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Self-Assembly of Pt(II) Spherical Complexes via Temporary Labilization of the Metal–Ligand Association in 2,2,2-Trifluoroethanol

Daishi Fujita, Asana Takahashi, Sota Sato, and Makoto Fujita*

Department of Applied Chemistry, School of Engineering, The University of Tokyo, and CREST, Japan Science and Technology Agency (JST), 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

S *Supporting Information*

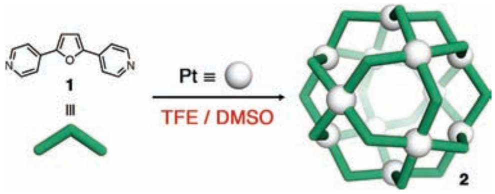
ABSTRACT: Thermodynamically controlled platinum(II) spherical complexes were synthesized via temporary labilization of inert Pt(II)–pyridine bonds by the addition of the strong hydrogen-bond donor 2,2,2-trifluoroethanol (TFE), which weakens the pyridine–metal interaction. The platinum complex was stably trapped after removal of TFE and showed higher acid durability than its palladium counterpart.

The switching of kinetically inert metal–ligand interactions into labile ones under certain external stimuli is termed temporary labilization (eq 1).[1,2] When inert coordination bonds are temporarily labilized, desired structures can be self-assembled from metal and ligand components under thermodynamic control and then turned into inert (stable) frameworks by "switching off" the labilization.

$$\underset{\text{(inert)}}{\mathrm{M}\!-\!\mathrm{L}}\ \underset{\text{labilization "off"}}{\overset{\text{labilization "on"}}{\rightleftarrows}}\ \underset{\text{(labile)}}{\mathrm{M}\cdots\mathrm{L}} \qquad (1)$$

Kinetically inert Pt(II)–pyridine coordination bonds have previously been labilized by salt-mediated nucleophilic activation[1] or photochemical activation[2] to give interlocked or cage structures that can otherwise be self-assembled only with analogous kinetically labile Pd(II)–pyridine bonds. However, these labilization methods are not suitable for practical use because the removal of the salt is troublesome and photoirradiation requires unconventional apparatus that limits practical synthesis and reaction scale-up. In addition, these methods are applicable only to self-assembly from a small number of metal and ligand components (typically, $n < 10$). When n is larger, these methods are no longer effective, and intractable mixtures are formed as a result of insufficient bond labilization, although there are some exceptions involving the self-assembly of Pt(II) complexes with large n.[3] Here we report that a strong H-bond-donor solvent, 2,2,2-trifluoroethanol (TFE),[4,5] considerably labilizes Pt(II)–pyridine bonds, allowing the formation of even giant, multicomponent $\mathrm{Pt(II)_{12}L_{24}}$ spheres from Pt(II) ions and pyridine ligands (L) (Scheme 1). The volatile TFE solvent (bp 78 °C) is easily removed, affording kinetically trapped stable Pt(II) assemblies. We demonstrate that the $\mathrm{Pt(II)_{12}L_{24}}$ sphere, whose structure is shown in Figure 1, is much more stable than its Pd(II) counterpart. Interestingly, when the ligand was made relatively flexible with acetylene spacers, the temporary labilization resulted in the trapping of a $\mathrm{Pt(II)_6L_{12}}$ cube rather than a $\mathrm{Pt(II)_{12}L_{24}}$ sphere.

Scheme 1. Schematic Representation of the Self-Assembly of $\mathrm{Pt(II)_{12}L_{24}}$ Complex 2 with the Weakly Acidic, H-Bond-Donating Solvent TFE



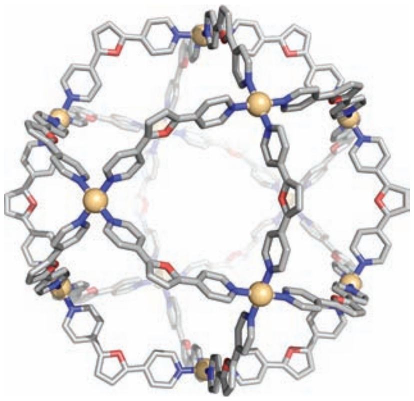


Figure 1. Crystal structure of $\mathrm{Pt(II)_{12}L_{24}}$ complex **2**. H atoms and the two $\mathrm{SbF_6^-}$ counterions that are present at the apical positions of each $\mathrm{Pt^{2+}}$ have been omitted for clarity.

TFE exhibits weakly acidic character and a H-bond donating ability comparable to that of phenol[4] and forms a stable 1:1 acid–base complex with pyridine.[5] We anticipated that the Pt(II)–pyridine coordination bond could be labilized in TFE because dissociated pyridine ligands are stabilized by strong H-bonds with TFE. Thus, ligand **1** (7.0 μmol), which forms a $\mathrm{Pd(II)_{12}L_{24}}$ sphere upon complexation with Pd(II) ions,[6] was treated with $\mathrm{Pt(NO_3)_2}$ (5.6 μmol) in 60:40 TFE/DMSO mixed solvent (700 μL). Time-dependent ^{1}H NMR analysis revealed that the spectrum gradually became simpler, and convergence

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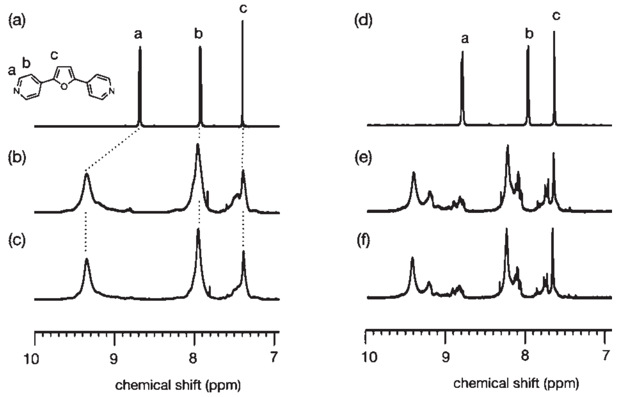


Figure 2. ^{1}H NMR (500 MHz, 300 K) observation of the self-assembly of $Pt(II)_{12}L_{24}$ complex **2** in (a−c) 60:40 TFE/DMSO and (d−f) DMSO. Shown are spectra of (a, d) free ligand **1** and the the mixture (b, e) 12 and (c, f) 24 h after complexation with $Pt(NO_3)_2$. The structure converged only in TFE/DMSO. It should be noted that signal broadening for giant Pt(II) complexes is inevitable because of their tumbling motion, which is slow on the NMR time scale.

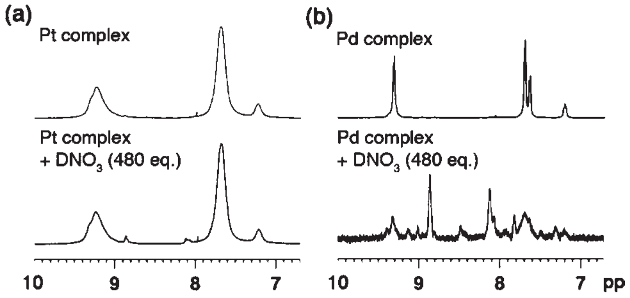
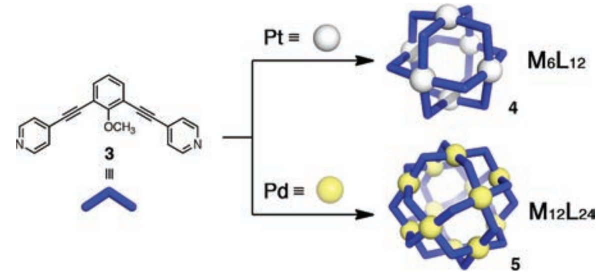


Figure 3. ^{1}H NMR spectra (500 MHz, DMSO-d_6, 300 K) of (a) Pt complex **2** and (b) its Pd analogue in DMSO upon the addition of excess DNO_3.

into a single product was observed after 24 h (Figure 2b,c). The considerable broadening of the signals was attributed to the tumbling motion of a giant product that was slow on the NMR time scale.[7] The diffusion-ordered spectroscopy (DOSY) NMR spectrum also indicated the formation of a single product with a diffusion coefficient of 6.31×10^{-11} m^2/s, which is comparable to that of the $Pd(II)_{12}L_{24}$ sphere formed from Pd(II) ions and ligand **1**.[8] This structural convergence was not observed without TFE: in DMSO only, the NMR spectrum of an initially formed, unassignable mixture remained unchanged over 24 h (Figure 2e,f). Addition of another protic solvent such as EtOH or acetic acid was ineffective.

The $Pt(II)_{12}L_{24}$ composition of **2** (SbF_6^- salt) was confirmed by cold-spray ionization time-of-flight mass spectrometry (CSI-TOF-MS)[9] from a series of $[M - n(SbF_6^-)]^{n+}$ peaks (n = 10−15), each of which was further resolved into an isotopic distribution pattern consistent with theoretical simulations (see the Supporting Information). The rigid shell framework of $Pt(II)_{12}L_{24}$ was revealed by X-ray crystallographic analysis (Figure 1). Single crystals were obtained by slow diffusion of isopropyl acetate vapor into a DMSO solution of **2** (SbF_6^- salt). Because of the severe disorder of solvent molecules and counterions in the large void of the crystals, the diffraction with a conventional X-ray diffractometer was too weak to be solved. However, high-flux, low-divergence synchrotron X-ray irradiation afforded high-quality data from which the $Pt(II)_{12}L_{24}$ spherical shell was confirmed. No unusual bond lengths or angles were observed, and almost perfect square-planar orientation of the four pyridyl groups around each Pt(II) center was confirmed. Importantly, these structural features of **2** are essentially the same as those of $Pd(II)_{12}L_{24}$ spheres with the same shell framework, whose crystal structures have been determined previously.[6]

Scheme 2. Schematic Representation of the Self-Assembly of the M_nL_{2n}-type Complexes Derived from Ligand 3



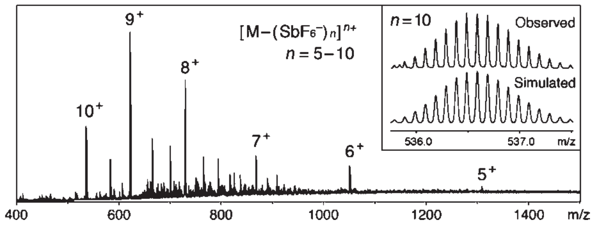


Figure 4. CSI-TOF mass spectrum of $Pt(II)_6L_{12}$ cube **4** (SbF_6^- salt). The inset shows expanded spectra of the n = 10 peak (observed and simulated).

The remarkable durability of **2** toward acidic solution is worthy of note. The NMR spectrum of **2** hardly changed upon addition of excess nitric acid (480 equiv) to a DMSO solution of **2** (Figure 3a). In contrast, the Pd(II) analogue could not tolerate acidic conditions and immediately decomplexed into a unassignable mixture of oligomers because of the labile nature of the Pd(II)−pyridine coordination (Figure 3b).

When the extended ligand **3** was employed, we unexpectedly observed the self-assembly of $Pt(II)_6L_{12}$ cube **4** rather than a $Pt(II)_{12}L_{24}$ sphere analogous to **2**, though the same ligand gave the the $Pd(II)_{12}L_{24}$ sphere (**5**) quantitatively (Scheme 2).[8,10] The formation of cube **4** was confirmed by CSI-TOF-MS and 1D and DOSY NMR spectroscopy (see the Supporting Information). After counterion exchange with SbF_6^-, CSI-TOF-MS revealed a series of $[M - n(SbF_6^-)]^{n+}$ peaks (n = 6−10) for **4** (Figure 4). All of the m/z values of these peaks agreed with the formulas of **4** (SbF_6^- salt) (e.g, m/z calcd for $[M - 9(SbF_6^-)]^{9+}$, 621.7547; found, 621.7552]. High acid durability (toward DNO_3) was again observed for cube **4** (Figure S5 in the Supporting Information).

We assume that the M_6L_{12} cube structure[11] exists as a metastable local-minimum structure on the potential surface for the self-assembly process. Even in the presence of TFE, the Pt(II)−pyridine interaction is much stronger than the Pd(II)−pyridine interaction. Thus, the $Pt(II)_6L_{12}$ cube is trapped at the local minimum and not further converted into the $Pt(II)_{12}L_{24}$ structure, whereas the Pd(II) counterpart is not deeply trapped in the cube structure and smoothly slips down to the minimum on the potential surface corresponding to the $Pd(II)_{12}L_{24}$ structure **5**.

In summary, we have demonstrated the self-assembly of giant multicomponent $Pt(II)_nL_{2n}$ complexes via the temporary labilization of Pt(II)−pyridine bonds in TFE. This conventional method offers practical applications for the construction of a variety of Pt(II)-linked coordination assemblies that efficiently self-assemble in TFE but are frozen after simple removal of the volatile TFE solvent.

■ ASSOCIATED CONTENT

Supporting Information. Synthesis, characterization data of the compounds, crystallographic data (CIF), and additional figures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

mfujita@appchem.t.u-tokyo.ac.jp

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