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Tetrakis(*tert*-butyl 3-oxobutanoato)zirconium(IV)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.047
wR factor = 0.102
Data-to-parameter ratio = 19.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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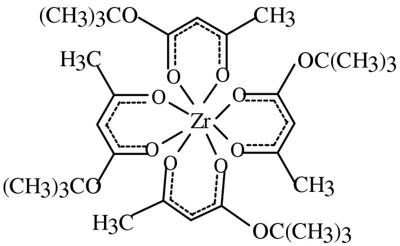
The structure of the title compound, $[Zr(C_8H_{13}O_3)_4]$, an MOCVD precursor, has been determined. The zirconium coordination geometry is dodecahedral and the chelate rings are significantly non-planar. The Zr atom lies on a $\overline{4}$ axis, so the asymmetric unit contains only one ligand.

Comment

The structure of the title zirconium complex, (I), an MOCVD precursor, has been determined. The molecular fourfold inversion symmetry ($\overline{4}$) is retained in the crystal structure, with the Zr atom occupying a special position. The coordination geometry is dodecahedral (Hoard & Silverton, 1963) and not a square antiprism, as in tetrakis(acetylacetonato)-zirconium(IV) (Clegg, 1987; Silverton & Hoard, 1963). The ligand has *tert*-butoxy as a substituent on one side and methyl on the other, as in the Fe complex, also an MOCVD precursor, reported by us previously (Urs *et al.*, 2000). The ligand bite O···O distance is 2.703 (2) Å. The six-membered chelate ring is significantly non-planar, the angle between the Zr1/O1/O2 and C1/C2/C3 planes being 3.8 (2)° (Nardelli, 1995). The packing is essentially by van der Waals interactions. There are two intramolecular short contacts of the C—H···O type involving the *tert*-butyl atoms C6 and C7, and the chelate ring atom O2, with C···O distances of 2.999 (3) and 2.906 (4) Å, and angles at H of 114.2 (2) and 116.6 (2)°, respectively.



(I)

Experimental

The title compound was synthesized by refluxing zirconium *n*-propoxide with *tert*-butyl 3-oxobutanoate in dry benzene, under flowing dry nitrogen. 10 mmol (2.31 g) of zirconium *n*-propoxide was placed in a three-necked round-bottomed flask connected to the dry nitrogen gas line. 40 mmol (6.12 g) of *tert*-butyl 3-oxobutanoate was added, using a pressure equalizer fitted to one of the necks. A reflux condenser fitted with calcium chloride guard tube was fitted to the third neck, to ensure that the system was moisture-free. The reaction mixture was refluxed for 3 h. The propanol-benzene mixture and the excess solvent were removed by distillation. The residue (4.42 g, 85%) was recrystallized from hot *n*-hexane.

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Crystal data

$[Zr(C_8H_{13}O_3)_4]$
$M_r = 719.96$
Tetragonal, $I4_1/a$
$a = 18.569$ (4) Å
$c = 10.818$ (3) Å
$V = 3730.2$ (16) Å^3
$Z = 4$
$D_x = 1.282$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 19 762 reflections
$\theta = 2.2$–27.5°
$\mu = 0.35$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.19 × 0.13 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.84$, $T_{max} = 0.98$
19 762 measured reflections

2111 independent reflections
1491 reflections with $I > 2\sigma(I)$
$R_{int} = 0.122$
$\theta_{max} = 27.5°$
$h = -23 \rightarrow 24$
$k = -23 \rightarrow 22$
$l = -14 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.102$
$S = 1.00$
2111 reflections
106 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Zr1—O1	2.1008 (16)	C2—C1	1.417 (3)
Zr1—O2	2.2786 (16)	O1—C3	1.283 (3)
C2—C3	1.357 (3)	O2—C1	1.234 (3)
O1^i—Zr1—O2	71.36 (6)	O1—C3—C2	124.8 (2)
C3—C2—C1	122.3 (2)	O1—C3—C4	115.2 (2)
C3—O1—Zr1	138.39 (15)	C2—C3—C4	120.0 (2)
O2—Zr1—O1—C3	−1.4 (2)	O1—Zr1—O2—C1	7.6 (2)
Zr1—O1—C3—C2	−2.6 (4)	Zr1—O2—C1—C2	−9.9 (3)
C1—C2—C3—O1	2.7 (4)	C3—C2—C1—O2	3.6 (4)

Symmetry codes: (i) $\frac{3}{4} - y, x - \frac{1}{4}, \frac{7}{4} - z$.

H atoms were positioned geometrically and allowed to ride on their respective parent atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997) and *CAMERON* (Watkin *et al.*, 1993); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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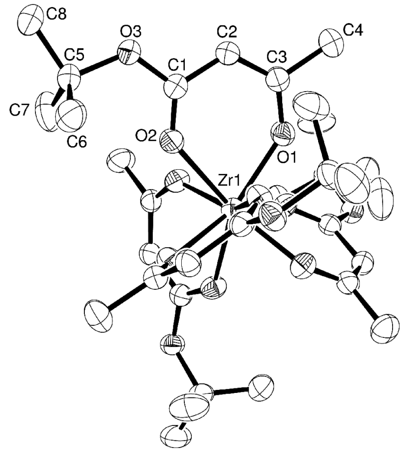

Figure 1
The molecular structure of the title compound, with displacement ellipsoids drawn at the 30% probability level. H atoms have been omitted for clarity and only the atoms of the asymmetric unit are labelled.

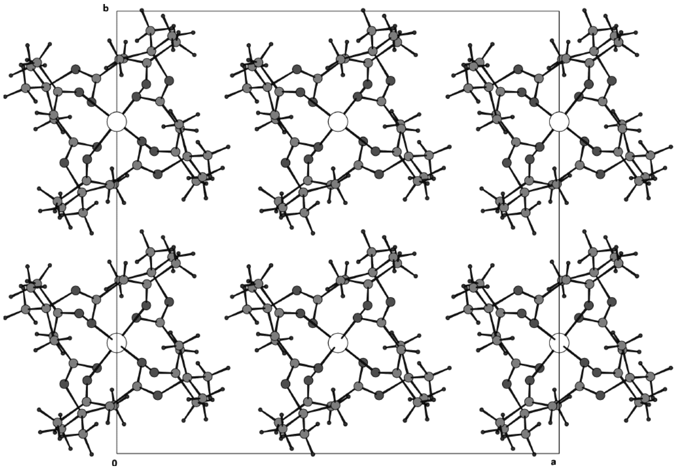

Figure 2
Packing of the molecules, viewed down the *c* axis.

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