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Synthesis and Structure of Phosphorus(V) Octaethylporphyrins That Contain a σ-Bonded Element−Carbon Bond: Characterization of a Porphyrin Bearing an R−P=O Bond and Relation of the Ruffling of the Porphyrin Core with the Electronegativity of the Axial Ligands

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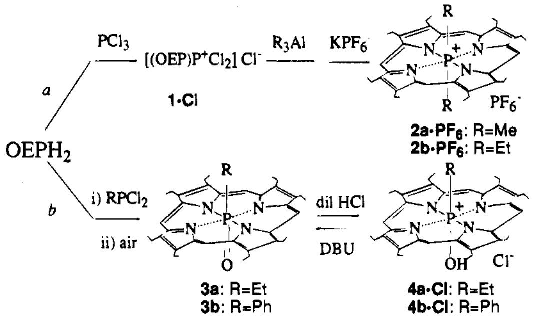
Phosphorus has been the smallest atom which can occupy the center of a porphyrin ring,[1] and phosphorus porphyrins have been attracting considerable interest recently.[2] However, acute attention has been paid neither to the electronic effect of the axial ligands on the degree of ruffling of the porphyrin core[3] nor to the possibility of forming a double bond.[4] Moreover, there has not been any example bearing a phosphorus−carbon bond. Here we report the synthesis and crystal structure of **3a** [(OEP)PEt(=O)] (OEP: octaethylporphyrinate) with a quite unique hexacoordinate hypervalent bonding system and the preliminary investigation of ruffling of several phosphorus porphyrins as a function of axial ligands. Although the effect of the porphyrin ring distortion on properties such as redox potentials,[5] electronic structures,[6] ^{59}Co NMR,[7] and so on[8] has been the subject of recent interest, no investigations of crystal structures of phosphorus porphyrins have been reported except for one example of (5,10,15,20-tetraphenylporphyrinato)dihydroxophosphorus(V) hydroxide dihydrate (**7**: TPPP(OH)$_2^+$-OH$^-$·2H$_2$O), which showed extensive ruffling of the porphyrin core.[9]

Scheme 1



Dialkylphosphorus(V) porphyrin could be prepared by the reaction of [(OEP)PCl$_2$]$^+$Cl$^-$ (**1-Cl**) with trialkylaluminum in dichloromethane according to the method recently reported by us for antimony porphyrins[10] (Scheme 1). The dimethyl compound [**2a-PF$_6$**; [(OEP)PMe$_2$]$^+$PF$_6^-$, 24%][11] showed a characteristic methyl signal at very high shielding[12] (^{1}H NMR (CDCl$_3$) δ −6.21, d, 6 H, $^2J_{PH}$ = 17 Hz) and a phosphorus signal at δ −191.3; the diethyl compound [**2b-PF$_6$**; [(OEP)PEt$_2$]$^+$PF$_6^-$, 20%][13] showed the corresponding signals, i.e., ^{1}H NMR (CDCl$_3$) δ −6.38 (dq, 4 H, $^2J_{PH}$ = 15 Hz, $^3J_{HH}$ = 8 Hz), −5.02 (dt, 6 H, $^3J_{PH}$ = 47 Hz, $^3J_{HH}$ = 8 Hz), and a phosphorus signal at δ −159.9.

Synthesis of the R−P=O compound **3** was successfully carried out by a straightforward reaction of OEPH$_2$ with EtPCl$_2$ in the presence of 2,6-dimethylpyridine (3 equiv) in dichloromethane at room temperature followed by rapid air oxidation during workup. **3a** was isolated as purple crystals in 28% yield.[14] The ^{1}H NMR spectrum showed a characteristic ethyl signal, i.e., δ −6.49 (dq, 2 H, $^2J_{PH}$ = 16 Hz, $^3J_{HH}$ = 8 Hz) and −5.08 (dt, 3 H, $^3J_{PH}$ = 45 Hz, $^3J_{HH}$ = 8 Hz). Notable downfield shifts of these protons toward δ −5.70 and −4.52, respectively, were observed by treating a solution of **3a** in dichloromethane with aqueous dilute HCl, suggesting the formation of [(OEP)-PEt(OH)]$^+$Cl$^-$ (**4a-Cl**). The OH proton of **4a-Cl** was acidic enough to regenerate **3a** after treatment of a solution of **4a-Cl** with DBU, and the pK_a value was determined by UV−vis spectrometry to be about 7.1 in water, although the insolubility of the compounds prevented precise measurement. Counteranion exchange of **4a-Cl** with NaClO$_4$ gave **4a-ClO$_4$**.[15]

Crystals of **3a** and **4a-ClO$_4$** suitable for X-ray analysis were obtained by recrystallization from dichloromethane for **3a** and from ethyl acetate for **4a-ClO$_4$**.[16] Figures 1 and 2 show the crystal structure of **3a** with a water molecule found incorporated in the crystal lattice, and **4a-ClO$_4$** with the perchlorate anion, respectively. Each of the geometries about the phosphorus atom is a distorted octahedron, of which the bond length of the P−O bond (1.487(8) Å) in **3a** is very short in contrast to the usual single-bond length (1.635(5) Å) as seen for **4a-ClO$_4$**. However, the oxygen atom in the P−O group in **3a** is hydrogen-bonded

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[11] **2a-PF$_6$**: UV−vis (CH$_2$Cl$_2$) λ_{max} (ϵ x 10^{-3}) 367 (35.7), 407 (50.7), 429 (253), 556 (13.9), 595 (8.63) nm. **2a-PF$_6$** (contained 1 mol of dichloromethane): R = 0.093, R_w = 0.070.

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[13] **2b-PF$_6$**: UV−vis (CH$_2$Cl$_2$) λ_{max} (ϵ × 10^{-3}) 365 (41.5), 408 (52.3), 430 (236), 554 (15.5), 594 (6.33) nm.

[14] **3a**: UV−vis (CH$_2$Cl$_2$) λ_{max} (ϵ x 10^{-3}) 347 (27.6), 417 (165), 539 (12.9), 572 (9.68) nm.

[15] **4a-ClO$_4$**: UV−vis (CH$_2$Cl$_2$) λ_{max} (ϵ x 10^{-3}) 356 (27.2), 417 (288), 548 (13.4), 590 (14.8) nm.

[16] **3a** (contained 1 mol of H$_2$O): R = 0.086, R_w = 0.090. **4a-ClO$_4$** (contained 0.5 mol of ethyl acetate): R = 0.087, R_w = 0.112. All five compounds in Table 1 gave correct elemental analyses.

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Table 1. Selected Bond Distances and the Degree of Ruffling of Phosphorus(V) Porphyrins

	1-PF$_6$	**4b-PF$_6$**	**4a-ClO$_4$**	**2a-PF$_6$**	**3a**	**7**[a]
P-axial (Å) (atom)	2.136(2) (Cl)	1.865(7) (C)	1.871(6) (C)	1.863(8) (C)	1.84(1) (C)	1.644(8) (O)
P-axial (Å) (atom)	2.140(2) (Cl)	1.636(5) (O)	1.635(5) (O)	1.864(8) (C)	1.487(8) (O)	1.545(8) (O)
averaged P–N bond distance (Å)	1.833(6)	1.873(5)	1.884(3)	1.974(6)	2.00(1)	1.8905(10)
deviation from the mean plane of the core porph (root mean square) (Å)[b]	0.514	0.481	0.465	0.057	0.070	0.488

[a] Reference 9: $[(TPP)P(OH)_2]^+OH^-\cdot 2H_2O$. [b] ($\Delta r$): root mean squares of displacements for entire 24 atom core.

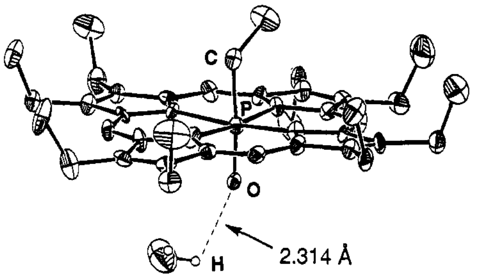

Figure 1. ORTEP diagram (30% probability ellipsoids) for **3a** with a water molecule found incorporated in the crystal lattice.

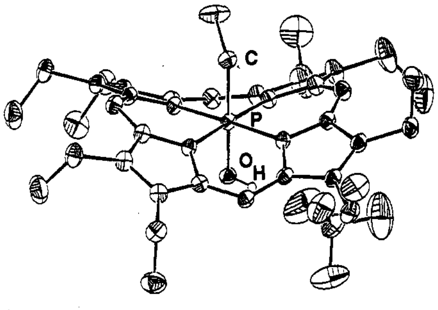

Figure 2. ORTEP diagram (30% probability ellipsoids) for **4a-ClO$_4$**.

with the water molecule (the distance between the oxygen atom in the P–O group and the closer hydrogen atom in the water molecule is 2.31 Å). The P–O bond in **3a** should be regarded as a double bond[4] since the P–O bond length is almost identical with the reported distance (1.483 Å) of that of triphenylphosphine oxide.[17] The bonding around the phosphorus atom in **3a** is quite unique, the first example of a hypervalent 12-P-6 compound bearing a P=O double bond. The only examples of compounds of this class bearing a P=O double bond are theoretically proposed species, i.e., $F_3P(=O)\cdot 2NH_3$ and $(HO)_3P(=O)\cdot 2NH_3$, concerning the mechanism of associated edge inversion in which two molecules of ammonia are coordinated with the phosphoryl group.[18]

Interestingly, the porphyrin core of **3a** is almost planar in contrast to **4a-ClO$_4$**, which is severely ruffled. In order to elucidate the relationship between ruffling of the porphyrin core and the nature of the axial ligands, the structures of **2a-PF$_6$**, **4b-PF$_6$**, and **1-PF$_6$** were determined by X-ray crystallographic analyses. Bond distances of the P-axial atom, the averaged P–N bond distance, and the degree of ruffling of the core (Δr) are shown in Table 1 together with the reported data for the dihydroxy compound **7**. There is a drastic change in ruffling between **4a-ClO$_4$** and **2a-PF$_6$**, and a P–N bond distance of about 1.95 Å seems to be the threshold between the extensively ruffled porphyrin core and the planar one. Among the series **1-PF$_6$**, **4b-PF$_6$**, **4a-ClO$_4$**, and **2a-PF$_6$**, the order of ruffling (Δr) corresponds to the inverse order of the averaged P–N bond distance, reflecting the effect of electronegativity of the axial ligands. It can be concluded that the more electronegative are the axial ligands, the shorter become the averaged P–N bond distances and the more ruffled is the porphyrin core, while the four nitrogens and the central phosphorus atom remain almost in a plane.

Finally the UV–vis spectra for these compounds should be mentioned briefly. It has well been established that metalloporphyrins containing low-valent main-group elements show unusual p-type hyper absorption spectra, in contrast to the normal absorptions of the corresponding higher valent ones.[1,19] The spectra (CH_2Cl_2) of dialkyl compounds, **2a-PF$_6$** and **2b-PF$_6$**, however, showed distinct hyper character even though these are higher valent phosphorus(V) compounds, i.e., **2a-PF$_6$** and **2b-PF$_6$** showed an extra Soret band with considerable intensity at 367 nm (ϵ 35 700) and at 365 nm (ϵ 41 500), respectively. Since the hyper band has been assigned as a charge transfer band from the central element of low valency to the ligand,[19] the electron-donating property of the hypervalent axial bond of dialkylphosphorus(V) porphyrin ($R-P^+-R$) was thus exemplified. Further synthetic and structural study is in progress.

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Supporting Information Available: Tables of ^{1}H NMR, ^{31}P NMR, and elemental analyses and of positional and thermal parameters and complete interatomic distances and angles for **1-PF$_6$**, **2a-PF$_6$**, **3a**, **4a-ClO$_4$**, and **4b-PF$_6$** including crystal data and ORTEP structure drawings (79 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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