	3	73	58
2	1	25	12	27	5
3	1	60	12	63	6

[a] $H_2O@[Pd_3L_2](BF_4)_6$. [b] $[Pd_3L_2](BF_4)_6$.

In conclusion, the present research undertook construction of thermodynamically stable C_{3h} skeletal cages that can reversibly associate and dissociate an isolated water molecule via conformational flexibility and the molecule's motion. To the best of our knowledge, this is a unique example of perfectly typical single water molecule behavior combined with dual liberal/restrictive properties. Specifically, a preliminary test showed significant C−C cross-coupling catalytic effects along with water molecule synergy effects. This result suggests potential applications to small-molecule-accommodating recognition systems, gas adsorption, and catalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Text and figures giving full experimental details, MS data for $[Pd_3L_2](BF_4)_6$, ^1H NMR spectra in a mixture of CD_3CN and D_2O, CD_3OD, and ethanol-d_6, respectively, IR spectra of $H_2O@[Pd_3L_2](X)_6$ ($X^- = BF_4^-$, ClO_4^-) showing the adsorption and desorption of the water molecule, temperature-dependent ^1H NMR reflecting incorporated water and free water in CD_3CN, COSY spectrum of $H_2O@[Pd_3L_2](BF_4)_6$ at −30 °C, and ^1H NMR of biphenyl formed via catalysis and CIF files giving crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Crystal data: $C_{81}H_{116}B_6N_{18}F_{24}O_{22}Pd_3$, $M = 2533.98$, rhombohedral, space group $R3$, $a = b = 15.5209(6)$ Å, $c = 39.827(2)$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 8308.8(6)$ Å^3, $Z = 3$, 15 285 reflections measured, 6243 unique reflections ($R_{\text{int}} = 0.0292$), $S = 1.038$, $\mu = 0.593$ mm^{-1}. The final R indices were R1 ($I > 2\sigma(I)$) = 0.0505 and wR2 (all data) = 0.1466.

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