Synthesis, characterization and X-ray crystal structure of the benzenedithiolatohafnium(IV) porphyrin complex

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Abstract

A novel hafnium porphyrin complex Hf(TPP)(bdt) (TPP = 5,10,15,20-tetraphenylporphyrinate; bdt = benzenedithiolate) was synthesized and characterized. The X-ray crystal structure of the complex revealed a six-coordinate Hf atom surrounded by 4 N atoms of the porphyrin and 2 S atoms of the bdt ligand. The two sulfur atoms of the bdt are in an eclipsed position with respect to the two opposite pyrrole nitrogen atoms of the porphyrin. Crystal data for Hf(TPP)(bdt): tetragonal, $P4_12_12$, $a = 12.471(2)$, $c = 26.966(3)$ Å, $V = 4038.2(7)$ Å^3, $Z = 4$; $R = 0.054$ and $R_w = 0.060$ for 2673 independent reflections with $I > 3\sigma(I)$.

Key words: Crystal structures; Hafnium complexes; Dithiolato complexes; Porphyrin complexes

Introduction

Until recently, only a few hafnium porphyrins had been reported in the literature [1] although the first one was reported as early as 1972 [1a]. Part of the difficulty in the synthesis and characterization of hafnium or other early transition metal porphyrin complexes may be attributed to their high oxophilicity and ease of hydrolysis [2]. Recently, we [3a] and Buchler *et al.* [3b, c] independently reported sandwich-type hafnium bisporphyrins in which the metal ion is encompassed by two porphyrin rings. Very recently, we have synthesized Hf(por)Cl_2 (por = 2,3,7,8,12,13,17,18-octaethylporphyrinate (OEP); and 5,10,15,20-tetraphenylporphyrinate (TPP)) [4] 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 [(n-$C_4H_9)_4N$][Hf(por)(P_3O_9)] [4] or Hf(por)$(Me)_2$ [5] by replacing the two Cl ions of the dichloro complexes with an oxygen tripod ligand $P_3O_9^{3-}$ or two methyl groups. Here we report the synthesis, characterization and X-ray crystal structure of another novel hafnium porphyrin complex Hf(TPP)(bdt) (bdt = benzenedithiolate) which is the first structurally characterized six-coordinate hafnium porphyrin complex.

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). The complex Hf(TPP)Cl_2 was prepared as described previously [4]. All solvents were distilled from their sodium-benzophenone solutions (benzene, thf and hexanes), or from P_2O_5 (CH_2Cl_2) under a nitrogen atmosphere. Deuterated solvents for NMR measurement were dried over P_2O_5($CDCl_3$, CD_2Cl_2) 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 spectra were recorded on an Hewlett Packard 8451A spectrometer. ^{1}H NMR spectra were obtained on a Bruker AM-300 spectrometer, and Fourier-transform IR data on a Bomem Michelson 100 spectrometer. Mass spectrometry using a VG70-SEQ mass spectrometer and elemental analysis were performed at Korea Basic Science Center.

Cyclic voltammetry was performed with an EG&G 273 potentiostat and standard three electrode cells. A glassy carbon electrode was used as the working electrode, a platinum wire as the counter electrode, and a silver wire as the pseudoreference electrode. Cyclic

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voltammograms were obtained on approximately 2×10^{-3} M solution of the samples in 0.2 M tetrabutylammonium perchlorate in dichloromethane. Ferrocene was added as an internal standard ($Cp_2Fe^{0/+}$: ~0.40 V versus Ag wire; ~0.46 V versus SCE).

Synthesis of benzenedithiolato(5,10,15,20-tetraphenylporphyrinato)hafnium(IV), Hf(TPP)(bdt)

To a solution of $Hf(TPP)Cl_2$ (100 mg, 0.12 mmol) in THF (30 ml) were added 2 equiv. of benzenedithiol (1 ml, 0.234 M in THF) and the mixture was stirred for 5 min. On addition of an excess amount of NEt_3 white solids precipitated. After 10 h stirring the reaction mixture was filtered to remove $NEt_3\cdot HCl$ and the filtrate was evaporated to dryness. The product was extracted with benzene and crystallized by the addition of hexane to the solution (40 mg, 37%). *Anal.* Calc. for $C_{50}H_{32}N_4HfS_2$: C, 64.47; H, 3.47; N, 6.02; S, 6.88. Found: C, 64.51; H, 3.59; N, 5.96; S, 6.67%. ^1H NMR (CD_2Cl_2, 300 MHz): 9.19 (s, 8H, H_β), 8.41 (d, 4H, H_o), 8.09 (d, 4H, H_o), 7.80 (m, 12H, $H_m+H_{m'}+H_p$), 5.98 (q, 2H, ph), 5.75 (q, 2H, ph). UV–Vis (THF, nm): 416 (soret), 538. IR (KBr, cm^{-1}): 1615(m), 1487(m), 1441(m), 1338(m), 1203(w), 1180(w), 1074(m), 999(s), 804(s), 754(s), 728(m), 702(s), 661(m), 465(br). MS (EI): 932 (M^+).

X-ray crystal structure determination of Hf(TPP)(bdt)

Crystals of Hf(TPP)(bdt) suitable for X-ray work were obtained from a solution of benzene and hexane. X-ray data were collected with an Enraf-Nonius CAD4 diffractometer using Mo Kα radiation at room temperature. Cell parameters and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections. Crystallographic data for Hf(TPP)(bdt) are summarized in Table 1. The intensities of three standard reflections, recorded every 3 h of X-ray exposure, showed no systematic changes. All the calculations were carried out with the Enraf-Nonius MolEN package [6]. The intensity data were corrected for Lorentz and polarization effects and empirical absorption corrections (DIFABS) [7] were also applied. The structures were solved by a combination of Patterson and difference Fourier methods and refined by full-matrix least-squares methods. All the non-hydrogen atoms were refined anisotropically. The positions of the hydrogen atoms were idealized (d(C–H) = 0.95 Å) and included in the calculations of the structure factors as fixed contributions. Each hydrogen atom was assigned an isotropic thermal parameter of 1.2 times that of the attached atom. The final cycle of refinement on F converged to the agreement indexes given in Table 1.

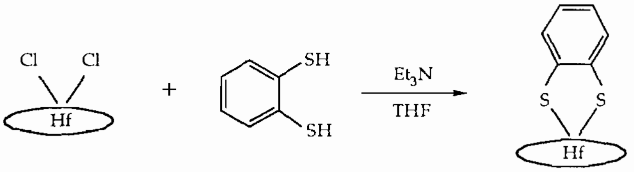
TABLE 1. Crystallographic data for Hf(TPP)(bdt)

Empirical formula	$C_{50}H_{32}N_4S_2Hf$
Formula weight	931.46
Crystal system	tetragonal
Space group	$P4_12_12$
a (Å)	12.471(2)
c (Å)	26.966(3)
V (Å^3)	4038.2(7)
Z value	4
D_{calc} (g/cm^3)	1.532
$F(000)$	1728
T (°C)	23
Crystal size (mm)	$0.25\times0.25\times0.30$
μ(Mo Kα) (cm^{-1})	26.99
Radiation	Mo Kα ($\lambda=0.71073$ Å)
No. observations ($I>3\sigma(I)$)	2673
No. of variables	258
Goodness of fit indicator	0.488
Scan mode	ω
ω-Scan width (°)	$1.0+0.35\tan\theta$
Scan speed[a] (°/min)	2.06
2θ Limits (°)	$3<2\theta<50$
Residuals: R; R_w[b]	0.054; 0.060

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

Results and discussion

In the presence of NEt_3 the reaction of $Hf(TPP)Cl_2$ with benzenedithiol in THF afforded Hf(TPP)(bdt). This compound has been characterized by various spectroscopic methods.



$Hf(TPP)Cl_2$

Hf(TPP)(bdt)

The electronic absorption spectrum of the compound shows the Soret band at 416 nm in THF solution as usually found in monomeric TPP complexes. On the basis of decoupling experiments and consideration of the porphyrin ring current, the two doublets at 8.41 and 8.09 ppm in the NMR spectrum were assigned to the *ortho* protons of the porphyrin phenyl rings and the multiplet at 7.80 ppm to the *meta* and *para* protons. The existence of two distinct resonance signals for the *ortho* protons indicates that the two sides of the porphyrin are not equivalent. The β-pyrrolic protons give a sharp singlet at 9.19 ppm which indicates that the rotation of the benzenedithiolate ligand around the metal is rapid on the NMR time scale. The phenyl proton signals of the benzenedithiolate ligand, which now appear at 5.98 and 5.75 ppm, are shifted to higher field due to the ring current effect of the porphyrin. The spectroscopic properties of Hf(TPP)(bdt) are similar to those of Ti(TPP)(tdt) (tdt = 3,4-toluenedithiolate) [8].

An ORTEP drawing of the compound is shown in Fig. 1 and selected bond distances and angles are given in Table 2. To our knowledge this is the first structurally characterized metalloporphyrin–benzenedithiolate complex. The molecule lies on a two-fold axis passing through the hafnium atom and the middle of the benzenedithiolate ligand. The Hf atom is coordinated by 4 N atoms of the porphyrin and 2 S atoms of the bdt ligand. This is the first six-coordinate hafnium porphyrin whose structure has been determined by X-ray crystallography. Interestingly, the two sulfur atoms bound to the metal are in an eclipsed position with respect to the two opposite pyrrole nitrogen atoms of the porphyrin; the dihedral angle between the plane of the dithiolato ring and the plane containing the N(2), Hf and N(2′) atoms is 5.1°. The Hf–N bond eclipsing the Hf–S bond is slightly longer than the other although the difference may not be significant at the 3σ level due to the large standard deviation: Hf–N(1) = 2.162(9), Hf–N(2) = 2.192(11) Å. Similar eclipsed conformations have been observed in η^2-peroxometalloporphyrin complexes [9], which are thought to be stabilized by the interaction between the d orbitals of the metal and the p orbitals of the oxygen atoms. Similar d_π–p_π (and/or –d_π) interactions between Hf and S may exist in Hf(TPP)(bdt). However, the β-pyrrolic proton signal in the NMR spectrum remains a sharp singlet even at −90 °C indicating that such interaction in Hf(TPP)(bdt) may not be significant at least in solution. The Hf–S bond distance is 2.496(4) Å and the 'bite angle', S–Hf–S, is 78.7(1)°. The hafnium atom lies 0.84 Å above the plane of the four nitrogen atoms. The displacement of the metal from the N_4 plane is much smaller than those in the eight-coordinate complex Hf(OEP)(OAc)$_2$ (1.012 Å) [10] or in the seven-coordinate complexes [(n-C$_4$H$_9$)$_4$N][Hf(OEP)(P$_3$O$_9$)] (1.007 Å) [4] and {[Hf(TPP)]$_2$(μ-OH)$_3$}(OH) (0.9903 Å) [11]. A formal diagram showing the out-of-plane displacement of the 24-atom porphyrin core is given in Fig. 2.

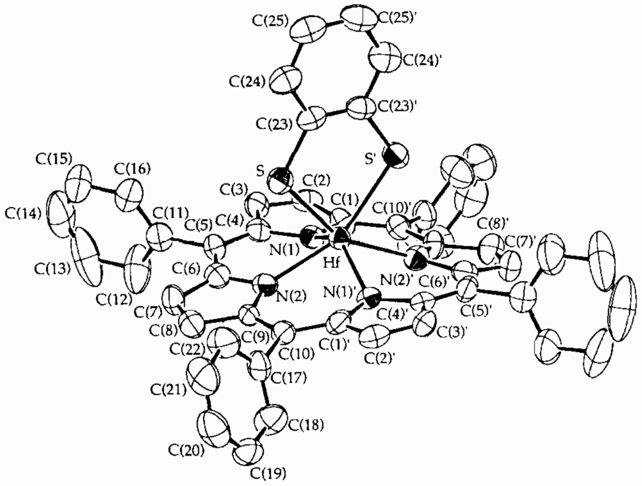


Fig. 1. ORTEP drawing of Hf(TPP)(bdt).

TABLE 2. Selected bond distances (Å) and angles (°) for Hf(TPP)(bdt)

Hf–S	2.496(4)	C(3)–C(4)	1.42(2)
Hf–N(1)	2.162(9)	C(4)–C(5)	1.38(2)
Hf–N(2)	2.19(1)	C(5)–C(6)	1.39(2)
N(1)–C(1)	1.39(2)	C(5)–C(11)	1.50(2)
N(1)–C(4)	1.38(2)	C(6)–C(7)	1.43(2)
N(2)–C(6)	1.40(2)	C(7)–C(8)	1.34(2)
N(2)–C(9)	1.40(2)	C(8)–C(9)	1.42(2)
C(1)–C(10)′	1.40(2)	C(9)–C(10)	1.39(2)
C(1)–C(2)	1.43(2)	C(10)–C(17)	1.50(2)
C(2)–C(3)	1.33(2)	S–C(23)	1.76(1)
S–Hf–S′	78.7(1)	Hf–N(1)–C(1)	126.0(8)
S–Hf–N(1)	109.5(3)	Hf–N(1)–C(4)	123.6(8)
S–Hf–N(1)	103.4(3)	C(1)–N(1)–C(4)	106.0(1)
S–Hf–N(2)	74.9(3)	Hf–N(2)–C(6)	124.4(8)
S–Hf–N(2)′	153.1(3)	Hf–N(2)–C(9)	127.9(8)
S′–Hf–N(1)	103.4(3)	C(6)–N(2)–C(9)	105.0(1)
N(1)–Hf–N(1)′	137.1(4)	N(1)–C(1)–C(2)	109.0(1)
N(1)–Hf–N(2)	81.3(4)	N(1)–C(1)–C(10)′	125.0(1)
N(1)–Hf–N(2)′	81.6(4)	C(2)–C(1)–C(10)′	126.0(1)
N(2)–Hf–N(2)′	131.8(4)	S–C(23)–C(23)′	121.0(1)
Hf–S–C(23)	109.8(5)	S–C(23)–C(24)	119.0(1)

A cyclic voltammetric study of Hf(TPP)(bdt) revealed two reversible one-electron reductions at −1.18 and −1.39 V versus Fc$^{0/+}$ (or *c.* −0.72 and −0.93 V versus SCE) in CH$_2$Cl$_2$ solution. No oxidation wave was observed until the potential reached the solvent limit in the cyclic voltammogram. The nature of the reductions remains to be established. The analogous titanium complex Ti(TPP)(tdt) exhibits two reversible one-elec-

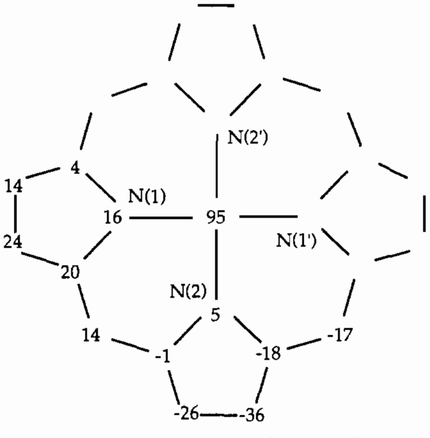


Fig. 2. A formal diagram showing the out-of-plane displacement of the 24-atom porphyrin core.

tron reductions at −0.87 and −1.30 V versus SCE; the first reduction has been assigned to occur at the porphyrin ring [8].

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 author upon request.

Acknowledgements

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