

Mo—C(9)	2.32 (1)	O(5)—C(4)	1.19 (2)
Mo—C(10)	2.32 (1)	O(6)—C(11)	1.19 (1)
Mo—C(11)	1.93 (1)	O(7)—C(12)	1.15 (2)
Mo—C(11')	3.16 (2)	C(4)—C(6)	1.49 (2)
Mo—C(12)	1.96 (2)	C(6)—C(7)	1.41 (2)
Mo—C(12')	3.15 (1)	C(6)—C(10)	1.44 (2)
P—O(1)	1.58 (1)	C(7)—C(8)	1.41 (2)
P—O(2)	1.590 (8)	C(8)—C(9)	1.40 (2)
P—O(3)	1.59 (1)	C(9)—C(10)	1.40 (2)
P—Mo—C(6)	116.0 (3)	C(9)—Mo—C(11)	102.9 (6)
P—Mo—C(7)	142.5 (4)	C(9)—Mo—C(12)	147.2 (4)
P—Mo—C(8)	121.5 (4)	C(10)—Mo—C(11)	135.5 (6)
P—Mo—C(9)	89.0 (3)	C(10)—Mo—C(12)	112.6 (5)
P—Mo—C(10)	85.4 (3)	C(11)—Mo—C(12)	104.2 (5)
P—Mo—C(11)	78.0 (4)	O(1)—P—O(2)	104.2 (5)
P—Mo—C(12)	79.0 (4)	O(1)—P—O(3)	99.1 (6)
C(6)—Mo—C(7)	34.2 (6)	O(2)—P—O(3)	105.4 (5)
C(6)—Mo—C(8)	57.3 (4)	P—O(1)—C(1)	124 (1)
C(6)—Mo—C(9)	58.5 (5)	P—O(2)—C(2)	131 (1)
C(6)—Mo—C(10)	35.6 (5)	P—O(3)—C(3)	127 (1)
C(6)—Mo—C(11)	154.3 (5)	C(4)—O(4)—C(5)	113 (1)
C(6)—Mo—C(12)	99.8 (5)	O(4)—C(4)—O(5)	125 (2)
C(7)—Mo—C(8)	34.0 (6)	O(4)—C(4)—C(6)	110 (2)
C(7)—Mo—C(9)	57.4 (5)	O(5)—C(4)—C(6)	125 (1)
C(7)—Mo—C(10)	57.8 (5)	C(4)—C(6)—C(7)	131 (1)
C(7)—Mo—C(11)	122.2 (6)	C(4)—C(6)—C(10)	122 (1)
C(7)—Mo—C(12)	119.4 (6)	C(7)—C(6)—C(10)	107 (1)
C(8)—Mo—C(9)	34.5 (4)	C(6)—C(7)—C(8)	109 (1)
C(8)—Mo—C(10)	57.8 (4)	C(7)—C(8)—C(9)	108 (1)
C(8)—Mo—C(11)	97.2 (5)	C(8)—C(9)—C(10)	109 (1)
C(8)—Mo—C(12)	153.4 (5)	C(6)—C(10)—C(9)	108 (1)
C(9)—Mo—C(10)	35.3 (5)		

Symmetry code: (i) $-x, 2 - y, -z$.

The title structure was solved by a combination of Paterson and subsequent Fourier methods. The structure was refined by full-matrix least-squares techniques. All calculations were carried out on a VAX-11/785 computer. Anomalous dispersion was corrected for according to Cromer & Waber (1974).

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1983). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *GCIF* (local program).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1083). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Adams, R. D., Collins, D. M. & Cotton, F. A. (1974). *Inorg. Chem.* **13**, 1086–1090.
- Adams, R. D., Katahira, D. A. & Yang, L. W. (1982). *Organometallics*, **1**, 231–235.
- Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- Curtis, M. D. & Klingler, R. J. (1978). *J. Organomet. Chem.* **161**, 23–37.
- Gilmore, G. J. (1983). *MITHRIL. Computer Program for the Automatic Solution of Crystal Structures from X-ray Data*. University of Glasgow, Scotland.
- Green, M. L. H., Poveda, M. L., Bashkin, J. & Prout, K. (1982). *J. Chem. Soc. Chem. Commun.* pp. 30–31.

- Johnson, C. K. (1976). *ORTEPII*. Report ORNI-5138. Oak Ridge National Laboratory, Tennessee, USA.
- Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- Molecular Structure Corporation (1988). *MSCIAFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Riess, J. G., Klement, U. & Wachter, J. (1985). *J. Organomet. Chem.* **280**, 215–224.
- Wilson, F. C. & Shoemaker, D. P. (1957). *J. Chem. Phys.* **27**, 809–810.

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(Tetraphenylporphyrinato)hafnium(IV) Diacetate Acetonitrile Solvate

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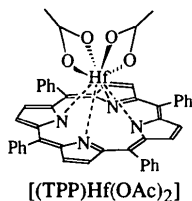
Abstract

The title metalloporphyrin bis(acetato-*O, O'*)[5,10-,15,20-tetraphenyl-21*H*,23*H*-porphinato(2-)-*N*²¹,*N*²²-,*N*²³,*N*²⁴]hafnium acetonitrile solvate, [Hf(C₂H₃O₂)₂-(C₄₄H₂₈N₄)]·CH₃CN, crystallizes in space group *C2/c* with *Z* = 4. The complex has twofold crystallographic symmetry. The two acetate ligands are coordinated in a mutually *cis* configuration and the geometry about the hafnium center approximates a square antiprism. The distance of the Hf atom from the porphyrin plane is 1.033 (5) Å. The average Hf—N and Hf—O bond distances are 2.26 (2) and 2.25 (3) Å, respectively. The bite angle of the diacetate (C_{carbonyl}—Hf—C_{carbonyl}) and average N—Hf—N($-x+1, y, -z+\frac{3}{2}$) angles are 83.8 (4) and 125.7 (4)°, respectively.

Comment

The title compound, [(TPP)Hf(OAc)₂].CH₃CN (TPP is tetraphenylporphyrinato), was prepared according to the literature method of Huhmann, Corey, Rath & Campana (1996) and recrystallized from CH₃CN at 296 K as the CH₃CN solvate, with one molecule of CH₃CN per molecule of the metalloporphyrin. The solvent molecule exhibits large anisotropic displacement

parameters arising from unresolved disorder. There are no unusual packing features or close intermolecular contacts resulting from the crystal packing. The acetonitrile solvent molecules are oriented such that the N atoms point away from the acetate O atoms. All of the porphyrin phenyl groups are planar within experimental error. The C11–C16 phenyl group is tilted from the N_4 plane by an angle of $98.6(3)^\circ$, while the C17–C22 phenyl group is tilted by $56.7(3)^\circ$ from the same plane.



This hafnium–porphyrin complex (Fig. 1) is isomorphous with the zirconium analog [(TPP)Zr(OAc)₂].CH₂Cl₂ (Huhmann, Corey & Rath, 1995). Both structures exhibit twofold crystallographic symmetry, with bidentate acetate ligands coordinated mutually *cis* and the geometries about both the hafnium and zirconium centers approximating square antiprisms. The distance from the metal atom to the N_4 porphyrin plane is similar in both compounds, 1.033(5) and 1.036(7) Å, as are the bite angles of the two acetate ligands, $83.8(4)^\circ$ and $85.1(4)^\circ$, for the hafnium and zirconium complexes, respectively. The porphyrin cores in both structures are domed markedly towards the metal centers. The extent of this doming for the title compound can be seen from

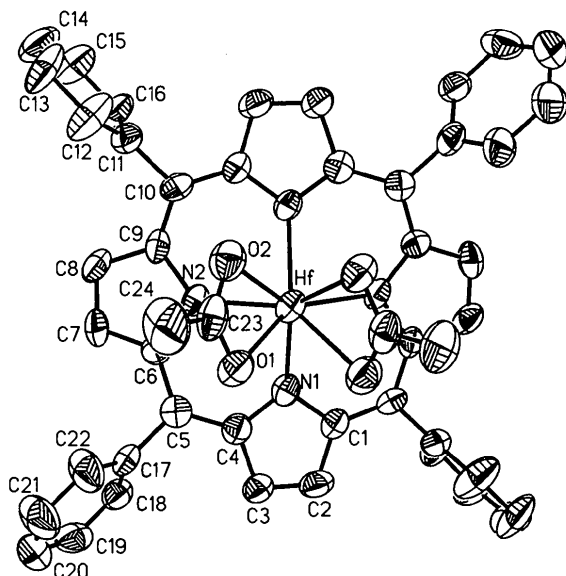


Fig. 1. View of the metal porphyrin showing the atom-labeling scheme for the non-H atoms. Displacement ellipsoids are shown at 30% probability levels and the solvent molecule has been omitted for clarity.

the out-of-plane displacement of the 24-atom porphyrin core. The related diacetate derivatives [(OEP)Zr(OAc)₂] and [(OEP)Hf(OAc)₂] (OEP is 2,3,7,8,12,13,17,18-octaethylporphyrinato) also exhibit similar geometric features, with eight-coordinate metal centers, bidentate *cis*-acetate ligands and domed porphyrin cores (Buchler *et al.*, 1971; Hoard, 1975).

Few mononuclear hafnium porphyrins have been crystallographically characterized. Those reported include [(OEP)HfCl₂(H₂O)]. $\frac{1}{2}$ C₆D₆, [NⁿBu₄][(OEP)Hf(P₃O₉)] (Ryu, Whang, Kim, Yeo & Kim, 1993) and [(TPP)Hf(S₂C₆H₄)] (Ryu, Whang, Yeo & Kim, 1994). Related zirconium porphyrins which have been crystallographically characterized are [(OEP)ZrCl₂]. $\frac{1}{2}$ Tol, [(OEP)Zr(O^tBu)₂], [(OEP)ZrMe₂].CH₂Cl₂ (Brand & Arnold, 1993), [(TPP)ZrCl₂].thf (Kim, Whang, Kim & Do, 1993) and [(OEP)Zr(CH₂SiMe₃)₂] (Brand & Arnold, 1992), where Tol is toluene and thf is tetrahydrofuran. All of the zirconium and hafnium porphyrins were shown to have *cis* coordination of ligands, with the metal positioned above the N_4 porphyrin plane.

There has been a growing interest in the development of hafnium and zirconium d^0 metalloporphyrins with *cis* coordination of their ligands due to the potential analogy to the versatile group IV d^0 metallocenes, which are used as catalysts in many Ziegler–Natta polymerization processes (Kaminsky & Simn, 1988). Finally, it has been shown that [(POR)*M*(OAc)₂] derivatives are suitable precursors to organometallic hafnium and zirconium porphyrin complexes [POR = TPP, *M* = Zr (Shibata, Aida & Inoe, 1992); POR = TPP or OEP, *M* = Hf or Zr (Huhmann, Corey, Rath & Campana, 1996)].

Experimental

The title compound was prepared according to the method of Huhmann, Corey, Rath & Campana (1996) and recrystallized from CH₃CN at 296 K.

Crystal data

[Hf(C₂H₃O₂)₂(C₄₄H₂₈N₄)]·
CH₃CN
M_r = 950.34
Monoclinic
*C*₂/*c*
a = 17.754(9) Å
b = 16.129(7) Å
c = 14.990(5) Å
 β = 103.33(3)°
V = 4177(3) Å³
Z = 4
D_x = 1.511 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71073 Å
Cell parameters from 2856
reflections
 θ = 1.73–20.82°
 μ = 2.550 mm⁻¹
T = 293(2) K
Needle
0.30 × 0.05 × 0.05 mm
Purple

Data collection

Siemens SMART CCD
diffractometer

2403 observed reflections
[*I* > 2σ(*I*)]

ω scans
Absorption correction:
semi-empirical from
equivalent reflections
(*XEMP* in *SHELXTL*-
V5.0; Sheldrick, 1994)
 $T_{\min} = 0.646$, $T_{\max} =$
0.845
8512 measured reflections
3653 independent reflections

$R_{\text{int}} = 0.106$
 $\theta_{\text{max}} = 24.99^\circ$
 $h = -18 \rightarrow 23$
 $k = -21 \rightarrow 21$
 $l = -19 \rightarrow 12$
50 standard reflections
measured at the start and
end of data collection
intensity decay: none

N1—C1	1.387 (10)	C8—C9	1.433 (10)
C1—C2	1.423 (11)	C9—C10	1.382 (10)
C2—C3	1.333 (11)	C23—C24	1.494 (13)
O1 ⁱ —Hf—O1	90.7 (3)	N1—Hf—O2 ⁱ	77.5 (3)
O1—Hf—N1	85.0 (2)	O1 ⁱ —Hf—O2	73.5 (2)
O1—Hf—N2	80.2 (2)	O1—Hf—O2	57.6 (2)
N1 ⁱ —Hf—N2	79.5 (2)	N2—Hf—O2	75.2 (2)
N1—Hf—N2	76.6 (2)	O2 ⁱ —Hf—O2	108.8 (3)
N2—Hf—N2 ⁱ	122.8 (3)	C23 ⁱ —Hf—C23	83.8 (4)

Symmetry code: (i) $1 - x, y, \frac{3}{2} - z$.

Refinement

Refinement on F^2
 $R(F) = 0.0780$
 $wR(F^2) = 0.1096$
 $S = 1.376$
3534 reflections
273 parameters
H-atom parameters not
refined
 $w = 1/[\sigma^2(F_o^2) + (0.015P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = -0.008$
 $\Delta\rho_{\text{max}} = 0.707 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.653 \text{ e } \text{\AA}^{-3}$
Extinction correction: none
Atomic scattering factors
from *International Tables*
for *Crystallography* (1992,
Vol. C, Tables 4.2.6.8 and
6.1.1.4)

The non-H atoms were refined anisotropically, while H atoms were treated using appropriate riding models. The solvent molecule exhibits large anisotropic displacement parameters due to unresolved disorder. The occupancy factor of the solvent molecule was refined. As the refined occupancy is approximately 50%, site occupancy was used.

Data collection: *SMART* (Siemens, 1994). Cell refinement: *SMART*. Data reduction: *SHELXTL*-V5.0 (Sheldrick, 1994). Program(s) used to solve structure: *SHELXTL*-V5.0. Program(s) used to refine structure: *SHELXTL*-V5.0. Molecular graphics: *SHELXTL*-V5.0. Software used to prepare material for publication: *SHELXTL*-V5.0.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: FG1145). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Brand, H. & Arnold, J. (1992). *J. Am. Chem. Soc.* **114**, 2266–2267.
Brand, H. & Arnold, J. (1993). *Organometallics*, **12**, 3655–3665.
Buchler, J. W., Eikermann, G., Puppe, L., Rohbock, K., Shennehage, H. H. & Weck, D. (1971). *Liebigs Ann. Chem.* **745**, 135–151.
Hoard, J. L. (1975). *Porphyryns and Metalloporphyryns*, edited by K. M. Smith, pp. 317–380. New York: Elsevier.
Huhmann, J. L., Corey, J. Y. & Rath, N. P. (1995). *Acta Cryst.* **C51**, 195–196.
Huhmann, J. L., Corey, J. Y., Rath, N. P. & Campana, C. F. (1996). *J. Organomet. Chem.* **513**, 17–26.
Kaminsky, W. & Simn, H. (1988). In *Transition Metals and Organometallics as Catalysts for Olefin Polymerization*. Berlin: Springer-Verlag.
Kim, H.-J., Whang, D., Kim, K. & Do, Y. (1993). *Inorg. Chem.* **32**, 360–362.
Ryu, S., Whang, D., Kim, J., Yeo, W. & Kim, K. (1993). *J. Chem. Soc. Dalton Trans.* pp. 205–209.
Ryu, S., Whang, D., Yeo, H. & Kim, K. (1994). *Inorg. Chim. Acta*, **221**, 51–54.
Sheldrick, G. M. (1994). *SHELXTL*-V5.0. *Program for the Solution and Refinement of Crystal Structures*. Siemens Analytical Instruments Inc., Madison, Wisconsin, USA.
Shibata, K., Aida, T. & Inoue, S. (1992). *Chem. Lett.* pp. 1173–1176.
Siemens (1994). *SMART Package for Data Collection and Integration*. Siemens Analytical Instruments Inc., Madison, Wisconsin, USA.

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j$$

	x	y	z	U_{eq}
Hf	1/2	0.18841 (4)	3/4	0.0456 (2)
O1	0.4593 (3)	0.2854 (3)	0.8335 (4)	0.057 (2)
O2	0.3958 (3)	0.2707 (4)	0.6921 (5)	0.062 (2)
N1	0.5514 (4)	0.1279 (4)	0.8855 (5)	0.042 (2)
C1	0.6299 (5)	0.1178 (5)	0.9229 (6)	0.044 (2)
C2	0.6439 (6)	0.1197 (6)	1.0203 (6)	0.055 (3)
C3	0.5760 (5)	0.1294 (5)	1.0427 (6)	0.051 (2)
C4	0.5162 (5)	0.1310 (5)	0.9586 (6)	0.046 (2)
C5	0.4370 (5)	0.1302 (5)	0.9519 (6)	0.041 (2)
N2	0.3975 (4)	0.1208 (4)	0.7842 (5)	0.043 (2)
C6	0.3815 (5)	0.1177 (5)	0.8691 (6)	0.043 (2)
C7	0.3035 (5)	0.0946 (6)	0.8609 (7)	0.058 (3)
C8	0.2696 (5)	0.0865 (5)	0.7719 (6)	0.051 (3)
C9	0.3270 (5)	0.1028 (5)	0.7209 (6)	0.042 (2)
C10	0.3143 (5)	0.1048 (5)	0.6264 (6)	0.045 (2)
C11	0.2328 (5)	0.0879 (7)	0.5736 (6)	0.053 (3)
C12	0.1796 (6)	0.1517 (7)	0.5496 (7)	0.092 (4)
C13	0.1052 (6)	0.1373 (9)	0.4991 (8)	0.097 (4)
C14	0.0849 (6)	0.0585 (10)	0.4718 (7)	0.088 (4)
C15	0.1348 (7)	-0.0038 (8)	0.4924 (7)	0.085 (4)
C16	0.2094 (5)	0.0099 (6)	0.5444 (6)	0.060 (3)
C17	0.4074 (5)	0.1417 (6)	1.0371 (6)	0.051 (3)
C18	0.4223 (5)	0.0857 (6)	1.1096 (6)	0.052 (2)
C19	0.3949 (6)	0.0981 (7)	1.1861 (6)	0.069 (3)
C20	0.3511 (6)	0.1685 (11)	1.1945 (8)	0.103 (5)
C21	0.3339 (6)	0.2213 (8)	1.1221 (9)	0.104 (5)
C22	0.3615 (6)	0.2087 (7)	1.0444 (7)	0.081 (4)
C23	0.4048 (5)	0.3100 (7)	0.7662 (8)	0.058 (2)
C24	0.3548 (6)	0.3824 (7)	0.7758 (7)	0.100 (4)
N3	1/2	0.552 (2)	3/4	0.42 (2)
C25	1/2	0.624 (2)	3/4	0.35 (2)
C26	1/2	0.711 (2)	3/4	0.58 (4)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Hf—O1	2.226 (5)	C3—C4	1.449 (11)
Hf—N1	2.249 (6)	C4—C5	1.386 (11)
Hf—N2	2.280 (7)	C5—C6	1.410 (11)
Hf—O2	2.280 (6)	N2—C6	1.367 (9)
O1—C23	1.289 (10)	N2—C9	1.415 (10)
O2—C23	1.257 (10)	C6—C7	1.412 (11)
N1—C4	1.382 (9)	C7—C8	1.338 (10)