

Preparation and Some Properties of a Phosphorus(V) Complex of Tetra-*tert*-butylphthalocyanine

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Introduction

The insertions of phosphorus into tetraphenylporphyrin² and octaethylporphyrin³ were reported by independent groups in 1977. Since then, their spectroscopic, electrochemical, and spectroelectrochemical investigations have been carried out^{4–7} along with an X-ray crystal structure determination of the tetraphenylporphyrin complex.⁸

Gouterman reported that reaction of phosphorus tribromide with phthalocyanine (pcH₂) in pyridine at 90–100 °C gave a phosphorus(III) complex with a minor product of phosphorus(V) complex.^{9,10} Later, the phosphorus(III) complex was proved to be a complex of α,β,γ -triazatetrabenzcorrole (tbcH₃),^{11,12} as was reported for the complexes of metalloid aluminum, silicon, gallium, and germanium.¹¹ Recently, a silicon complex of substituted tbcH₃ was also prepared.¹³ As to the phosphorus(V) complex, there has been no detailed report until now.¹⁴ Herein we report the synthesis and some properties of a phosphorus(V) complex (**1**) of tetra-*tert*-butylphthalocyanine (tbcH₂).

Experimental Section

Materials. Dichloromethane was purified by a method described elsewhere.¹⁵ The other reagents were of analytical grade or of the highest grade available and were used without further purification.

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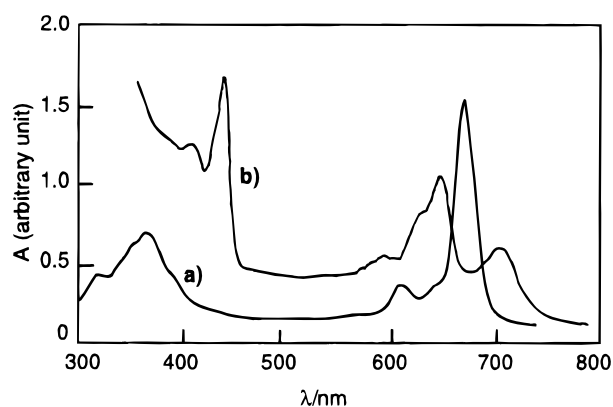


Figure 1. Absorption spectral change of **1** (a) to the tbc complex (b) in pyridine.

Preparation of 1. *N*-Ethyl-diisopropylamine (DIEA) (1.1 mL, 6.3 mmol) and phosphorus trichloride (0.1 mL, ca. 0.7 mmol) were poured into 30 mL of dichloromethane containing tbcH₂¹⁶ (200 mg, 0.27 mmol), and the mixture was stirred magnetically at room temperature for 1 h. Then, the mixture was diluted with 30 mL of dichloromethane, washed with 5% NaHCO₃ (3 × 25 mL), dried (Na₂SO₄), and filter. The filtrate was concentrated to an adequate amount and poured onto a silica gel column. An unreacted ligand was first eluted out with benzene, and small amounts of green tbc complex were subsequently eluted out with the solvent mixture of benzene and ethyl acetate (5:1). Finally, the blue complex **1** was eluted out with the solvent mixture of benzene and ethyl acetate (1:10), being precipitated by the addition of hexane to the eluent (58 mg, 27% yield). Anal. Calcd for C₄₈H₄₈N₈PO(OH)•H₂O: C, 70.40; H, 6.28; N, 13.68; P, 3.78. Found: C, 70.49; H, 6.25; N, 13.19; P, 4.05. λ_{abs} (CHCl₃, log ϵ): 350 (4.85), 615 (4.40), 680 (5.19) nm. ν_{OH} (KBr): 3450 cm⁻¹. ¹H NMR (DMSO-*d*₆) δ 1.79 (d, 36H, *tert*-butyl), 8.37 (s, 4H, aromatic ring), 9.37 (d, 8H, aromatic ring). FABMS: m/z 801.38 (M + H)⁺, 783.36 (M - OH)⁺ where M is C₄₈H₄₈N₈PO(OH). The complex **1** was also obtained using phosphorus tribromide instead of phosphorus trichloride (52 mg, 24% yield).

Measurements. UV-vis, infrared (KBr pellets), and fluorescence spectra were recorded on Shimadzu UV-3100, Hitachi 260-50, and Hitachi 850 spectrometers, respectively. ¹H NMR spectra were measured with a JEOL GX270 spectrometer at 270 MHz. The chemical shifts were determined in ppm using TMS as an internal standard. Elemental analyses (C, H, N) were carried out using a Yanako CHN Corder MT-5. Phosphorus was colorimetrically analyzed by a Shimadzu UV-210A spectrometer. FAB mass spectra were recorded with a JMS-700 MStation mass spectrometer using *m*-nitrobenzyl alcohol (*m*-TBA) as a matrix. A cyclic voltammogram (CV) was obtained in a dichloromethane solution containing tetrabutylammonium perchlorate (TBAP) on a Hokuto Denko HA-501 potentiostat with a Hokuto Denko HF-201 function generator. A glassy carbon disk (3 mm diameter), a platinum coil, and a saturated calomel electrode (SCE) were used as the working electrode, the counter electrode, and the reference electrode, respectively.

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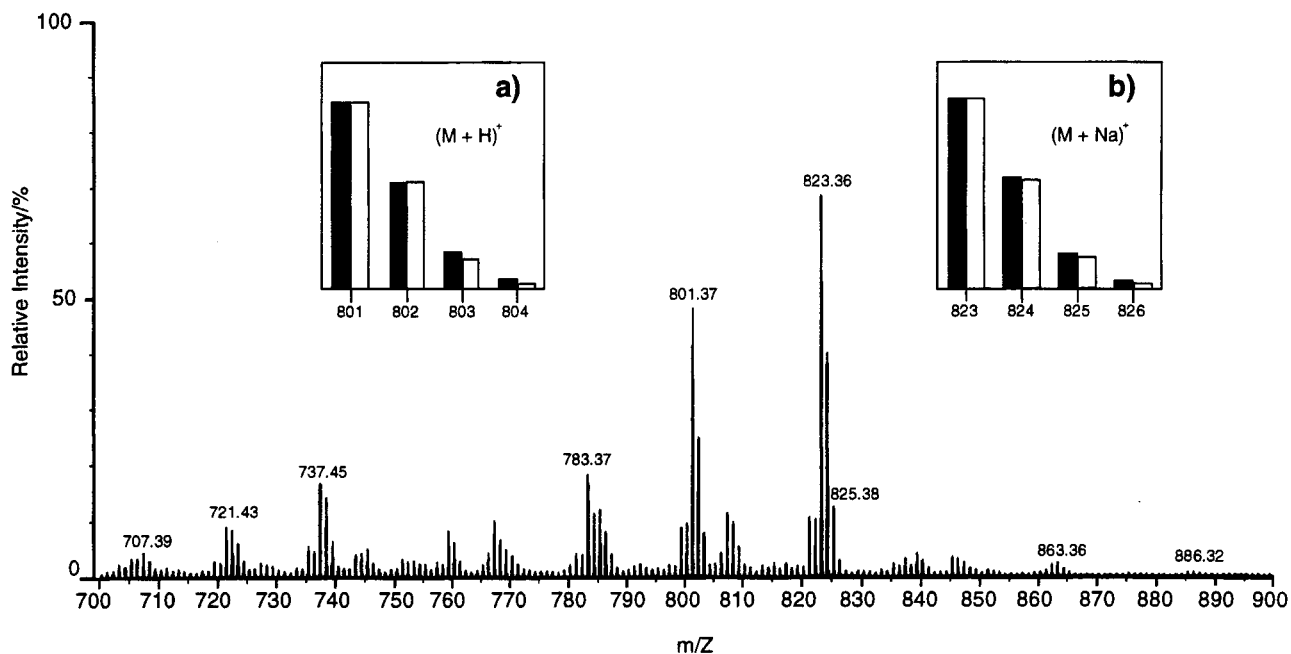


Figure 2. Mass spectra of **1**. The multiplet signals' observed (■) and calculated (□) relative isotopic abundances for $(M + H)^+$ and $(M + Na)^+$ are shown in insets a and b, respectively (the mass values are rounded off to whole numbers).

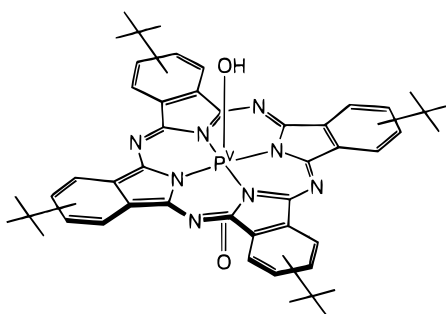


Figure 3. Proposed structure for **1**.

Results and Discussion

It turned out that heating the pyridine solution of phthalocyanine and phosphorus halide gave the tbc complex as a main product formed via a pc ring-constrictive reaction of the ligand.^{11,12} Recently, a pure magnesium(II) complex of tbcP₂ was prepared by allowing a dichloromethane solution of the ligand and magnesium halide in the presence of a noncoordinating base DIEA to stand at room temperature.¹⁷ Applying this method to the preparation of the phosphorus complex, **1** was obtained as a main product with a small amount of the tbc complex. The blue complex **1** dissolved in such common organic solvents as benzene, chloroform, dichloromethane, and dimethyl sulfoxide, but gradually turned pale in the air. However, it dissolved in methanol without decomposition even in the air.

The complex **1** shows a spectral feature similar to those for usual metallophthalocyanines; B and Q bands are located at 350 and 660 nm in chloroform. The solution showed a fluorescence

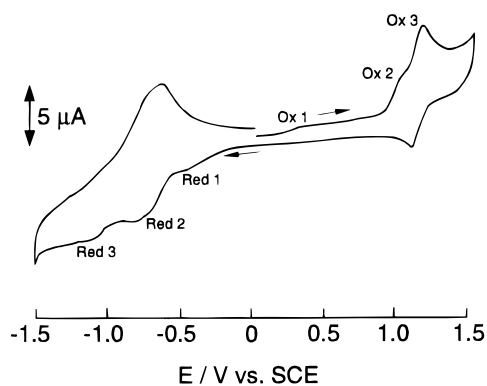


Figure 4. CV for **1** in dichloromethane. $[I] = 1 \times 10^{-3}$ M and $[TBAP] = 0.1$ M. Scan rate was 100 mV/s. $(E_{pa} + E_{pc})/2 = 1.16$ V vs SCE for Ox 3. $E_{pa/2} = 1.03$ V vs SCE for Ox 2 and 0.30 V vs SCE for Ox 1. $E_{pc/2} = -0.35$ V vs SCE for Red 1, -0.69 V vs SCE for Red 2, and -1.06 V vs SCE for Red 3.

peak at 680 nm. By warming the pyridine solution of **1** at ca. 60 °C, a new absorption band characteristic of the tbc complex appeared at 440 nm, showing the change of **1** to the tbc complex in the coordinative solvent (Figure 1).

A FAB mass spectrum of **1** showed peaks at $m/z = 801.38$ and 783.36 corresponding to $(M + H)^+$ and $(M - OH)^+$, respectively. By mixing sodium iodide with the *m*-NBA matrix, a new peak corresponding to $(M + Na)^+$ also appeared at 823.36, which indicates that **1** has a molecular weight 800.37 (Figure 2). The multiplet signals observed around $m/z = 800$ and 823 reflect the relative isotopic abundances of the constituent elements, of which analytical data confirm the formula of C₄₈H₄₉N₈O₂P for **1**. The formula is consistent with that for the tbcP(V) core with axial oxo and hydroxo groups; the hydroxo one was characterized by the IR spectrum. The most likely structure is shown in Figure 3, in which the axial oxo and hydroxo groups are oriented to the different directions with respect to the pc ring.

The cyclic voltammogram of **1** was measured in the range -1.5 to 1.5 V (vs SCE) (Figure 4). The quasireversible wave

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Ox 3 at 1.16 V ($|E_{pa} - E_{pc}| = 75$ mV) could be assigned to the ring oxidation. However, our effort to assign the other redox processes was in vain. The reductions of the ring and phosphorus(V) ion might both occur in the reduction side, being accompanied by the decomposition of the complex.

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Additions and Corrections

1996, Volume 35

Colin L. Beswick, Richard D. Shalders, and Thomas W. Swaddle* Volume Profile for Substitution in Labile Chromium(III) Complexes: Reactions of Aqueous [Cr(Hedta)OH₂] and [Cr(edta)]⁻ with Thiocyanate Ion

Page 992: In eq 2, a division sign is missing, and in the final term r_i and r_o are interchanged. The correct equation is

$$\epsilon_p = \epsilon_0 b_0 (A_p / A_0) / \{ (b_0 - l) + (r_i / r_o)^2 l \} + (V_0 / V_p) \{ 1 - (r_i / r_o)^2 \} l \quad (2)$$

These errors are typographical; all reported data were calculated using the correct eq 2.

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1999, Volume 38

Igor V. Kourkine, Caroline S. Slone, Chad A. Mirkin,* Louise M. Liable-Sands, and Arnold L. Rheingold: Small Molecule-Induced Intramolecular Electron "Pitch and Catch" in a Rhodium^I Complex with Substitutionally Inert Redox-Active Ligands.

Page 2758: The correct list of authors is as follows: Igor V. Kourkine, Caroline S. Slone, Elizabeth T. Singewald, Chad A. Mirkin, Louise M. Liable-Sands, and Arnold L. Rheingold. Elizabeth Singewald was inadvertently omitted from this list.

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