

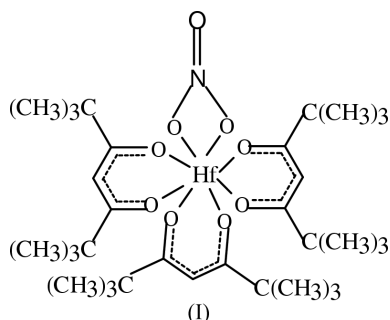
Nitratotrakis(2,2,6,6-tetramethyl-3,5-heptadionato)hafnium(IV)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.012 \text{ \AA}$
Disorder in main residue
R factor = 0.061
wR factor = 0.137
Data-to-parameter ratio = 18.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.The title compound, $[\text{Hf}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3(\text{NO}_3)]$, is a mixed-ligand MOCVD precursor. Hf has distorted square antiprismatic coordination. Of the six *tert*-butyl groups present, four are found to be disordered.Received 11 November 2002
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Comment

The structure of the title compound, (I), a mixed-ligand MOCVD precursor, has been analysed. The hafnium coordination polyhedron is a distorted square antiprism, with each ligand spanning the opposite edges of the two square faces of the antiprism. The nitrate ligand has a very small bite [2.110 (7) Å] and hence this square face is highly distorted, but it is more planar than the other square face of the antiprism. The angle between the mean planes fitted to the two square faces is 1.3 (1)° (Nardelli, 1995), close to the ideal value of zero. The bite distances for the three acetylacetonate ligands are 2.608 (7), 2.638 (6) and 2.611 (6) Å. In a zirconium complex with similar ligands, the coordination polyhedron was found to be a distorted dodecahedron, with the distortion arising due to the small bite of the nitrate ligand (Muller *et al.*, 1976).

The tertiary butyl groups have high displacement parameters, and four of these groups have positional disorder, with each of the three methyl C atoms having two positions with partial occupancies for each group. This makes these groups very labile, a favourable feature for chemical vapour deposition.

Experimental

The title complex was synthesized by dissolving 2,2,6,6-tetramethyl-3,5-heptadione (15 mmol, 2.76 g) and potassium hydroxide (15 mmol, 1.68 g) in 25 ml of 30% ethanol. This was followed by the addition of hafnium nitrate (5 mmol, 2.13 g), dissolved in 20 ml of distilled water. The mixture was stirred at room temperature for 3 h and the resulting yellow precipitate was filtered, dried and recrystallized from *n*-hexane.

Crystal data

$[\text{Hf}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3(\text{NO}_3)]$
 $M_r = 790.29$
 Triclinic, $P\bar{1}$
 $a = 10.156$ (9) Å
 $b = 10.590$ (9) Å
 $c = 19.277$ (17) Å
 $\alpha = 79.683$ (16)°
 $\beta = 75.336$ (16)°
 $\gamma = 83.579$ (16)°
 $V = 1969$ (3) Å³

$Z = 2$
 $D_x = 1.333$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 21660
 reflections
 $\theta = 1.1$ – 27.6 °
 $\mu = 2.70$ mm⁻¹
 $T = 293$ (2) K
 Prism, pale yellow
 $0.52 \times 0.36 \times 0.23$ mm

Data collection

Bruker SMART CCD area-detector
 diffractometer
 ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.438$, $T_{\max} = 0.538$
 21660 measured reflections

8429 independent reflections
 4904 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.092$
 $\theta_{\text{max}} = 27.6$ °
 $h = -13 \rightarrow 13$
 $k = -13 \rightarrow 13$
 $l = -24 \rightarrow 25$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.061$
 $wR(F^2) = 0.137$
 $S = 0.92$
 8429 reflections
 463 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0539P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.013$
 $\Delta\rho_{\text{max}} = 0.82$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.51$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Hf1—O3	2.098 (5)	Hf1—O4	2.147 (5)
Hf1—O6	2.132 (5)	Hf1—O2	2.165 (5)
Hf1—O1	2.134 (5)	Hf1—O8	2.297 (5)
Hf1—O5	2.136 (5)	Hf1—O7	2.337 (5)
O6—Hf1—O5	75.42 (18)	O1—Hf1—O2	74.68 (19)
O3—Hf1—O4	76.85 (19)	O8—Hf1—O7	54.15 (19)

The four tertiary butyl groups are disordered, with two distinct positions with partial occupancies for methyl C atoms in each group. The occupancies for the four disordered groups are 0.55:0.45(5), 0.595:0.405(12), 0.557:0.443(16), and 0.569:0.431(18), respectively. These disordered atoms were refined with anisotropic displacement parameters. Positional parameters of all the H atoms were calculated geometrically and were allowed to ride on the C atoms to which they are bonded, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 1998); cell refinement: SAINT (Bruker, 1998; data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine

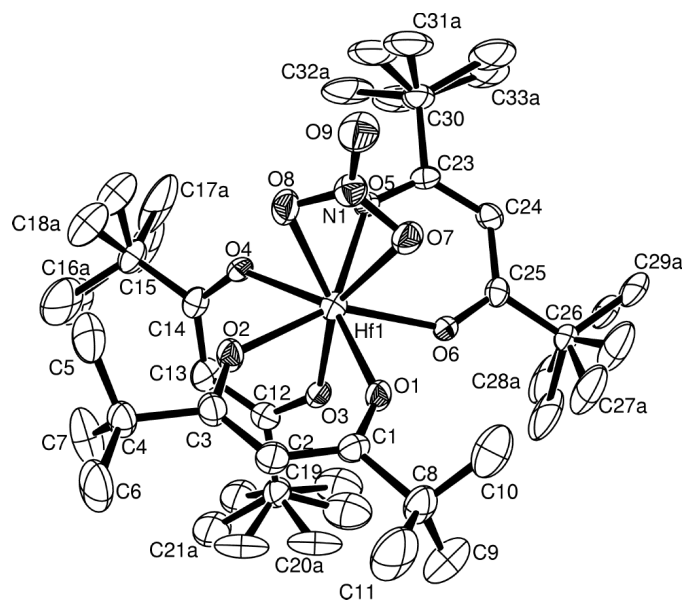


Figure 1

View of the title compound with the disordered *tert*-butyl groups. Displacement ellipsoids are drawn at the 30% probability level. H atoms are omitted for clarity, and disordered C atoms labelled with the suffix 'a' have higher occupancy.

structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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