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Key indicators

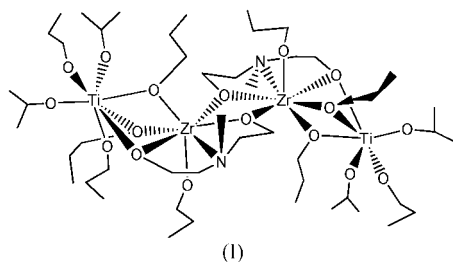
Single-crystal X-ray study
 $T = 170\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.011\text{ \AA}$
H-atom completeness 61%
Disorder in main residue
 R factor = 0.068
 wR factor = 0.215
Data-to-parameter ratio = 21.3For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.A centrosymmetric triply alkoxo-bridged titanium- μ_2 -
O-zirconium tetranuclear complex: $[\text{TiZr}(\mu_2\text{-O}, \mu_2\text{-O}'\text{-}$
methyliminodiethanolate) $(\mu_2\text{-O-}n\text{-propanolate})_2\text{-}$
 $(n\text{-propanolate})_{2.7}(\text{isopropanolate})_{1.3}]_2$

The centrosymmetric tetranuclear title compound, bis(methyliminodiethanolato)dodecapropanolatodititaniumdizirconium, $[\text{Ti}_2\text{Zr}_2(\text{C}_3\text{H}_7\text{O})_{12}(\text{C}_5\text{H}_{11}\text{NO}_2)_2]$, has a zigzag TiZr_2Ti arrangement including novel triple-oxo $\text{Ti}\cdots\text{Zr}$ bridges. The methyliminodiethanolate ligand is bound to the zirconium in a meridional configuration, with the ethanolate O atoms bridging both the $\text{Ti}\cdots\text{Zr}$ and $\text{Zr}\cdots\text{Zr}$ centres. Two n -propanolate O atoms provide the other two $\text{Ti}\cdots\text{Zr}$ bridges. The remaining propanolate ligands are attached to either Zr or Ti, completing seven- and six-coordination, respectively. The distorted pentagonal bipyramidal $[\text{ZrO}_5\text{N}_2]$ units edge-share with each other and face-share with the distorted octahedral $[\text{TiO}_6]$ units. As well as some conventional conformational disorder involving alternative carbon-chain conformations, there is some iso- and n -propanolate chemical disorder around the Ti atoms.

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Comment

The title compound, (I), was prepared as part of a study of possible precursor compounds for zirconium titanates. The analysis was required as the chemical structure was not unambiguously determined, particularly by elemental analyses (Kemmitt *et al.*, 2002). The crystal structure consists of independent centrosymmetric $[\text{TiZr}(\text{MDEA})(n\text{-propanolate})_{4.7}(\text{isopropanolate})_{1.3}]_2$ (MDEA is methyliminodiethanolate) molecules (Fig. 1) with only weak intermolecular contacts, *e.g.* $\text{C}33\text{A}\cdots\text{H}63\text{B}^i$ [symmetry code: (i) $x - 1, y + 1, z$], with $\text{C}\cdots\text{H} = 2.686\text{ \AA}$. Within the complex, there is one weak intramolecular contact $\text{C}71-\text{H}71\text{A}\cdots\text{O}1$, with $\text{C}\cdots\text{O} = 3.055(10)\text{ \AA}$ and $\text{C}-\text{H}\cdots\text{O} = 117^\circ$, which may prevent atom C71 from existing in alternative conformations as for atom C72. For clarity, Fig. 1 shows only the major conformation (*a*) rings. The titanium is in a typical distorted octahedral coordination environment; the octahedra share a common face with the distorted pentagonal $[\text{ZrO}_5\text{N}_2]$ bipyramids, which edge-share with each other.



The $\text{Ti}\cdots\text{Zr}$ distance of 3.165 \AA is much shorter than the distances of $3.413(12)$ and $3.4117(12)\text{ \AA}$ found in the otherwise similar doubly oxo-bridged titanium and zirconium

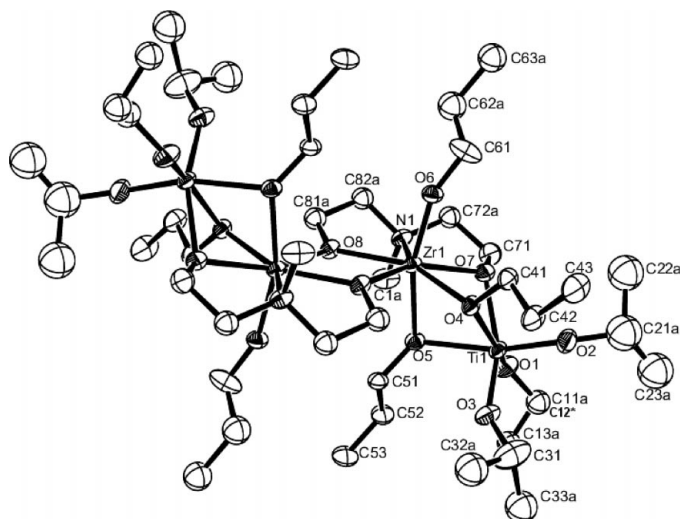


Figure 1

The molecular structure of (I) (Farrugia, 1997). Displacement ellipsoids are drawn at the 20% probability level. H atoms and minor chemical/conformational conformers (see text) have been excluded for clarity. Atom C12* is obscured behind C11a.

pinacolate complexes reported by Zechmann *et al.* (1998) (hereafter JARSUQ and JARWEE). There are no other triply oxo-bridged Ti···Zr compounds reported in the Cambridge Structural Database, and currently only eight compounds with Ti···Zr bridges (Cambridge Structural Database, 2002; Allen & Kennard, 1993). Moraru *et al.* (2001) report Ti and Zr butanolate/methacrylate mixed compounds, derived from zigzag chains of ZrO₈, ZrO₇ and TiO₆ polyhedra. The metals in these latter compounds are not in the near-linear relationship observed here, being related to the Ti₄O₄ motif (*F*) noted by Johnson *et al.* (2001). Only the chloro-bridged example (Chen & Cotton, 1996) has the zigzag structure, while the imido compound (Abarca *et al.*, 2000) displays another motif [Ti₄(μ₃-O)₄, *E*; Johnson *et al.*, 2001].

Triply oxo-bridged zirconium complexes are well known (Fleeting *et al.*, 1999). The metal atoms zigzag, with Ti1···Zr1···Zr1 = 132.8°, compared with a value of 154° in JARSUQ. The MDEA adopts a meridional configuration, with a Zr1—N1 distance of 2.419 (5) Å, similar to that found recently of 2.397 (3) Å, being shorter than the more conventional facial (twist) conformation length of 2.443 (3) Å (Gainsford *et al.*, 2002, hereafter KEMM). A comparable twist Zr—N distance of 2.427 Å is found in the complex [N,N-bis(2-(mesitylamido)ethyl)methylamine]zirconium (Schrock *et al.*, 2000). The Zr—O distances are similar to those found recently (KEMM), with distances to the μ-O atoms of 2.182 (2) and 2.222 (2) Å, compared with the mean of 2.206 (3) Å here. The Zr—O lengths of the bound isopropanolate ligands in JARSUQ are similar to those for the *n*-propanolate here, at 1.940 (4) Å. All the Ti—O bond lengths are similar to those found previously, with the typically longer bridging bonds [2.140 (4), 2.171 (4) and 2.174 (4) Å] comparable with previous mean values of 2.107 (Kemmitt *et al.*, 1999) and 2.103 Å (Sevast'yanov *et al.*, 2001).

The O atoms bound to the titanium (O3, O2, O5 and O7) are coplanar, with an average deviation of 0.023 (3) Å, Ti1 being 0.209 (3) Å from the plane. This plane makes an angle of 67.2 (1)° to the five-atom plane through atoms O8, O8', O4, N1 and O7 [average deviation out of plane is 0.020 (3) Å]; Zr1 is 0.190 (2) Å from this plane, with an O6—Zr1—O5 angle of 162.6 (2)°.

Experimental

The title compound was prepared by mixing titanium tetraisopropoxide, zirconium tetrapropoxide and *N*-methyldiethanolamine (MDEAH₂) in a 1:1:1 molar ratio in dry benzene. After evaporating the solvent, the resulting white solid was recrystallized from benzene to afford colourless crystals.

Crystal data

[Ti₂Zr₂(C₃H₇O)₁₂(C₅H₁₁NO₂)₂]
M_r = 1221.57
 Triclinic, *P*1̄
a = 10.573 (3) Å
b = 11.360 (4) Å
c = 13.731 (5) Å
 α = 87.593 (5)°
 β = 78.464 (4)°
 γ = 81.396 (4)°
V = 1597.7 (9) Å³

Z = 1
D_x = 1.270 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 5923 reflections
 θ = 2.8–25.3°
 μ = 0.61 mm⁻¹
T = 170 (2) K
 Rod, colourless
 0.62 × 0.20 × 0.13 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (Blessing, 1995)
*T*_{min} = 0.688, *T*_{max} = 0.923
 20 444 measured reflections

6398 independent reflections
 3540 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.066
 θ_{max} = 26.3°
h = -6 → 13
k = -14 → 14
l = -17 → 17

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.068
wR(*F*²) = 0.215
S = 1.02
 6398 reflections
 300 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.1187P)^2 + 0.4988P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.63 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.81 \text{ e \AA}^{-3}$

Table 1

Selected interatomic distances (Å).

Zr1—O6	1.940 (4)	Ti1—O2	1.837 (5)
Zr1—O5	2.124 (4)	Ti1—O3	1.839 (5)
Zr1—O4	2.174 (4)	Ti1—O1	1.851 (5)
Zr1—O7	2.201 (5)	Ti1—O7	2.140 (4)
Zr1—O8	2.203 (4)	Ti1—O4	2.171 (4)
Zr1—O8 ⁱ	2.209 (4)	Ti1—O5	2.174 (4)
Zr1—N1	2.418 (5)		

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

H atoms, where reasonable to include [on the MDEA and bridging *n*-propanolates (O4 and O5) and C atoms, C32A and C34B], were constrained to *U*_{iso} = 1.2 *U*_{eq} of their parent atom. The refinement included conformational disorder in the methyliminodiethanolate (MDEA) and in two *n*-propanolate ligands (O6 and O1). Chemical disorder (*iso*-*n*-propanolate) was also included in the final model for the two propanolate ligands bound to Ti1. The disordered atoms were refined with isotropic displacement parameters and without bound H atoms (see refine_special_details in CIF).

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996) and *SADABS* (Sheldrick, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* in *WinGX* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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References

- Abarca, A., Martin, A., Mena, M. & Yelamos, C. (2000). *Angew. Chem. Int. Ed.* **39**, 3460–3463.
- Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Cambridge Structural Database (2002). *ConQuest*. Version 1.3. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.
- Chen, L. F. & Cotton, F. A. (1996). *Inorg. Chem.* **35**, 7364–7369.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Fleeting, K. A., O'Brien, P., Jones, A. C., Otway, D. J., White, A. J. P. & Williams, D. J. (1999). *J. Chem. Soc. Dalton Trans.* pp. 2853–2859.
- Gainsford, G. J., Al-Salim, N. I. & Kemmitt, T. (2002). *Acta Cryst.* **C58**, m509–m510.
- Johnson, B. F. G., Klunduk, M. C., O'Connell, T. J., McIntosh, C. & Ridland, J. (2001). *J. Chem. Soc. Dalton Trans.* pp. 1553–1555.
- Kemmitt, T., Al-Salim, N. I. & Gainsford, G. J. (1999). *Eur. J. Inorg. Chem.* pp. 1847–1849.
- Kemmitt, T., Al-Salim, N. I. & Gainsford, G. J. (2002). *Aust. J. Chem.* In the press.
- Moraru, B., Kickelbick, G. & Schubert, U. (2001). *Eur. J. Inorg.* **5**, 1295–1301.
- Schrock, R. R., Casado, A. L., Goodman, J. T., Liang, L.-C., Bonitatebus, P. J. Jr & Davis, W. M. (2000). *Organometallics*, **19**, 5325–5341.
- Sevast'yanov, D. V., Sevast'yanov, V. G., Simonenko, E. P., Kemmitt, T., Gainsford, G. J. & Kuznetsov, N. T. (2001). *Thermochim. Acta*, **381**, 173–180.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97* and *SHELXS97*. University of Göttingen, Germany.
- Siemens (1996). *SMART* and *SAINT*. Versions 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Zechmann, C. A., Huffman, J. C., Foltling, K. & Caulton, K. G. (1998). *Inorg. Chem.* **37**, 5856–5861.