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Spectroscopic Observation of Self-Assembly of a Macrocyclic Tetranuclear Complex Composed of Pt^{2+} and 4,4'-Bipyridine

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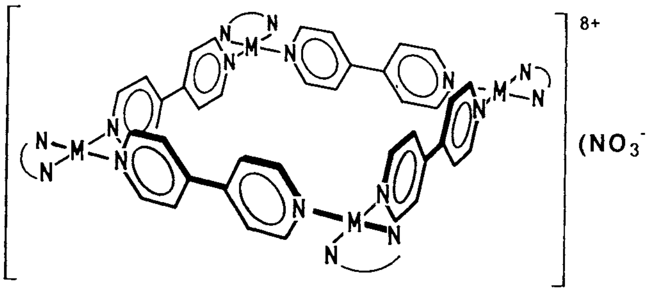
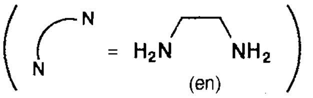
Macrocyclic tetranuclear Pt(II) complex $[(en)Pt(4,4'\text{-}bpy)]_4(NO_3)_8$ (en = ethylenediamine; bpy = bipyridine) assembled by treating $(en)Pt(NO_3)_2$ with 4,4'-bpy in water. The assembling was monitored by ^1H NMR.

Coordination of polydentate ligands to metal cations often gives rise to polynuclear complexes having unique and highly integrated structures.1) Although these complexes seem to assemble spontaneously, there are no example of the observation of the dynamic assembling process. We recently reported preparation of a macrocyclic Pd(II) complex **1** from $(en)Pd(NO_3)_2$ and 4,4'-bipyridine.2) Now we succeeded in spectroscopic monitoring of the self-assembling process of the analogous Pt(II) macrocyclic complex **2**.



1:M = Pd; 2:M = Pt



The self-assembly of **2** was observed by ^1H NMR. Treatment of $(en)Pt(NO_3)_2$3) with 4,4'-bipyridine (1 mol equiv.) in D_2O initially formed an intractable mixture (Fig. 1(a)) that may be composed of oligomers $(\{\text{-}[(en)Pt(4,4'\text{-}bpy)]_n\text{-}\}^{2n+}(NO_3^-)_{2n})$. Surprisingly, on heating the mixture at 100 °C, the NMR spectrum became simpler and finally converged to a set of two doublet-like signals at δ = 7.84 and 8.87 (Fig. 1(b), (c)). This dramatic spectral change should be attributed to the transformation of kinetically distributed products into the thermodynamically most stable component.4) Apparently the complex **2** is the latter. Although more than four weeks were required to accomplish this assembling, employment of 4,4'-bpy•$2HNO_3$ instead of

4,4'-bpy itself was effective for saving the reaction period and the convergence to **2** at 100 °C completed within a week.

Addition of ethanol to the resulting solution caused precipitation of pale yellow powder (79-81% yield) that was fully characterized by elemental analysis and spectroscopic measurements (Fig. 1(d)). Since its spectral data were quite similar to those of previously prepared Pd(II) complex **1**,(2) the structure of the Pt(II) complex was assigned to be a cyclic tetramer **2**.(5) Physical data of **2** are as follows: mp 230-240 °C dec; ^{1}H NMR (400 MHz, D_2O)(6) δ 2.84 (s, 16 H, $-CH_2CH_2-$) 7.84 (d-like, J = 6.8 Hz, 16 H, Ar$H\beta$), 8.87 (d-like, J = 6.8 Hz, 16 H, Ar$H\alpha$); ^{13}C NMR (100 MHz, D_2O)(6) δ 50.33 (CH_2), 128.0 ($C\beta$), 149.2 ($C\gamma$), 155.5 ($C\alpha$); IR (KBr) 1610, 825 cm^{-1}. Found: C, 26.08; H, 3.07; N, 14.78%. Calcd for $C_{48}H_{64}N_{24}O_{24}Pt_4 \cdot 5H_2O$:(7) C, 25.83; H, 3.34; N, 15.06%.

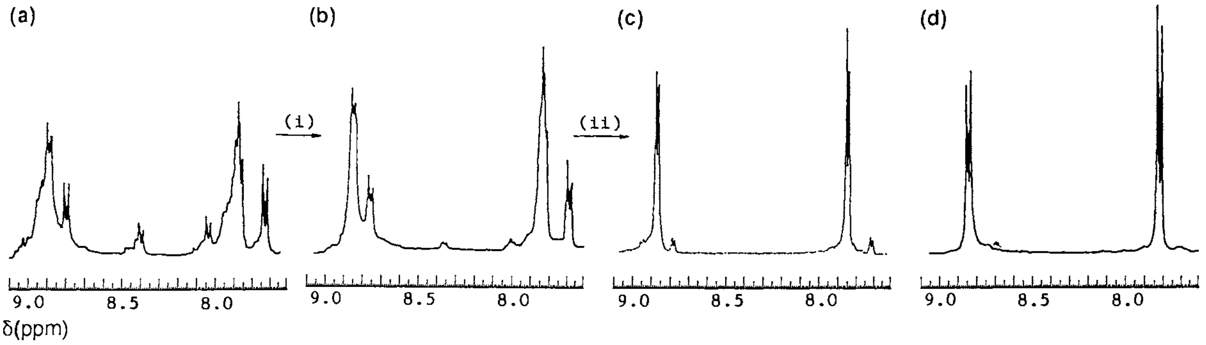


Fig. 1. Spectroscopic observation of the assembly of **2**.

(a)-(c): Spectral variation in the reaction of (en)Pt$(NO_3)_2$ and 4,4'-bpy. Conditions are: (i) room temperature, 1 week, then, 100 °C, 1 week; (ii) 100 °C, 4 weeks. (d) Spectrum of **2** after isolation ((a), (b), (d): 270 MHz; (c) 500 MHz).

References

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2) M. Fujita, J. Yazaki, and K. Ogura, *J. Am. Chem. Soc.*, **112**, 5645 (1990).
3) (en)Pt$(NO_3)_2$ was prepared by treating (en)PtCl_2 with $AgNO_3$ (2 mol equiv.) in H_2O at 100 °C for 2 h. Preparation of (en)PtCl_2: F. Basolo, J. C. Bailar, and B. R. Tarr, *J. Am. Chem. Soc.*, **72**, 2433 (1950).
4) The same self-assembly mechanism must work in the formation of Pd complex **1**. However the equilibrium seems very rapid in the reaction of (en)Pd$(NO_3)_2$ with 4,4'-bipyridine and no kinetic products were observed even at the early stage of the reaction (room temperature, 1 min).
5) Aqueous complexation of **2** with aromatic compounds will appear elsewhere.
6) Sodium 2,2,3,3-tetradeuterio-3-(trimethylsilyl)propanoate (a D_2O solution) sealed in a capillary was used as an external standard.
7) The hydrate number may vary owing to hygroscopic property of this complex.

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