# Synthesis, Characterization and Crystal Structures of Novel Hafnium Porphyrins†

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Dichlorohafnium porphyrin complexes [Hf(por)Cl$_2$] [por = 2,3,7,8,12,13,17,18-octaethylporphyrinate (oep) or 5,10,15,20-tetraphenylporphyrinate (tpp)] which are potentially useful precursors for various hafnium porphyrin complexes, were synthesised and characterized. The structure of [Hf(oep)Cl$_2$(H$_2$O)] has been determined by X-ray crystallography; the co-ordination geometry around the Hf atom can be described as a 4:3 piano-stool with the square base occupied by the porphyrin N atoms and the legs by the two Cl atoms and a water molecule. Treatment of [Hf(por)Cl$_2$] with [NBu$^n_4$]$_3$[P$_3$O$_9$] gave [NBu$^n_4$][Hf(por)(P$_3$O$_9$)] (por = oep and tpp). The crystal structure of the oep complex revealed a seven-co-ordinate Hf atom surrounded by 4 N atoms of the porphyrin and 3 O atoms of the P$_3$O$_9$$^{3-}$ ligand. The N$_4$ and O$_3$ planes are almost parallel and the Hf atom is located 1.007 Å above the N$_4$ plane and 1.476 Å below the O$_3$ plane. Crystal data for [Hf(oep)Cl$_2$(H$_2$O)]·C$_6$H$_6$: triclinic, space group $P\bar{1}$, $a$ = 11.977(2), $b$ = 12.261(1), $c$ = 14.677(2) Å, $\alpha$ = 76.74(1), $\beta$ = 85.41(1), $\gamma$ = 74.41(1)°, $Z$ = 2; $R$ = 0.081 and $R'$ = 0.092 for 3325 independent reflections with $I > 3\sigma(I)$. Crystal data for [NBu$^n_4$][Hf(oep)(P$_3$O$_9$)]·2CHCl$_3$: monoclinic, space group $P2_1/n$, $a$ = 15.490(2), $b$ = 19.133(1), $c$ = 22.761(4) Å, $\beta$ = 99.425(7)°, $Z$ = 4; $R$ = 0.036 and $R'$ = 0.037 for 4823 independent reflections with $I > 3\sigma(I)$.

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The chemistry of early transition-metal porphyrin complexes, especially of second- and third-row metal complexes, still remains in large part undeveloped mainly due to their high oxophilicity and ease of hydrolysis.[2] We have been particularly interested in exploring the chemistry of zirconium and hafnium porphyrins because a rich co-ordination and organometallic chemistry may be developed with them. Until recently, only a few zirconium and hafnium prophyrins have been reported in the literature[3] although the first ones were reported as early as 1971.[3a] We[4a] and other workers[4b,c] recently reported sandwich-type zirconium and hafnium bis(porphyrins) in which the metal ions are encompassed by two porphyrin rings. Very recently, Arnold and co-workers[5] and we[1,6] have prepared [Zr(por)Cl$_2$] (por = oep and tpp) and several organometallic zirconium porphyrin complexes derived from them. We also have prepared [Hf(por)Cl$_2$] [por = 2,3,7,8,12,13,17,18-octaethylporphyrinate (oep) or 5,10,15,20-tetraphenylporphyrinate (tpp)] which can be used as precursors for various hafnium porphyrins. Here we report the details of their syntheses and the crystal structure of [Hf(oep)Cl$_2$(H$_2$O)]. Preparation of the novel complexes [NBu$^n_4$][Hf(por)(P$_3$O$_9$)] by replacing the two Cl ions of the dichloro complexes with an oxygen tripod ligand P$_3$O$_9$$^{3-}$ and the crystal structure of the oep complexes are also presented.

## 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 compound H$_2$tpp was prepared by the literature method[7] and H$_2$oep was purchased from Aldrich. The complexes [HfCl$_4$(thf)$_2$][8] and [Li(thf)$_4$][Li(oep)][9] (thf = tetrahydrofuran) were prepared by the literature procedures. All solvents were distilled from their sodium–benzophenone solutions (toluene, thf and hexanes), or from P$_2$O$_5$ (CH$_2$Cl$_2$) under a nitrogen atmosphere.

All manipulations of oxygen- and water-sensitive materials were performed either in a Vacuum Atmospheres glove-box under a nitrogen atmosphere or in Schlenkwares under a purified argon atmosphere. The UV/VIS spectra were recorded on an Hewlett-Packard 8452A spectrometer, $^1$H and $^{31}$P NMR spectra on a Bruker AM-300 spectrometer ($^{31}$P spectra referenced to external 85% H$_3$PO$_4$ by the sample replacement method), Fourier-transform IR data on a Bomem michelson 100 spectrometer, and mass spectra on a VG70-SEQ mass spectrometer at Korea Basic Science Center. Elemental analyses were performed at Korea Basic Science Center.

*Synthesis of the Hafnium Complexes.*—[Hf(oep)Cl$_2$] **1a**. The salt [Li(thf)$_4$][Li(oep)] (0.17 g, 0.203 mmol) and [HfCl$_4$(thf)$_2$] (0.28 g, 0.61 mmol) were placed in a round-bottomed flask (100 cm$^3$) to which was added toluene (60 cm$^3$). The mixture was refluxed for 2 h, the resulting dark red solution was filtered to remove LiCl and the filtrate was allowed to cool to −20 °C for 1 d. The red solid was filtered off, washed with hexanes and dried under vacuum to yield complex **1a** (0.090 g, 58%) (Found: C, 53.1; H, 5.50; N, 6.75. C$_{36}$H$_{44}$Cl$_2$N$_4$Hf·0.5CH$_2$Cl$_2$ requires C, 53.2; H, 5.50; N, 6.80%). The sample for the elemental analysis was recrystallized from CH$_2$Cl$_2$ and the presence of CH$_2$Cl$_2$ has been confirmed by $^1$H NMR spectroscopy; $\lambda_{max}$/nm(CH$_2$Cl$_2$) 330, 398, 504, 526 and 564 (log ε/dm$^3$ mol$^{-1}$ cm$^{-1}$ 3.99, 5.02, 3.63, 4.01 and 4.27); $\nu_{max}$(KBr) 1631m, 1460s, 1375m, 1269w, 1147m, 1057m, 1017m, 958s, 851w, 745w and 700w cm$^{-1}$; $\delta_H$(300 MHz, solvent CDCl$_3$) 10.60 (4 H, s, *meso* H), 4.21 (16 H, m, C$H_2$CH$_3$) and 1.90 [24 H, t, $J$(HH) 7.5 Hz, CH$_2$C$H_3$]; $m/z$ (electron impact, EI) 782 ($M^+$), 747 ($M$ − Cl) and 711 ($M$ − 2Cl).

[Hf(tpp)Cl$_2$] **1b**. The synthesis is analogous to that of **1a** (0.085 g, 60%) (Found: C, 62.6; H, 3.65; N, 6.00. C$_{44}$H$_{28}$Cl$_2$HfN$_4$·0.5C$_7$H$_8$ requires C, 62.8; H, 3.55; N, 6.15%); $\lambda_{max}$/nm (CH$_2$Cl$_2$) 412, 497, 502 and 538 (log ε/dm$^3$ mol$^{-1}$ cm$^{-1}$ 4.97, 3.87, 3.87 and 4.26); $\nu_{max}$(KBr) 1596w, 1487w, 1441w, 1339m, 1071m, 1002s, 992s, 806s, 756s and 702s cm$^{-1}$; $\delta_H$(300 MHz,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

**Table 1** Crystallographic data for complexes **1a′** and **2a**

| Complex | **1a′** | **2a** |
|---|---|---|
| Formula | $C_{36}H_{46}Cl_2HfN_4O\cdot C_6D_6$ | $C_{52}H_{80}HfN_5O_9P_3\cdot 2CHCl_3$ |
| $M$ | 878.37 | 1429.41 |
| Crystal system | Triclinic | Monoclinic |
| Space group | $P\bar{1}$ | $P2_1/n$ |
| $a$/Å | 11.977(2) | 15.490(2) |
| $b$/Å | 12.261(1) | 19.133(1) |
| $c$/Å | 14.677(2) | 22.761(4) |
| α/° | 76.74(1) | |
| β/° | 85.41(1) | 99.425(7) |
| γ/° | 74.41(1) | |
| $U$/Å$^3$ | 2020.1(4) | 6655(2) |
| $Z$ | 2 | 4 |
| $F$(000) | 892 | 2928 |
| $T$/°C | 23 | 23 |
| $D_c$/g cm$^{-3}$ | 1.44 | 1.43 |
| μ/cm$^{-1}$ | 27.2 | 19.2 |
| Crystal size (mm) | 0.25 × 0.25 × 0.10 | 0.40 × 0.40 × 0.25 |
| Scan mode | ω–2θ | ω |
| ω-Scan width/° | 0.80 + 0.35 tanθ | 0.72 + 0.35 tanθ |
| Scan speed[a]/° min$^{-1}$ | 2.75 | 2.06 |
| 2θ Limits/° | $4 < 2\theta < 40$ | $3 < 2\theta < 44$ |
| Unique data with $I > 3\sigma(I)$ | 3325 | 4823 |
| No. of variables | 216 | 703 |
| $R$[b] | 0.081 | 0.036 |
| $R'$[c] | 0.092 | 0.037 |
| Goodness of fit | 2.46 | 2.95 |

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

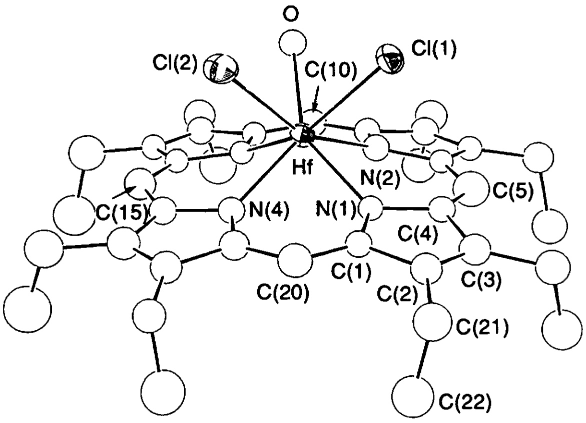

**Fig. 1** An ORTEP[12] drawing of complex **1a′** with the atom labelling scheme

solvent $CDCl_3$) 9.10 (8 H, s, pyrrole H), 8.45 (4 H, br), 8.05 (4 H, br) and 7.82 (12 H, br); $m/z$ (EI) 863 ($M^+$) and 828 ($M$ – Cl).

$[NBu^n_4][Hf(oep)(P_3O_9)]$ **2a**. To a solution of $[Hf(oep)Cl_2]$ (0.060 g, 0.077 mmol) in $CH_2Cl_2$ (20 cm$^3$) was added $[NBu^n_4]_3[P_3O_9]$ (0.079 g, 0.078 mmol) in $CH_2Cl_2$ (5 cm$^3$) and the mixture was stirred at room temperature for 1 h. The mixture was then filtered to remove $[NBu^n_4]Cl$ and the filtrate was evaporated to dryness *in vacuo*. The residue was redissolved in $CH_2Cl_2$ and slow addition of hexane yielded red precipitates of complex **2a** (0.080 g, 88%) (Found: C, 53.4; H, 6.80; N, 5.60. $C_{52}H_{80}HfN_5O_9P_3\cdot 0.5C_6H_{14}$ requires C, 53.5; H, 7.10; N, 5.70%); $\lambda_{max}$/nm($CH_2Cl_2$) 375, 394, 490, 498, 526 and 564 (log ε/dm$^3$ mol$^{-1}$ cm$^{-1}$ 4.24, 4.97, 3.55, 3.56, 3.79 and 4.07); $\nu_{max}$(KBr) 2952s, 1471m, 1334s, 1301s, 1125s, 938s, 778m and 548m; $\delta_H$(300 MHz, solvent $CDCl_3$) 10.41 (4 H, s, *meso*-H), 4.16 (16 H, m, $CH_2CH_3$), 2.89 (8 H, br, $CH_2$), 1.82 [24 H, t, $J$(HH) 7.6, $CH_2CH_3$], 1.32 (8 H, br, $CH_2$), 1.20 (8 H, br, $CH_2$), 0.80 [12 H, t, $J$(HH) 6.9 Hz, $CH_3$]; $\delta_P$(121 MHz, solvent $CDCl_3$) –21.78; $m/z$ (fast atom bombardment, FAB) 1191 ($M$ + H$^+$) and 950 ($M$ – $NBu^n_4$).

$[NBu^n_4][Hf(tpp)(P_3O_9)]$ **2b**. The synthesis is analogous to that of **2a** (0.030 g, 72%) (Found: C, 56.3; H, 5.10; N, 5.40. $C_{60}H_{64}HfN_5O_9P_3$ requires C, 56.7; H, 5.10; N, 5.50%); $\lambda_{max}$/nm($CH_2Cl_2$) 394, 412, 498, 502 and 538 (log ε/dm$^3$ mol$^{-1}$ cm$^{-1}$ 4.54, 4.95, 3.85, 3.85 and 4.33); $\nu_{max}$(KBr) 1332s, 1301s, 1127s, 941s, 783m and 549m cm$^{-1}$; $\delta_H$(300 MHz, solvent $CDCl_3$) 8.96 (8 H, s, pyrrole H), 8.39 (4 H, br), 8.05 (4 H, br), 7.73 (12 H, br), 2.60 [8 H, t, $J$(HH) 8.27, $CH_2$], 1.14 (8 H, br, $CH_2$), 1.03 (8 H, m, $CH_2$) and 0.72 [12 H, t, $J$(HH) 7.13 Hz, $CH_3$]; $\delta_P$(121 MHz, solvent $CDCl_3$) –21.98; $m/z$ (FAB) 1272 ($M$ + H$^+$) and 1030 ($M$ – $NBu^n_4$).

*X-Ray Crystal Structure Determination of Complexes* **1a′** *and* **2a**.—Dark red crystals of $[Hf(oep)Cl_2(H_2O)]\cdot C_6D_6$ **1a′** were obtained from a $C_6D_6$ solution of **1a** stored at room temperature after the NMR measurement and dark red crystals of **2a** were grown by slow diffusion of hexane into a $CHCl_3$ solution. Crystals were sealed in glass capillaries before being mounted on an Enraf-Nonius CAD4 diffractometer equipped with graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å). Unit-cell parameters were determined by least-squares refinement of 25 reflections. Crystallographic data for **1a′** and **2a** are summarized in Table 1. The intensities of three standard reflections, measured every 3 h of X-ray exposure, showed no systematic changes for **2a**. However, a linear decay in intensity was observed for **1a′**. The crystal was replaced with a new crystal when it lost 25% of its initial intensity. Three crystals were used before the data collection was finished. The three intensity data sets of **1a′** were merged before use for further calculations. All the calculations were carried out with the Enraf-Nonius MOLEN package.[10] The intensity data were corrected for Lorentz and polarization effects and empirical absorption corrections (DIFABS)[11] were also applied. The structures were solved by a combination of Patterson and Fourier difference methods and refined by full-matrix least-squares methods. All non-hydrogen atoms for **2a**, however, and the hafnium and two chloride atoms only for **1a′** were refined anisotropically owing to the limited number of data with $I > 3\sigma(I)$ for the latter. The positions of hydrogen atoms (except for the solvate molecules) were calculated (C–H 0.95 Å) and were included as fixed contributions to the structure factor. Each hydrogen atom was assigned an isotropic thermal parameter 1.2 times that of the atom to which it is attached. The final cycles of refinement on $F$ converged to the agreement indices given in Table 1. Positional parameters for **1a′** and **2a** are listed in Tables 2 and 3, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

## Results and Discussion

Treatment of $[Li(thf)_4][Li(por)]$[9] (por = oep or tpp) with $[HfCl_4(thf)_2]$[8] in toluene gives the dichlorohafnium complexes, $[Hf(por)Cl_2]$. The complexes have been characterized by UV–VIS, IR and $^1H$ NMR spectroscopy. They are stable in air as solids, but slowly decompose in solution. In the $^1H$ NMR spectrum of $[Hf(oep)Cl_2]$ the appearance of the diastereotopic methylene proton signals indicates that the Cl atoms are *cis* to each other and the structure has been confirmed by X-ray crystallography (Fig. 1). Large crystals were obtained from a $C_6D_6$ solution of **1a** kept on the bench after the NMR measurement. X-Ray structure analysis of the crystal revealed an additional water molecule co-ordinated to the Hf atom and a benzene solvate molecule. The source of the water is not clear but it may originate from a trace amount of water present in $C_6D_6$. Selected bond distances and angles for $[Hf(oep)Cl_2(H_2O)]$ **1a′** are given in Table 4.

**Table 2** Positional parameters for complex **1a′**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Hf | 0.088 88(7) | 0.115 40(8) | 0.128 30(7) |
| Cl(1) | 0.184 0(4) | 0.083 5(4) | −0.028 7(4) |
| Cl(2) | −0.089 2(4) | 0.208 9(5) | 0.029 7(4) |
| O | 0.038 9(9) | −0.041(1) | 0.104 9(9) |
| N(1) | 0.225(1) | 0.213(1) | 0.114(1) |
| N(2) | 0.242(1) | −0.027(1) | 0.187(1) |
| N(3) | 0.014(1) | 0.034(1) | 0.263(1) |
| N(4) | 0.002(1) | 0.269(1) | 0.188(1) |
| C(1) | 0.204(1) | 0.333(2) | 0.088(1) |
| C(2) | 0.312(2) | 0.363(2) | 0.049(2) |
| C(3) | 0.396(2) | 0.263(2) | 0.057(2) |
| C(4) | 0.343(1) | 0.170(2) | 0.090(1) |
| C(5) | 0.403(2) | 0.052(2) | 0.119(2) |
| C(6) | 0.360(1) | −0.041(2) | 0.164(1) |
| C(7) | 0.424(1) | −0.153(2) | 0.197(1) |
| C(8) | 0.351(2) | −0.211(2) | 0.246(2) |
| C(9) | 0.238(1) | −0.136(2) | 0.244(1) |
| C(10) | 0.141(2) | −0.158(2) | 0.293(2) |
| C(11) | 0.038(1) | −0.080(2) | 0.306(1) |
| C(12) | −0.055(1) | −0.107(2) | 0.367(2) |
| C(13) | −0.140(1) | −0.005(2) | 0.361(1) |
| C(14) | −0.098(1) | 0.082(2) | 0.297(1) |
| C(15) | −0.158(2) | 0.198(2) | 0.278(2) |
| C(16) | −0.112(1) | 0.289(2) | 0.230(1) |
| C(17) | −0.168(2) | 0.410(2) | 0.217(2) |
| C(18) | −0.094(2) | 0.469(2) | 0.170(2) |
| C(19) | 0.011(2) | 0.383(2) | 0.150(1) |
| C(20) | 0.104(2) | 0.413(2) | 0.101(2) |
| C(21) | 0.323(2) | 0.487(2) | 0.026(2) |
| C(22) | 0.332(2) | 0.532(2) | 0.112(2) |
| C(23) | 0.528(2) | 0.242(2) | 0.038(2) |
| C(24) | 0.592(2) | 0.229(2) | 0.130(2) |
| C(25) | 0.554(2) | −0.192(2) | 0.179(2) |
| C(26) | 0.618(2) | −0.158(2) | 0.257(2) |
| C(27) | 0.378(2) | −0.340(2) | 0.301(2) |
| C(28) | 0.398(2) | −0.349(2) | 0.401(2) |
| C(29) | −0.056(2) | −0.223(2) | 0.427(2) |
| C(30) | 0.015(2) | −0.251(2) | 0.518(2) |
| C(31) | −0.256(2) | 0.015(2) | 0.415(2) |
| C(32) | −0.244(2) | 0.053(3) | 0.504(2) |
| C(33) | −0.291(2) | 0.456(2) | 0.251(2) |
| C(34) | −0.289(2) | 0.469(3) | 0.351(2) |
| C(35) | −0.109(2) | 0.600(2) | 0.146(2) |
| C(36) | −0.051(2) | 0.636(2) | 0.219(2) |
| C(37) | 0.427(3) | 0.243(4) | 0.434(3) |
| C(38) | 0.407(3) | 0.177(4) | 0.377(3) |
| C(39) | 0.315(3) | 0.198(4) | 0.329(3) |
| C(40) | 0.240(3) | 0.299(3) | 0.335(3) |
| C(41) | 0.241(3) | 0.383(4) | 0.389(3) |
| C(42) | 0.347(3) | 0.340(4) | 0.447(3) |

**Table 3** Positional parameters for complex **2a**

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Hf | 0.013 86(2) | 0.245 97(2) | 0.069 93(1) |
| P(1) | −0.032 1(1) | 0.183 0(1) | −0.070 0(1) |
| P(2) | −0.052 3(1) | 0.328 6(1) | −0.061 8(1) |
| P(3) | −0.176 8(1) | 0.237 8(1) | −0.027 02(9) |
| O(1) | 0.015 8(3) | 0.183 9(3) | −0.007 2(2) |
| O(2) | −0.003 1(3) | 0.324 4(3) | 0.001 1(3) |
| O(3) | −0.125 2(3) | 0.236 4(3) | 0.034 0(2) |
| O(4) | −0.024 3(3) | 0.259 8(4) | −0.096 0(2) |
| O(5) | −0.153 3(3) | 0.309 4(3) | −0.059 1(3) |
| O(6) | −0.134 7(4) | 0.181 6(3) | −0.066 2(3) |
| O(7) | −0.010 1(5) | 0.130 7(4) | −0.112 1(3) |
| O(8) | −0.049 0(4) | 0.390 5(4) | −0.098 1(3) |
| O(9) | −0.271 5(3) | 0.229 2(4) | −0.036 0(3) |
| N(1) | 0.124 5(3) | 0.169 2(3) | 0.095 8(3) |
| N(2) | 0.128 2(3) | 0.318 1(3) | 0.093 1(3) |
| N(3) | −0.037 2(3) | 0.324 4(3) | 0.128 4(3) |
| N(4) | −0.039 8(3) | 0.174 5(3) | 0.133 4(3) |
| C(1) | 0.109 0(4) | 0.099 1(4) | 0.094 1(4) |
| C(2) | 0.182 3(5) | 0.061 0(4) | 0.078 1(4) |
| C(3) | 0.242 9(5) | 0.109 6(5) | 0.070 9(4) |
| C(4) | 0.207 5(4) | 0.177 0(4) | 0.080 9(4) |
| C(5) | 0.247 4(4) | 0.240 8(5) | 0.075 5(4) |
| C(6) | 0.211 6(4) | 0.305 3(4) | 0.080 8(4) |
| C(7) | 0.254 1(5) | 0.371 2(4) | 0.072 4(4) |
| C(8) | 0.198 2(5) | 0.423 8(4) | 0.078 8(4) |
| C(9) | 0.119 8(5) | 0.389 6(4) | 0.094 4(4) |
| C(10) | 0.047 7(5) | 0.425 5(4) | 0.107 8(4) |
| C(11) | −0.022 6(5) | 0.394 7(4) | 0.124 7(4) |
| C(12) | −0.095 3(5) | 0.434 0(5) | 0.145 3(4) |
| C(13) | −0.150 2(5) | 0.383 1(4) | 0.161 9(4) |
| C(14) | −0.114 7(5) | 0.315 9(5) | 0.152 7(4) |
| C(15) | −0.146 4(4) | 0.251 9(6) | 0.167 0(3) |
| C(16) | −0.111 1(4) | 0.187 1(4) | 0.159 8(4) |
| C(17) | −0.142 9(5) | 0.122 9(5) | 0.180 4(4) |
| C(18) | −0.095 3(5) | 0.070 1(4) | 0.164 0(4) |
| C(19) | −0.030 0(4) | 0.103 2(4) | 0.134 4(3) |
| C(20) | 0.037 7(5) | 0.067 3(4) | 0.111 6(4) |
| C(21) | 0.184 2(5) | −0.015 0(5) | 0.064 1(4) |
| C(22) | 0.149 6(9) | −0.028 6(7) | −0.000 6(6) |
| C(23) | 0.334 4(6) | 0.096 2(6) | 0.058 6(6) |
| C(24) | 0.399 4(7) | 0.084(1) | 0.115(1) |
| C(25) | 0.345 2(5) | 0.379 5(5) | 0.056 7(5) |
| C(26) | 0.416 0(6) | 0.379(1) | 0.109 4(7) |
| C(27) | 0.209 0(5) | 0.499 9(5) | 0.070 9(4) |
| C(28) | 0.177 1(9) | 0.521 1(7) | 0.005 7(6) |
| C(29) | −0.100 3(5) | 0.510 7(5) | 0.150 6(4) |
| C(30) | −0.056(1) | 0.540 7(7) | 0.208 8(8) |
| C(31) | −0.236 0(5) | 0.396 5(6) | 0.185 6(5) |
| C(32) | −0.311 5(8) | 0.397(1) | 0.136 9(9) |
| C(33) | −0.218 0(5) | 0.115 2(6) | 0.215 5(5) |
| C(34) | −0.188 9(8) | 0.117(1) | 0.281 5(6) |
| C(35) | −0.104 9(5) | −0.006 7(5) | 0.171 6(4) |
| C(36) | −0.046 7(9) | −0.036 0(6) | 0.225 4(6) |

The co-ordination geometry around the metal centre in [Hf(oep)$Cl_2$($H_2O$)] is similar to that in [Zr(tpp)$Cl_2$(thf)]:[6] a 4:3 piano-stool with the square base occupied by the porphyrin N atoms and the 'legs' by the two Cl atoms and a water molecule. The two Hf–Cl distances are somewhat different [2.552(5) for Cl(1) and 2.526(5) Å for Cl(2)] with the Cl(1)–Hf–Cl(2) angle of 82.7(2)°. The average Hf–Cl distance [2.539(13) Å]* is significantly longer than the average M–Cl distances in [Zr(tpp)$Cl_2$(thf)] [2.473(13) Å][6] or in [Hf($\eta^8$-$C_8H_8$)$Cl_2$(thf)] [2.468(2) Å].[13] The Hf–O ($H_2O$) distance is 2.264(14) Å which is much shorter than the Zr–O(thf) distance [2.412(3) Å] in [Zr(tpp)$Cl_2$(thf)][6] but slightly longer than the Hf–O(thf) distance [2.233(9) Å] in [Hf($\eta^8$-$C_8H_8$)$Cl_2$(thf)].[13] The Hf–N distances are equal within experimental errors with the average value of 2.235(16) Å, which is slightly shorter than the $(Zr–N)_{av}$ [2.262(9) Å] in [Zr(tpp)$Cl_2$(thf)]. The Hf atom lies 1.013 Å above the $N_4$ plane; the displacement is somewhat smaller than that in [Zr(tpp)$Cl_2$(thf)] (1.064 Å) presumably due to the smaller ionic radius of $Hf^{4+}$ (0.76 Å) *vs.* $Zr^{4+}$ (0.78 Å).

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* The estimated standard deviation in parentheses following an average value is the larger of that calculated for an individual observation from the inverse matrix or on the assumption that the values averaged are from the same populations.

**Table 4** Selected bond distances (Å) and angles (°) for complex **1a′**

| | | | |
|---|---|---|---|
| Hf–Cl(1) | 2.552(5) | Hf–N(1) | 2.237(16) |
| Hf–Cl(2) | 2.526(5) | Hf–N(2) | 2.241(13) |
| Hf–O | 2.264(14) | Hf–N(3) | 2.241(14) |
| | | Hf–N(4) | 2.221(16) |
| Cl(1)–Hf–Cl(2) | 82.7(2) | O–Hf–N(1) | 147.6(5) |
| Cl(1)–Hf–O | 75.4(3) | O–Hf–N(2) | 79.1(5) |
| Cl(2)–Hf–O | 78.3(3) | O–Hf–N(3) | 72.5(5) |
| Cl(1)–Hf–N(1) | 78.6(4) | O–Hf–N(4) | 135.6(5) |
| Cl(1)–Hf–N(2) | 83.6(4) | N(1)–Hf–N(2) | 79.2(5) |
| Cl(1)–Hf–N(3) | 145.6(4) | N(1)–Hf–N(3) | 125.7(6) |
| Cl(1)–Hf–N(4) | 135.6(4) | N(1)–Hf–N(4) | 76.8(5) |
| Cl(2)–Hf–N(1) | 117.2(4) | N(2)–Hf–N(3) | 78.8(5) |
| Cl(2)–Hf–N(2) | 155.8(5) | N(2)–Hf–N(4) | 126.4(6) |
| Cl(2)–Hf–N(3) | 102.1(4) | N(3)–Hf–N(4) | 77.8(5) |
| Cl(2)–Hf–N(4) | 76.6(4) | | |

**Table 5** Selected bond distances (Å) and angles (°) for complex **2a**

| | | | |
|---|---|---|---|
| Hf–O(1) | 2.124(6) | P(1)–O(7) | 1.464(8) |
| Hf–O(2) | 2.152(6) | P(2)–O(8) | 1.446(7) |
| Hf–O(3) | 2.181(4) | P(3)–O(9) | 1.455(5) |
| Hf–N(1) | 2.258(6) | P(1)–O(4) | 1.594(7) |
| Hf–N(2) | 2.236(6) | P(1)–O(6) | 1.603(6) |
| Hf–N(3) | 2.233(7) | P(2)–O(4) | 1.623(6) |
| Hf–N(4) | 2.243(6) | P(2)–O(5) | 1.616(5) |
| P(1)–O(1) | 1.497(6) | P(3)–O(5) | 1.619(6) |
| P(2)–O(2) | 1.511(6) | P(3)–O(6) | 1.601(7) |
| N(1)–Hf–N(2) | 78.6(2) | O(1)–Hf–O(2) | 78.6(2) |
| N(3)–Hf–N(4) | 79.6(2) | O(1)–Hf–O(3) | 77.8(2) |
| N(1)–Hf–N(4) | 77.4(2) | | |
| N(1)–Hf–N(3) | 127.4(2) | | |
| N(2)–Hf–N(4) | 125.8(2) | | |

The porphyrin core is domed away from the Hf–Cl bonds; the average deviation from the mean 24-atom plane is 0.11 Å. All the peripheral ethyl groups also point toward the opposite side of the Hf–Cl bonds. The domed porphyrin core and the ethyl groups provide a 'pocket' for the benzene solvate molecule as seen in the crystal packing diagram (Fig. 2). The packing diagram also reveals the intermolecular interactions between the two [Hf(oep)$Cl_2(H_2O)$] molecules related by an inversion symmetry. The co-ordinated water of one molecule appears to form hydrogen bonds with the Cl atoms of the other molecule [O $\cdots$ Cl(1′) 3.183(14), O $\cdots$ Cl(2′) 3.081(15) Å] and *vice versa*.

The dichlorohafnium complexes **1a** and **1b** are potentially useful precursors for various novel hafnium porphyrin complexes including organometallic complexes as Arnold and co-workers[5] and we[1,6] have recently demonstrated with the analogous dichlorozirconium porphyrins. Syntheses of organometallic derivatives is currently in progress in our laboratory. In the meantime, the high oxophilicity of hafnium porphyrins and their tendency to form complexes of co-ordination number higher than six prompted us to study the replacement of the two chloride ions of the dichloride complexes with an oxygen tripod ligand trimetaphosphate ion ($P_3O_9^{3-}$).

Tetrabutylammonium trimetaphosphate[14] readily reacts with [Hf(por)$Cl_2$] in $CH_2Cl_2$ to afford [$NBu^n_4$][Hf(por)($P_3O_9$)] (por = oep or tpp) which are stable in air and moisture. Co-ordination of the $P_3O_9$ ligand to the Hf atom in a $\kappa^3$-*O,O′,O″* fashion was indicated by the splitting of the strong band near 1300 $cm^{-1}$ into two bands in the IR spectra of both **2a** and **2b**, a common feature of all the known metal complexes containing such a ligand.[14] As in **1a**, the appearance of diastereotopic methylene protons in the NMR spectrum of **2a** also suggested the co-ordination of $P_3O_9^{3-}$ to one side of the (oep)Hf moiety. The structure of **2a** was confirmed by X-ray crystallography (Fig. 3). Selected bond distances and angles are given in Table 5.

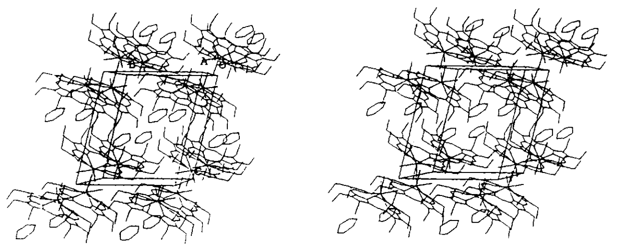

**Fig. 2** Crystal packing diagram of complex **1a′**

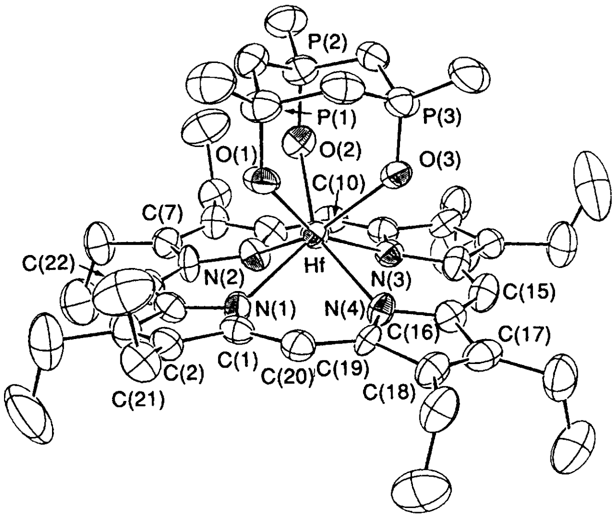

**Fig. 3** An ORTEP drawing of complex **2a** with the atom labelling scheme

The co-ordination geometry around the Hf atom is also a 4 + 3 type with the square base provided by the porphyrin N atoms and the trigonal-planar cap provided by the O atoms of the $P_3O_9^{3-}$. The planes of the square base and the trigonal-planar cap are nearly parallel (dihedral angle 4.9°). The Hf atom is 1.007 Å above the porphyrin $N_4$ plane and 1.476 Å below the $O_3$ plane. The average Hf–N and Hf–O bond distances are 2.243(10) and 2.152(23) Å, respectively. The average O–Hf–O angle is 78.2(4)° which is smaller than those in any known $P_3O_9^{3-}$ complexes[14,15] including [$NBu^n_4$][Fe{HB(pz)$_3$}($P_3O_9$)] (89.8°) (pz = pyrazolyl) the crystal structure of which was determined recently.[16] The steric bulk of the porphyrin ligand may be responsible for the small 'bite' angle of the $P_3O_9^{3-}$ ligand in **2a**. Interestingly, the Hf–O(1) and Hf–N(1) bonds are nearly eclipsed [when the Hf–O(1) bond is projected on the $N_4$ plane the angle O(1)–Hf–N(1) is 3.5°]. It may also be worth mentioning that the Hf–O(1) bond [2.124(6) Å] is slightly *shorter* than the other two Hf–O bonds [2.152(6) and 2.181(4) Å]. The structure suggests that the eclipsed conformation may be stabilized by the interactions between the p orbitals of the oxygen(s) and the d orbitals of the metal as in the metalloporphyrin peroxo complexes.[17]

The structure may be compared with that of the eight-co-ordinate complex [Hf($O_2CMe$)$_2$(oep)].[18] In the latter the Hf atom is displaced 1.012 Å from the plane of the nitrogen atoms with (Hf–N)$_{av}$ 2.257(3) Å and (Hf–O)$_{av}$ 2.278(3) Å. The much shorter Hf–O bond distances in **2a** *versus* those in the diacetate complex indicate that the $P_3O_9^{3-}$ ion binds more strongly to the Hf atom than the acetate ions do. A single resonance signal in $^{31}P$ NMR spectra of **2a** and **2b**, however, indicates that rotation of the $P_3O_9^{3-}$ moiety (and/or that of the porphyrin) around the metal is rapid on the NMR time-scale.

Other bond parameters associated with the $P_3O_9$ ligand are not exceptional. The P–O bonds for the oxygens that bridge phosphorus and hafnium atoms $[(P–O_c)_{av}$ 1.498(10) Å] are somewhat longer than the terminal P–O bonds $[(P–O_t)_{av}$ 1.455(7) Å] but are much shorter than the P–O bonds for the oxygens that bridge two phosphorus atoms $[(P–O_b)_{av}$ 1.610(10) Å].

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## References

1 H.-J. Kim, S. Ryu, K. Kim, W. Yeo and Y. Do, presented in part at the 68th Annual Meeting of the Korean Chemical Society, Chang-Won, October, 1991.

2 J. W. Buchler, in *The Porphyrins*, ed. D. Dolphin, Academic Press, New York, 1978, vol. 1, p. 436.

3 (*a*) J. W. Buchler, G. Eikelmann, L. Puppe, K. Rohbock, H. H. Schneehage and D. D. Weck, *Liebigs Ann. Chem.*, 1971, **745**, 135; (*b*) J. W. Buchler, M. Folz, H. Habets, J. van Kaam and H. H. Schneehage, *Chem. Ber.*, 1976, **109**, 1477.

4 (*a*) K. Kim, W. S. Lee, H.-J. Kim, S.-H. Cho, S. S. Girolami, P. A. Gorlin and K. S. Suslick, *Inorg. Chem.*, 1991, **30**, 2652; 1992, **31**, 716 (corrections); (*b*) J. W. Buchler, A. De Cian, J. Fischer, D. Hammerschmitt and R. Weiss, *Chem. Ber.*, 1991, **124**, 1051; (*c*) J. W. Buchler, A. De Cian, S. Elschner, J. Fischer, D. Hammerschmitt and R. Weiss, *Chem. Ber.*, 1992, **125**, 107.

5 (*a*) H. Brand and J. Arnold, *J. Am. Chem. Soc.*, 1992, **114**, 2266; (*b*) J. Arnold, S. E. Johnson, C. B. Knobler and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1992, **114**, 3996.

6 H.-J. Kim, D. Whang, Y. K. Do and K. Kim, *Inorg. Chem.*, in the press.

7 A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmatcher, J. Assour and T. Korsakoff, *J. Org. Chem.*, 1967, **32**, 476.

8 L. E. Manzer, *Inorg. Synth.*, 1982, **21**, 136.

9 J. Arnold, *J. Chem. Soc., Chem. Commun.*, 1990, 976.

10 MOLEN, An Interactive Structure Solution Procedure, Enraf-Nonius, Delft, 1990.

11 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

12 G. K. Johnson, ORTEP II, Report ORNL 5138, Oak Ridge National Laboratory, TN, 1976.

13 P. Berno, C. Floriani, A. Chiesi-Villa and C. Rizzoli, *J. Chem. Soc., Dalton Trans.*, 1991, 3093.

14 C. J. Besecker, V. W. Day and W. G. Klemperer, *Organometallics*, 1985, **4**, 564.

15 V. W. Day, W. G. Klemperer and D. J. Main, *Inorg. Chem.*, 1990, **29**, 2345; V. W. Day, W. G. Klemperer, S. P. Lockledge and D. J. Main, *J. Am. Chem. Soc.*, 1990, **112**, 2031.

16 K.-N. Han, D. Whang, H. J. Lee, Y. Do and K. Kim, submitted for publication.

17 B. Chevrier, Th. Diebold and R. Weiss, *Inorg. Chim. Acta*, 1976, **19**, L57; R. Guilard, J.-M. Latour, C. Lecomte, J.-C. Marchon, J. Protas and D. Ripoll, *Inorg. Chem.*, 1978, **17**, 1228; R. B. VanAtta, C. E. Strouse, L. K. Hanson and J. S. Valentine, *J. Am. Chem. Soc.*, 1987, **109**, 1425.

18 J. L. Hoard, in *Porphyrins and Metalloporphyrins*, ed. K. M. Smith, Elsevier, Amsterdam, 1975, pp. 347 and 348.

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