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Synthesis and Characterization of New Platinum(II) and Platinum(IV) Triphyrin Complexes

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Supporting Information

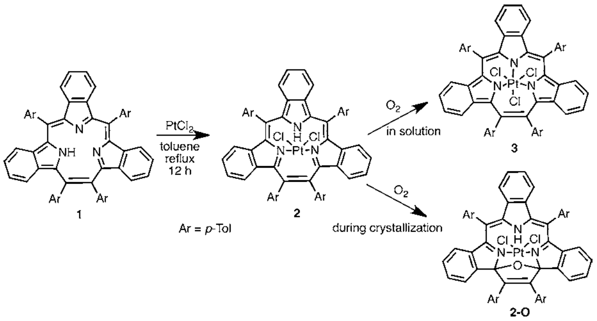
ABSTRACT: Metalation of 6,13,20,21-tetrakis(4-methylphenyl)-22*H*-tribenzo[14]triphyrin(2.1.1) with $PtCl_2$ gave a platinum(II) complex having a square-planar coordination structure with two pyrrolic nitrogen atoms and two chloride ions, with a saddle-shaped macrocycle. This platinum(II) complex was easily oxidized by air to an octahedral platinum(IV) complex coordinated by three pyrrolic nitrogen atoms as a tridentate monoanionic cyclic ligand and three chloride ions. When platinum(II) triphyrin was crystallized in air, an oxygen atom was incorporated between two α-carbon atoms of the pyrroles as an oxygen bridge to intercept the 14π aromatic system.

Contracted porphyrins, a new branch of the porphyrin family, have attracted considerable attention in recent years because of their potential applications in a variety of high-technology fields.[1] With the exception of subpyriporphyrin and some [18]triphyrins,[2] ring-contracted porphyrinoids(1.1.1) commonly contain three pyrrole or isoindoline moieties and exist only as boron compounds.[3] Moreover, removal of the central boron atom of these porphyrinoids(1.1.1) has not been achieved. In 2008, using a modified Lindsey condensation method, we first reported a facile synthesis of *meso*-aryl-substituted free-base [14]triphyrin(2.1.1) (TriP, **1**).[4] Since then, *meso*-free and β-free triphyrins have been prepared by McMurry coupling or [2 + 1] condensation reactions.[5,6] These novel complexes have made metalation of contracted porphyrins possible, which has attracted increasing attention in tuning the optical and electric properties.[4b,5]

Among metalloporphyrins, platinum-based complexes have received special attention in light of chromophores for a variety of applications, such as organic field-effect transistors,[7,8] organic light-emitting diodes,[9−11] and photodynamic therapy (PDT).[12,13] In general, platinum(II) and platinum(IV) porphyrins were prepared using platinum(II) and platinum(IV) reagents, respectively.[14] Platinum(II) porphyrins tend to give a square-planar structure, and platinum(IV) porphyrins give an octahedral structure with two more anionic ligands. The direct oxidation of a platinum(II) complex to a platinum(IV) complex was reported only by an electrochemical procedure.[15]

We have described the formation of octahedral metal complexes of [14]triphyrin(2.1.1) with Mn^{I}, Re^{I}, and Ru^{II} ions so far.[4b,5] The triangle macrocycle is a good tridentate monoanionic ligand for octahedral coordination. Considering the tridentate structure of [14]triphyrin(2.1.1), it is challenging to make the square-planar platinum(II) complex. In the present study, we will report the successful metalation of **1** with $PtCl_2$ in toluene to give $Pt^{II}TriP$ (**2**). The platinum(II) complex was easily oxidized to $Pt^{IV}TriP$ (**3**) in the presence of oxygen in solution (Scheme 1) or was bridged by an oxygen atom between α-carbon atoms of neighboring pyrroles ($Pt^{II}OTriP$, **2-O**) during crystallization.

Scheme 1. Synthesis of 2, 2-O, and 3



The synthesis of **1** was already reported.[4a] **1** was treated with $PtCl_2$ following the conventional procedure generally used for the synthesis of platinum(II) porphyrins.[9] A toluene solution of **1** in a Schlenk flask was refluxed for 12 h in the presence of 10 equiv of $PtCl_2$ under a nitrogen atmosphere. Subsequent separation over silica gel column chromatography using $CHCl_3$ as the eluent provided **3** as a green fraction ($R_f = 0.71$) as a trace amount and then **2** as a yellow-green fraction ($R_f = 0.12$) in 59% yield. Next the same reaction was performed in air, and then **2** and **3** were obtained in 47% and 11% yield, respectively. High-resolution electrospray ionization mass spectrometry (ESI-MS) analysis of **2** and **3** gave parent ion peaks that match well with the calculated ones (Figures S1 and S2 in the Supporting Information, SI). ^{1}H

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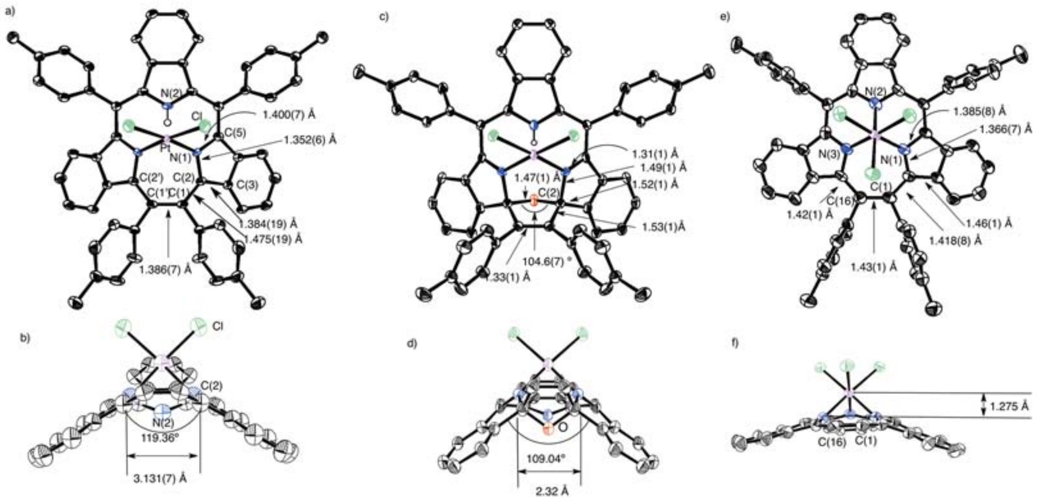

Figure 1. ORTEP diagrams of **2**, **2-O**, and **3**. Top views: (a) **2**, (c) **2-O**, and (e) **3**. Side views: (b) **2**, (d) **2-O**, and (f) **3**. Thermal ellipsoids are drawn at 50% probability with the phenyl groups omitted. Solvent molecules and hydrogen atoms, except N−H in part a, are also omitted for clarity.

NMR spectra of **2** and **3** are shown in Figure S3 in the SI along with that of **1**. In line with the symmetric structure, **2** shows a simple spectrum of the aromatic protons and two singlet peaks at 2.69 and 2.41 ppm for the methyl protons of the tolyl groups. The ^{1}H NMR spectrum of **3** is rather broad at room temperature (Figure S3c in the SI), but the peaks at 8.45, 7.82, 7.48, and 7.21 ppm become increasingly sharper upon a decrease in temperature to 213 K, indicating that the broad spectrum is due to conformational flexibility (Figure S3e in the SI). Broadening of the *meso*-aryl groups was also observed for rhenium(I) and ruthenium(II) complexes of tetraaryltribenzotriphyrins.[4b,5,16]

The transformation from **2** to **3** was confirmed by ^{1}H NMR investigation in $CDCl_3$. When the change of the ^{1}H NMR spectra of **2** in air was measured (Figure S4 in the SI), the two methyl peaks of the platinum(IV) complex at 2.76 and 2.49 ppm started to be observed at 2 h and the two methyl peaks of the platinum(II) complex at 2.69 and 2.41 ppm disappeared completely after 96 h. On the other hand, when the air in the NMR tube was changed to a strict argon atmosphere using a freeze−thaw method, this transformation did not occur after 96 h (Figure S5 in the SI). These results suggest that **2** is oxidized to **3** by oxygen gas. **3** was also obtained as the sole product in 41% yield by the reaction of **1** with $(Bu_4N)_2PtCl_6$, as a platinum(IV) source, in a mixture of toluene and acetic acid.

Crystallization of **2** was performed with a N_2-bubbled solvent (CH_2Cl_2/CH_3OH) under a nitrogen atmosphere in a glovebox. The crystal structure of **2** is shown in Figures 1a,b and S6a in the SI and summarized in Tables S1−S6 in the SI. The Pt^{II} ion was coordinated to two pyrrolic nitrogen atoms and two chloride ions with the following bond lengthes: 2.021(4) Å for Pt−N(1) and 2.314(1) Å for Pt−Cl in a *cis* configuration to form a rigid square-planar conformation. The triphyrin macrocycle shows a saddle shape with C_s symmetry. The mutual angle between two pyrrole rings coordinated to a Pt^{II} ion is 119.36° with a C(2)−C(2)′ distance of 3.131(7) Å. The angle between the noncoordinated pyrrole ring and the NNClCl plane was 43.69° (Figure S6a ni the SI).

When **2** was crystallized from a CH_2Cl_2/EtOH solution in air, green plate-shaped crystals were obtained. It was a new Pt^{II}TriP complex, **2-O**, with an oxygen adduct between two pyrrole rings, as shown in Figures 1c,d and S6b and Tables S1−S6 in the SI. The space group of the crystal for **2-O** was $P2_1/m$, and the molecule **2-O** was positioned in a mirror plane. In **2-O**, an oxygen atom is incorporated between the C(2) and C(2′) atoms to form a 2,5-dihydrofuran ring, with a C(2)−O bond length of 1.47(1) Å. The whole molecular π-conjugation system of **2-O** is interrupted with sp^3 C(2) atoms. The bond length of C(1)−C(1′) [1.331(1) Å] was close to that of a normal C═C double bond and significantly shorter than that of **2** [1.386(7) Å]. The bond lengths connected to the C(2) atom [1.53 (1) Å for C(1)−C(2); 1.52(1) Å for C(2)−C(3); 1.49(1) Å for C(2)−N(1)] in **2-O** are obviously longer than the corresponding bond lengths of **2**, 1.475(19), 1.384(19), and 1.352(6) Å, respectively. The newly formed dihydrofuran moiety showed chair shape, bent by 33.18° at the C(1)−C(1′) axis (Figure S6b in the SI). The mutual angle between two pyrrole rings coordinated to a platinum ion was 109.04°, and the C(2)−C(2′) distance was only 2.32 Å, indicating a deeper saddle shape compared with **2**. The angle between the noncoordinated pyrrole ring and the NNClCl plane of **2-O** was 46.53°, lifting the platinum plane 2.86° more than **2**.

Single crystals of **3** were obtained from a toluene/*n*-hexane solution. X-ray structure analysis (Figures 1e,f and S6c and Tables S1−S6 in the SI) revealed a bowl-shaped conformation for **3**, similar to that of rhenium(I) complex.[4b] The distance between the Pt^{IV} ion and the NNN plane was 1.275 Å and was shorter than the corresponding distance in the rhenium(I) complex by 0.201 Å, and platinum(IV) complex was flatter than that of the rhenium(I) complex. The bond length of C(1)−C(16) [1.43(1) Å] was longer than those of **2** and **2-O**, and the bond lengths of the macrocyclic ring suggested clear 14π conjugation (Table S2 in the SI).

Absorption spectra of **2** and **3** along with free-base **1** are shown in Figure 2. Platinum complexes show broad Soret bands at the region around 470 nm and Q bands in the region from 600 to 700 nm, respectively, which are considerably red-shifted and broadened compared with those of **1**. The Soret band of **3** is more red-shifted and the Q band is more blue-shifted than those of **2**. Unfortunately, the absorption spectrum of **2-O** was not obtained because the spectrum of **2-O** in solution was the same as that of **2**. **2-O** will be unstable in solution.

The electrochemical properties of **2** and **3** were examined by cyclic and differential pulse voltammetry (Table S7 and Figures S7 and S8 in the SI) in CH_2Cl_2 containing 0.1 M Bu_4NPF_6 at room temperature. Complex **2** gave four irreversible waves with

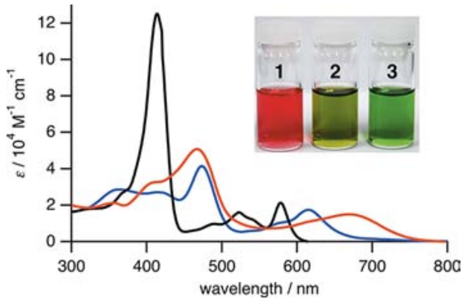

Figure 2. Absorption spectra of **1** (black line), **2** (red line), and **3** (blue line) in CH_2Cl_2.

potentials at 0.62, 0.85, 1.00, and 1.12 V (vs Fc/Fc^+) and two irreversible waves at −0.94 and −1.33 V (vs Fc/Fc^+) accompanied by one quasi-reversible wave at −1.62 V (vs Fc/Fc^+). The first oxidation potential [0.62 V (vs Fc/Fc^+)] was assigned to oxidation of the central Pt^{II} ion. Complex **3** showed one reversible oxidation peak at 0.84 V, one irreversible oxidation wave at 1.22 V (vs Fc/Fc^+), and three irreversible reduction potentials at −0.90, −1.33, and −1.60 V (vs Fc/Fc^+).

In conclusion, we have successfully prepared and characterized novel **2** and **3** by treating free-base **1** with $PtCl_2$. **2** was air-sensitive in solution and formed **3**. Furthermore, we happened to get the crystal of the oxygen-incorporated adduct, **2-O**, during crystallization of **2** in air. Further studies about the mechanism of oxidation of **2** and bioapplication on these novel platinum compounds are currently underway.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, synthetic details, NMR spectra, cyclic voltammograms, and crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to the memory of Dr. Christian G. Claessens.

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