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Note

Synthesis and characterization of the first organometallic hafnium porphyrin complex Hf(TPP)(Me)$_2$ (TPP = 5,10,15,20-tetraphenylporphyrinate) and crystal structure of its hydrolysis product [Hf(TPP)]$_2$(μ-O)(μ-OH)$_2$

Sanghoon Ryu [a,b], Jaheon Kim [a], Hwanjin Yeo [b], Kimoon Kim [a,*]

[a] *Department of Chemistry and Center for Biofunctional Molecules, Pohang University of Science and Technology, PO Box 125, Pohang 790-600, South Korea*

[b] *Department of Chemical Education, Kyungpook National University, Taegu 702-701, South Korea*

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Abstract

The first organometallic hafnium(IV) porphyrin complex Hf(TPP)(Me)$_2$ (TPP = 5,10,15,20-tetraphenylporphyrinate) was synthesized and characterized. The ^{1}H NMR spectrum of the complex suggested that the methyl groups are *cis* to each other. An attempt to crystallize the complex yielded the trioxygen-bridged dimer complex [Hf(TPP)]$_2$(μ-O)(μ-OH)$_2$ which was presumably formed by hydrolysis. The structure of the hydrolysis product has been determined by X-ray crystallography. The crystal structure revealed two hydroxo and one oxo groups bridging two hafnium porphyrin moieties. Crystal data for [Hf(TPP)]$_2$(μ-O)(μ-OH)$_2$: orthorhombic, space group *Fdd*2, $a = 25.476(4)$, $b = 39.361(8)$, $c = 14.848(2)$ Å, $Z = 8$; $R = 0.046$ and $R_w = 0.049$ for 1609 independent reflections with $I > 3\sigma(I)$.

Keywords: Crystal structures; Hydrolysis; Hafnium complexes; Porphyrin complexes; Organometallic complexes; Trioxygen-bridged dimer

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1. Introduction

Although organometallic chemistry of the late transition metal porphyrins [1–3] has been studied quite extensively, that of the early transition metal porphyrins, particularly Group 4 and 5 metal complexes [4–7], still remains largely undeveloped. This is because the early transition metal porphyrins are highly oxophilic and in some cases there was no precursor suitable for organometallic transformation. Recently, we have synthesized Hf(por)Cl$_2$ [8] (por = 2,3,7,8,12,13,17,18-octaethylporphyrinate (OEP), 5,10,15,20-tetraphenylporphyrinate (TPP)) which can be used as precursors for various hafnium porphyrins. The synthetic utility of the dichloro complexes has been demonstrated by the preparation of the novel complexes [NBu$^n{}_4$](Hf(por)(P$_3$O$_9$)] [8] and Hf(TPP)(bdt) [9] (bdt = benzenedithiolate) by replacing the two Cl ions of the dichloro complexes with an oxygen tripod ligand P$_3$O$_9{}^{3-}$ or benzenedithiolate ligand. We now report the synthesis and characterization of the first organometallic hafnium porphyrin complex Hf(TPP)(Me)$_2$. In an attempt to grow crystals of the dimethyl complex we accidentally obtained the trioxygen-bridged dimer complex [Hf(TPP)]$_2$(μ-O)(μ-OH)$_2$ which was formed presumably as a result of the hydrolysis of the dimethyl complex. We also report the crystal structure of the hydrolysis product.

2. Experimental

All chemicals were of reagent grade and were used without further purification except as noted below. Argon was purified by passage through successive columns of activated molecular sieves 13X (Aldrich) and Ridox (Fisher). Methyllithium (1.4 M in diethyl ether) was purchased from Aldrich. The complex Hf(TPP)Cl$_2$ was prepared as described previously [8]. Toluene and hexanes were distilled from their sodium-benzophenone solutions under a nitrogen atmosphere. Deuterated

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[*] Corresponding author.

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solvent for NMR measurement was dried over sodium-benzophenone solution (C_6D_6) and vacuum-distilled before used.

Reactions performed under an inert atmosphere were carried out in Schlenkware under a purified argon atmosphere or in a Vacuum Atmosphere glovebox under argon. The UV–Vis spectrum was recorded on an Hewlett Packard 8451A spectrometer, ^1H NMR spectrum on a Bruker AM-300 spectrometer, and Fourier-transform IR data on a Bomem michelson 100 spectrometer. Elemental analysis was performed at Korea Basic Science Center.

2.1. Synthesis of Hf(TPP)(Me)$_2$ (1)

To a suspension of Hf(TPP)Cl_2 (0.050 g, 0.058 mmol) in toluene (30 ml) was added 0.087 ml of LiMe (0.122 mmol, 1.4 M in diethyl ether). The reaction mixture was stirred at room temperature for 1 h in the dark and then filtered. The filtrate was concentrated and allowed to cool to −25 °C. The resulting purple microcrystalline solid was filtered, washed with hexanes and dried under vacuum to yield complex **1** (0.010 g, 23%). *Anal.* Calc for $C_{46}H_{34}N_4Hf$: C, 67.3; H, 4.20; N, 6.80. Found: C, 67.5; H, 4.40; N, 6.60%. ^1H NMR (300 MHz, C_6D_6): 9.03 (8H, s, H_β), 8.26 (4H, br, ph), 7.90 (4H, br, ph), 7.46 (12H, br, ph), −3.66 (6H, s, Hf–CH_3). UV–Vis (toluene, nm) (log ϵ): 414 (4.80), 548 (3.52). IR (KBr, cm^{-1}): 1596(w), 1482(w), 1440(w), 1333(w), 1070(m), 998(s), 801(s), 752(s), 727(s), 700(s), 659(w), 575(w), 466(w), 431(w).

2.2. Formation of [Hf(TPP)]$_2$(μ-O)(μ-OH)$_2$·H$_2$O·C$_6$D$_6$ (2)

In an attempt to grow crystals of Hf(TPP)$(Me)_2$ in C_6D_6 solution after the NMR measurement, dark purple crystals of **2** were formed presumably as a result of the hydrolysis of the dimethyl complex. It was characterized by X-ray crystallography.

2.3. X-ray crystal structure determination of [Hf(TPP)]$_2$(μ-O)(μ-OH)$_2$·H$_2$O·C$_6$D$_6$ (2)

A crystal sealed in a Lindemann capillary was mounted on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Unit-cell parameters were determined by a least-squares refinement of 25 reflections. Intensity data were measured at room temperature. The intensities of three standard reflections, measured every 3 h of X-ray exposure, showed no significant decay during the data collection. Crystal data for the title compound and the details of the data collection are summarized in Table 1. The intensity data were corrected for Lorentz and polarization effects. Absorption correction was not applied to the data. The structures were solved by a combination of Patterson (SHELXS86) and difference Fourier methods. Owing to the small number of observed data, only the hafnium and two oxygen atoms (O(1) and O(2)) were refined anisotropically; the other non-hydrogen atoms were refined isotropically by the full-matrix least-squares method. The benzene solvate molecule showed large thermal motion and the initial refinement led to a geometry deviating significantly from that of the normal benzene molecule. Therefore, its six carbon atoms (three in the asymmetric unit and the others generated by a two-fold symmetry) were fitted to a regular hexagon with C–C = 1.395(1) Å and C–C–C = 120(1)°; the generated coordinates were fixed and their thermal parameters only were refined as a group. The positions of the hydrogen atoms were calculated with C–H = 0.95 Å and their thermal parameters were fixed with 1.3 times those of the attached carbon atoms. The final cycles of refinement on F converged to the R indices listed in Table 1. All calculations except for the Patterson method were performed with the Enraf-Nonius MolEN package [10].

Table 1
Crystallographic data for complex **2**

Formula	$C_{88}H_{58}N_8O_3Hf_2 \cdot H_2O \cdot C_6D_6$
M	1728.66
Crystal system	orthorhombic
Space group	*Fdd*2
a (Å)	25.476(4)
b (Å)	39.361(8)
c (Å)	14.848(2)
U (Å^3)	14888(5)
Z	8
$F(000)$	3424.0
T (°C)	23
D_c (g cm^{-3})	1.542
μ (cm^{-1})	28.2
Crystal size (mm)	0.25 × 0.20 × 0.10
Scan mode	ω
ω-Scan width (°)	$0.70 + 0.35 \tan\theta$
Scan speed[a] (° min^{-1})	1.65
2θ Limits (°)	$4 < 2\theta < 47$
Unique data with $I > 3\sigma(I)$	1609
No. variables	220
R[b]	0.046
R_w[c]	0.049
Goodness of fit	0.90

[a] For reflections with $I < 3\sigma(I)$ rescans were forced to achieve $I > 3\sigma(I)$ up to 80 s total scan time.

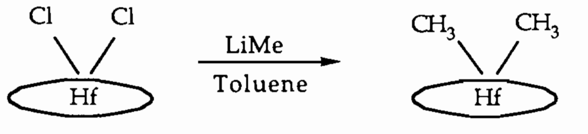
[b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[c] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 4F_o^2/\sigma^2(F_o^2)$; $\sigma(F_o^2) = [\sigma(I) + (pI)^2]^{1/2}$.

3. Results and discussion

The dimethyl complex Hf(TPP)$(Me)_2$ was prepared by treating Hf(TPP)Cl_2 with 2 equiv. of LiMe in toluene.

To our knowledge this is the first organometallic hafnium(IV) porphyrin complex. This complex is somewhat stable in the solid state, but very sensitive to air, moisture and chlorinated solvents. The electronic absorption spectrum of **1** shows a soret band at 414 nm indicating that this compound is a monomeric porphyrin complex



Hf(TPP)Cl$_2$ Hf(TPP)(Me)$_2$ (**1**)

The ^1H NMR spectrum of the diamagnetic product indicates that the two sides of the porphyrin planes are not equivalent. A sharp singlet of β-pyrrolic protons appears at 9.03 ppm and two multiplets (8.26 and 7.90 ppm) arise from the two magnetically inequivalent *ortho* protons of the phenyl ring. A singlet signal at −3.66 ppm corresponding to six protons was assigned to the two methyl groups coordinated to the Hf atom. The upfield shift of the methyl ligand resonances, relative to those of the free methyl groups, are attributed to the effect of the porphyrin ring current.

This chemical shift of the methyl groups bound to the metal center is comparable to that of the corresponding zirconium complex Zr(TPP)(Me)$_2$ (−3.26 ppm) [7], however, it has a lower negative value than those of Co(III) [11], Rh(III) [12] and Al(III) [13] porphyrin methyl complexes M(TPP)Me (M = Co, Rh or Al) (−4.75, −5.80 and −6.03 ppm, respectively). Two reasons are attributed to this: (i) the complexes with more electronegative metals normally give signals at lower fields [14] and (ii) the methyl groups in Hf(TPP)(Me)$_2$ or Zr(TPP)(Me)$_2$ [7] are not axially oriented as in M(TPP)Me (M = Al, Co or Rh) but rather at an angle with the normal to the porphyrin plane, which removes the H atoms of the methyl groups from the center of the shielding zone. Thus far we have been unable to obtain single crystals of **1** suitable for X-ray crystallography. The crystal structure of its congener Zr(OEP)(Me)$_2$ has been reported recently [15].

In an attempt to grow single crystals of **1** we accidentally obtained a hydrolysis product which was identified as the three oxygen-bridged dimeric compound, [Hf(TPP)]$_2$(μ-O)(μ-OH)$_2$·H$_2$O·C$_6$D$_6$ (**2**) on the basis of its X-ray diffraction study. The structure of **2** is isomorphous with the previously determined structure of [Zr(TPP)]$_2$(μ-O)(μ-OH)$_2$·C$_6$D$_6$ [16].

The crystal structure of the dimeric complex **2** revealed that the two hafnium porphyrin moieties are joined by one oxo and two hydroxo ligands. A two-fold axis passes through the bridging oxo ligand and the midpoint between the two Hf atoms (Fig. 1). Selected bond distances and angles for **2** are given in Table 2. In this structure the oxo and hydroxo ligands were clearly distinguished: the Hf–O(1)(oxo) distance (1.977(13) Å) is shorter than the Hf–O(2)(hydroxo) distances (2.167(14) and 2.206(14) Å); the Hf–O(1)–Hf′ angle for the oxo (101.6(9)°) is larger than that for the hydroxo (88.9(5)°). The bond parameters involved in the Hf–(μ-O)(μ-OH)$_2$–Hf core are comparable with those of the corresponding Zr complex [16]. A water molecule disordered over two sites (O(3) and O(3′)) appears to form a hydrogen bond with the bridging oxo ligand (O(1)···O(3) distances of 2.83(5) Å). The presence of the water molecule makes the two porphyrin planes no longer parallel (dihedral angle, 12.0(2)°). The Hf···Hf distance, 3.064(1) Å is slightly shorter than the Zr···Zr distance (3.071(1) Å) in the corresponding Zr complex [16]. The average Hf–N distance amounts to 2.27(3) Å. The displacement of the metal from the

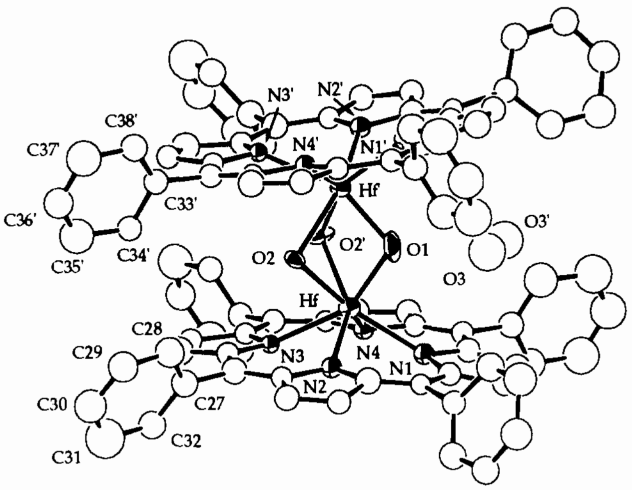


Fig. 1. Crystal structure of complex **2**. A disordered water molecule (O3 and O3′) forms a hydrogen bond with the bridging oxo ligand (O1).

Table 2
Selected bond distances (Å) and angles (°) for complex **2**

Hf–Hf′	3.0635(14)	Hf–N(1)	2.201(17)
Hf–O(1)	1.977(13)	Hf–N(2)	2.292(13)
Hf–O(2)	2.167(14)	Hf–N(3)	2.303(16)
Hf–O(2′)	2.206(14)	Hf–N(4)	2.279(14)
O(1)···O(3)	2.83(5)		
Hf–O(1)–Hf′	101.6(9)	Hf–O(2)–Hf′	88.9(5)
O(1)–Hf–O(2)	75.4(5)	O(2′)–Hf–N(1)	136.3(6)
O(1)–Hf–O(2′)	74.5(5)	O(2′)–Hf–N(2)	144.9(6)
O(2)–Hf–O(2′)	67.6(5)	O(2′)–Hf–N(3)	83.3(5)
O(1)–Hf–N(1)	84.7(6)	O(2′)–Hf–N(4)	76.7(5)
O(1)–Hf–N(2)	110.4(5)	N(1)–Hf–N(2)	78.4(7)
O(1)–Hf–N(3)	151.5(6)	N(1)–Hf–N(3)	123.8(6)
O(1)–Hf–N(4)	114.9(4)	N(1)–Hf–N(4)	78.1(6)
O(2)–Hf–N(1)	143.0(6)	N(2)–Hf–N(3)	78.3(7)
O(2)–Hf–N(2)	79.8(6)	N(2)–Hf–N(4)	126.1(5)
O(2)–Hf–N(3)	79.8(6)	N(3)–Hf–N(4)	76.0(6)
O(2)–Hf–N(4)	138.6(6)		

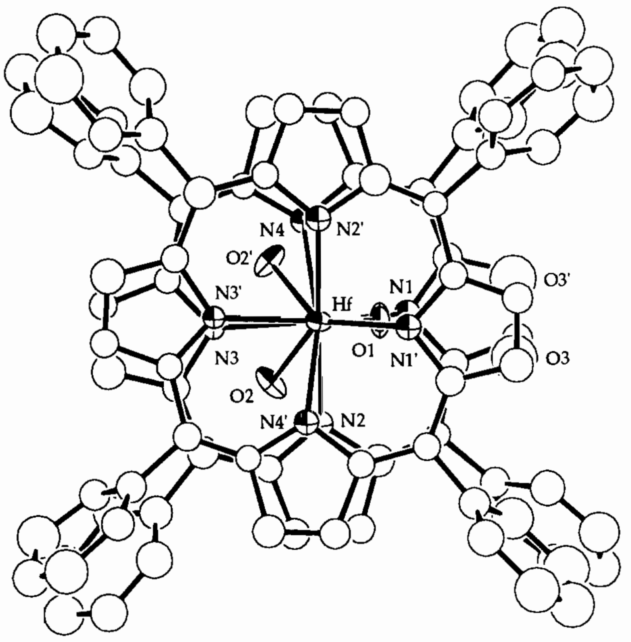


Fig. 2. Top view of complex **2**.

N_4 plane (1.048(1) Å) is somewhat smaller than that of the Zr complex (1.057 Å) presumably due to the smaller ionic radius of Hf^{4+} (0.76 Å) versus Zr^{4+} (0.78 Å).

Interestingly, as in $[Zr(TPP)]_2(\mu\text{-}O)(\mu\text{-}OH)_2$ [16] the two porphyrin rings are almost eclipsed (Fig. 2): the N(1)–Hf–Hf′–N(1′) torsional angle is 9.5(5)°. The near eclipsed conformation of the porphyrin cores leads to the close contacts of the peripheral phenyl groups on the two opposite porphyrin rings (Fig. 1); the shortest intramolecular C· · ·C distance (C28· · ·C34′) is 3.37(3) Å. One of the Hf–O bonds (Hf–O(1)(oxo)) also eclipses an Hf–N bond (Hf–N(1)) (twist angle, 4.8°), which may cause the Hf–N(1) bond (2.201(17) Å) to be slightly shorter than the other Hf–N bonds (2.279(14)–2.303(16) Å). The eclipsed conformation of the two porphyrin rings and the concomitant eclipsed configuration of one of the Hf–O bonds with respect to an Hf–N bond suggest that such a conformation for the $N_4HfO_3HfN_4$ unit may be stabilized by d_π–p_π interactions between the Hf atoms and the O and N atoms.

4. Conclusions

We have synthesized and characterized the first organometallic hafnium porphyrin complex $Hf(TPP)(Me)_2$. The dimethyl complex was easily hydrolyzed to yield the novel trioxygen-bridged dimer complex $[Hf(TPP)]_2(\mu\text{-}O)(\mu\text{-}OH)_2$. Synthesis of other organometallic hafnium porphyrin complexes and their reaction chemistry are currently under investigation.

5. Supplementary material

Tables of positional parameters, bond distances and angles, and anisotropic thermal parameters, and a listing of observed and calculated structure factors are available from the corresponding author upon request.

Acknowledgements

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