Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Multiple bridging modes in a novel trinuclear titanium 1,3-dioxypropane compound, Ti_3(methyliminodiethanolate)$_2$(1,3-propanediolate)$_4$

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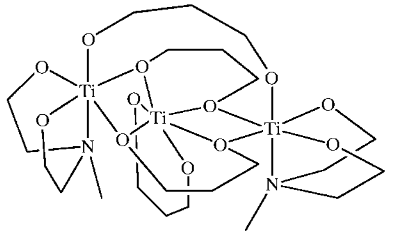
Received 15 March 2002
Accepted 8 April 2002
Online 30 April 2002

The title compound, bis(2,2′-methyliminodiethanolato)-$1\kappa^3O,N,O'$;$3\kappa^3O,N,O'$-di-μ_3-propane-1,3-diolato-1:2:$3\kappa^8O:O,O':O'$-μ-propane-1,3-diolato-1:$3\kappa^2O:O'$-propane-1,3-diolato-$2\kappa^2O,O'$-trititanium(IV), $[Ti_3(C_5H_{11}NO_2)_2(C_3H_6O_2)_4]$, has four 1,3-propanediolate ligands binding in three different modes. Two ligands chelate adjacent Ti atoms with normal μ_3-O bridges, giving typical edge-sharing of the Ti distorted octahedra, one chelating to the central Ti atom with no μ-bridging, and the other spanning the cluster, binding only to the outermost Ti atoms. The two methyliminodiethanolate ligands each coordinate to the outer Ti atoms *via* their N and two O atoms. The Ti—O bond lengths range, in a self-consistent fashion, from 1.816 (2) to 2.082 (2) Å, while the average Ti—N distance is 2.391 (3) Å.

Comment

Titanium alkoxides can be modified to provide complexes with properties designed for specific applications. Chelating diols and amino alcohols have been demonstrated to improve the stability of alkoxide complexes and their solutions (Takahashi & Matsuoka, 1988; Tanaka *et al.*, 1995). The chelating amine function acts to increase coordinative saturation at the metal centre, reducing the tendency of the ligands to form bridges. This is a useful strategy in producing low-nuclearity complexes for metal–organic chemical vapour deposition (Jones *et al.*, 1998, 2001; Lee *et al.*, 1999). Sterically demanding ligands have also been used to limit nuclearity (Damo *et al.*, 2000; Boyle *et al.*, 1995). Titanium complexes containing bulky diol ligands in tandem with 2,2′-methyliminodiethanol (or *N*-methyldiethoxoamine, MDEA) produce volatile dimeric complexes (Sevast'yanov *et al.*, 2001). As part of this study, we have employed the less sterically demanding 1,3-propanediol to form the title compound, (I), in order to illustrate the influence which steric factors have on the structure of the complex. The present analysis was required as the chemical structure was not unambiguously determined by other techniques.



(I)

The crystal structure of (I) consists of independent $Ti_3(MDEA)_2$(1,3-propanediolate)$_4$ molecules (Fig. 1), with only weak intermolecular contacts, *e.g.* C13—H13*A*···H13*A*^{i} 2.22 Å [symmetry code: (i) $1 - x$, $1 - y$, $-z$]. Both MDEA ligands adopt two conformations, which were modelled using total linked occupancies of 1 for the two resolvable atom sets around N1 and N2 (C11/C12/C14 and C19/C20/C22, respectively). For clarity, Fig. 1 shows only the major conformation of the rings (suffix *A*), corresponding to occupancies of 0.772 (7) and 0.52 (1) for the N1 and N2 sets, respectively. Trititanium alkoxy compounds adopt either this chain configuration or a triangular arrangement which permits the coordination of at least one O atom (μ_3-O) to all three Ti atoms (*e.g.* Boyle *et al.*, 1999).

The outer Ti atoms, Ti1 and Ti3, have a similar distorted octahedral coordination, with an approximate square plane through the edge-sharing and MDEA O atoms, with a mean deviation of 0.040 (2) Å from the plane through atoms O1, O2, O4 and O5; atom Ti1 deviates by −0.282 (1) Å and atom Ti2 by −0.0342 (2) from this plane. The Ti2 octahedral distortion is greater, approaching a trigonal antiprism coordination, consistent with the wider variation in Ti—O bond lengths.

Methyl- and dimethyl-substituted ethoxoamine ligands (MDEA and DMEA) bound to titanium oxide species form a wide range of products under controlled hydrolysis (Kemmitt, Al-Salim & Gainsford, 1999; Kemmitt, Al-Salim, Gainsford & Henderson, 1999; Johnson *et al.*, 2001, and references therein). For compound (I), the two MDEA ligands do not provide any of the Ti-bridging O atoms, each being bound by the two O atoms [Ti—O 1.848 (2)–1.878 (2) Å] and one N atom [average Ti—N 2.405 (3) Å] to the outer two Ti atoms.

In contrast with the MDEA ligands, the 1,3-propanediolate ligand is coordinated to the trititanium cluster in three different modes. The first of these is an 'ubiquitous' mode (Boyle *et al.*, 1997), in which the μ_3-O atoms (*e.g.* atoms O1 and O7 in O1—C1—C2—C3—O7) are linked to the central and outer Ti atoms (Davis *et al.*, 2001; Minhas *et al.*, 1992). Two of these ligands provide the edge-sharing of the distorted octahedra. As observed previously (Corden *et al.*, 1999; Boyle *et al.*, 1997), these Ti—O bonds are much longer than normal non-bridged Ti—O bonds, varying, in (I), from 1.988 (2) to 2.082 (2) Å, with mean values for Ti—O—C, Ti···Ti and Ti—O of 123.6°, 3.322 (1) Å and 2.04 Å, respectively. These values are at the upper end of the spectrum of published values; in a subset of titanium six-coordinate oxo complexes, where one Ti

DOI: 10.1107/S0108270102006273

binds an N atom (as here), the Ti—O range is 1.939–2.49 Å, with mean values for Ti—O—C, Ti···Ti and Ti—O of 122°, 3.12 Å and 1.99 Å, respectively (*ConQuest*, 33 hits; Cambridge Structural Database, 2001; Allen & Kennard, 1993).

The second mode involves coordination to one Ti atom, Ti2 (O9 and O10), with an average Ti2—O distance of 1.851 (3) Å. There are no complete reports of this ligand bound in this manner in metal oxide complexes, although a rhenium compound has been studied (Nunes *et al.*, 1998). In the related five-coordinate [Ti(2,4-dimethyl-2,4-pentanediolate)$_2$]$_2$ dimer, the Ti—O lengths range from 1.802 (2) to 1.816 (2) Å (Damo *et al.*, 2000). In six-coordinate titanium complexes with unsymmetrically substituted neutral glycols (Steinhuebel & Lippard, 1999), the Ti—O distances are comparable, varying from 1.862 (4) to 1.888 (2) Å.

The third and novel coordination mode involves linking the outer two Ti atoms, like the handle of the basket formed by the remainder of the cluster, with a shorter average Ti—O length of 1.820 (3) Å. This coordination has apparently not been reported before (*ConQuest*; Cambridge Structural Database, 2001). The nearest equivalent to this, with a similar span between Ti atoms, is the coordination of tris(hydroxymethylpropane) in a tetratitanium compound (Boyle *et al.*, 1995), although, in this case, all the O atoms also bind two Ti atoms (μ_2-O type). The shorter Ti—O lengths of 1.750 (4) Å in [TiCl$_2$(cyclopentadienyl)]$_2$(1,3-propanediolate) (Huang & Stephan, 1995), where the TiCpCl$_2$ entities are only linked by the diolate, and 1.776 (2) Å in [Ti(triethoxoamine)]$_2$-[OC(CH$_3$)$_2$C(CH$_3$)$_2$O] (Naiini *et al.*, 1993), where the titanatranyl entities are linked by the pinacolate, reflect the less crowded four-coordinate trigonal–pyramidal titanium stereochemistry. The angles subtended at the O atom (Ti—O—C) in these two reference structures are also quite different (158.1 and 159.6°, respectively), compared with 128.5 (2) and 129.0 (2)° in (I). The propane-chain dihedral angles [59.7 (4) and 57.3 (4)°] indicate there is little strain in this mode of coordination, although these values are also similar to those in the other 1,3-propanediolate ligands in (I).

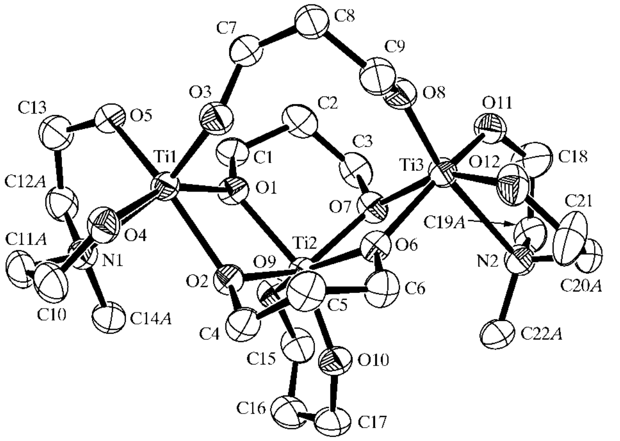


Figure 1
A view of the molecule of (I). Only the major conformations for the MDEA rings are shown (see *Comment*). Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

Experimental

Ti(isopropoxide)$_4$ was reacted at room temperature with equimolar amounts of 2,2′-methyliminodiethanol and 1,3-propanediol in toluene. Evaporation of liberated 2-propanol under reduced pressure allowed the slow growth of crystals of (I) as the only isolable product (*ca* 30% yield). Adjustment of the reactant stoichiometries to reflect the product formula resulted in slight improvement of yields (45%).

Crystal data

[Ti$_3$(C$_5$H$_{11}$NO$_2$)$_2$(C$_3$H$_6$O$_2$)$_4$]
M_r = 674.31
Monoclinic, $P2_1/n$
a = 11.732 (4) Å
b = 18.415 (6) Å
c = 13.703 (5) Å
β = 92.842 (5)°
V = 2956.9 (17) Å^3
Z = 4
D_x = 1.515 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5609 reflections
θ = 2.2–26.3°
μ = 0.85 mm^{-1}
T = 168 (2) K
Block, colourless
0.65 × 0.30 × 0.24 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{\min}$ = 0.679, $T_{\max}$ = 0.815
37 694 measured reflections
5953 independent reflections
4627 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.046
$\theta_{\max}$ = 26.4°
$h = -14 \rightarrow 14$
$k = -22 \rightarrow 22$
$l = -17 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.121
S = 1.09
5953 reflections
403 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0575P)^2 + 2.8442P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.001
$\Delta\rho_{\max}$ = 0.34 e Å^{-3}
$\Delta\rho_{\min}$ = −0.60 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ti1—O3	1.825 (2)	Ti2—O7	1.992 (2)
Ti1—O4	1.848 (2)	Ti2—O1	2.057 (2)
Ti1—O5	1.878 (2)	Ti2—O6	2.061 (2)
Ti1—O1	2.031 (2)	Ti3—O8	1.816 (2)
Ti1—O2	2.082 (2)	Ti3—O11	1.854 (2)
Ti1—N1	2.380 (3)	Ti3—O12	1.873 (2)
Ti2—O10	1.843 (2)	Ti3—O6	2.027 (2)
Ti2—O9	1.859 (2)	Ti3—O7	2.084 (2)
Ti2—O2	1.988 (2)	Ti3—N2	2.401 (2)
O3—Ti1—O4	98.72 (10)	O10—Ti2—O2	94.54 (9)
O3—Ti1—O5	94.90 (10)	O9—Ti2—O2	115.25 (9)
O4—Ti1—O5	105.51 (10)	O10—Ti2—O7	113.00 (9)
O3—Ti1—O1	97.22 (9)	O9—Ti2—O7	91.96 (9)
O4—Ti1—O1	155.68 (9)	O2—Ti2—O7	142.05 (8)
O5—Ti1—O1	91.25 (9)	O10—Ti2—O1	159.07 (9)
O3—Ti1—O2	103.75 (9)	O9—Ti2—O1	84.46 (9)
O4—Ti1—O2	88.82 (8)	O2—Ti2—O1	70.93 (8)
O5—Ti1—O2	154.54 (9)	O7—Ti2—O1	87.01 (8)
O1—Ti1—O2	69.57 (7)	O10—Ti2—O6	84.59 (9)
O3—Ti1—N1	168.34 (9)	O9—Ti2—O6	157.56 (9)
O4—Ti1—N1	77.02 (9)	O2—Ti2—O6	86.65 (8)
O5—Ti1—N1	76.10 (9)	O7—Ti2—O6	71.31 (8)
O1—Ti1—N1	90.46 (9)	O1—Ti2—O6	108.73 (8)
O2—Ti1—N1	87.13 (9)	C1—O1—Ti1	129.50 (17)
O10—Ti2—O9	88.59 (10)	Ti1—O1—Ti2	108.68 (9)
O1—C1—C2—C3	61.5 (3)	O3—C7—C8—C9	59.7 (4)
C1—C2—C3—O7	−64.9 (4)	C7—C8—C9—O8	57.3 (4)
O2—C4—C5—C6	−64.7 (3)	O9—C15—C16—C17	−65.4 (4)
C4—C5—C6—O6	59.8 (4)	C15—C16—C17—O10	40.3 (4)

All H atoms were constrained (C—H = 0.98 and 0.99 Å) to an isotropic displacement parameter 1.2 times that of the equivalent U of their parent atom. Atoms C11/C12/C14 and C19/C20/C22 (and their riding H atoms) were refined over two sites, with two common occupancies for each set and a total occupancy of 1.

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 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

The authors thank Dr J. Wikaira, University of Canterbury, New Zealand, for her assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1372). Services for accessing these data are described at the back of the journal.

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