Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

An oxo-bridged centrosymmetric tetranuclear titanium compound

Tim Kemmitt, Graeme J. Gainsford* and Najeh I. Al-Salim

Industrial Research Limited, PO Box 31-310, Lower Hutt, New Zealand
Correspondence e-mail: g.gainsford@irl.cri.nz

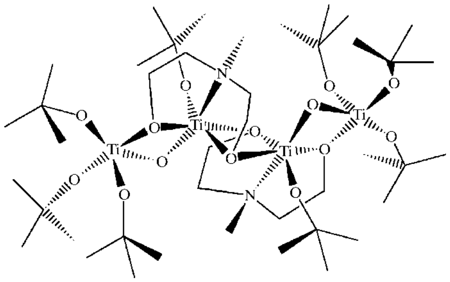
Received 20 October 2003
Accepted 3 December 2003
Online 10 January 2004

The title compound, octa-*tert*-butoxybis[μ_3-2,2′-(*N*-methylimino)diethanolato]di-μ-oxo-tetratitanium(IV), $[Ti_2O\{(OCH_2CH_2)_2(NCH_3)\}\{(CH_3)_3CO\}_4]_2$ or $[Ti_4(C_5H_{11}NO_2)_2(C_4H_9O)_8O_2]$, lies about an inversion centre, and displays the less usual zigzag configuration. One O atom of the *N*-methyldiethoxoamine ligand bridges the symmetry-related Ti atoms, while the other bridges the two independent Ti atoms, with the N atom binding to give a facial configuration. Four ^{t}BuO$^-$ ligands and a bridging oxide complete the respective five- and sixfold coordination of the two Ti atoms. The Ti—O bond lengths range in a self-consistent fashion from 1.7624 (17) to 2.0878 (18) Å, while the Ti—N bond length is 2.374 (2) Å.

Comment

This study is part of a programme aimed at modifying metal alkoxides as precursors to high-tech oxides. A recent review (Hubert-Pfalzgraf, 2003) discussed many structural features and applications of this class of compound. The varied coordination chemistry of *N*-methyldiethoxoamine (MDEA) has been of great interest to us in forming volatile complexes (Sevast'yanov *et al.*, 2001; Kemmitt *et al.*, 2004), mixed metal alkoxides (Gainsford *et al.*, 2002*a*,*b*), an oxoalkoxide structure (Kemmitt, Al-Salim & Gainsford, 1999) and other complexes with different metal–ligand ratios (Kemmitt, Al-Salim, Gainsford & Henderson, 1999; Kemmitt, Al-Salim & Gainsford, 2002; Kemmitt, Gainsford & Robson-Marsden, 2002). Aminoalkoxide ligands influence the formation of partial hydrolysis condensates, as noted by the contrasting structures observed in the cyclic hexanuclear MDEA oxotitanate (Kemmitt, Al-Salim & Gainsford, 1999), dimethylaminoethoxide (DMAE) oxotitanate, which forms a Ti_4O_4 cluster core (Johnson *et al.*, 2001), and the isolated linear oxo bridges observed in triethanolaminotitanates (Kemmitt *et al.*, 2000). The title titanium complex, (I), has fewer amine functions and retains some alkoxide ligands, resulting in a new structural type for partial hydrolysis condensates.

The crystal structure of (I) consists of independent centrosymmetric $[Ti_2O(N\text{-methyldiethoxoamine})(tert\text{-butoxide})_4]_2$ complexes (Fig. 1). There are a few weak intermolecular contacts, *e.g.* C13—H13*A*···H13*A*($1-x$, $1-y$, $-z$) of 2.22 Å. The four Ti atoms are arranged in the less usual zigzag configuration, with a Ti1···Ti2···Ti2^{i} angle of 117.40 (2)° [symmetry code: (i) $-x$, $-y$, $1-z$]. The terminal Ti1 atoms are pentacoordinate, while the linking Ti2 atoms are hexacoordinate.



(I)

The Ti1 stereochemistry can best be described as distorted bipyramidal, with apical atoms O1 and O7 of the MDEA bridging ligand and one *tert*-butoxide, and equatorial atoms O5, O6 and O3 from two *tert*-butoxides and the bridging oxide, respectively (mean O—Ti—O = 118.4°).

The hexacoordinate Ti2 stereochemistry approaches a trigonal antiprism arrangement. One trigonal face of the antiprism is occupied by the three coordinating atoms of the MDEA ligand (O1, O2 and N1), where atom O2 bridges the two symmetry-related Ti2 atoms and atom O1 bridges the two independent atoms Ti1 and Ti2. The other face of the antiprism is occupied by atoms O3, O4 and O2 from the bridging oxide, a *tert*-butoxide and the arm of the symmetry-related MDEA ligand, respectively. The Ti—μ_3-O [1.7624 (17)–2.0878 (18) Å] and Ti—N [2.374 (2) Å] bond lengths are within the normal ranges for this type of complex.

The Ti1···Ti2 and Ti2···Ti2^{i} distances of 3.0459 (7) and 3.3101 (10) Å compare with the values of 3.307 (3) and 3.242 (4) Å in the similar zigzag Ti_4 structure $[Ti_4(O^iPr)_8(\mu,\eta^2\text{-}OCH_2CH{=}CHCH_2O)_2(\mu_3,\eta^2\text{-}OCH_2CH{=}CHCH_2O)_2]$ found by Miele-Pajot *et al.* (1999). The shorter Ti1···Ti2 distance in (I) is expected from the smaller less constrained bridging between atoms Ti1 and Ti2. Ti···Ti distances in the range 2.952–3.570 Å are observed in other Ti—O—Ti bridged complexes.

Tetratitanium oxygen-bridged complexes adopt eight different configurations, as observed in a search of the Cambridge Structural Database (CSD, July 2003 update; Allen, 2002). A previous analysis of multititanium oxygen-bridged compounds was given by Boyle *et al.* (1997). In the following list, the items are 'type' followed by, in brackets, the number found of that type, an example CSD code and the reference for that example: square (13; RONBUR; Troyanov & Gorbenko, 1997), cube (ten; GOXMUB; Guerrero *et al.*, 1999), capped parallelogram (ten; NEMBIQ; Weymann-Schildknetch & Henry, 2001), butterfly (one; GOMVIN; Boyle *et al.*, 1998), planar linear (two; JUKQUB; Franceschi *et al.*, 1999), planar with a μ_3-O—Ti bridge (three; NOCYOT; Moran *et al.*, 1998), bowed linear or plate (one; FETMIA; Pedersen *et al.*, 1987) and zigzag [two; (I) and WOGLEJ; Miele-Pajot *et al.*, 1999]. In most cases (except the last two),

DOI: 10.1107/S0108270103027902

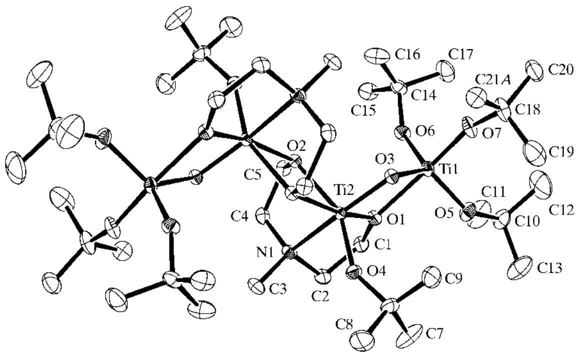


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

the Ti atoms are six-coordinate. It is noted that the zigzag configuration is found in a related Zr_4 compound, $[Zr_2(\mu_2$-O,μ_2-O'-methyliminodiethanolate)(μ_2-O-n-propanolate)$_3$(n-propanolate)$_3]_2$, and an analogous $TiZr_2Ti$ compound, but with the MDEA ligands adopting planar meridional binding conformations around the Zr atoms (Gainsford *et al.*, 2002*b*,*c*).

Experimental

Crystals of (I) were isolated from liquid $Ti_2(MDEA)(O^tBu)_6$, prepared by the addition of Ti(*tert*-butoxide)$_4$ (27.2 g, 0.08 mol) to a solution of MDEA (4.76 g, 0.04 mol) in anhydrous toluene (100 ml) at room temperature. After stirring for 4 h, the solvent was distilled off, leaving the crude product as a mobile oil. The extremely moisture-sensitive liquid was exposed briefly to atmospheric air and then stored in an airtight flask. Within minutes, feathery crystals of (I) appeared around the neck of the flask. X-ray quality crystals grew slowly from the liquid over a period of several months.

Crystal data

$[Ti_4(C_5H_{11}NO_2)_2(C_4H_9O)_8O_2]$
$M_r = 1042.79$
Monoclinic, $P2_1/n$
$a = 9.2937\ (10)$ Å
$b = 23.058\ (3)$ Å
$c = 13.5360\ (16)$ Å
$\beta = 102.436\ (2)°$
$V = 2832.7\ (6)$ Å^3
$Z = 2$
$D_x = 1.223$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5496 reflections
$\theta = 2.3$–$23.8°$
$\mu = 0.60$ mm^{-1}
$T = 163\ (2)$ K
Block, colourless
0.36 × 0.15 × 0.15 mm

Data collection

Siemens SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.678$, $T_{max} = 0.914$
33 365 measured reflections
5693 independent reflections
3634 reflections with $I > 2\sigma(I)$
$R_{int} = 0.081$
$\theta_{max} = 26.4°$
$h = -11 \rightarrow 6$
$k = -28 \rightarrow 28$
$l = -16 \rightarrow 16$

Table 1
Selected interatomic distances (Å).

Ti1—O7	1.794 (2)	Ti2—O4	1.8034 (18)
Ti1—O6	1.7957 (19)	Ti2—O1	1.9755 (18)
Ti1—O5	1.810 (2)	Ti2—O2^i	2.0044 (17)
Ti1—O3	1.9488 (18)	Ti2—O2	2.0751 (17)
Ti1—O1	2.0878 (18)	Ti2—N1	2.374 (2)
Ti2—O3	1.7624 (17)		

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

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.098$
$S = 1.01$
5693 reflections
291 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0351P)^2 + 1.5206P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}

Atom C21 was disordered over two sites and each was given a common isotropic displacement parameter.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1996) and *SADABS* (Sheldrick, 1996); structure solution: *SHELXS*97 (Sheldrick, 1997); structure refinement: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 (Farrugia, 1997).

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

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1427). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Boyle, T. J., Alam, T. M., Mechenbier, E. R., Scott, B. L. & Ziller, J. W. (1997). *Inorg. Chem.* **36**, 3293–3300.
Boyle, T. J., Alam, T. M., Tafoya, C. J. & Scott, B. L. (1998). *Inorg. Chem.* **37**, 5588–5594.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Franceschi, F., Solari, E., Floriani, C., Rosi, M., Chiesi-Villa, A. & Rizzoli, C. (1999). *Chem. Eur. J.* **5**, 708–721.
Gainsford, G. J., Al-Salim, N. I. & Kemmitt, T. (2002*a*). *Acta Cryst.* C**58**, m509–m510.
Gainsford, G. J., Al-Salim, N. I. & Kemmitt, T. (2002*b*). *Acta Cryst.* E**58**, m636–m638.
Gainsford, G. J., Al-Salim, N. I. & Kemmitt, T. (2002*c*). *Acta Cryst.* E**58**, m619–m621.
Guerrero, G., Mehring, M., Mutin, P. H., Dahan, F. & Vioux, A. (1999). *J. Chem. Soc. Dalton Trans.* pp. 1537–1538.
Hubert-Pfalzgraf, L. G. (2003). *Inorg. Chem. Commun.* **6**, 102–120.
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. (2000). *Inorg. Chem.* **39**, 6067–6071.
Kemmitt, T., Al-Salim, N. I. & Gainsford, G. J. (2002). *Aust. J. Chem.* **55**, 513–517.
Kemmitt, T., Al-Salim, N. I., Gainsford, G. J. & Henderson, W. (1999). *Aust. J. Chem.* **52**, 915–919.
Kemmitt, T., Al-Salim, N. I., Gainsford, G. J., Robson-Marsden, H. & Sevast'yanov, D. V. (2003). *Aust. J. Chem.* **56**, 1147–1152.
Kemmitt, T., Gainsford, G. J. & Robson-Marsden, H. (2002). *Acta Cryst.* C**58**, m310–m312.
Miele-Pajot, N., Hubert-Pfalzgraf, L. G., Papiernik, R., Vaissermnann, J. & Collier, R. (1999). *J. Mater. Chem.* **9**, 3027–3033.
Moran, P. D., Rickard, C. E. F., Bowmaker, G. A., Cooney, R. P., Bartlett, J. R. & Woolfrey, J. L. (1998). *Inorg. Chem.* **37**, 1417–1419.
Pedersen, S. F., Dewan, J. C., Eckman, R. R. & Sharpless, K. B. (1987). *J. Am. Chem. Soc.* **109**, 1279–1282.
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). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Siemens (1996). *SMART* and *SAINT*. Versions 4.0. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Troyanov, S. I. & Gorbenko, O. Yu. (1997). *Polyhedron*, **16**, 777–780.
Weymann-Schildknetch, S. & Henry, M. (2001). *J. Chem. Soc. Dalton Trans.* pp. 2425–2428.