

Bis(μ -2-hydroxymethyl-2-methylpropane-1,3-diolato)bis[dichlorido-titanium(IV)] diethyl ether disolvate

Alastair J. Nielson,^{a*} Chaohong Shen^{b‡} and Joyce M. Waters^a

^aChemistry, Institute of Natural and Mathematical Sciences, Massey University at Albany, PO Box 102904 North Shore Mail Centre, Auckland, New Zealand, and

^bChemistry, Institute of Fundamental Sciences, Massey University at Albany, PO Box 102904 North, Shore Mail Centre, Auckland, New Zealand

Correspondence e-mail: a.j.nielson@massey.ac.nz

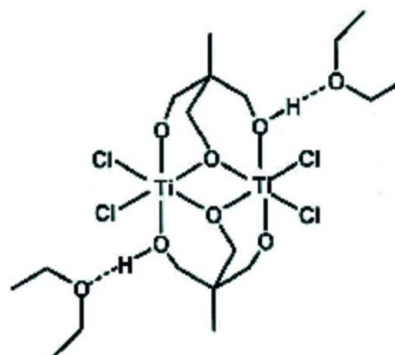
Received 7 November 2013; accepted 19 November 2013

Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.022; wR factor = 0.061; data-to-parameter ratio = 17.5.

The title complex, $[\text{Ti}_2\text{Cl}_4\{\text{CH}_3\text{C}(\text{CH}_2\text{O})_2(\text{CH}_2\text{OH})_2\}]_2$, lies across a centre of symmetry with a diethyl ether solvent molecule hydrogen bonded to the $-\text{CH}_2\text{OH}$ groups on either side of it. The Ti^{IV} atom is coordinated in a distorted octahedral geometry by a tripodal ligand and two terminal chloride atoms. There are three coordination modes for the tripodal ligand distinguishable on the basis of their very different $\text{Ti}-\text{O}$ bond lengths. For the terminal alkoxo ligand, the $\text{Ti}-\text{O}$ distance is 1.760 (1) Å, the asymmetric bridge system has $\text{Ti}-\text{O}$ bond lengths of 1.911 (1) and 2.048 (1) Å. The $\text{Ti}-\text{O}$ bond length for the alcohol O atom is the longest at 2.148 (1) Å.

Related literature

For general background to $\text{Ti}-\text{O}$ and $\text{Ti}-\text{Cl}$ bonds, see: Gau *et al.* (1996); Wu *et al.* (1996). For closely related structures, see: Talbot-Eeckelaers *et al.* (2006); Chang *et al.* (1993); Salta & Zubieta (1997); Chen *et al.* (1997). For cluster compounds of this ligand type, see: Boyle *et al.* (1995); Delmont *et al.* (2000); Liu *et al.* (1990).



Experimental

Crystal data

$[\text{Ti}_2\text{Cl}_4(\text{C}_5\text{H}_{10}\text{O}_3)_2] \cdot 2\text{C}_4\text{H}_{10}\text{O}$
 $M_r = 622.10$
 Triclinic, $P\bar{1}$
 $a = 7.9617$ (3) Å
 $b = 9.6379$ (4) Å
 $c = 10.5783$ (5) Å
 $\alpha = 71.351$ (1)°
 $\beta = 82.023$ (1)°

$\gamma = 66.757$ (1)°
 $V = 706.60$ (5) Å³
 $Z = 1$
 Mo $K\alpha$ radiation
 $\mu = 0.98$ mm⁻¹
 $T = 150$ K
 $0.26 \times 0.24 \times 0.10$ mm

Data collection

Siemens SMART CCD diffractometer
 Absorption correction: multi-scan (Blessing, 1995)
 $T_{\text{min}} = 0.766$, $T_{\text{max}} = 0.892$

6510 measured reflections
 2661 independent reflections
 2417 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.015$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.061$
 $S = 1.04$
 2661 reflections
 152 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\text{max}} = 0.31$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.27$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O3}-\text{H3}\cdots\text{O11}$	0.74 (2)	1.89 (2)	2.6233 (14)	168 (2)

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL97*.

We are grateful to Massey University for the award of a Post-Doctoral Fellowship to CS, and to Ms T. Groutso of the University of Auckland for the data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG5360).

‡ Former address.

References

- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.
- Boyle, T. J., Schwartz, R. W., Doedens, R. J. & Ziller, J. W. (1995). *Inorg. Chem.* **34**, 1110–1120.
- Chang, Y., Chen, Q., Khan, M. I., Salta, J. & Zubieta, J. (1993). *J. Chem. Soc. Chem. Commun.* pp. 1872–1874.
- Chen, Q., Chang, Y. D. & Zubieta, J. (1997). *Inorg. Chim. Acta*, **258**, 257–262.
- Delmont, R., Proust, A., Robert, F., Herson, P. & Gourzerh, P. (2000). *Chimie*, **3**, 147–155.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Gau, H.-M., Lee, C.-S., Lin, C.-C. & Jiang, M.-K. (1996). *J. Am. Chem. Soc.* **118**, 2936–2941.
- Liu, S., Ma, L., McGowty, D. & Zubieta, J. (1990). *Polyhedron*, **9**, 1541–1553.
- Salta, J. & Zubieta, J. (1997). *Inorg. Chim. Acta*, **257**, 83–88.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Siemens (1995). *SAINT* and *SMART*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Talbot-Eeckelaers, C. E., Rajaraman, G., Cano, J., Aromí, G., Ruiz, E. & Brechin, E. K. (2006). *Eur. J. Inorg. Chem.* pp. 3382–3392.
- Wu, Y.-T., Ho, Y.-C., Lin, C.-C. & Gau, H.-M. (1996). *Inorg. Chem.* **35**, 5948–5952.

supporting information

Acta Cryst. (2013). E69, m676–m677 [doi:10.1107/S1600536813031504]

Bis(μ -2-hydroxymethyl-2-methylpropane-1,3-diolato)bis[dichloridotitanium(IV)] diethyl ether disolvate

Alastair J. Nielson, Chaohong Shen and Joyce M. Waters

S1. Comment

Transition metal complexes that arise from the *tris*-hydroxymethyl ethane ligand $\text{CH}_3\text{C}(\text{CH}_2\text{OH})_3$ are not widely reported in the literature. Structures identified by X-ray crystallography include the triply deprotonated form in cluster compounds of molybdenum and tungsten (Liu *et al.* 1990; Delmont *et al.* 2000) and dimeric and cluster compounds of chromium (Talbot-Eeckelaers *et al.* 2006), the doubly deprotonated form in dimeric vanadium-oxo complexes (Chang *et al.* 1993; Salta & Zubieta 1997) and the fully protonated form in monomeric yttrium complexes (Chen *et al.* 1997). For titanium only μ 3–O and μ 2–O coordination modes have been identified (Boyle *et al.* 1995).

When TiCl_4 in diethyl ether was reacted with a mixture of $\text{CH}_3\text{C}(\text{CH}_2\text{OSiMe}_3)_3$ and $\text{CH}_3\text{C}(\text{CH}_2\text{OSiMe}_3)_2(\text{CH}_2\text{OH})$ we obtained a small amount of colourless crystals analysing as $\text{TiCl}_2[(\text{OCH}_2)_2(\text{HOCH}_2)\text{CCH}_3]$. 0.5 diethyl ether. One crystal was characterized by X-ray crystallography. The structure consists of a centrosymmetric dimer made up of two $[(\text{OCH}_2)_2(\text{HOCH}_2)\text{CCH}_3]$ ligands forming a tripodal bridging system across two titanium atoms each of which also contain two terminal chloro ligands. One tripodal ligand is positioned above the two Ti atoms and out towards the rear of the molecule and the other is below and out the front with the two related by an inversion centre. The distorted octahedral geometry about Ti is made from one arm of a terminal alkoxo ligand (O2), another from an alcohol ligand (O3) and a third arm from the bridging alkoxo atoms (O1 and O1ⁱ). These latter each lie in *trans*-positions to the two *cis*-related chloro ligands.

For the terminal alkoxo ligand the Ti–O2 distance is 1.760 (1) Å which is indicative of strong π -bonding (see later). The asymmetric bridge system has Ti–O bond lengths of 1.991 (1) and 2.048 (7) Å and the Ti–Cl bonds *trans* to these bridging O atoms also show differences in length, 2.3184 (4) Å for Ti–Cl11 which is *trans* to the longer Ti–O1 and 2.3292 (4) Å for Ti–Cl12 which lies *trans* to the shorter Ti–O1ⁱ bond. The Ti–O bond length for the alcohol oxygen (Ti–O3) is the longest at 2.148 (1) Å. The strongly π -bonded terminal alkoxo ligand O atoms (O2, O2ⁱ) lie *trans* to the weak dative bonds made by the alcohol ligand O atoms (O3ⁱ, O3).

The overall coordination geometry and deprotonation features of the two ligands are identical with that found in the vanadium (v) complex $\{\text{V}_2\text{O}_2\text{Cl}_2[(\text{OCH}_2)_2(\text{HOCH}_2)\text{CCH}_3]_2\}$ (Chang *et al.* 1993; Salta & Zubieta 1997). In $\{\text{M}_2\text{O}_4[(\text{OCH}_2)_3\text{CCH}_3]_2\}^{2-}$ (M = Mo, W) all three arms of the tripod are deprotonated (Liu *et al.* 1990; Delmont *et al.* 2000). Single deprotonation occurs in $\{\text{Cr}_2\text{Cl}_4[(\text{OCH}_2)\text{HOCH}_2]_2(\text{CET})_2\}$ (Talbot-Eeckelaers *et al.* 2006).

The Ti–O bond lengths in the present complex reflect the various coordination modes in the molecule. The Ti–O1 bond lengths [1.991 (1) and 2.048 (1) Å] show the asymmetric nature of the bridging system across the two Ti atoms. The short Ti–O2 bond length [1.760 (1) Å] is associated with an alkoxo ligand. In comparison, terminal alkoxo ligand Ti–O bond lengths range from 1.702 (4) to 1.742 (6) Å in a variety of *iso*-propoxo Ti complexes (Gau *et al.* 1996). The dative nature of the alcohol ligand is shown by the longer Ti–O3 bond length [2.148 (1) Å] in the present complex being slightly longer

than observed for isopropyl alcohol ligated to titanium [bond lengths 2.087 (4) and 2.093 (4) Å] (Wu *et al.* 1996). The Ti–Cl1 and Ti–Cl2 bond lengths [2.3184 (4) and 2.3292 (4) Å] do not differ significantly from each other and are typical of Ti–Cl bonds observed elsewhere. (Gau *et al.* 1996; Wu *et al.* 1996).

The strong π -donor nature of the alkoxo ligand oxygen is shown by the way other coordinated atoms push away from it [O2–Ti–O1, 86.71 (4); O2–Ti–O1ⁱ, 101.78 (5); O–2–Ti–Cl1, 97.18 (4); O2–Ti–Cl2, 93.95 (4)°]. For the dative Ti–O bond all the associated O3ⁱ–Ti–Y angles are 90° or below [range 80.17 (4) to 90.02 (3)°]. The bond angle associated with the bridging Ti–O1–Tiⁱ system [103.17 (4)°] does not differ significantly from comparable angles observed in other complexes. In this regard, it is noted that all known complexes have an alkoxo ligand making up the bridging system. The largest terminal Ti–O–C bond angle is associated with the alkoxo ligand [alkoxo Ti–O2–C3 angle 138.33 (9)° *cf.* alcohol Tiⁱ–O3–C4 angle 126.66 (9)°]. To accommodate the coordination mode of the various oxygen ligands across the two Ti atoms, the O–C–C bond angles of the tripod [range, 112.4 (1) to 113.3 (1)°] are slightly greater than the ideal tetrahedral angle.

S2. Experimental

Using normal bench-top techniques for air-sensitive compounds, TiCl₄ (1.25 g, 6.59 mmol) was cooled to dry-ice temperature and diethyl ether (50 ml) chilled to -20 °C was added. The mixture was warmed to room temperature, heated until all the yellow solid had dissolved and 1,1,1-tris(hydroxymethyl)ethane (2.2 g, 6.6 mmol) in diethyl ether (50 ml) was added to the rapidly stirred solution whereupon a dense colourless precipitate was formed. The mixture was refluxed for 3 h, cooled to room temperature and the remaining solid allowed to settle and the solution was filtered. The volume was reduced to *ca* 30 ml and the solution stood at -20 °C whereupon a mass of crystalline colourless material was deposited. Found: C, 31.06; H, 6.15%. C₁₄H₃₀Cl₄O₆Ti₂ (*i.e.* C₁₀H₂₀Cl₄O₆Ti₂.diethyl ether) requires C, 31.61; H, 5.69%. A crystal was chosen from the mass and the X-ray crystal structure obtained. This molecule corresponded to C₁₀H₂₀Cl₄O₆Ti₂.*bis*-diethyl ether.

S3. Refinement

All H atoms (except H3) were included in calculated positions and refined using a riding model with $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for H on secondary C atoms and $1.5U_{\text{eq}}(\text{C})$ for those on tertiary C atoms. C–H distances of 0.99Å and 0.96Å were assumed for tertiary C and secondary C atoms respectively. H3 was located on a difference map and its *x*, *y*, *z* co-ordinates and isotropic thermal parameter refined.

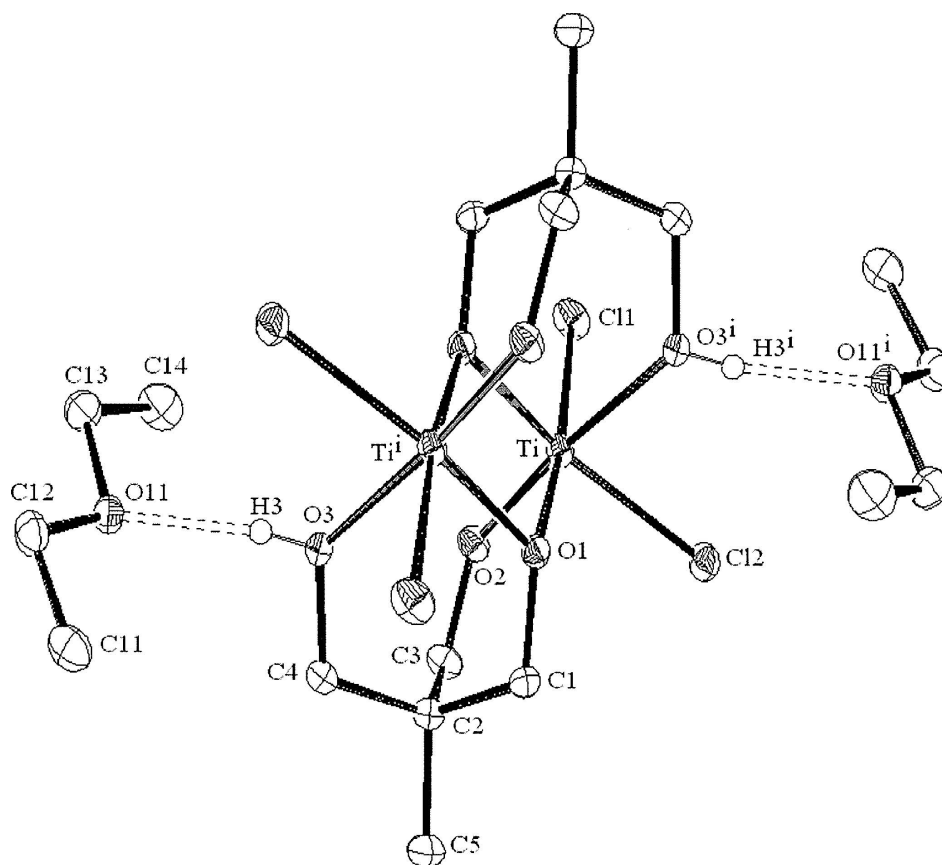


Figure 1

ORTEP diagram of molecule, at the 50% probability level, showing the numbering system. Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Bis(μ -2-hydroxymethyl-2-methylpropane-1,3-diolato)bis[dichloridotitanium(IV)] diethyl ether disolvate

Crystal data

$[\text{Ti}_2\text{Cl}_4(\text{C}_5\text{H}_{10}\text{O}_3)_2] \cdot 2\text{C}_4\text{H}_{10}\text{O}$

$M_r = 622.10$

Triclinic, $P\bar{1}$

Hall symbol: $-P\ 1$

$a = 7.9617\ (3)\ \text{\AA}$

$b = 9.6379\ (4)\ \text{\AA}$

$c = 10.5783\ (5)\ \text{\AA}$

$\alpha = 71.351\ (1)^\circ$

$\beta = 82.023\ (1)^\circ$

$\gamma = 66.757\ (1)^\circ$

$V = 706.60\ (5)\ \text{\AA}^3$

$Z = 1$

$F(000) = 324$

$D_x = 1.462\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 5595 reflections

$\theta = 2\text{--}25^\circ$

$\mu = 0.98\ \text{mm}^{-1}$

$T = 150\ \text{K}$

Plate, colourless

$0.26 \times 0.24 \times 0.10\ \text{mm}$

Data collection

Siemens SMART CCD
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Area detector ω scans

Absorption correction: multi-scan
(Blessing, 1995)

$T_{\min} = 0.766, T_{\max} = 0.892$

6510 measured reflections

2661 independent reflections

2417 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.015$
 $\theta_{\text{max}} = 25.7^\circ$, $\theta_{\text{min}} = 2.0^\circ$
 $h = -9 \rightarrow 9$

$k = -10 \rightarrow 11$
 $l = 0 \rightarrow 12$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.022$
 $wR(F^2) = 0.061$
 $S = 1.04$
 2661 reflections
 152 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: inferred from
 neighbouring sites
 H atoms treated by a mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 0.2355P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.31 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.27 \text{ e } \text{\AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ti	0.58094 (3)	0.61520 (3)	0.39188 (2)	0.01725 (9)
Cl1	0.74357 (5)	0.59557 (5)	0.19464 (4)	0.02805 (11)
Cl2	0.47954 (5)	0.88725 (4)	0.35265 (4)	0.02495 (10)
O1	0.43149 (13)	0.59722 (11)	0.56614 (9)	0.0177 (2)
O2	0.76654 (13)	0.57443 (12)	0.48899 (10)	0.0217 (2)
O3	0.66826 (14)	0.32177 (13)	0.70683 (10)	0.0197 (2)
C1	0.4634 (2)	0.65978 (17)	0.66438 (14)	0.0209 (3)
H1A	0.3764	0.6490	0.7400	0.025*
H1B	0.4384	0.7737	0.6237	0.025*
C2	0.6586 (2)	0.57709 (17)	0.71785 (15)	0.0211 (3)
C3	0.7972 (2)	0.60351 (19)	0.60594 (15)	0.0248 (3)
H3A	0.7897	0.7137	0.5832	0.030*
H3B	0.9221	0.5328	0.6382	0.030*
H3	0.721 (3)	0.236 (3)	0.737 (2)	0.038 (6)*
C4	0.6997 (2)	0.40296 (17)	0.78961 (15)	0.0227 (3)
H4A	0.8288	0.3514	0.8178	0.027*
H4B	0.6216	0.3934	0.8709	0.027*
C5	0.6733 (2)	0.65305 (19)	0.82181 (16)	0.0296 (4)
H5A	0.5924	0.6323	0.8981	0.044*
H5B	0.6371	0.7672	0.7813	0.044*
H5C	0.7997	0.6079	0.8522	0.044*

O11	0.89033 (14)	0.03405 (12)	0.82316 (10)	0.0220 (2)
C11	0.7018 (2)	0.0355 (2)	1.01998 (16)	0.0309 (4)
H11A	0.7672	0.0891	1.0464	0.046*
H11B	0.6635	-0.0316	1.0999	0.046*
H11C	0.5939	0.1143	0.9687	0.046*
C12	0.8258 (2)	-0.06469 (18)	0.93561 (16)	0.0276 (3)
H12A	0.9306	-0.1496	0.9889	0.033*
H12B	0.7584	-0.1142	0.9041	0.033*
C13	1.0030 (2)	-0.0498 (2)	0.73231 (17)	0.0305 (4)
H13A	0.9318	-0.0910	0.6945	0.037*
H13B	1.1090	-0.1401	0.7797	0.037*
C14	1.0679 (2)	0.0633 (2)	0.62220 (18)	0.0375 (4)
H14A	0.9624	0.1497	0.5732	0.056*
H14B	1.1492	0.0074	0.5610	0.056*
H14C	1.1343	0.1064	0.6609	0.056*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ti	0.01564 (14)	0.01876 (14)	0.01493 (14)	-0.00583 (10)	0.00015 (10)	-0.00266 (10)
C11	0.0258 (2)	0.0379 (2)	0.01864 (19)	-0.01292 (16)	0.00543 (15)	-0.00699 (16)
C12	0.0292 (2)	0.01963 (18)	0.0251 (2)	-0.01055 (15)	-0.00415 (15)	-0.00208 (14)
O1	0.0167 (5)	0.0178 (5)	0.0160 (5)	-0.0040 (4)	0.0002 (4)	-0.0047 (4)
O2	0.0178 (5)	0.0266 (5)	0.0192 (5)	-0.0073 (4)	-0.0004 (4)	-0.0058 (4)
O3	0.0222 (5)	0.0149 (5)	0.0202 (5)	-0.0041 (4)	-0.0047 (4)	-0.0046 (4)
C1	0.0239 (7)	0.0196 (7)	0.0181 (7)	-0.0051 (6)	0.0006 (6)	-0.0084 (6)
C2	0.0241 (7)	0.0200 (7)	0.0196 (7)	-0.0070 (6)	-0.0026 (6)	-0.0070 (6)
C3	0.0248 (8)	0.0308 (8)	0.0221 (8)	-0.0129 (6)	-0.0025 (6)	-0.0078 (6)
C4	0.0273 (8)	0.0217 (7)	0.0188 (7)	-0.0074 (6)	-0.0051 (6)	-0.0057 (6)
C5	0.0405 (9)	0.0274 (8)	0.0245 (8)	-0.0122 (7)	-0.0050 (7)	-0.0108 (7)
O11	0.0222 (5)	0.0197 (5)	0.0201 (5)	-0.0051 (4)	0.0000 (4)	-0.0042 (4)
C11	0.0341 (9)	0.0376 (9)	0.0224 (8)	-0.0189 (8)	0.0021 (7)	-0.0046 (7)
C12	0.0321 (9)	0.0237 (8)	0.0244 (8)	-0.0124 (7)	-0.0032 (7)	0.0002 (6)
C13	0.0270 (8)	0.0294 (8)	0.0296 (9)	-0.0014 (7)	-0.0008 (7)	-0.0130 (7)
C14	0.0289 (9)	0.0492 (11)	0.0312 (9)	-0.0110 (8)	0.0069 (7)	-0.0151 (8)

Geometric parameters (Å, °)

Ti—O2	1.7601 (10)	C3—H3B	0.9900
Ti—O1 ⁱ	1.9911 (10)	C4—H4A	0.9900
Ti—O1	2.0478 (10)	C4—H4B	0.9900
Ti—O3 ⁱ	2.1481 (11)	C5—H5A	0.9800
Ti—C11	2.3184 (4)	C5—H5B	0.9800
Ti—C12	2.3292 (4)	C5—H5C	0.9800
Ti—Ti ⁱ	3.1649 (5)	O11—C13	1.4374 (19)
O1—C1	1.4501 (17)	O11—C12	1.4413 (18)
O1—Ti ⁱ	1.9911 (10)	C11—C12	1.502 (2)
O2—C3	1.4243 (18)	C11—H11A	0.9800

O3—C4	1.4473 (18)	C11—H11B	0.9800
O3—Ti ⁱ	2.1481 (11)	C11—H11C	0.9800
O3—H3	0.74 (2)	C12—H12A	0.9900
C1—C2	1.533 (2)	C12—H12B	0.9900
C1—H1A	0.9900	C13—C14	1.509 (3)
C1—H1B	0.9900	C13—H13A	0.9900
C2—C4	1.523 (2)	C13—H13B	0.9900
C2—C3	1.533 (2)	C14—H14A	0.9800
C2—C5	1.542 (2)	C14—H14B	0.9800
C3—H3A	0.9900	C14—H14C	0.9800
O2—Ti—O1 ⁱ	101.78 (5)	C2—C3—H3A	109.1
O2—Ti—O1	86.71 (4)	O2—C3—H3B	109.1
O1 ⁱ —Ti—O1	76.83 (4)	C2—C3—H3B	109.1
O2—Ti—O3 ⁱ	172.39 (5)	H3A—C3—H3B	107.9
O1 ⁱ —Ti—O3 ⁱ	80.17 (4)	O3—C4—C2	112.55 (12)
O1—Ti—O3 ⁱ	86.59 (4)	O3—C4—H4A	109.1
O2—Ti—C11	97.18 (4)	C2—C4—H4A	109.1
O1 ⁱ —Ti—C11	93.21 (3)	O3—C4—H4B	109.1
O1—Ti—C11	169.89 (3)	C2—C4—H4B	109.1
O3 ⁱ —Ti—C11	90.02 (3)	H4A—C4—H4B	107.8
O2—Ti—C12	93.95 (4)	C2—C5—H5A	109.5
O1 ⁱ —Ti—C12	158.75 (3)	C2—C5—H5B	109.5
O1—Ti—C12	90.05 (3)	H5A—C5—H5B	109.5
O3 ⁱ —Ti—C12	82.46 (3)	C2—C5—H5C	109.5
C11—Ti—C12	98.956 (16)	H5A—C5—H5C	109.5
O2—Ti—Ti ⁱ	95.24 (4)	H5B—C5—H5C	109.5
O1 ⁱ —Ti—Ti ⁱ	39.05 (3)	C13—O11—C12	112.91 (12)
O1—Ti—Ti ⁱ	37.78 (3)	C12—C11—H11A	109.5
O3 ⁱ —Ti—Ti ⁱ	81.61 (3)	C12—C11—H11B	109.5
C11—Ti—Ti ⁱ	132.238 (18)	H11A—C11—H11B	109.5
C12—Ti—Ti ⁱ	125.940 (16)	C12—C11—H11C	109.5
C1—O1—Ti ⁱ	124.13 (8)	H11A—C11—H11C	109.5
C1—O1—Ti	118.13 (8)	H11B—C11—H11C	109.5
Ti ⁱ —O1—Ti	103.17 (4)	O11—C12—C11	108.69 (13)
C3—O2—Ti	138.33 (9)	O11—C12—H12A	110.0
C4—O3—Ti ⁱ	126.66 (9)	C11—C12—H12A	110.0
C4—O3—H3	106.5 (16)	O11—C12—H12B	110.0
Ti ⁱ —O3—H3	117.1 (16)	C11—C12—H12B	110.0
O1—C1—C2	113.32 (11)	H12A—C12—H12B	108.3
O1—C1—H1A	108.9	O11—C13—C14	108.13 (14)
C2—C1—H1A	108.9	O11—C13—H13A	110.1
O1—C1—H1B	108.9	C14—C13—H13A	110.1
C2—C1—H1B	108.9	O11—C13—H13B	110.1
H1A—C1—H1B	107.7	C14—C13—H13B	110.1
C4—C2—C1	110.95 (12)	H13A—C13—H13B	108.4
C4—C2—C3	112.76 (13)	C13—C14—H14A	109.5
C1—C2—C3	110.72 (12)	C13—C14—H14B	109.5

C4—C2—C5	107.06 (12)	H14A—C14—H14B	109.5
C1—C2—C5	108.02 (12)	C13—C14—H14C	109.5
C3—C2—C5	107.07 (13)	H14A—C14—H14C	109.5
O2—C3—C2	112.41 (12)	H14B—C14—H14C	109.5
O2—C3—H3A	109.1		

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

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O3—H3...O11	0.74 (2)	1.89 (2)	2.6233 (14)	168 (2)