

内孔に結合する直鎖状二座配位子の長さに応じた環状六核パラジウム錯体の構造変化

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Structural Change of a Macrocyclic Hexanuclear Palladium Complex According to the Lengths of Bidentate Ligands Binding to Its Inner Cavity (¹*Degree Programs in Pure and Applied Sciences, University of Tsukuba*, ²*Faculty of Pure and Applied Sciences, University of Tsukuba*)
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We previously reported that the binding of six molecules of pyridine derivatives to a palladium complex of hexapap, a cyclic hexamer of chelating unit pap, leads to a twisted conformation in which each coordination site of the Pd(pap) complex is directed up-up-down-up-up-down¹⁾. In this work, we have found that the coordination of various lengths of linear diamines $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$ let the hexanuclear palladium complex $[\text{1Pd}_6\text{L}_6]^{6+}$ (L: an exchangeable ligand) adopt different binding modes and macrocyclic conformations according to the number of methylene groups (n). In the case of $n = 4-7$, it took an alternate conformation in which each coordination site is directed up-down-up-down-up-down by binding three diamines. Meanwhile, it took a twisted conformation upon binding two 1,8-diaminooctanes ($n = 8$), and three 1,12-diaminododecanes ($n = 12$) also resulted in a twisted conformation.

Keywords : Macrocyclic; Palladium; Diamine; Supramolecular Chemistry; Multinuclear Complex

我々は以前、キレート配位部位 pap の環状六量体 hexapap のパラジウム錯体にピリジン誘導体を 6 分子結合することで、Pd(pap)錯体の各配位サイトが順に上上下下上下の向きになる捻れた配座をとることを報告した¹⁾。今回、パラジウム 6 核錯体 $[\text{1Pd}_6\text{L}_6]^{6+}$ (L は交換可能な配位子) の内孔に、種々の長さの直鎖状ジアミン $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$ を配位させたところ、メチレンの数 (n) に応じて異なる結合様式と環状骨格の配座をとることがわかった。 $n = 4-7$ の場合はジアミン 3 分子が結合して各配位サイトが交互に上下上下上下の向きになる配座をとった。一方で、 $n = 8$ では 2 分子が結合して捻れた配座、 $n = 12$ では 3 分子が結合して捻れた配座となった。

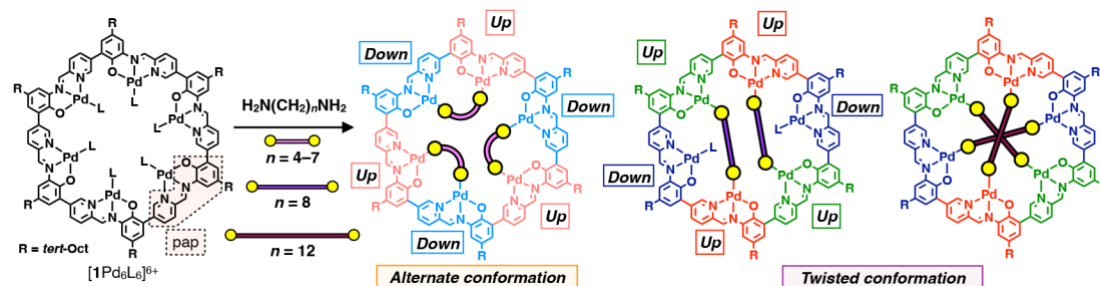


Figure. Structural change of hexanuclear palladium complex $[\text{1Pd}_6\text{L}_6]^{6+}$ according to the lengths (n) of diamines $\text{H}_2\text{N}(\text{CH}_2)_n\text{NH}_2$.

1) A. Nagai, T. Nakamura, T. Nabeshima, *Chem. Commun.* **2019**, 55, 2421.