

A novel titanium– μ -O–zirconium complex: bis(μ -methyliminodiethanolato- $1\kappa^3O,N,O'$; $1:2\kappa^2O$)(methyliminodiethanolato- $2\kappa^3O,N,O'$)dipropanolato- $1\kappa O,2\kappa O$ -titanium(IV)-zirconium(IV)

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Received 25 July 2002

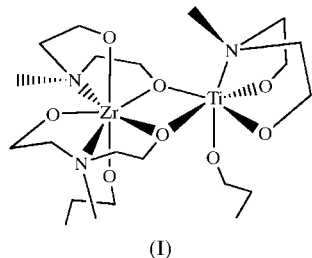
Accepted 27 August 2002

Online 30 September 2002

The title compound, $[\text{TiZr}(\text{C}_5\text{H}_{11}\text{NO}_2)_3(\text{C}_3\text{H}_7\text{O})_2]$, contains three methyliminodiethanolate ligands, two in different μ -oxo bridging coordination modes and one bound only to the Ti atom. The Ti and Zr atoms have distorted octahedral and pentagonal–bipyramidal coordinations, respectively, which share edges. As well as some conformational disorder in the carbon chains, there is chemical disorder at one Ti site, with a mix of *n*- and isopropanolate ligands.

Comment

The title compound, (I), was prepared as part of a study of possible precursor compounds for zirconium titanates and lead zirconate titanate (PZT). An X-ray analysis was required as the chemical structure could not be unambiguously determined by other techniques (Kemmitt, Al-Salim & Gainsford, 2002).



The crystal structure of (I) (Fig. 1) consists of independent $[\text{TiZr}(\text{MDEA})_3(n\text{-propanolato})_{1.6}(\text{isopropanolato})_{0.4}]$ molecules (MDEA is methyliminodiethanolate) with only weak intermolecular contacts, e.g. $\text{C}33\text{A}—\text{H}332\cdots\text{O}22^i$, with a $\text{C}\cdots\text{O}$ distance of 3.476 (9) Å [symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$]. Within the complex, there is one weak intramolecular $\text{C}15—\text{H}15\text{B}\cdots\text{O}22$ hydrogen-bond contact, with a $\text{C}\cdots\text{O}$ distance of 3.280 (5) Å and a $\text{C}—\text{H}\cdots\text{O}$ angle of 148°. For

clarity, Fig. 1 shows only the major conformation rings (suffix A) and the major (60% occupancy) *n*-propanolate ligand bound to the Ti atom *via* the O41 atom.

The Ti atom is in a typical distorted octahedral coordination environment, while the Zr is seven-coordinate, highly distorted from bipyramidal–pentagonal symmetry. The $\text{Ti}\cdots\text{Zr}$ distance of 3.459 (1) Å is considerably longer than the values of 3.413 and 3.4117 (12) Å found in the oxo-bridged titanium and zirconium pinacolate complexes reported by Zechmann *et al.* (1998) [Cambridge Structural Database (CSD; Allen & Kennard, 1993) refcodes JARSUQ and JARWEE]. The latter are the only two oxo-bridged $\text{Ti}\cdots\text{Zr}$ complexes in the CSD (*ConQuest*; Cambridge Structural Database, 2002).

Both of the MDEA ligands bound to the Zr atom in (I) have one O atom bridging the two metal centres. One adopts a facial conformation, as previously observed by Kemmitt, Al-Salim & Gainsford (1999), while the other is meridionally bound [see examples in Sevast'yanov *et al.* (2001)]. The latter MDEA ligand, with its flattened conformation, has a $\text{Zr}—\text{N}$ distance of 2.397 (3) Å, which is shorter than the usual facial (twist) conformation length ($\text{Zr}—\text{N}21$) of 2.443 (3) Å. A comparable twist $\text{Zr}—\text{N}$ distance of 2.427 Å is found in the complex $\{N,N\text{-bis}[2\text{-(mesitylamido)ethyl}]\text{methylamine}\}\text{zirconium}$ (Schrock *et al.*, 2000).

The $\text{Zr}—\text{O}$ distances in (I) are similar to those found in JARSUQ and JARWEE, which have distances to the μ -O atom of 2.135 (3), 2.178 (4), 2.174 (5) and 2.164 (5) Å, compared with values of 2.182 (2) and 2.222 (2) Å in (I). The $\text{Ti}—\text{O}$ lengths of the bound isopropanolate ligand in JARSUQ and JARWEE [mean 1.791 (5) Å] are identical to that for the *n*-propanolate ligand in (I) [1.786 (3) Å]. This suggests that the mixture of iso- and *n*-propanolate ligands bound to the Ti atom through oxygen (site O41) found by model trials is, structurally speaking, a reasonable possibility (see *Experimental*).

The third MDEA ligand is only bound to the Ti atom, adopting a facial conformation with a $\text{Ti}—\text{N}$ distance of

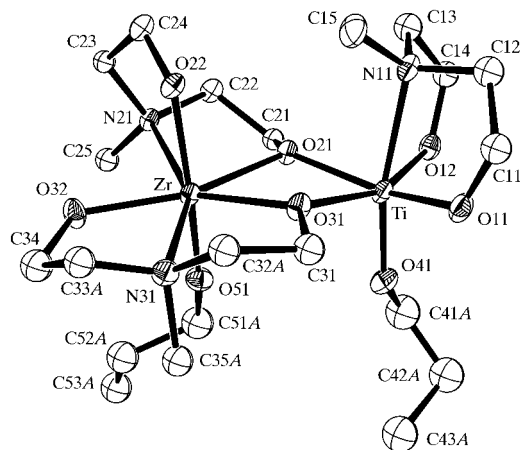


Figure 1

A view of the molecular structure of (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms, minor conformers and the isopropanolate ligand at O41 (see text) have been omitted for clarity.

2.346 (3) Å, slightly shorter than the values of 2.380 (3) and 2.401 (2) Å found in [Ti₃(MDEA)₂(1,3-propanolate)₄] (hereinafter KEMM1; Kemmitt, Gainsford & Robson-Marsden, 2002), and the maximum of 2.422 (2) Å observed in [Ti(MDEA)₂] (Kemmitt, Al-Salim *et al.*, 1999). The folding in the MDEA is normal, with N–C–C–O dihedral angles of 44.9 (5) and 37.0 (4)° (for the *A* conformations), compared with means of 43.8 and 30.7° in KEMM1.

All the Ti–O(MDEA) bond lengths in (I) are similar to those found previously. The mean Ti–O(MDEA) in (I) is 1.883 (3) Å, which is comparable with the range of 1.848–1.878 Å found in KEMM1, and the usually longer bridging bonds (2.014 and 2.067 Å) are comparable with mean values observed in related compounds of 2.107 (Kemmitt, Al-Salim & Gainsford, 1999) and 2.103 Å (Sevast'yanov *et al.*, 2001).

Atoms O11, O12, O21 and O31 are planar, with an average deviation of 0.024 (3) Å, and the Ti atom is 0.279 (1) Å from the plane. This plane makes an angle of 10.3 (1)° with the plane through the four approximately planar atoms O21, O31, O32 and N31 (average deviation out of the plane 0.08 Å) bound to Zr; atoms Zr and N21 are 0.022 (2) and 0.446 (5) Å, respectively, from this plane.

Experimental

Titanium tetraisopropoxide (5.97 g, 21 mmol) and zirconium tetra-*n*-propoxide (9.83 g, 21 mmol) were added to *N*-methyl-diethoxoamine (5.0 g, 42 mmol) in anhydrous benzene at room temperature. The mixture was stirred under an inert atmosphere at 323 K for 1 h, and the solvent was then evaporated at 323–343 K under vacuum to give a viscous material. This was dissolved in anhydrous benzene (2 ml), from which approximately cubic colourless crystals of (I) separated out (*ca* 30% yield).

Crystal data

[TiZr(C₅H₁₁NO₂)₃(C₃H₇O)₂]
M_r = 608.74
 Monoclinic, *C*2/*c*
a = 31.172 (10) Å
b = 10.407 (3) Å
c = 19.116 (6) Å
 β = 116.002 (3)°
V = 5574 (5) Å³
Z = 8

D_x = 1.451 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 5093 reflections
 θ = 2.6–25.8°
 μ = 0.71 mm⁻¹
T = 163 (2) K
 Cubic block, colourless
 0.30 × 0.27 × 0.25 mm

Data collection

Siemens SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.686, *T_{max}* = 0.837
 19 935 measured reflections

5613 independent reflections
 3723 reflections with *I* > 2σ(*I*)
R_{int} = 0.056
 θ_{\max} = 26.4°
h = -38 → 35
k = -12 → 12
l = -8 → 23

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.043
wR (*F*²) = 0.104
S = 0.95
 5613 reflections
 272 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0537P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.60 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.59 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.00051 (7)

Table 1

Selected geometric parameters (Å, °).

Zr–O51	1.977 (3)	Ti–O41	1.786 (3)
Zr–O22	2.046 (2)	Ti–O12	1.877 (2)
Zr–O32	2.068 (2)	Ti–O11	1.887 (2)
Zr–O31	2.182 (2)	Ti–O21	2.014 (2)
Zr–O21	2.222 (2)	Ti–O31	2.067 (2)
Zr–N31	2.397 (3)	Ti–N11	2.346 (3)
Zr–N21	2.443 (3)		
O51–Zr–O31	98.93 (10)	O21–Zr–N31	136.14 (9)
O32–Zr–O31	143.18 (9)	O31–Zr–N21	135.17 (9)
O22–Zr–O21	88.84 (9)	O21–Zr–N21	71.94 (8)
O32–Zr–N31	72.55 (10)	O12–Ti–N11	76.37 (11)
O31–Zr–N31	71.05 (9)	O11–Ti–N11	76.51 (11)
O11–Ti–O21–Zr	-57.9 (3)	O31–Ti–O21–Zr	-16.06 (10)

The positions of the H atoms on atoms C31 and C34 were refined. Other H atoms were placed in calculated positions, with C–H = 0.98–0.99 Å. Subsequently, all H atoms were constrained, with *U*_{iso}(H) = 1.2*U*_{eq} of their parent atom. There was conformational disorder in one methyliminodiethanolate ligand and in the *n*-propanolate ligand bound to Zr. Chemical disorder (*iso/n*-propanolate) was modelled for the ligand bound to Ti; full details are given in the archived CIF. No H atoms were included for the poorly ordered *iso*-propanolate C atoms.

Data collection and cell refinement: *SMART* (Siemens, 1996); data reduction: *SAINT* (Siemens, 1996) and *SADABS* (Sheldrick, 1996); structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* in *WinGX* (Farrugia, 1997, 1999).

The authors thank Dr J. Wikaira and Professor Ward T. Robinson of the University of Canterbury, New Zealand, for their assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1389). Services for accessing these data are described at the back of the journal.

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