Pt Complexes of N-Confused Porphyrin

Facile Formation of *N*-Confused Porphyrin Dimers by Platinum(II) Coordination to the Outer-Nitrogen Atoms

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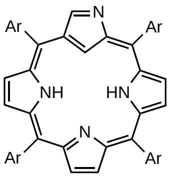
Recently, metal assisted porphyrin assembly has attracted much interest as one of the useful strategies employed to create polyporphyrin architectures in supramolecular chemistry.[1] For such studies, a combination of Pd^{II} or Pt^{II} ions, and amines such as pyridine, which can form stable tetracoordinated square-planar complexes, are frequently used as external bridging metal ions and ligands, respectively.[2] The edge-to-edge distances between two adjacent porphyrin rings in these systems depend on the size of the linker, thus, one way of generating the shortest connection might be to form a bond between the bridging metal atom and the porphyrin framework in which the coordinating atom is embedded.

In the course of studying *N*-confused porphyrin (NCP, **1**),[3,4] we discovered the formation of a doubly linked Pd^{II}–NCP-dimer complex, or "double decker" (**2**), in which two Pd centers were directly bonded to an outwardly pointing nitrogen atom of the confused pyrrole ring, an *ortho*-carbon atom of *meso*-aryl group, and two inner core nitrogens of the countered porphyrin.[5] The unique structure of **2** was derived as the result of the distortion from planarity of both the porphyrin ring and the coordinated Pd^{II} center. In this regard, we have been interested in Pt^{II}-ion complexation because rigid square-planar Pt^{II} complexes are known.[6] This attribute might force the porphyrin ring to be distorted significantly if the NCP formed a similar type of dimer to that of complex **2** with Pt^{II} ions. Interestingly, the Pt dimer complexes (**3, 4**) were singly linked dimers with the ratio of Pt to NCP being 1:2. Herein, we report the syntheses and structural characterization of novel Pt^{II}–NCP dimer complexes and an inner coordinated monomer complex (**5**). To the best of our knowledge, the complexes **3** and **4** are the first NCP dimers linked by a metal at the peripheral core nitrogens.



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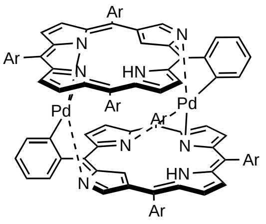

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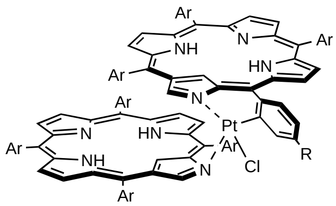

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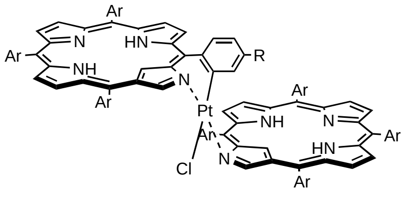

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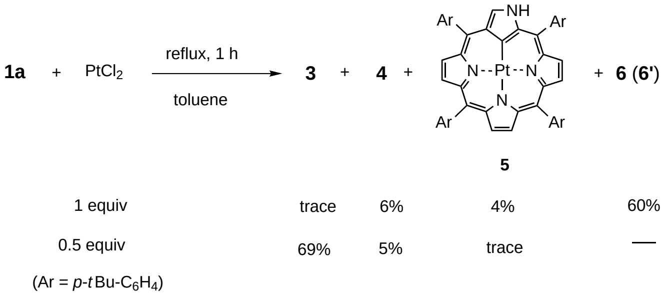
When *N*-confused 5,10,15,20-tetrakis(4′-*tert*-butylphenyl)porphyrin (**1a**)[7] was treated with one equivalent of PtCl$_2$ in refluxing toluene for 1 h, green dimer complexes **3** and **4** were isolated in trace and 6 % yield, respectively. Apart from these, inner coordinated monomer complex **5** and an isomeric mixture of reddish dimer complexes **6** and **6′** (see below) were produced in 4 and 60 % yields, respectively. On the other hand, when 0.5 equivalents of PtCl$_2$ was subjected to the reaction, the dimers **3** and **4** were isolated in 69 and 5 % yields, respectively, but the monomer **5** was obtained only in trace amounts and the formation of neither **6** nor **6′** were observed (Scheme 1).

The structures of dimer complexes **3** and **4** were established by single crystal X-ray analyses (Figure 1).[8] Both complexes consist of one Pt atom, two NCP units, and one chloride atom. The Pt center was connected with two outer-nitrogen atoms of NCP molecules, an *ortho*-carbon atom of a



Scheme 1. Reactions of NCP **1a** with Pt^{II}Cl$_2$.

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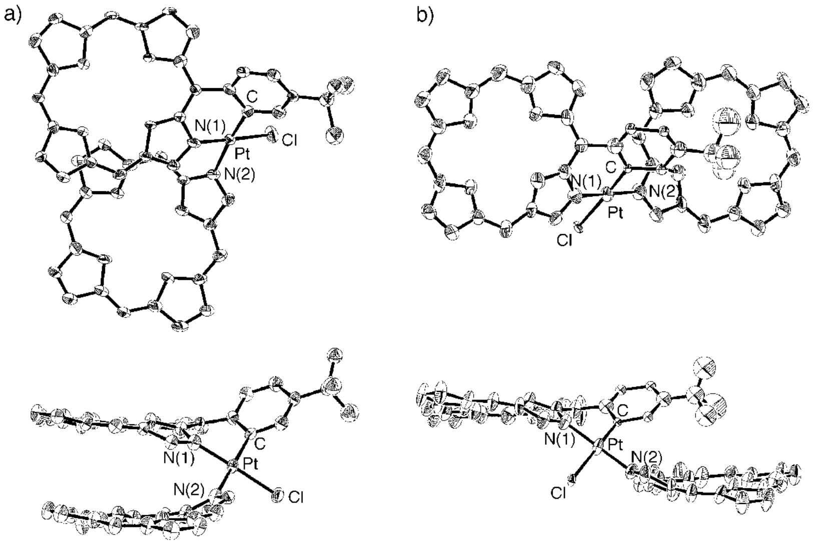


Figure 1. Molecular structure and coordination geometries of a) **3** and b) **4**; top view (top) and side view (bottom; ORTEP drawing, ellipsoids set at the 50% probability level). Uncoordinated *meso*-aryl groups were omitted for clarity. Selective bond lengths [Å] and angles [°]: a) Pt-N(1) 1.97(1), Pt-N(2) 2.12, Pt-C 1.98(1), Pt-Cl 2.313(4), N(1)-Pt-N(2) 91.8(5), N(1)-Pt-C 87.8(5), N(2)-Pt-Cl 88.3(3), C-Pt-Cl 92.4(4); b) Pt-N(1)(=Pt-N(2)) 2.007(9), Pt-C 1.892(8), Pt-Cl 2.512(5), N(1)-Pt-C 85.6(5), N(2)-Pt-Cl 86.9(1).

meso-aryl group, and a chloride atom in a square-planar fashion. The two confused pyrrole rings in **3** and **4** were located around the Pt center in a *cis* and *trans* configuration, respectively. The confused pyrrole rings, which were serving as metallocyclic ligands, were tilted 20.94° for **3** and 28.72° for **4** to the mean planes consisting a core of 24 atoms. In both the complexes, the two core planes were nearly parallel with dihedral angles of 7.71 and 7.42°, respectively, and in the case of **3**, these planes were partially overlapped. Noteworthy, the binding mode of the second NCP molecule to a Pt center is a simple outer-N coordination, in just the same fashion as nucleobase adducts to cisplatin.[9] In fact, this NCP ligand was quantitatively replaced with triphenylphosphane in toluene at room temperature.[10] The structure of **5** was also established from the X-ray analysis of the corresponding NCP derivative,[11] which showed Pt^{II} ion in the center of the NCP core with a carbon–metal atom bond similar to that of Pd^{II} monomer complex (see Supporting Information).

The ^1H NMR spectrum of *cis* **3** showed the two inner-CH signals at $\delta = -5.08$ and -4.76 ppm in $CDCl_3$ at room temperature. At $-40\,°C$, the two pairs of inner N-bonded H atoms were observed unequivocally at $\delta = -3.25$, -2.05 ppm, and $\delta = -1.09$, -0.68 ppm, respectively. The folded arrangement of the two porphyrin rings in **3** was reflected in the outer-CH signals of confused pyrrole rings at $\delta = 4.26$ and 9.60 ppm, in which the diamagnetic shielding effect of the former proton was manifested because it partially overlaps the countered porphyrin. The ^1H NMR spectrum of *trans* complex **4** showed the two inner-CH signals at $\delta = -4.38$ and -4.32 ppm, but the outer-CH signals were observed in the normal aromatic region at $\delta = 8.84$ and 9.44 ppm, which is also consistent with the extended arrangement of the two porphyrin rings shown by the molecular structure of **4**. In both the complexes, the ^1H signals of *meso*-aryl groups above the NCP planes were observed in the range from $\delta = 3$ to 4.5 ppm at $-40\,°C$ owing to the ring-current shielding effect. These data suggest that the structures of the dimers **3** and **4** in the $CDCl_3$ solution are rigid and similar to those observed in the solid states.

The absorption spectra of **3** and **4**, recorded in $CHCl_3$, were similar and displayed the Soret band at $\delta = 447$ and 458 nm, and Q bands in the region of 563–820 and 580–820 nm, respectively (Figure 2). In comparison with the free base **1a**, the Soret band and the Q band at the longest wavelength transition of **3** were 4 and 84 nm red-shifted probably because of the interaction between the two NCP rings and the distortion of the NCP planes.

With regards to the structures of unseparated **6** and **6'**, we believe the complexes are an isomeric pair of bisplatinum complexes as depicted in Scheme 2. Quantitative transformation of the mixture to triphenylphosphane complex **7** and **7'**(Scheme 2, path A), the similar absorption spectrum to that of **7** (**7'**), the inner CH signals at $\delta = -4.27$ and -4.07 ppm in the same

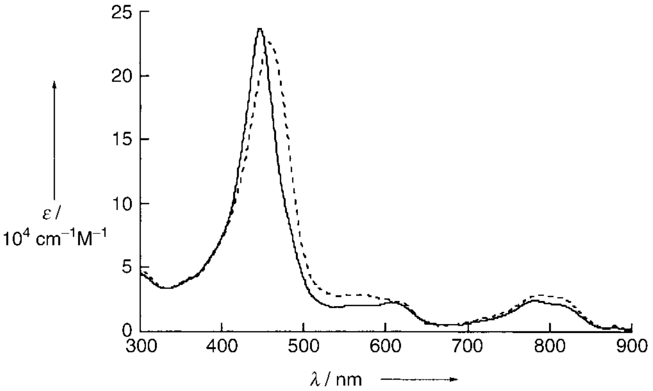
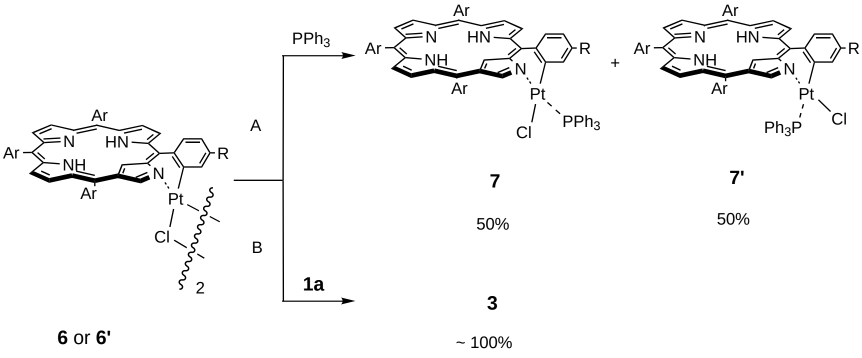


Figure 2. Absorption spectra of **3** (——) and **4** (-----) recorded in $CHCl_3$.



Scheme 2. Reactions of **6** (**6'**) with triphenylphosphane (path A) and **1a** (path B).

region to that of **7** (**7′**) at $\delta = -4.07$ (-4.11) ppm, and the FABMS peak at m/z 2137.7, all these data support the structures suggested for **6** (**6′**). The lower yield of **3** in the reaction with one equivalent of $PtCl_2$ arises from the formation of intermediates **6** (**6′**) because these intermediates are transformed into **3** quantitatively by the reaction with free base **1a** (Scheme 2, path B).[12] From a mechanistic point of view, outer-N coordination and succeeding *ortho* platination seem to be faster than the inner coordination as judged by the lower yield of **5**, especially in the reaction with 0.5 equivalents $PtCl_2$.

In summary, we have synthesized the NCP dimer complexes with Pt^{II} ions and shown that the outer nitrogen of the confused pyrrole in NCP can serve as a good coordinating ligand and that the formation of a metallocycle using an *ortho*-carbon atom of the *meso*-aryl group is not only restricted to Pd^{II} metal. By introducing a second confusion in the NCP ring,[13] the NCP oligomers with Pt^{II} connectors may be accessible. Such a strategy would be useful to build porphyrin arrays for the study of molecular wires, which are of current interest.[14]

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[7] 4-*tert*-Butylphenyl-substituted NCP (**1a**) was used to increase the solubility of the Pt^{II} complexes.

[8] Crystal data for **3**: $C_{120}H_{123}N_8PtCl \cdot 3\,CH_2Cl_2$, $M_W = 2162.69$, triclinic $P\bar{1}$ (No. 2), $a = 10.5849(5)$, $b = 18.0888(9)$, $c = 30.344(2)$ Å, $\alpha = 80.344(2)$, $\beta = 90.992(2)$, $\gamma = 79.960(1)°$, $V = 5633.4(5)$ Å^3, $T = 123$ K, $\rho_{calcd} = 1.275$ g cm^{-3}, $Z = 2$. For 18054 reflections measured; $R = 0.090$, $wR = 0.112$ for 12171 reflections with $[I > 3\sigma(I)]$, $GOF = 0.131$. Crystal data for **4**: $C_{120}H_{123}N_8PtCl \cdot 3\,C_6H_{14} \cdot CH_2Cl_2$, $M_W = 2253.37$, monoclinic $C2/c$ (No. 15), $a = 15.739(1)$, $b = 23.184(2)$, $c = 34.791(2)$ Å, $\beta = 91.927(3)°$, $V = 12687.4(1)$ Å^3, $T = 123$ K, $\rho_{calcd} = 1.180$ g cm^{-3}, $Z = 4$. For 19858 reflections measured; $R = 0.099$, $wR = 0.120$ for 8349 reflections with $[I > 3\sigma(I)]$, $GOF = 1.652$. CCDC-200335 (**3**) and 200334 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[10] When **3** was stirred with triphenylphosphane for 1 h at room temperature, the dimer complex was completely converted to the monomer to afford free base **1a** and the triphenylphosphane-coordinated monomer complex **7**, quantitatively. See Supporting Information.

[11] A single crystal with good quality for X-ray analysis was obtained from 3,5-di-*tert*-butylphenyl substituted NCP complex. K. Ariga, T. Kunitake, H. Furuta, *J. Chem. Soc. Perkin Trans. 2*, **1996**, 667 – 672.

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