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Methylzinc *tert*-butoxide tetrahydrofuran solvate

Andrew D. Bond,* David J. Linton and Andrew E. H. Wheatley

Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, England

Correspondence e-mail: adb29@cam.ac.uk

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Key indicators

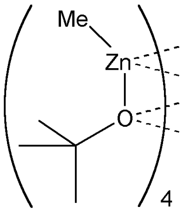
Single-crystal X-ray study
T = 230 K
Mean σ(C–C) = 0.005 Å
Disorder in solvent or counterion
R factor = 0.039
wR factor = 0.110
Data-to-parameter ratio = 22.1

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

The crystal structure of tetra-μ_3-*tert*-butoxo-tetrakis(methylzinc) tetrahydrofuran (THF) solvate, $[Zn_4(CH_3)_4(C_4H_9O)_4]\cdot C_4H_8O$, has been determined at 230 (1) K. The structure is based on a $(^t\text{BuOZnMe})_4$ pseudo-cube and contains one lattice molecule of tetrahydrofuran per $(^t\text{BuOZnMe})_4$ unit. Comparison with a previously reported unsolvated structure of methylzinc *tert*-butoxide suggests that this also contains lattice THF.

Comment

Lithiated derivatives of zinc compounds have been shown to exhibit unique and useful properties in organic synthesis (*e.g.* Harada *et al.*, 1992; Kondo *et al.*, 1996; Uchiyama *et al.*, 1998). Intermediate species in processes of this type are often highly oxophilic; this observation has led to recent investigations into the methods and selectivities with which they scavenge oxygen from the environment (Wheatley *et al.*, 2001). Accordingly, treatment with molecular oxygen of the presumed lithium zincate product resulting from sequential treatment of *N*-methylbenzamide with $ZnMe_2$ and ^{t}BuLi affords colourless blocks of the title compound, (I)·THF, as the sole crystalline product.



(I)

Complex (I)·THF crystallizes in the high-symmetry tetragonal space group $I4_1/acd$. The solid-state structure reveals tetrameric molecules of methylzinc *tert*-butoxide (Fig. 1). Such pseudo-cubic tetramers are a common structure type in alkoxide structural chemistry, not only of Group 12 elements (Boersma, 1982; Nöth & Thomann, 1995), but also of many main group elements (Lindsell, 1982; Rothfuss *et al.*, 1993; Wright & Beswick, 1995) and transition metals (Geerts *et al.*, 1983; McNeese *et al.*, 1984; Darensbourg *et al.*, 1998). In (I)·THF, the tetrameric aggregates form an approximate face-centred-cubic lattice, with the octahedral sites occupied by positionally disordered THF molecules (Fig. 2).

A previous crystallographic study of methylzinc *tert*-butoxide has been reported (Herrmann *et al.*, 1992) in which the unit-cell parameters are comparable with those reported here: $I4_1/acd$, $a = b = 14.935$ (1) Å, $c = 30.220$ (2) Å at T =

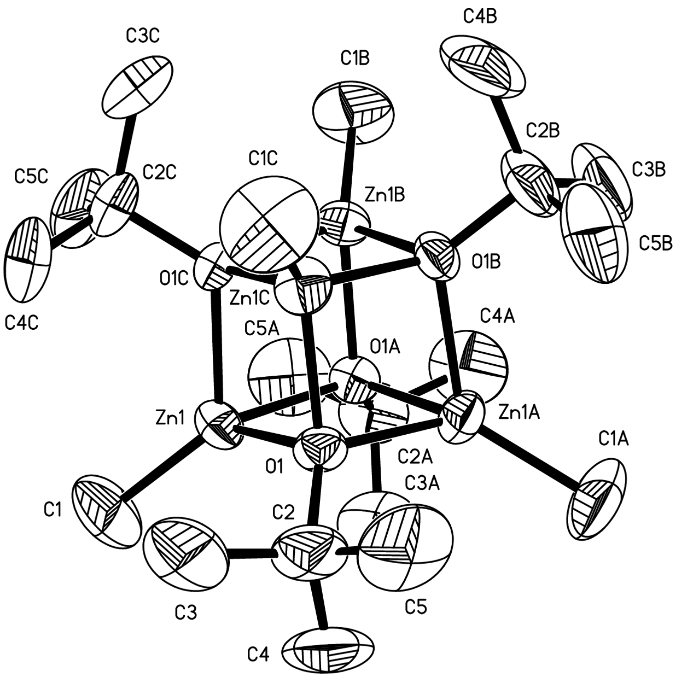


Figure 1
Pseudo-cubic molecular unit in (I)·THF showing displacement ellipsoids at the 50% probability level. H atoms have been omitted for clarity (*XP*; Sheldrick, 1993).

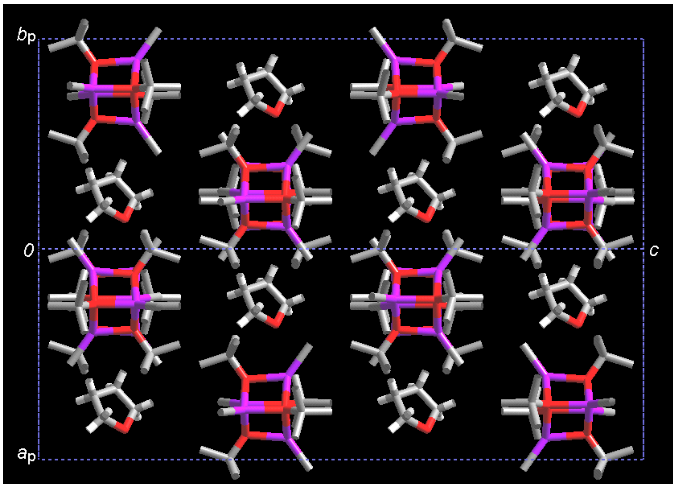


Figure 2
Projection onto (110) showing the approximate face-centred-cubic arrangement of (^{t}BuOZnMe)$_4$ units (H atoms omitted) with THF molecules in all octahedral sites. For clarity, only one orientation of the THF molecules is shown (*Cerius*^{2}; Molecular Simulations Inc., 1999).

295 (1) K; the observed unit-cell expansion relative to the present study can be attributed to the difference in temperature between the two investigations. This structure was refined to give an apparently acceptable *R* factor (*R*1 = 0.077), with residual electron density reported as 0.49 and −0.27 e Å^{-3}. Inspection of the structure, however, reveals that the tetramers form an approximate face-centred-cubic lattice identical to that reported here, but with the octahedral sites left vacant. Inclusion at these sites of the disordered solvent molecules affords an *R*1 value of 0.039 for our refinement [for reflections with $I > 4\sigma(I)$, directly comparable with that reported by Herrmann *et al.* (1992)], and a goodness-of-fit value (*S*) of 1.076, compared with 3.157 for the previously reported refinement. Omission of the THF molecules in our structure increases *R*1 by only a very small amount to 0.053 [$I > 4\sigma(I)$], but the solvent molecules are readily apparent in a difference Fourier map (maximum residual electron density 1.05 e Å^{-3}). Given that the work of Herrmann *et al.* (1992) employed dimethylzinc in THF as a metallating agent, it is highly likely that the previously reported structure also incorporates lattice THF molecules but that these could not be resolved in the original study. It is probable that the decreased temperature of our study facilitates their location and subsequent refinement.

Experimental

A solution of *N*-methylbenzamide (0.14 g, 1 mmol) in toluene (1 ml) was treated with ZnMe$_2$ (0.5 ml, 1 mmol, 2 *M* in toluene) at ambient temperature. The mixture was stirred for 10 min whereupon it was cooled to 195 K and ^{t}BuLi (0.6 ml, 1 mmol, 1.7 *M* in pentane) was added. The resultant suspension was allowed to warm to room temperature before being treated with excess dry O$_2$. Dissolution was effected by the addition of THF (1.25 ml). Filtration, reduction to half-volume and storage at 243 K for 2 d gave (I)·THF.

Crystal data

$[Zn_4(CH_3)_4(C_4H_9O)_4]\cdot C_4H_8O$
$M_r = 686.17$
Tetragonal, $I4_1/acd$
$a = 14.8323$ (7) Å
$c = 30.0976$ (10) Å
$V = 6621.4$ (5) Å^3
$Z = 8$
$D_x = 1.377$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 6316 reflections
$\theta = 1.0$–27.5°
$\mu = 2.89$ mm^{-1}
$T = 230$ (2) K
Block, colourless
0.23 × 0.23 × 0.23 mm

Data collection

Nonius KappaCCD diffractometer
Thin-slice ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.425$, $T_{max} = 0.515$
10 143 measured reflections
1876 independent reflections
1421 reflections with $I > 2\sigma(I)$
$R_{int} = 0.055$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 19$
$k = -19 \rightarrow 19$
$l = -38 \rightarrow 39$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.110$
$S = 1.08$
1876 reflections
85 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0531P)^2 + 5.7820P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.016$
$\Delta\rho_{max} = 0.40$ e Å^{-3}
$\Delta\rho_{min} = -0.53$ e Å^{-3}

All H atoms were placed geometrically and allowed to ride during subsequent refinement with an isotropic displacement parameter fixed at 1.5 times U_{iso} for the C atom to which the H atom was attached. The solvent molecule is disordered extensively around the special position at $(0,\frac{3}{4},\frac{7}{8})$ (point symmetry 222). The C—C and C—O bond distances in the THF solvent molecule were restrained to a common value with an s.u. of 0.02 Å and 1,3-distances were also restrained to ensure a reasonable molecular geometry. The C and O atoms in this solvent molecule were refined with a single common isotropic displacement parameter.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL*

Acta Cryst. (2001). E**57**, m298–m300 Andrew D. Bond *et al.* • $[Zn_4(CH_3)_4(C_4H_9O)_4]\cdot C_4H_8O$ **m299**

DENZO (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

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m300 Andrew D. Bond *et al.* • $[Zn_4(CH_3)_4(C_4H_9O)_4]\cdot C_4H_8O$ *Acta Cryst.* (2001). E**57**, m298–m300