

Synthesis and Crystal Structure of an 8-Coordinated Tetrakis[2-(phenylamido)pyridine]hafnium(IV) and Comparison with a 4-Coordinated Tetrakis(diphenylamido)hafnium(IV)

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The crystal structure of tetrakis[2-(phenylamido)pyridine]hafnium has been determined. The complex has been obtained in a direct reaction between hafnium(IV) chloride and 2-(phenylamino)pyridine. Ligand precursors lose amino protons and form very small chelate rings, with an average N–Hf–N angle of 58.3(3)°. The complex crystallizes in the monoclinic *C*-centered space group *C2/c* with the unit cell parameters *a* = 24.213(11) Å, *b* = 7.916(8) Å, *c* = 20.432(9) Å, and β = 112.01(3)°. The hafnium atom lies on the diad axis at *x* = 1/2, *z* = 3/4 and leaves half of the molecule crystallographically independent. Hafnium possesses coordination number eight, and thus the coordination sphere can be roughly defined as a triangulated dodecahedron. Data were collected at 193 K.

Crystal structures of homoleptic aminopyridine complexes are rarities: the only known complexes are quadruply bonded dichromium, dimolybdenum and ditungsten complexes.^{1,2} Those most closely relating ones to the present compound are tetrakis(phenylamido)pyridine)ditungsten(II) and the analogous molybdenum(II) complex.² As far as we know tetrakis[2-(phenylamido)pyridine]hafnium has no monometallic analogues. In contrast, the chemistry of homoleptic dialkylamido complexes has been widely studied,^{3,4} and also several crystal structures have been reported.^{5,6} Since the synthesis of tetrakis(diethylamido)uranium(IV),⁷ complexes of this type have been prepared from lithiated ligand precursors, and tetrakis(diphenylamido)hafnium(IV)⁸ was also prepared according to this method. The synthesis of tetrakis[2-(phenylamido)pyridine]hafnium was carried without lithiation of the ligand precursor.

Growing interest has been focused on homoleptic dialkylamido complexes as possible precursors in the deposition of nitride thin film by chemical vapor deposition. The most widely studied complex is tetrakis(dimethylamido)titanium(IV), [Ti(NMe₂)₄], because of the importance of TiN films,⁹ but other transition-metal (viz. Zr, Hf,¹⁰ V, Nb and Ta,¹¹) and main-group metal (viz. Al,¹² Ga¹³ and Si¹⁴) alkylamido complexes have been studied as well. In the CVD process ammonia is

used to enhance nitride formation. The advantages of the alkylamido precursors include good volatility, low deposition temperatures, the possibility of atmospheric pressure processing and the good quality of the films. We have studied the deposition of several nitride films by atomic layer epitaxy from different volatile precursors^{15–18} and in the future the use of amido complexes will be examined.

Experimental

Syntheses. 2-(Phenylamino)pyridine (1.92 g, 11.3 mmol) was suspended in 70 ml of toluene and cooled down to –50 °C. Hafnium(IV) chloride (0.92 g, 2.9 mmol) was added to the vigorously stirred suspension. The solution slowly turned to pale yellow when its temperature was allowed to rise to room temperature. The solution was heated for 2 h at 90 °C; it was then filtered, and pale yellow prismatic crystals were obtained after 20 h. All reaction steps were carried out under an argon atmosphere using standard Schlenk techniques.

X-Ray crystallography. A portion of the thermally stable crystals was transferred to perfluoroether. The crystal selected for X-ray measurements was mounted on a glass fiber using the oil drop method.²⁰ Intensity data sets were recorded on an automated four-circle Rigaku AFC-7S diffractometer using graphite monocromatised

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Table 1. Crystal data and structure refinement for [Hf(PhNPy)₄].

Compound	[Hf(PhNPy) ₄]
Empirical formula	C ₄₄ H ₃₆ HfN ₈
Formula weight	855.30
Temperature/K	193(1)
Wavelength/Å	0.71073
Crystal system	Monoclinic
Space group	C2/c
a/Å	24.213(11)
b/Å	7.916(8)
c/Å	20.432(9)
β/°	112.01(3)
V/Å ³	3631(4)
Z	4
Density (calculated)/Mg m ⁻³	1.565
Absorption coefficient/cm ⁻¹	29.18
F(000)	1712
Crystal size/mm	0.30 × 0.25 × 0.25
Scan mode	2θ-ω
θ _{max}	25.01
No. of independent reflections	3091
No. of observed reflections	2938
No. of variables	240
Goodness-of-fit on F ²	1.153
Final R-indices [I > 2σ(I)]	R ₁ = 0.0876, wR ₂ = 0.2417
R-indices (all data)	R ₁ = 0.0893, wR ₂ = 0.2442
Largest diff. peak and hole/eÅ ⁻³	4.547 and -9.960

Mo Kα (λ = 0.7173 Å) radiation. Reflection intensities over background were collected using 2θ-ω scans. Intensities of three standard reflections, which were recorded after every 200 intensity scans, showed only standard fluctuations. The intensities were corrected for Lorentz and polarization effects and psi-scans were used for absorption (0.8599–1.0000) correction. The data set was compressed to reflection files with TEXSAN single-crystal structure-analysis software.²¹ Structures were solved with the SHELXTL PC 4.1 program package²²

using direct methods which showed the positions of the non-hydrogen atoms. Further refinement with full-matrix least-squares on F² was carried out with SHELXL 93²³ using all collected reflections. In each case non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced into calculated positions with a fixed C–H distance of 0.95 Å and 1.3 × displacement factors to host carbon atoms. The largest positive residual electron density peaks found from the Fourier map were located near (within 0.9–1.0 Å of) the hafnium atom. Crystallographic data are presented in Table 1. Fractional atom coordinates for the complex are presented in Table 2. Structure factors and thermal parameters are available from the authors as supplementary material.

Results and discussion

Tetrakis(diphenylamido)hafnium was found to crystallize in the triclinic space group *P* $\bar{1}$, and one molecule formed the asymmetric unit, whereas the title complex crystallizes in the monoclinic *C*-centered space group *C2/c*. The hafnium atom lies on the diad axis at *x* = 1/2, *z* = 3/4, and thus the asymmetric unit is formed by only half of the molecule. The coordination sphere in the title complex can be roughly defined as a triangulated dodecahedron. It is a typical case in which a polyhedron can be viewed as a pair of two interpenetrating tetrahedra having two different types of edges due to the four didentate ligands with relatively short bite.¹³ In the current complex phenylamido pyridines do have a short bite, as the small N–Hf–N angle [58.3(3)°] indicates. When the tetrahedron formed by the amido bonds is considered, clear distortion from the ideal tetrahedral symmetry can be recognized. These angles vary between 87.0(4) and 143.7(3)°. The tetrahedron formed by the heterocyclic nitrogen atoms is equally distorted: N–Hf–N

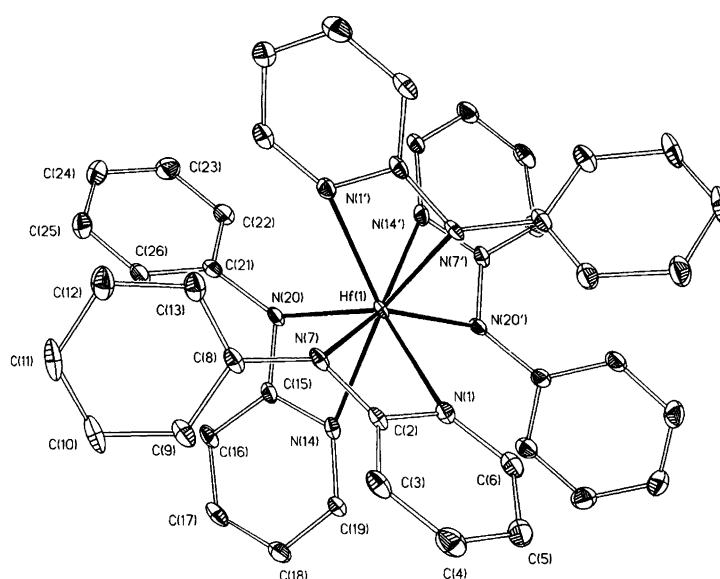


Fig. 1. A perspective view of [Hf(PhNPy)₄] showing the labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for $[\text{Hf}(\text{PhNPY})_4]$.

Atom	x	y	z	$U(\text{eq})^a$
Hf(1)	5000	2373 (1)	7500	24 (1)
N(1)	5444 (4)	3742 (10)	8588 (4)	28 (2)
N(7)	4537 (4)	4390 (10)	7835 (5)	27 (2)
N(14)	4675 (4)	975 (11)	8292 (5)	28 (2)
N(20)	4216 (3)	731 (11)	7143 (4)	27 (2)
C(2)	4946 (4)	4740 (13)	8469 (5)	29 (2)
C(3)	4939 (5)	5864 (15)	8991 (6)	40 (3)
C(4)	5422 (6)	5995 (15)	9607 (7)	46 (3)
C(5)	5924 (5)	4974 (16)	9730 (6)	45 (3)
C(6)	5915 (5)	3891 (14)	9189 (6)	38 (2)
C(8)	3942 (5)	4939 (14)	7632 (6)	31 (2)
C(9)	3609 (5)	4511 (15)	8033 (7)	40 (3)
C(10)	3016 (5)	5000 (17)	7821 (8)	52 (3)
C(11)	2747 (5)	5877 (17)	7197 (8)	55 (4)
C(12)	3064 (5)	6281 (16)	6776 (7)	48 (3)
C(13)	3668 (5)	5827 (14)	7010 (6)	37 (2)
C(15)	4180 (5)	379 (13)	7771 (6)	28 (2)
C(16)	3721 (5)	-428 (14)	7929 (6)	34 (2)
C(17)	3807 (5)	-554 (14)	8633 (6)	41 (3)
C(18)	4299 (5)	102 (14)	9158 (6)	39 (3)
C(19)	4729 (4)	838 (14)	8969 (5)	33 (2)
C(21)	3707 (5)	444 (13)	6501 (5)	31 (2)
C(22)	3769 (5)	-524 (14)	5959 (6)	37 (2)
C(23)	3296 (6)	-732 (17)	5335 (6)	49 (3)
C(24)	2755 (6)	7 (19)	5230 (7)	53 (3)
C(25)	2697 (5)	969 (18)	5760 (7)	48 (3)
C(26)	3166 (5)	1194 (15)	6394 (6)	37 (2)

^a $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected bond lengths (in \AA) for $[\text{Hf}(\text{PhNPY})_4]$.

Hf(1)–N(20)	2.187 (8)	N(7)–C(2)	1.331 (14)
Hf(1)–N(7)	2.202 (8)	N(7)–C(8)	1.410 (13)
Hf(1)–N(14)	2.327 (9)	N(14)–C(19)	1.344 (13)
Hf(1)–N(1)	2.341 (8)	N(14)–C(15)	1.355 (14)
N(1)–C(6)	1.331 (14)	N(20)–C(15)	1.348 (13)
N(1)–C(2)	1.386 (13)	N(20)–C(21)	1.41 (13)

angles vary between $73.4(3)$ and $136.5(3)^\circ$. For comparison in $[\text{Hf}(\text{NPh}_2)_4]$ the tetrahedral N–Hf–N angles vary only between $101.63(14)$ and $121.33(14)^\circ$.

In the present complex Hf–N distances are $2.187(8)$ and $2.202(8) \text{\AA}$ for Hf(1)–N(20) and Hf(1)–N(7)

Table 4. Selected bond angles (in \AA) for $[\text{Hf}(\text{PhNPY})_4]$.

N(20)–Hf(1)–N(14)	58.2 (3)	N(20)–Hf(1)–N(1)	128.7 (3)
N(7)–Hf(1)–N(1)	58.4 (3)	N(14)–Hf(1)–N(1)	136.5 (3)
N(14)–Hf(1)–N(1)	73.4 (3)	N(20)–Hf(1)–N(7)	143.7 (3)
N(7)–Hf(1)–N(14)	77.6 (3)	N(7)–Hf(1)–N(14')	154.8 (3)
N(7)–Hf(1)–N(1)	81.6 (3)	C(6)–N(1)–Hf(1)	147.9 (7)
N(20)–Hf(1)–N(1')	85.7 (3)	C(2)–N(1)–Hf(1)	92.2 (6)
N(7)–Hf(1)–N(7)	87.0 (4)	C(2)–N(7)–Hf(1)	100.0 (6)
N(20)–Hf(1)–N(14')	87.8 (3)	C(8)–N(7)–Hf(1)	135.6 (7)
N(20)–Hf(1)–N(7)	93.2 (3)	C(19)–N(14)–Hf(1)	145.7 (7)
N(20)–Hf(1)–N(20)	107.1 (5)	C(15)–N(14)–Hf(1)	92.8 (6)
N(14)–Hf(1)–N(14)	123.2 (4)	C(15)–N(20)–Hf(1)	99.3 (6)
N(1)–Hf(1)–N(1')	124.8 (4)	C(21)–N(20)–Hf(1)	137.4 (6)

Symmetry transformation used to generate equivalent atoms ('): $-x+1, y, -z+3/2$.

σ -bonds, respectively. These bond lengths are longer than the corresponding bonds in $[\text{Hf}(\text{NPh}_2)_4]$, where distances vary between $2.047(4)$ and $2.085(4) \text{\AA}$. Pyridine nitrogen atoms have Hf–N distances of $2.327(9)$ and $2.341(4) \text{\AA}$ in Hf(1)–N(14) and Hf(1)–N(1), respectively. Pyridine coordination is not linear, since Hf–N–X angles where X is at the center of a six-membered ring deviate clearly from linearity being on average $151.6(4)^\circ$. The hafnium atom clearly deviates from the pyridine plane numbered as N(14)–C(19), $[0.411(15) \text{\AA}]$, whereas deviation from the pyridine plane N(1)–C(6) is less significant, being only $0.141(10) \text{\AA}$. Amido nitrogen atoms deviate from the plane of neighbouring atoms only a little, namely $0.141(10) \text{\AA}$ for N(7) and $0.169(10) \text{\AA}$ for N(20). Deviations of the nitrogen atoms from the Hf–C $_{\alpha}$ –C $_{\alpha}$ plane in the case of $[\text{Hf}(\text{NPh}_2)_4]$ were between $0.024(4)$ and $0.124(4) \text{\AA}$.

Although the appearance of the tetrakis[2-(phenylamido)pyridine]hafnium is similar to that of tetrakis(diphenylamido)hafnium(IV), where four C–H units are replaced with nitrogen atoms, these complexes have interesting chemical differences. Because all four amido-pyridine ligands are in bidentate coordination, hafnium has high 8-coordination. The saturated coordination sphere also results in low reactivity.

Tetrakis[2-(phenylamido)pyridine]hafnium, with average mesh size 0.2 mm , can stand several hours of exposure to air moisture without noticeable changes in crystallinity, and can be rapidly washed with ethanol, acetone or even water, whereas similar sized crystals of tetrakis(diphenylamido)hafnium decompose after a few seconds of exposure to moisture or protic agents.

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