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Dichlorido-1 κ Cl,3 κ Cl-hexakis-[1,1,2,2,3,3(η^5)-methylcyclopentadienyl]di- μ_2 -oxido-1:2 κ^2 O:O;2:3 κ^2 O:O-trihafnium(IV)

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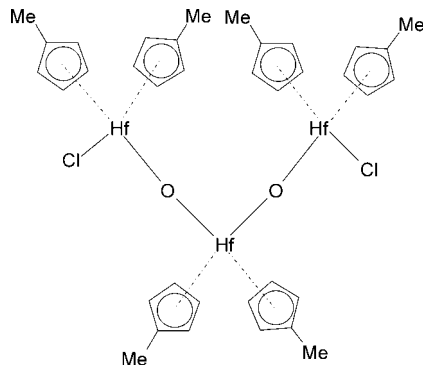
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 Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.034$ Å; disorder in main residue; R factor = 0.061; wR factor = 0.185; data-to-parameter ratio = 20.4.

The title compound, $[\text{Hf}_3(\text{C}_6\text{H}_7)_6\text{Cl}_2\text{O}_2]$, is a trinuclear molecule having two $(\text{MeCp})_2\text{HfCl}$ units (MeCp is methylcyclopentadienyl) each connected to an $(\text{MeCp})_2\text{Hf}$ unit by an oxide bridge. The two Hf—O—Hf bridges are nearly linear. The geometry of the three Hf atoms is tetrahedral (assuming the MeCp group occupies one coordination site); the O—Hf—O angle is $99.8(5)^\circ$. One of the Cl atoms is disordered, with site occupancies of 0.61 (7) and 0.39 (7).

Related literature

For another dichloridobis(η^5 -methylcyclopentadienyl)-hafnium(IV) compound, see: Wisniewska *et al.* (2007). For tris(μ_2 -oxo)-tris(hafnocene) toluene solvate, see: Rogers *et al.* (1982). For (μ_2 -oxo)-bis(methylhafnocene), see: Fronczek *et al.* (1976). For (μ_2 -oxo)-bis(chlorohafnocene), see: Parkanyi *et al.* (1993).



Experimental

Crystal data

$[\text{Hf}_3(\text{C}_6\text{H}_7)_6\text{Cl}_2\text{O}_2]$
 $M_r = 1113.07$
 Monoclinic, $P2_1/c$
 $a = 18.9598(10)$ Å
 $b = 12.9710(5)$ Å
 $c = 14.6178(6)$ Å
 $\beta = 108.466(4)^\circ$

$V = 3409.8(3)$ Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 9.30$ mm⁻¹
 $T = 120(2)$ K
 $0.1 \times 0.08 \times 0.04$ mm

Data collection

Oxford Diffraction KM4 CCD diffractometer
 Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2006)
 $T_{\min} = 0.283$, $T_{\max} = 0.434$

11353 measured reflections
 5801 independent reflections
 4052 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.057$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.185$
 $S = 1.06$
 5801 reflections
 284 parameters

6 restraints
 H-atom parameters constrained
 $\Delta\rho_{\max} = 2.41$ e Å⁻³
 $\Delta\rho_{\min} = -2.70$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Hf1—O1	1.925 (12)	Hf2—O2	2.019 (11)
Hf1—Cl1	2.446 (4)	Hf3—O2	1.859 (11)
Hf2—O1	1.953 (12)	Hf3—Cl2	2.479 (13)
O1—Hf1—Cl1	96.7 (4)	Hf1—O1—Hf2	173.3 (7)
O1—Hf2—O2	99.8 (5)	Hf3—O2—Hf2	178.7 (8)
O2—Hf3—Cl2	103.5 (10)		

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors thank Dr Jarosław Chojnacki for helpful comments.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2389).

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supplementary materials

Acta Cryst. (2008). E64, m361 [doi:10.1107/S1600536807061417]

Dichlorido-1 κ Cl,3 κ Cl-hexakis[1,1,2,2,3,3(η^5)-methylcyclopentadienyl]di- μ_2 -oxido-1:2 κ^2 O:O;2:3 κ^2 O:O-trihafnium(IV)

A. Wisniewska, K. Baranowska and J. Pikies

Comment

The molecular structure of (**1**) is shown in Fig.1. The crystal structure of (**1**) is build up of discrete molecules. The geometry of the central Hf atom in (**1**) is distorted pseudotetrahedral (O1—Hf2—O2 angle is 99.99 °) similar to the geometry of Cl—Hf—Cl in [$(\eta^5$ -C₅H₄Me)₂HfCl₂] (Wisniewska *et al.*, 2007). The Hf—Cl distances are in the typical range for hafnocene dichlorides. The Hf1—O1—Hf2 and Hf3—O2—Hf2 angles are large (172.91 and 178.82°). It is typical for Hf—O—Hf moieties (Fronczek *et al.*, 1976; Parkanyi *et al.*, 1993). The related angles in cyclic tris(μ_2 -Oxo)-tris(hafnocene) are smaller (142.61°.) (Rogers *et al.*, 1982). The Hf—O distances 1.852Å - 2.024 Å are in typical range for hafnocene - oxygen moieties.

Experimental

The title compound [$(\eta^5$ -CH₃C₅H₄)₂HfCl-O-(η^5 -CH₃C₅H₄)₂Hf—O-(η^5 -CH₃C₅H₄)₂HfCl] (**1**) has been isolated as a colourless crystals in a reaction of (CpMe)₂HfCl₂ with (iPr₂N)₂P—P(SiMe₃)Li 2,5 THF in Toluene. After standing for 1 day at room temperature, the mixture was dried under vacuum at 1 mTorr (1 Torr = 133.322 Pa) for 1 h, and the residue dissolved in pentane (4 ml) and filtered. After 2 days at 243 K, the solution yielded small colorless crystals of (**1**).

Explanation. [$(\eta^5$ -CH₃C₅H₄)₂HfCl-O-(η^5 -CH₃C₅H₄)₂Hf—O-(η^5 -CH₃C₅H₄)₂HfCl] (**1**) is a byproduct in the reaction of (CH₃C₅H₄)Li with HfCl₄ in mol ratio 2:1. The commercially available hafnium tetrachloride contains probably Cl₃Hf—O—HfCl₂—O—HfCl₃, which reacts with (CH₃C₅H₄)Li yielding small amounts of (**1**).

Refinement

All H atoms were refined as riding on C atoms with aromatic C—H = 0.95 Å, methyl C—H = 0.98 Å, and $U_{iso}(H) = 1.2U_{eq}(C)$ for CH groups, $1.5U_{eq}(C)$ for CH₃ groups. Atom Cl2 is disordered (0.61 (7)/0.39 (7)). Two methylcyclopentadienyl molecules (C13—C18 and C19—C24) were constrained to be flat.

The largest peak/deepest hole in the final difference Fourier map was in the vicinity of the hafnium atoms.

Figures

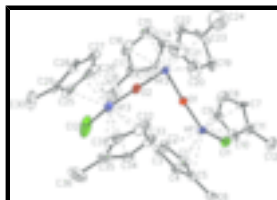


Fig. 1. The molecular structure of (**1**), with atom labels and 50% probability displacement ellipsoids for non-H atoms.

Dichlorido-1κCl,3κCl-hexakis[1,1,2,2,3,3(η⁵)-methylcyclopentadienyl]di-μ₂-oxido-1:2κ²O:O;2:3κ²O:O-trihafnium(IV)

Crystal data

[Hf₃(C₆H₇)₆Cl₂O₂]

M_r = 1113.07

Monoclinic, *P*2₁/*c*

Hall symbol: -*P* 2ybc

a = 18.9598 (10) Å

b = 12.9710 (5) Å

c = 14.6178 (6) Å

β = 108.466 (4)°

V = 3409.8 (3) Å³

Z = 4

*F*₀₀₀ = 2096

D_x = 2.168 Mg m⁻³

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 6065 reflections

θ = 1.9–32.4°

μ = 9.30 mm⁻¹

T = 120 (2) K

Prism, colourless

0.1 × 0.08 × 0.04 mm

Data collection

Oxford Diffraction KM4 CCD
diffractometer

Monochromator: graphite

Detector resolution: 8.1883 pixels mm⁻¹

T = 120(2) K

ω scans, 0.75 deg width

Absorption correction: analytical
(CrysAlis RED; Oxford Diffraction, 2006)

*T*_{min} = 0.283, *T*_{max} = 0.434

11353 measured reflections

5801 independent reflections

4052 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.057

θ_{max} = 25.1°

θ_{min} = 1.9°

h = -21→22

k = -7→15

l = -16→17

Refinement

Refinement on *F*²

Least-squares matrix: full

R [*F*² > 2σ(*F*²)] = 0.061

wR(*F*²) = 0.185

S = 1.06

5801 reflections

284 parameters

6 restraints

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

H-atom parameters constrained

w = 1/[σ²(*F*_o²) + (0.1162*P*)² + 4.6904*P*]

where *P* = (*F*_o² + 2*F*_c²)/3

(Δ/σ)_{max} = 0.002

Δρ_{max} = 2.41 e Å⁻³

Δρ_{min} = -2.70 e Å⁻³

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
Hf1	0.11659 (4)	0.32908 (5)	0.39912 (5)	0.0309 (2)	
Hf2	0.31749 (4)	0.38207 (5)	0.56434 (5)	0.0279 (2)	
Hf3	0.30910 (4)	0.67984 (5)	0.58248 (5)	0.0331 (2)	
O1	0.2183 (6)	0.3553 (8)	0.4746 (9)	0.037 (3)	
O2	0.3134 (7)	0.5372 (8)	0.5725 (10)	0.049 (4)	
Cl1	0.0620 (3)	0.3676 (3)	0.5261 (4)	0.0450 (11)	
Cl2	0.2938 (12)	0.741 (3)	0.4165 (7)	0.056 (7)	0.61 (7)
Cl2A	0.319 (2)	0.693 (3)	0.4198 (12)	0.051 (8)	0.39 (7)
C1	0.0637 (13)	0.3899 (16)	0.2276 (16)	0.059 (6)	
H1	0.0484	0.3399	0.1776	0.07*	
C2	0.1362 (13)	0.4306 (14)	0.2644 (15)	0.052 (5)	
H2	0.1777	0.411	0.2452	0.062*	
C3	0.1366 (13)	0.5039 (13)	0.3334 (15)	0.049 (5)	
H3	0.1774	0.5461	0.3676	0.059*	
C4	0.0661 (11)	0.5041 (13)	0.3434 (15)	0.046 (5)	
H4	0.0514	0.5446	0.3884	0.056*	
C5	0.0181 (11)	0.4330 (14)	0.2745 (16)	0.050 (5)	
C6	-0.0606 (12)	0.4165 (17)	0.261 (2)	0.070 (7)	
H6A	-0.0777	0.3549	0.2211	0.105*	
H6B	-0.0891	0.4765	0.2285	0.105*	
H6C	-0.0679	0.4069	0.3237	0.105*	
C7	0.1181 (10)	0.1447 (13)	0.4586 (17)	0.051 (5)	
H7	0.1331	0.1332	0.5262	0.061*	
C8	0.1654 (14)	0.1518 (14)	0.398 (3)	0.075 (9)	
H8	0.2179	0.1437	0.4181	0.09*	
C9	0.1227 (14)	0.1712 (15)	0.3092 (19)	0.059 (6)	
H9	0.14	0.1812	0.2555	0.07*	
C10	0.0499 (14)	0.1749 (12)	0.3057 (16)	0.051 (5)	
H10	0.0084	0.1868	0.2498	0.062*	
C11	0.0472 (13)	0.1584 (14)	0.3974 (19)	0.057 (6)	
C12	-0.0240 (13)	0.1464 (17)	0.426 (2)	0.068 (7)	
H12A	-0.038	0.0735	0.4228	0.102*	
H12B	-0.0643	0.186	0.3809	0.102*	

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H12C	-0.0149	0.1722	0.4915	0.102*
C13	0.3497 (13)	0.3140 (18)	0.4161 (18)	0.066 (3)
H13	0.311	0.2875	0.3627	0.079*
C14	0.3922 (12)	0.2589 (19)	0.4995 (17)	0.066 (3)
H14	0.3862	0.1879	0.5112	0.079*
C15	0.4404 (13)	0.3201 (17)	0.5573 (19)	0.066 (3)
H15	0.4749	0.3	0.6174	0.079*
C16	0.4349 (13)	0.4140 (19)	0.5209 (17)	0.066 (3)
H16	0.4644	0.4717	0.5502	0.079*
C17	0.3762 (12)	0.4144 (18)	0.4285 (17)	0.066 (3)
C18	0.3580 (13)	0.5119 (17)	0.3697 (18)	0.066 (3)
H18A	0.3902	0.5173	0.329	0.08*
H18B	0.3662	0.5715	0.413	0.08*
H18C	0.3059	0.5103	0.3289	0.08*
C19	0.2593 (18)	0.283 (2)	0.6744 (16)	0.081 (3)
H19	0.2137	0.2478	0.6448	0.097*
C20	0.2703 (18)	0.381 (2)	0.7065 (15)	0.081 (3)
H20	0.2309	0.4285	0.702	0.097*
C21	0.3378 (18)	0.404 (2)	0.7429 (15)	0.081 (3)
H21	0.3542	0.4707	0.7685	0.097*
C22	0.3828 (19)	0.330 (2)	0.7422 (16)	0.081 (3)
H22	0.4355	0.3331	0.7667	0.097*
C23	0.3394 (17)	0.242 (2)	0.6982 (13)	0.081 (3)
C24	0.3580 (17)	0.1362 (19)	0.6783 (17)	0.081 (3)
H24A	0.3199	0.1103	0.6205	0.08*
H24B	0.36	0.092	0.7334	0.08*
H24C	0.4065	0.1358	0.6676	0.08*
C25	0.3903 (12)	0.8149 (18)	0.6894 (18)	0.064 (3)
H25	0.366	0.8746	0.7023	0.076*
C26	0.3995 (12)	0.7254 (17)	0.7377 (18)	0.064 (3)
H26	0.3831	0.7127	0.7918	0.076*
C27	0.4380 (12)	0.6501 (18)	0.6960 (18)	0.064 (3)
H27	0.4519	0.5816	0.7172	0.076*
C28	0.4500 (12)	0.7013 (17)	0.6182 (18)	0.064 (3)
H28	0.4721	0.6717	0.5745	0.076*
C29	0.4241 (12)	0.8036 (18)	0.6143 (18)	0.064 (3)
C30	0.4338 (12)	0.8816 (17)	0.5436 (17)	0.064 (3)
H30A	0.3889	0.924	0.5204	0.08*
H30B	0.4424	0.8461	0.4889	0.08*
H30C	0.4765	0.9258	0.5752	0.08*
C31	0.2248 (13)	0.7771 (18)	0.658 (2)	0.071 (3)
H31	0.244	0.8231	0.7109	0.086*
C32	0.2150 (13)	0.6754 (18)	0.665 (2)	0.071 (3)
H32	0.2312	0.6363	0.7229	0.086*
C33	0.1776 (13)	0.6357 (19)	0.574 (2)	0.071 (3)
H33	0.1589	0.5675	0.5608	0.086*
C34	0.1724 (13)	0.7119 (17)	0.508 (2)	0.071 (3)
H34	0.1526	0.7046	0.4403	0.086*
C35	0.2015 (14)	0.8040 (18)	0.559 (2)	0.071 (3)

C36	0.2008 (13)	0.9084 (16)	0.520 (2)	0.071 (3)
H36A	0.1504	0.9368	0.5024	0.08*
H36B	0.2166	0.9057	0.462	0.08*
H36C	0.2349	0.9525	0.5683	0.08*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Hf1	0.0263 (4)	0.0324 (4)	0.0300 (4)	-0.0008 (3)	0.0031 (3)	-0.0028 (3)
Hf2	0.0227 (4)	0.0375 (4)	0.0232 (4)	-0.0005 (3)	0.0069 (3)	0.0003 (3)
Hf3	0.0318 (4)	0.0381 (4)	0.0296 (4)	-0.0057 (3)	0.0101 (3)	-0.0056 (3)
O1	0.032 (7)	0.036 (6)	0.041 (7)	0.001 (5)	0.009 (6)	0.003 (5)
O2	0.039 (8)	0.031 (6)	0.078 (11)	-0.008 (5)	0.019 (8)	-0.003 (6)
Cl1	0.039 (3)	0.046 (2)	0.054 (3)	0.0013 (19)	0.021 (2)	-0.009 (2)
Cl2	0.068 (9)	0.058 (15)	0.042 (5)	-0.007 (9)	0.019 (5)	0.010 (5)
Cl2A	0.086 (15)	0.028 (13)	0.043 (8)	0.005 (12)	0.026 (8)	0.011 (6)
C1	0.058 (15)	0.058 (12)	0.044 (13)	-0.004 (11)	-0.005 (11)	-0.001 (10)
C2	0.068 (15)	0.048 (10)	0.042 (12)	0.000 (10)	0.021 (12)	0.012 (9)
C3	0.066 (15)	0.030 (8)	0.050 (13)	0.003 (9)	0.018 (11)	0.004 (9)
C4	0.045 (12)	0.035 (8)	0.050 (13)	-0.001 (8)	0.003 (10)	0.002 (9)
C5	0.043 (12)	0.043 (10)	0.059 (14)	0.004 (9)	0.009 (11)	0.020 (10)
C6	0.043 (13)	0.060 (12)	0.10 (2)	0.016 (10)	0.013 (14)	0.026 (13)
C7	0.021 (10)	0.041 (9)	0.067 (15)	0.001 (7)	-0.018 (10)	-0.013 (10)
C8	0.047 (14)	0.032 (10)	0.15 (3)	-0.003 (9)	0.035 (18)	-0.024 (14)
C9	0.061 (16)	0.057 (12)	0.066 (16)	0.023 (11)	0.031 (14)	0.002 (11)
C10	0.076 (16)	0.030 (9)	0.043 (13)	-0.004 (9)	0.010 (12)	-0.007 (8)
C11	0.056 (14)	0.038 (10)	0.080 (17)	-0.018 (9)	0.024 (13)	-0.009 (10)
C12	0.051 (15)	0.064 (13)	0.10 (2)	-0.008 (11)	0.035 (14)	-0.006 (13)
C13	0.070 (7)	0.081 (6)	0.059 (6)	0.005 (5)	0.035 (6)	-0.003 (5)
C14	0.070 (7)	0.081 (6)	0.059 (6)	0.005 (5)	0.035 (6)	-0.003 (5)
C15	0.070 (7)	0.081 (6)	0.059 (6)	0.005 (5)	0.035 (6)	-0.003 (5)
C16	0.070 (7)	0.081 (6)	0.059 (6)	0.005 (5)	0.035 (6)	-0.003 (5)
C17	0.070 (7)	0.081 (6)	0.059 (6)	0.005 (5)	0.035 (6)	-0.003 (5)
C18	0.070 (7)	0.081 (6)	0.059 (6)	0.005 (5)	0.035 (6)	-0.003 (5)
C19	0.106 (10)	0.087 (7)	0.057 (7)	0.004 (7)	0.038 (7)	0.015 (6)
C20	0.106 (10)	0.087 (7)	0.057 (7)	0.004 (7)	0.038 (7)	0.015 (6)
C21	0.106 (10)	0.087 (7)	0.057 (7)	0.004 (7)	0.038 (7)	0.015 (6)
C22	0.106 (10)	0.087 (7)	0.057 (7)	0.004 (7)	0.038 (7)	0.015 (6)
C23	0.106 (10)	0.087 (7)	0.057 (7)	0.004 (7)	0.038 (7)	0.015 (6)
C24	0.106 (10)	0.087 (7)	0.057 (7)	0.004 (7)	0.038 (7)	0.015 (6)
C25	0.038 (5)	0.078 (6)	0.069 (7)	-0.027 (5)	0.007 (5)	-0.018 (5)
C26	0.038 (5)	0.078 (6)	0.069 (7)	-0.027 (5)	0.007 (5)	-0.018 (5)
C27	0.038 (5)	0.078 (6)	0.069 (7)	-0.027 (5)	0.007 (5)	-0.018 (5)
C28	0.038 (5)	0.078 (6)	0.069 (7)	-0.027 (5)	0.007 (5)	-0.018 (5)
C29	0.038 (5)	0.078 (6)	0.069 (7)	-0.027 (5)	0.007 (5)	-0.018 (5)
C30	0.038 (5)	0.078 (6)	0.069 (7)	-0.027 (5)	0.007 (5)	-0.018 (5)
C31	0.047 (6)	0.066 (5)	0.091 (8)	0.010 (5)	0.009 (6)	-0.015 (6)
C32	0.047 (6)	0.066 (5)	0.091 (8)	0.010 (5)	0.009 (6)	-0.015 (6)

supplementary materials

C33	0.047 (6)	0.066 (5)	0.091 (8)	0.010 (5)	0.009 (6)	-0.015 (6)
C34	0.047 (6)	0.066 (5)	0.091 (8)	0.010 (5)	0.009 (6)	-0.015 (6)
C35	0.047 (6)	0.066 (5)	0.091 (8)	0.010 (5)	0.009 (6)	-0.015 (6)
C36	0.047 (6)	0.066 (5)	0.091 (8)	0.010 (5)	0.009 (6)	-0.015 (6)

Geometric parameters (Å, °)

Hf1—O1	1.925 (12)	C10—H10	0.95
Hf1—C11	2.446 (4)	C11—C12	1.54 (3)
Hf1—C9	2.46 (2)	C12—H12A	0.98
Hf1—C8	2.482 (19)	C12—H12B	0.98
Hf1—C2	2.493 (18)	C12—H12C	0.98
Hf1—C4	2.498 (18)	C13—C17	1.39 (3)
Hf1—C1	2.51 (2)	C13—C14	1.42 (3)
Hf1—C10	2.524 (18)	C13—H13	0.95
Hf1—C3	2.538 (18)	C14—C15	1.30 (3)
Hf1—C7	2.541 (19)	C14—H14	0.95
Hf1—C5	2.543 (19)	C15—C16	1.32 (3)
Hf1—C11	2.571 (18)	C15—H15	0.95
Hf2—O1	1.953 (12)	C16—C17	1.45 (4)
Hf2—O2	2.019 (11)	C16—H16	0.95
Hf2—C15	2.498 (18)	C17—C18	1.51 (3)
Hf2—C20	2.510 (19)	C18—H18A	0.98
Hf2—C14	2.511 (17)	C18—H18B	0.98
Hf2—C21	2.53 (2)	C18—H18C	0.98
Hf2—C16	2.536 (18)	C19—C20	1.36 (4)
Hf2—C19	2.57 (2)	C19—C23	1.54 (4)
Hf2—C13	2.586 (19)	C19—H19	0.95
Hf2—C22	2.59 (2)	C20—C21	1.26 (4)
Hf2—C17	2.599 (15)	C20—H20	0.95
Hf2—C23	2.606 (17)	C21—C22	1.29 (4)
Hf3—O2	1.859 (11)	C21—H21	0.95
Hf3—C26	2.44 (2)	C22—C23	1.44 (4)
Hf3—C12A	2.447 (17)	C22—H22	0.95
Hf3—C32	2.45 (3)	C23—C24	1.47 (3)
Hf3—C12	2.479 (13)	C24—H24A	0.98
Hf3—C34	2.51 (2)	C24—H24B	0.98
Hf3—C27	2.51 (2)	C24—H24C	0.98
Hf3—C25	2.52 (2)	C25—C26	1.34 (3)
Hf3—C33	2.52 (2)	C25—C29	1.44 (3)
Hf3—C35	2.54 (2)	C25—H25	0.95
Hf3—C31	2.55 (2)	C26—C27	1.46 (3)
Hf3—C28	2.57 (2)	C26—H26	0.95
C1—C5	1.38 (3)	C27—C28	1.40 (3)
C1—C2	1.41 (3)	C27—H27	0.95
C1—H1	0.95	C28—C29	1.41 (3)
C2—C3	1.39 (3)	C28—H28	0.95
C2—H2	0.95	C29—C30	1.50 (3)
C3—C4	1.39 (3)	C30—H30A	0.98

C3—H3	0.95	C30—H30B	0.98
C4—C5	1.45 (3)	C30—H30C	0.98
C4—H4	0.95	C31—C32	1.34 (3)
C5—C6	1.46 (3)	C31—C35	1.43 (4)
C6—H6A	0.98	C31—H31	0.95
C6—H6B	0.98	C32—C33	1.39 (4)
C6—H6C	0.98	C32—H32	0.95
C7—C11	1.37 (3)	C33—C34	1.36 (4)
C7—C8	1.45 (3)	C33—H33	0.95
C7—H7	0.95	C34—C35	1.42 (3)
C8—C9	1.31 (4)	C34—H34	0.95
C8—H8	0.95	C35—C36	1.47 (3)
C9—C10	1.37 (3)	C36—H36A	0.98
C9—H9	0.95	C36—H36B	0.98
C10—C11	1.37 (3)	C36—H36C	0.98
O1—Hf1—C11	96.7 (4)	C1—C2—Hf1	74.5 (12)
O1—Hf1—C9	104.2 (7)	C3—C2—H2	125.8
C11—Hf1—C9	132.8 (6)	C1—C2—H2	125.8
O1—Hf1—C8	81.9 (7)	Hf1—C2—H2	116
C11—Hf1—C8	116.4 (7)	C2—C3—C4	107.1 (19)
C9—Hf1—C8	30.9 (8)	C2—C3—Hf1	72.2 (10)
O1—Hf1—C2	89.2 (6)	C4—C3—Hf1	72.4 (10)
C11—Hf1—C2	134.2 (5)	C2—C3—H3	126.5
C9—Hf1—C2	88.5 (7)	C4—C3—H3	126.5
C8—Hf1—C2	109.5 (9)	Hf1—C3—H3	120.7
O1—Hf1—C4	103.7 (5)	C3—C4—C5	109.8 (19)
C11—Hf1—C4	81.5 (5)	C3—C4—Hf1	75.6 (11)
C9—Hf1—C4	131.4 (8)	C5—C4—Hf1	75.0 (10)
C8—Hf1—C4	160.9 (9)	C3—C4—H4	125.1
C2—Hf1—C4	53.1 (7)	C5—C4—H4	125.1
O1—Hf1—C1	121.8 (6)	Hf1—C4—H4	116.2
C11—Hf1—C1	124.2 (6)	C1—C5—C4	104.4 (19)
C9—Hf1—C1	78.4 (8)	C1—C5—C6	130 (2)
C8—Hf1—C1	108.3 (10)	C4—C5—C6	125 (2)
C2—Hf1—C1	32.7 (7)	C1—C5—Hf1	73.0 (12)
C4—Hf1—C1	53.1 (7)	C4—C5—Hf1	71.6 (11)
O1—Hf1—C10	133.6 (6)	C6—C5—Hf1	120.5 (13)
C11—Hf1—C10	108.2 (5)	C5—C6—H6A	109.5
C9—Hf1—C10	31.8 (7)	C5—C6—H6B	109.5
C8—Hf1—C10	52.1 (8)	H6A—C6—H6B	109.5
C2—Hf1—C10	99.5 (7)	C5—C6—H6C	109.5
C4—Hf1—C10	118.0 (7)	H6A—C6—H6C	109.5
C1—Hf1—C10	74.7 (7)	H6B—C6—H6C	109.5
O1—Hf1—C3	79.4 (6)	C11—C7—C8	105 (2)
C11—Hf1—C3	104.7 (5)	C11—C7—Hf1	75.7 (11)
C9—Hf1—C3	120.3 (7)	C8—C7—Hf1	71.0 (12)
C8—Hf1—C3	136.4 (8)	C11—C7—H7	127.5
C2—Hf1—C3	32.0 (6)	C8—C7—H7	127.5
C4—Hf1—C3	32.0 (6)	Hf1—C7—H7	118.1

supplementary materials

C1—Hf1—C3	53.3 (7)	C9—C8—C7	108 (2)
C10—Hf1—C3	127.8 (7)	C9—C8—Hf1	73.5 (13)
O1—Hf1—C7	94.0 (5)	C7—C8—Hf1	75.4 (11)
C11—Hf1—C7	83.9 (5)	C9—C8—H8	126.1
C9—Hf1—C7	53.2 (8)	C7—C8—H8	126.1
C8—Hf1—C7	33.6 (8)	Hf1—C8—H8	117.1
C2—Hf1—C7	141.2 (7)	C8—C9—C10	110 (2)
C4—Hf1—C7	158.2 (6)	C8—C9—Hf1	75.7 (14)
C1—Hf1—C7	126.4 (7)	C10—C9—Hf1	76.8 (11)
C10—Hf1—C7	52.3 (7)	C8—C9—H9	124.9
C3—Hf1—C7	169.6 (7)	C10—C9—H9	124.9
O1—Hf1—C5	133.8 (5)	Hf1—C9—H9	114.5
C11—Hf1—C5	92.6 (5)	C9—C10—C11	108 (2)
C9—Hf1—C5	102.0 (8)	C9—C10—Hf1	71.4 (12)
C8—Hf1—C5	132.6 (9)	C11—C10—Hf1	76.3 (11)
C2—Hf1—C5	54.1 (7)	C9—C10—H10	126.1
C4—Hf1—C5	33.5 (6)	C11—C10—H10	126.1
C1—Hf1—C5	31.7 (7)	Hf1—C10—H10	118.2
C10—Hf1—C5	84.5 (7)	C7—C11—C10	109 (2)
C3—Hf1—C5	54.5 (7)	C7—C11—C12	125 (2)
C7—Hf1—C5	132.1 (6)	C10—C11—C12	126 (2)
O1—Hf1—C11	125.0 (6)	C7—C11—Hf1	73.3 (11)
C11—Hf1—C11	81.1 (5)	C10—C11—Hf1	72.5 (11)
C9—Hf1—C11	52.2 (7)	C12—C11—Hf1	125.0 (14)
C8—Hf1—C11	52.6 (7)	C11—C12—H12A	109.5
C2—Hf1—C11	130.6 (7)	C11—C12—H12B	109.5
C4—Hf1—C11	129.6 (7)	H12A—C12—H12B	109.5
C1—Hf1—C11	102.7 (8)	C11—C12—H12C	109.5
C10—Hf1—C11	31.3 (7)	H12A—C12—H12C	109.5
C3—Hf1—C11	154.6 (8)	H12B—C12—H12C	109.5
C7—Hf1—C11	31.1 (7)	C17—C13—C14	106 (2)
C5—Hf1—C11	101.1 (7)	C17—C13—Hf2	75.0 (10)
O1—Hf2—O2	99.8 (5)	C14—C13—Hf2	70.9 (9)
O1—Hf2—C15	128.9 (7)	C17—C13—H13	127
O2—Hf2—C15	112.2 (6)	C14—C13—H13	127
O1—Hf2—C20	92.0 (8)	Hf2—C13—H13	119.1
O2—Hf2—C20	85.6 (7)	C15—C14—C13	110 (2)
C15—Hf2—C20	128.0 (9)	C15—C14—Hf2	74.4 (10)
O1—Hf2—C14	99.8 (7)	C13—C14—Hf2	76.7 (9)
O2—Hf2—C14	133.9 (7)	C15—C14—H14	125
C15—Hf2—C14	30.1 (7)	C13—C14—H14	125
C20—Hf2—C14	134.6 (8)	Hf2—C14—H14	115.8
O1—Hf2—C21	120.8 (8)	C14—C15—C16	111 (3)
O2—Hf2—C21	79.7 (7)	C14—C15—Hf2	75.5 (10)
C15—Hf2—C21	103.9 (9)	C16—C15—Hf2	76.3 (9)
C20—Hf2—C21	28.9 (8)	C14—C15—H15	124.7
C14—Hf2—C21	122.9 (9)	C16—C15—H15	124.7
O1—Hf2—C16	126.6 (7)	Hf2—C15—H15	115.3
O2—Hf2—C16	84.6 (6)	C15—C16—C17	108 (2)

C15—Hf2—C16	30.4 (7)	C15—C16—Hf2	73.2 (9)
C20—Hf2—C16	141.2 (9)	C17—C16—Hf2	76.0 (10)
C14—Hf2—C16	50.6 (8)	C15—C16—H16	125.8
C21—Hf2—C16	112.4 (9)	C17—C16—H16	125.8
O1—Hf2—C19	79.5 (8)	Hf2—C16—H16	117
O2—Hf2—C19	115.5 (7)	C13—C17—C16	105 (2)
C15—Hf2—C19	117.1 (8)	C13—C17—C18	135 (2)
C20—Hf2—C19	31.0 (8)	C16—C17—C18	120 (2)
C14—Hf2—C19	108.9 (8)	C13—C17—Hf2	74.0 (9)
C21—Hf2—C19	50.7 (9)	C16—C17—Hf2	71.2 (9)
C16—Hf2—C19	145.6 (9)	C18—C17—Hf2	119.7 (7)
O1—Hf2—C13	79.0 (6)	C17—C18—H18A	109.5
O2—Hf2—C13	114.4 (6)	C17—C18—H18B	109.5
C15—Hf2—C13	52.0 (8)	H18A—C18—H18B	109.5
C20—Hf2—C13	159.0 (8)	C17—C18—H18C	109.5
C14—Hf2—C13	32.4 (7)	H18A—C18—H18C	109.5
C21—Hf2—C13	154.7 (9)	H18B—C18—H18C	109.5
C16—Hf2—C13	52.2 (8)	C20—C19—C23	102 (3)
C19—Hf2—C13	128.1 (8)	C20—C19—Hf2	72.2 (10)
O1—Hf2—C22	132.9 (7)	C23—C19—Hf2	74.1 (10)
O2—Hf2—C22	102.4 (7)	C20—C19—H19	128.8
C15—Hf2—C22	78.6 (9)	C23—C19—H19	128.8
C20—Hf2—C22	49.5 (10)	Hf2—C19—H19	117.6
C14—Hf2—C22	93.8 (8)	C21—C20—C19	113 (3)
C21—Hf2—C22	29.1 (8)	C21—C20—Hf2	76.5 (12)
C16—Hf2—C22	96.6 (9)	C19—C20—Hf2	76.8 (10)
C19—Hf2—C22	53.4 (9)	C21—C20—H20	123.4
C13—Hf2—C22	126.0 (8)	C19—C20—H20	123.4
O1—Hf2—C17	94.0 (7)	Hf2—C20—H20	114.8
O2—Hf2—C17	85.3 (6)	C20—C21—C22	114 (3)
C15—Hf2—C17	52.4 (8)	C20—C21—Hf2	74.6 (12)
C20—Hf2—C17	169.8 (8)	C22—C21—Hf2	78.0 (11)
C14—Hf2—C17	52.1 (7)	C20—C21—H21	123
C21—Hf2—C17	143.8 (9)	C22—C21—H21	123
C16—Hf2—C17	32.9 (8)	Hf2—C21—H21	115.7
C19—Hf2—C17	158.9 (8)	C21—C22—C23	108 (3)
C13—Hf2—C17	31.0 (7)	C21—C22—Hf2	72.9 (12)
C22—Hf2—C17	128.7 (9)	C23—C22—Hf2	74.5 (11)
O1—Hf2—C23	105.7 (8)	C21—C22—H22	125.9
O2—Hf2—C23	130.6 (7)	C23—C22—H22	125.9
C15—Hf2—C23	83.0 (8)	Hf2—C22—H22	118.6
C20—Hf2—C23	52.4 (8)	C22—C23—C24	134 (3)
C14—Hf2—C23	82.2 (8)	C22—C23—C19	102 (2)
C21—Hf2—C23	50.9 (8)	C24—C23—C19	124 (3)
C16—Hf2—C23	111.0 (9)	C22—C23—Hf2	73.3 (11)
C19—Hf2—C23	34.7 (8)	C24—C23—Hf2	119.6 (8)
C13—Hf2—C23	111.5 (8)	C19—C23—Hf2	71.3 (10)
C22—Hf2—C23	32.1 (8)	C23—C24—H24A	109.5
C17—Hf2—C23	132.9 (8)	C23—C24—H24B	109.5

supplementary materials

O2—Hf3—C26	106.2 (7)	H24A—C24—H24B	109.5
O2—Hf3—Cl2A	88.4 (10)	C23—C24—H24C	109.5
C26—Hf3—Cl2A	129.8 (8)	H24A—C24—H24C	109.5
O2—Hf3—C32	94.1 (7)	H24B—C24—H24C	109.5
C26—Hf3—C32	87.4 (8)	C26—C25—C29	107 (2)
Cl2A—Hf3—C32	140.3 (12)	C26—C25—Hf3	71.2 (12)
O2—Hf3—Cl2	103.5 (10)	C29—C25—Hf3	77.8 (12)
C26—Hf3—Cl2	131.5 (6)	C26—C25—H25	126.3
Cl2A—Hf3—Cl2	18.0 (4)	C29—C25—H25	126.3
C32—Hf3—Cl2	127.7 (9)	Hf3—C25—H25	116.8
O2—Hf3—C34	101.3 (7)	C25—C26—C27	111 (2)
C26—Hf3—C34	133.3 (8)	C25—C26—Hf3	77.6 (14)
Cl2A—Hf3—C34	87.3 (13)	C27—C26—Hf3	75.4 (13)
C32—Hf3—C34	53.3 (9)	C25—C26—H26	124.5
Cl2—Hf3—C34	74.9 (9)	C27—C26—H26	124.5
O2—Hf3—C27	80.9 (7)	Hf3—C26—H26	114.4
C26—Hf3—C27	34.3 (7)	C28—C27—C26	105 (2)
Cl2A—Hf3—C27	107.3 (12)	C28—C27—Hf3	76.3 (14)
C32—Hf3—C27	112.3 (9)	C26—C27—Hf3	70.3 (13)
Cl2—Hf3—C27	118.9 (8)	C28—C27—H27	127.7
C34—Hf3—C27	165.4 (9)	C26—C27—H27	127.7
O2—Hf3—C25	135.0 (7)	Hf3—C27—H27	118
C26—Hf3—C25	31.3 (7)	C27—C28—C29	110 (2)
Cl2A—Hf3—C25	109.7 (7)	C27—C28—Hf3	71.8 (13)
C32—Hf3—C25	96.2 (8)	C29—C28—Hf3	76.6 (13)
Cl2—Hf3—C25	104.2 (8)	C27—C28—H28	125.2
C34—Hf3—C25	119.8 (8)	C29—C28—H28	125.2
C27—Hf3—C25	54.7 (8)	Hf3—C28—H28	118.2
O2—Hf3—C33	80.7 (6)	C28—C29—C25	107 (2)
C26—Hf3—C33	119.3 (8)	C28—C29—C30	123 (2)
Cl2A—Hf3—C33	110.2 (10)	C25—C29—C30	130 (2)
C32—Hf3—C33	32.4 (8)	C28—C29—Hf3	72.0 (11)
Cl2—Hf3—C33	102.6 (8)	C25—C29—Hf3	69.7 (11)
C34—Hf3—C33	31.4 (8)	C30—C29—Hf3	124.5 (15)
C27—Hf3—C33	137.4 (8)	C29—C30—H30A	109.5
C25—Hf3—C33	125.9 (8)	C29—C30—H30B	109.5
O2—Hf3—C35	132.4 (7)	H30A—C30—H30B	109.5
C26—Hf3—C35	105.7 (8)	C29—C30—H30C	109.5
Cl2A—Hf3—C35	97.3 (14)	H30A—C30—H30C	109.5
C32—Hf3—C35	53.3 (9)	H30B—C30—H30C	109.5
Cl2—Hf3—C35	79.9 (11)	C32—C31—C35	108 (2)
C34—Hf3—C35	32.7 (7)	C32—C31—Hf3	70.4 (14)
C27—Hf3—C35	139.5 (8)	C35—C31—Hf3	73.2 (14)
C25—Hf3—C35	87.2 (8)	C32—C31—H31	126
C33—Hf3—C35	53.0 (8)	C35—C31—H31	126
O2—Hf3—C31	125.1 (7)	Hf3—C31—H31	122
C26—Hf3—C31	80.1 (8)	C31—C32—C33	110 (3)
Cl2A—Hf3—C31	129.7 (14)	C31—C32—Hf3	78.6 (16)
C32—Hf3—C31	31.0 (7)	C33—C32—Hf3	76.8 (16)

Cl2—Hf3—C31	111.9 (11)	C31—C32—H32	125.1
C34—Hf3—C31	53.2 (9)	C33—C32—H32	125.1
C27—Hf3—C31	113.7 (8)	Hf3—C32—H32	111.8
C25—Hf3—C31	74.3 (8)	C34—C33—C32	108 (2)
C33—Hf3—C31	52.2 (8)	C34—C33—Hf3	73.6 (14)
C35—Hf3—C31	32.6 (8)	C32—C33—Hf3	70.9 (14)
O2—Hf3—C28	93.2 (6)	C34—C33—H33	126
C26—Hf3—C28	53.6 (8)	C32—C33—H33	126
Cl2A—Hf3—C28	78.4 (10)	Hf3—C33—H33	121.2
C32—Hf3—C28	140.8 (9)	C33—C34—C35	108 (3)
Cl2—Hf3—C28	87.5 (7)	C33—C34—Hf3	74.9 (14)
C34—Hf3—C28	159.4 (8)	C35—C34—Hf3	74.7 (14)
C27—Hf3—C28	31.9 (8)	C33—C34—H34	125.9
C25—Hf3—C28	53.7 (8)	C35—C34—H34	125.9
C33—Hf3—C28	169.1 (8)	Hf3—C34—H34	116.5
C35—Hf3—C28	134.3 (8)	C34—C35—C31	106 (2)
C31—Hf3—C28	127.8 (8)	C34—C35—C36	128 (3)
Hf1—O1—Hf2	173.3 (7)	C31—C35—C36	126 (2)
Hf3—O2—Hf2	178.7 (8)	C34—C35—Hf3	72.6 (13)
C5—C1—C2	110.2 (19)	C31—C35—Hf3	74.2 (13)
C5—C1—Hf1	75.3 (12)	C36—C35—Hf3	123.1 (17)
C2—C1—Hf1	72.8 (11)	C35—C36—H36A	109.5
C5—C1—H1	124.9	C35—C36—H36B	109.5
C2—C1—H1	124.9	H36A—C36—H36B	109.5
Hf1—C1—H1	118.7	C35—C36—H36C	109.5
C3—C2—C1	108 (2)	H36A—C36—H36C	109.5
C3—C2—Hf1	75.8 (11)	H36B—C36—H36C	109.5

Fig. 1

