A centrosymmetric μ_2-alkoxo-bridged zirconium tetrameric complex: [Zr$_2$(μ_2-O,μ_2-O′-methyliminodiethanolate)-(μ_2-O-n-propanolate)$_2$(n-propanolate)$_4$]$_2$

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Key indicators

Single-crystal X-ray study
$T = 170$ K
Mean σ(C–C) = 0.014 Å
Disorder in main residue
R factor = 0.057
wR factor = 0.181
Data-to-parameter ratio = 21.0

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

The centrosymmetric tetrameric title compound, bis(methyl-iminodiethanolato-$\kappa^5 O$:O,N,O′:O′)tetra-μ-n-propanolato-$\kappa^8 O$:O-octa-n-propanolato-κO-tetrazirconium, [Zr$_4$(C$_5$H$_{11}$N-O$_2$)$_2$(C$_3$H$_7$O)$_{12}$], contains eight μ_2-O-atom Zr—O—Zr bridges. Each methyliminodiethanolate ligand is bound to one of the two central Zr atoms with a Zr—N distance of 2.412 (5) Å in a meridional configuration(s), with the ethanolate O atoms bridging both the central Zr atoms. Four n-propanolate ligands provide O atoms to bridge other pairs of Zr atoms. The remaining propanolate ligands bind terminally to one metal atom each, to make up 7- and 6-coordination for the the central and outer Zr atoms, respectively. The distorted ZrO$_6$ octahedra each share a face with one of the central ZrO$_6$N pentagonal bipyramids; these edge-share with each other across the centre of symmetry.

Comment

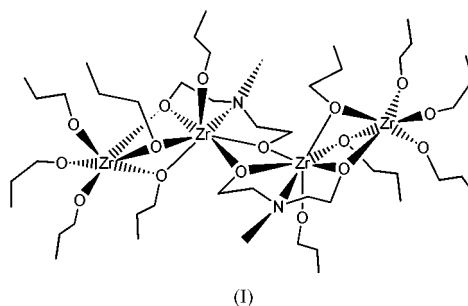The title compound, (I), was prepared as part of a study of possible precursor compounds for zirconia and lead zirconate titanate (PZT) thin film materials. The analysis was required as the chemical structure was not unambiguously determined by other techniques, specifically elemental analysis (Kemmitt *et al.*, 2002*a*).

(I)

The crystal structure consists of centrosymmetric [Zr$_2$-(MDEA)(n-propanolate)$_6$]$_2$ molecules (MDEA is methyl-iminodiethanolate) (Fig. 1) with no significant intermolecular contacts. For clarity, Fig. 1 shows only the major conformation rings. The terminal zirconium is in a typical distorted octahedral coordination environment (Fleeting *et al.*, 1999). The central Zr atoms are seven-coordinate, having a distorted pentagonal–bipyramidal geometry, with axial atoms O4 (bridging n-propanolate) and O6 (terminal n-propanolate) subtending an angle of 164.83 (16)° at Zr2; they each share a face with a terminal octahedron and an edge with the centrosymmetrically related ZrO$_6$N unit.

Dimeric zirconium complexes with three μ_2-O bridges are well known (Fleeting *et al.*, 1999; Evans *et al.*, 1999). Other zirconium configurations containing such bridges do exist;
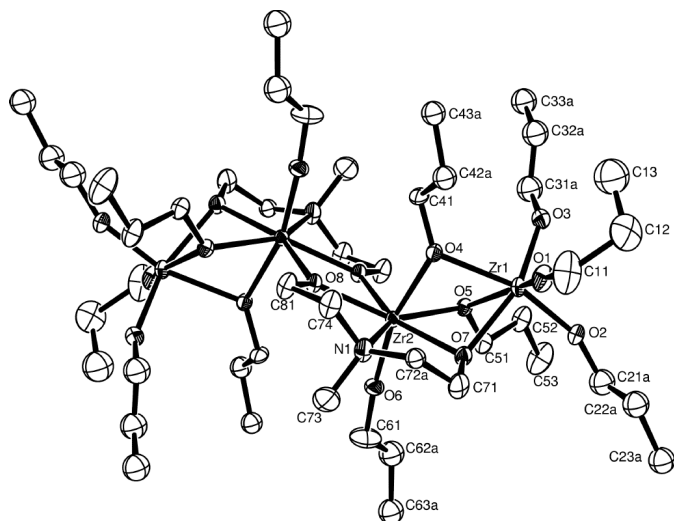
Figure 1
The molecular structure of (I) (Farrugia, 1997). Displacement ellipsoids are drawn at the 30% probability level. H atoms and minor disorder components have been excluded for clarity (see text).

examples are the triangular Zr_3 compound reported by Evans *et al.* (1998) and the zigzag di-*tert*-butyl-catecholate tetrameric complex reported by Chi *et al.* (2000). The Zr⋯Zr distance of 3.2538 (10) Å in (I) compares with 3.2936 (6) Å in the similar triply O-bridged zirconium compound [Zr_2(isopropanolate)$_6$(1-dimethylaminopropan-2-olate)$_2$] (Fleeting *et al.*, 1999); shorter distances, such as 3.215 Å (Evans *et al.*, 1999), have extended the ranges previously noted (3.31–3.50 Å) by Boyle *et al.* (1995).

Oxo-bridged Zr⋯Zr distances (Cambridge Crystallographic Data Centre, 2002; Allen & Kennard, 1993) vary considerably, from 3.06 Å in two bridging tetraphenylporphyrinate complexes (Huhmann *et al.*, 1996) to 3.98 Å in a hexazirconium compound (Kickelbick & Schubert, 1999). The longer Zr2⋯Zr2′ distance in the title compound, of 3.6729 (13) Å, is close to the value of 3.62 Å found in bis(μ_3-O-propoxo)tetrakis(μ_4-O-propoxo)decakis(propoxy)-tetrazirconium (Day *et al.*, 2001). The metal atoms form a zigzag, with Zr2′⋯Zr2⋯Zr1 = 130.87 (3)°, compared with the similar Ti,Zr compound with Ti1⋯Zr1⋯Zr1′ = 132.80 (6)° (Kemmitt *et al.*, 2002*b*, hereafter TIZR), and with 154/151.6° in the doubly oxo-bridged titanium and zirconium pinacolate complexes reported by Zechmann *et al.* (1998), hereafter JARSUQ & JARWEE. The Zr—O length of the pinacolate O atom bound to zirconium in JARWEE [1.936 (4) Å] is similar to those found in (I) for the *n*-propanolate ligands [1.929 (4)–1.965 (5) Å, mean 1.95 Å].

The MDEA ligand is in a meridional configuration, with Zr—N = 2.412 (5) Å, identical to the distance found in the related TIZR [2.415 (5) Å], both being shorter than the facial configuration MDEA length of 2.443 (3) Å (Kemmitt *et al.*, 2002*c*, hereafter KEMM). The Zr—O distances involving the MDEA ligand are similar to those found recently, with distances to the μ-O atom of 2.182 (2) and 2.222 (2) Å (KEMM) compared with the mean of 2.20 Å here. The *n*-

propanolate Zr—μ-O bond lengths range from 2.144 (4) to 2.255 (4) Å.

The O atoms bound to Zr1 (O3, O5, O7 O1) are coplanar, with an average deviation of 0.002 (4) Å, the Zr atom being 0.247 (2) Å from the plane. This plane makes an angle of 69.32 (9)° with the mean plane through atoms O8, O8′, N1, O5 and O7 [average out-of-plane deviation 0.110 (3) Å], with Zr2 0.212 (2) Å out of this plane.

Experimental

The title compound was prepared by reacting zirconium tetrapropoxide with methyliminodiethanolamine in a 2:1 molar ratio in dry benzene at 323 K. The solvent was evaporated, to obtain a white solid, which was then recrystallized from benzene.

Crystal data

[$Zr_4(C_5H_{11}NO_2)_2(C_3H_7O)_{12}$]	Mo $K\alpha$ radiation
$M_r = 1308.2$	Cell parameters from 8192
Orthorhombic, *Pbca*	reflections
$a = 18.271$ (6) Å	$\theta = 2.5$–24.8°
$b = 16.941$ (5) Å	$\mu = 0.71$ mm^{-1}
$c = 20.221$ (6) Å	$T = 170$ (2) K
$V = 6259$ (3) Å^3	Block, colourless
$Z = 4$	$0.70 \times 0.40 \times 0.20$ mm
$D_x = 1.388$ Mg m^{-3}	

Data collection

Siemens SMART CCD area-detector diffractometer	6435 independent reflections
φ and ω scans	4298 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (Blessing, 1995)	$R_{int} = 0.095$
	$\theta_{max} = 26.5°$
$T_{min} = 0.555$, $T_{max} = 0.868$	$h = -22 \rightarrow 22$
75801 measured reflections	$k = -21 \rightarrow 18$
	$l = -25 \rightarrow 25$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0932P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.057$	$+ 16.9738P]$
$wR(F^2) = 0.181$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.02$	$(\Delta/\sigma)_{max} = 0.001$
6435 reflections	$\Delta\rho_{max} = 1.14$ e Å^{-3}
306 parameters	$\Delta\rho_{min} = -1.05$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Zr1—O1	1.944 (4)	Zr2—O4	2.143 (4)
Zr1—O2	1.962 (4)	Zr2—O5	2.158 (4)
Zr1—O3	1.965 (5)	Zr2—O8	2.183 (3)
Zr1—O7	2.202 (4)	Zr2—O8^i	2.199 (3)
Zr1—O5	2.253 (4)	Zr2—O7	2.202 (4)
Zr1—O4	2.256 (4)	Zr2—N1	2.412 (5)
Zr2—O6	1.929 (4)	N1—C73	1.465 (11)

O3—Zr1—O7	157.25 (16)	O6—Zr2—O4	164.83 (16)

Symmetry code: (i) $-x, 1 - y, 1 - z$.

H atoms, included in calculated positions (C—H methylene = 0.99 Å and tertiary = 0.99 Å) on *n*-propanolate C atoms (C11–C13, C41 and C51–C53) and MDEA C atoms (C81, C71, C72*a*, C72*b* and C74) were constrained to the same occupancy and to U_{iso} values of 1.2U_{eq} of the parent atom. There was conformational disorder in the methyliminodiethanolate (MDEA), in one of the bridging *n*-propanolate ligands (O4) and in all three terminal *n*-propanolate ligands, mostly modelled using atoms in the two alternative conformations (*a*/*b*), with a common refined isotropic displacement para-

meter (see refine_special_details in CIF). Only the H atoms on C41, of the 28 H atoms on the four disordered propanolate groups, could be included in the refinement.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996) and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 in *WinGX* (Farrugia, 1997, 1999); software used to prepare material for publication: *SHELXL*97.

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