

Concerning the structures of Lewis base adducts of titanium(IV) hexafluoroisopropoxide

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The reaction of titanium(IV) chloride with sodium hexafluoroisopropoxide, carried out in hexafluoroisopropanol, produces titanium(IV) hexafluoroisopropoxide, which is a liquid at room temperature. Recrystallization from coordinating solvents, such as acetonitrile or tetrahydrofuran, results in the formation of bis-solvate complexes. These compounds are of interest as possible Ziegler–Natta polymerization catalysts. The acetonitrile complex had been structurally characterized previously and adopts a distorted octahedral structure in which the nitrile ligands adopt a *cis* configuration, with nitrogen lone pairs coordinated to the metal. The low-melting tetrahydrofuran complex has not provided crystals suitable for single-crystal X-ray analysis. However, the structure of chloridotris(hexafluoroisopropoxido- κO)bis(tetrahydrofuran- κO)titanium(IV), $[\text{Ti}(\text{C}_3\text{HF}_6\text{O})_3\text{Cl}(\text{C}_4\text{H}_8\text{O})_2]$, has been obtained and adopts a distorted octahedral coordination geometry, with a facial arrangement of the alkoxide ligands and adjacent tetrahydrofuran ligands, coordinated by way of metal–oxygen polar coordinate interactions.

1. Introduction

Early transition-metal coordination chemistry involving Group IV metals (Ti, Hf, and Zr) has been of interest for many years, with applications as Ziegler–Natta (ZN)-type polymerization catalysts (Ziegler *et al.*, 1955). It is generally accepted that effective ZN catalysts involve alkylated and coordinatively unsaturated species that complex an olefin monomer, and then allow for insertion into the metal–carbon bond by way of the so-called Cossee–Arlman mechanism (Hartwig, 2010). Theoretical studies predict that the electron densities of the titanium ion play a major role in the effectiveness of the catalyst (Piovano *et al.*, 2021). Previously, the author and co-workers published a description of a series of titanium fluoroalkoxide complexes, obtained primarily by alcohol-exchange reactions. The nature of the products appeared to depend upon the acidity and steric requirements of the fluoroalcohol and the alkyl groups of the titanium alkoxide starting materials (Campbell *et al.*, 1994; Fisher *et al.*, 1993). In several cases, the products adopted dimeric structures with bridging alkoxide ligands and/or coordinated alcohol ligands to satisfy the coordinative unsaturation of the titanium(IV) ions. In at least one case, a titanium coordination site was filled by the interaction with an F atom, that wrapped around and formed a weak interaction. The primary impetus of this work was to use the electron-withdrawing fluoroalkoxide ligands as pseudohalides to provide significantly more Lewis acidity to the metal ion, yet retain the steric control associated with the alkoxide ligands. Sawamoto & Kamigaito (1996) have described using $\text{TiCl}_2(\text{OR})_2$ compounds, where OR represents both alkyl alkoxides and

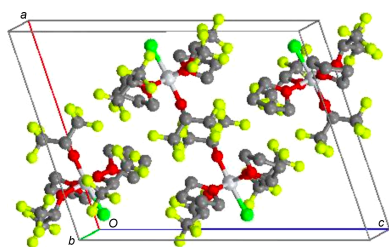
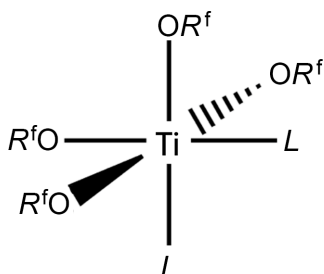


Table 1
 Experimental details.

Crystal data	
Chemical formula	[Ti(C ₃ HF ₆ O) ₃ Cl(C ₄ H ₈ O) ₂]
<i>M_r</i>	728.67
Crystal system, space group	Monoclinic, <i>P</i> ₂ ₁ / <i>c</i>
Temperature (K)	100
<i>a</i> , <i>b</i> , <i>c</i> (Å)	14.050 (4), 10.701 (3), 18.692 (5)
β (°)	108.450 (3)
<i>V</i> (Å ³)	2665.9 (13)
<i>Z</i>	4
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.58
Crystal size (mm)	0.26 × 0.18 × 0.18
Data collection	
Diffractometer	Bruker APEX CCD
Absorption correction	Multi-scan [TWINABS (Sheldrick, 2015c) and SADABS (Krause <i>et al.</i> , 2015)]
<i>T</i> _{min} , <i>T</i> _{max}	0.864, 0.904
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	67346, 4968, 3934
<i>R</i> _{int}	0.058
(sin θ / λ) _{max} (Å ⁻¹)	0.610
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.042, 0.123, 0.98
No. of reflections	4968
No. of parameters	379
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.56, -0.71

Computer programs: APEX2 (Bruker, 2007), SAINT (Bruker, 2007), SHELXT (Sheldrick, 2015a), SHELXL2018 (Sheldrick, 2015b), and Mercury (Macrae *et al.*, 2020).

phenoxides, as living polymerization catalysts that are potentially stereospecific. As part of prior work on the related titanium(IV) fluoroalkoxides, the author and co-workers described the preparation and characterization of two hexafluoroisopropoxide complexes with the general formula Ti(OR^f)₄L₂, where *L* represents the coordinating solvents acetonitrile (in complex **1**) and tetrahydrofuran (THF) (in **2**). A single-crystal X-ray structure determination of the acetonitrile complex indicated a monomeric structure in which the coordination geometry of the titanium was essentially octahedral, with *cis*-nitrile ligands acting as Lewis bases (Fig. 1), coordinating by way of nitrogen lone pairs. This result was somewhat interesting, but not terribly surprising, and consistent with the structures of other similar complexes that had been characterized previously (Bradley, 1959; Bradley *et al.*, 1978).


Figure 1
 The presumed octahedral structure of monomeric bis-Lewis base adducts of titanium(IV) alkoxides.

On the other hand, we did not report the crystal structure of the tetrahydrofuran complex **2**. In fact, we attempted to obtain a single-crystal X-ray structure of this compound on several occasions, but were unable to obtain crystals of suitable quality to publish the results. However, the diffraction data we did obtain appeared to be most consistent with an auto-ionization isomer, in which an octahedrally coordinated [Ti(OR^f)₂L₄]²⁺ cation and a [Ti(OR^f)₆]²⁻ anion had formed. We have structurally characterized one other example of an octahedrally coordinated Ti^{IV} dianionic hexakisfluorophenoxide, Na₂Ti(OC₆F₅)₆(THF)₂, so at least the formation of the dianion is plausible. [We have recently described the X-ray structures of the tetrakis(pentafluorophenoxide)bis(tetrahydrofuran)titanium(IV) complex and the hexakis(pentafluorophenoxide)titanium(IV) complex anion (Van Der Sluys *et al.*, 2018).]

There are a limited number of examples of cationic titanium(IV) alkoxides which also include cyclopentadienyl ligands (Fandos *et al.*, 2007). Perhaps the most relevant example that we are aware of is a cyclopentadienyl titanium(IV) trication, in which there are coordinated acetonitrile ligands and three SbCl₆⁻ anions that act as counter-ions (Willey *et al.*, 1994). Our spectroscopic evidence for auto-ionization, based on NMR and IR spectroscopic and conductivity measurements, was inconclusive at best and we were unsure if the ionization isomer represented a minor component or was representative of the bulk of the material. While ionization isomers for metal complexes are known (Barbier *et al.*, 1972), we were unwilling to publish our speculative results. More recent results concerning the auto-ionization of metal coordination compounds (Tebbe & Muetterties, 1967; Kamata *et al.*, 2012; Giesbrecht *et al.*, 2004; Xie *et al.*, 1996; Niemeyer, 2001) has encouraged a revisit of this work. Described herein are the most recent efforts, including the X-ray crystal structure of a mixed chloride/fluoroalkoxide complex, which adopts a structure similar to that of the neutral acetonitrile complex.

2. Experimental

2.1. Synthesis

All synthetic procedures were carried out using standard Schlenk techniques or in a purified nitrogen atmosphere using a Braun UNILab glove-box. Solvents were purified by distillation from a sodium benzophenone ketal solution and stored in glass containers fitted with solvent seal fittings. IR spectra were recorded as KBr pellets, by grinding small portions of the sample with dried potassium bromide using an agate mortar and pestle in the glove-box. The Fourier transform IR (FT-IR) spectra were recorded on a ThermoScientific Nicolet iS10 FT-IR spectrometer. A background spectrum was subtracted to produce the percent transmittance spectrum of the sample. Residual gaseous carbon dioxide asymmetric vibrations were sometimes observed in the 2400 cm⁻¹ region, due to incomplete background subtraction, and calibration was checked regularly using a film of polystyrene. NMR spectra were

collected using a Bruker DPX 300 MHz spectrometer. Deuterated solvents, such as benzene- d_6 (≥ 99.6 atom% D) and dichloromethane- d_2 (≥ 99.9 atom% D) were purchased from Aldrich and degassed using a freeze–pump–thaw (FPT) method, and stored in the glove-box over molecular sieves.

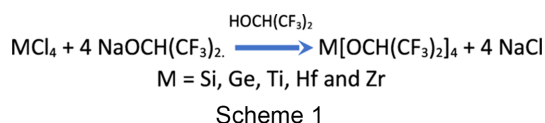
2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The selected crystal was twinned by non-merohedry. The twinning in intensity data was effectively removed by the integration and absorption correction programs. The positions of the H atoms were initially determined by geometry and were refined using a riding model. H-atom displacement parameters were set at 1.2 times the isotropic equivalent displacement parameters of the bonded atoms.

3. Results and discussion

3.1. Synthesis

Mazdiyasi *et al.* (1971) described the synthesis of a series of hexafluoroisopropoxides of the Group IV elements by way of a metathesis approach, in which the metal chlorides were reacted with four equivalents of sodium hexafluoroisopropoxide, with the corresponding alcohol as solvent (Scheme 1). The titanium(IV) compound is a colorless liquid that can be obtained in high yield by distillation. Mazdiyasi reported that these compounds could be recrystallized from a variety of solvents, including benzene, acetone, diethyl ether, and tetrahydrofuran (THF), and indicated that the ethers reacted to form solvate complexes, but did not provide structural characterization data for these solvate complexes.



In our laboratory, we first prepared the sodium hexafluoroisopropoxide *in situ* by reacting sodium hydride with excess hexafluoroisopropanol and, after the evolution of hydrogen stopped, titanium(IV) chloride was added slowly while stirring. The product was recovered by first removing the excess hexafluoroalcohol *in vacuo* and then gently heating the somewhat less volatile titanium(IV) hexafluoroisopropoxide and condensing the liquid product in a liquid-nitrogen-cooled trap, which usually resulted in excellent yields. We typically accessed the purity of the product based on NMR spectroscopy, but we suspect that there is rapid ligand exchange on the NMR time scale at room temperature between various species that might be present in solution. Borden & Hammer (1970) also observed rapid ligand exchange at room temperature for a mixture of TiCl_4 and TiF_4 in THF solution. At -60°C , exchange was slowed sufficiently to observe several species in solution. The ^{19}F NMR data were most easily interpreted as having resulted from a complex mixture

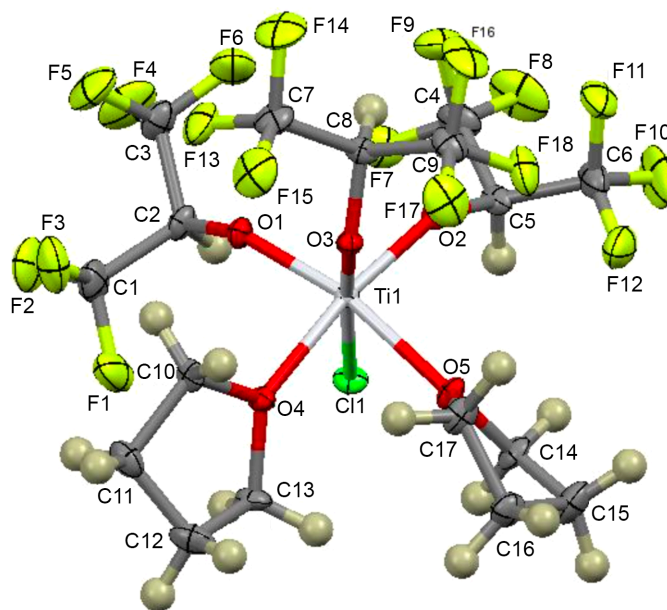


Figure 2
The molecular structure of compound **3**, showing the numbering scheme used. Displacement ellipsoids are drawn at the 50% probability level.

of compounds in which *cis*- $\text{TiF}_4(\text{THF})_2$ was present, but also that there were additional compounds having both chloride and fluoride coordinated to monomeric octahedrally coordinated titanium(IV) species with two THF molecules occupying *cis*, but not *trans*, positions. While their interpretation of the data is very well reasoned, it is not totally clear that these data eliminate the possible presence of ionic species as well, such as $\text{TiF}_5(\text{THF})^-$, TiF_6^{2-} , $\text{TiF}_3(\text{THF})_3^+$, and $\text{TiF}_2(\text{THF})_4^{2+}$, as additional components in solution.

When the titanium(IV) hexafluoroisopropoxide is recrystallized from coordinating solvents, such as acetonitrile or THF, the bis-solvate complexes, $\text{Ti}(\text{OR}^f)_4\text{L}_2$, are formed based on combustion elemental analysis and spectroscopic techniques, such as NMR and IR (Campbell *et al.*, 1994; Fisher *et al.*, 1993). The acetonitrile complex is a very stable crystalline solid that can be sublimed intact to form large nearly cubic crystals. The THF complex is extremely soluble in THF and has a relatively low melting point, which is slightly above room temperature (Campbell *et al.*, 1994). Unfortunately, it has not been possible to produce single crystals of compound **2** of suitable quality for a convincing single-crystal X-ray analysis. However, on at least one occasion, recrystallization from a mixture of hexane and THF at -20°C , produced a small number of crystals which were suitable for X-ray analysis. It appears that this higher-melting crystalline material was a minor component, with the formula $\text{TiCl}[\text{OCH}(\text{CF}_3)_2]_3(\text{THF})_2$ (**3**), resulting from incomplete substitution of chlorides for fluoroalkoxides in the metathesis reaction.

3.2. Crystal structure

The molecular structure of **3** shown in Fig. 2 emphasizes the nearly octahedral coordination geometry of the Ti atom. The fluoroalkoxide ligands form a facial arrangement, with the

Table 2
 Selected geometric parameters (Å, °).

Ti1—O1	1.8386 (17)	Ti1—O4	2.1043 (17)
Ti1—O2	1.8426 (17)	Ti1—O5	2.1593 (17)
Ti1—O3	1.8679 (17)	Ti1—Cl1	2.3399 (9)
O1—Ti1—O2	100.14 (8)	O2—Ti1—Cl1	90.52 (5)
O1—Ti1—O3	94.69 (7)	O3—Ti1—Cl1	172.19 (6)
O2—Ti1—O3	92.72 (7)	O4—Ti1—Cl1	90.02 (5)
O1—Ti1—O4	88.84 (7)	O5—Ti1—Cl1	85.92 (5)
O2—Ti1—O4	170.98 (7)	C2—O1—Ti1	140.75 (15)
O3—Ti1—O4	85.68 (7)	C5—O2—Ti1	142.97 (15)
O1—Ti1—O5	167.56 (7)	C8—O3—Ti1	130.80 (15)
O2—Ti1—O5	92.10 (7)	C13—O4—Ti1	129.17 (14)
O3—Ti1—O5	86.87 (7)	C10—O4—Ti1	120.92 (13)
O4—Ti1—O5	78.95 (6)	C14—O5—Ti1	129.22 (14)
O1—Ti1—Cl1	91.72 (6)	C17—O5—Ti1	121.54 (13)

chloride and two THF ligands on opposing sides. Table 2 provides relevant bond length and angle data. Fractional coordinates and other crystallographic data can be found in the supporting information.

The coordination geometry of **3** is best described as distorted octahedral. The average fluoroalkoxide Ti—O bond length [1.85 (1) Å] compares very well with the average fluoroalkoxide Ti—O bond lengths reported previously for compound **1** [1.84 (1) Å]. Not surprisingly, the longest metal–ligand bond length is the bond between the titanium and chloride [2.3399 (9) Å], which is similar to the terminal Ti—Cl distances observed in other octahedrally coordinated titanium compounds (Sarsfield *et al.*, 1999; McCarthy *et al.*, 2020; Nielson *et al.*, 2001; Wright & Williams, 1968). There appears to be a slight but significant *trans* influence (Burdett & Albright, 1979) in the Ti—OR^f bond lengths, with the Ti—O3 bond length, which is *trans* to the chloride ligand, being slightly longer than the Ti—O1/O2 bond lengths, which are *trans* to the coordinated THF ligands. The Ti—O bond lengths for the coordinated THF ligands are significantly longer than the alkoxide bond lengths [average 2.13 (1) Å], consistent with the weaker polar coordinate interactions of these ligands. The *trans* influence is due to the weakly coordinating neutral THF ligands that allow the *trans*-fluoroalkoxides to bond more strongly to titanium than the alkoxide that is *trans* to the formally anionic chloride ligand.

The large Ti—O—C angles of the fluoroalkoxides are also comparable to those observed in compound **1** and consistent with other structurally characterized Ti^{IV} alkoxide complexes (Schubert *et al.*, 2020). These angles are best interpreted as resulting from significant oxygen-to-titanium $p\pi \rightarrow d\pi$ bonding. Titanium(IV) has a $3d^0$ electronic configuration and therefore in an octahedral ligand field, the empty t_{2g} set (d_{xy} , d_{xz} , and d_{yz}) of d orbitals can accept electrons from π -donor ligands, such as alkoxides. Presumably this is tempered somewhat in fluoroalkoxide ligands due to the electron-withdrawing nature of the —CF₃ groups, as compared with alkyl-alkoxide ligands, making the Ti—OR^f interactions more halide-like in nature. The presumed order of π -bonding is proposed to be OR^f > Cl > THF, consistent with the *trans*-influence effects that we observe in **3** and consistent with the order of F > Cl > THF used by Borden & Hammer (1970) to

justify their proposed stereochemical interpretation of the ¹⁹F solution NMR data for the TiF₄/TiCl₄/THF system. Perhaps even more straightforward, the *trans* influence in these compounds can be interpreted based on hard–soft Lewis acid–base theory (Pearson, 1963; Jolly, 1984).

4. Conclusions

While the crystal structure of compound **3** reported here clearly indicates a monomeric molecular coordination compound and not an ionization isomer, as speculated for compound **2**, it is not totally clear if replacing the final chloride ligand would tip the scale in favor of such a structure. There may be a subtle balance between the steric factors of the coordinated ligands, the degree of covalency or ionic interactions associated with the metal cation and the ligands, as well as intermolecular forces of attraction between the coordination complex and the solvent. The initial hypothesis suggested that an increase in the ionic nature of the alkoxide ligands would produce favorable properties that would facilitate polymerization catalysis. Coordinately unsaturated cationic transition-metal species are particularly promising in this regard. We note that the ionic radius of the titanium(IV) ion (0.745 Å), is smaller than the highly ionic lanthanide ions (1.00–1.17 Å) (Shannon, 1976), with the latter producing autoionization in certain cases (Fandos *et al.*, 2007). It is also not clear if there are several structural possibilities that might exist in solution, all of which are rapidly exchanging, and that crystallization of a solid does not necessarily indicate what species are present in solution. It is hoped that the solvent molecules are labile enough to provide open coordination sites and that alkylation of these compounds will produce effective olefin polymerization catalysts. Further studies are currently in progress.

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William G. Van Der Sluys

Computing details

Chloridotris(hexafluoroisopropoxido- κ O)bis(tetrahydrofuran- κ O)titanium(IV)

Crystal data

[Ti(C₃HF₆O)₃Cl(C₄H₈O)₂]

$M_r = 728.67$

Monoclinic, $P2_1/c$

$a = 14.050$ (4) Å

$b = 10.701$ (3) Å

$c = 18.692$ (5) Å

$\beta = 108.450$ (3)°

$V = 2665.9$ (13) Å³

$Z = 4$

$F(000) = 1448$

$D_x = 1.816$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 9958 reflections

$\theta = 2.2$ – 24.3 °

$\mu = 0.57$ mm⁻¹

$T = 100$ K

Block, colourless

$0.26 \times 0.18 \times 0.18$ mm

Data collection

Bruker APEX CCD
diffractometer

φ and ω scans

Absorption correction: multi-scan

[TWINABS (Sheldrick, 2015c) and SADABS
(Krause *et al.* (2015))]

$T_{\min} = 0.864$, $T_{\max} = 0.904$

67346 measured reflections

4968 independent reflections

3934 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.058$

$\theta_{\max} = 25.7$ °, $\theta_{\min} = 2.2$ °

$h = -16$ → 16

$k = 0$ → 13

$l = 0$ → 22

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.042$

$wR(F^2) = 0.123$

$S = 0.98$

4968 reflections

379 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier
map

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.090P)^2 + 0.4P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.56$ e Å⁻³

$\Delta\rho_{\min} = -0.71$ e Å⁻³

Special details

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

Refinement. A colorless block-shaped crystal of dimensions 0.180 × 0.182 × 0.262 mm was selected for structural analysis. Intensity data for this compound were collected using a diffractometer with a Bruker APEX CCD area detector and graphite-monochromated Mo *K*α radiation ($\lambda = 0.71073 \text{ \AA}$). The sample was cooled to 100(±2) K. Cell parameters were determined from a least-squares fit of 9958 peaks in the range $2.22 < \theta < 24.29^\circ$. A total of 67346 data were measured in the range $2.223 < \theta < 25.677^\circ$ using ω oscillation frames. The data were corrected for absorption by the empirical method giving minimum and maximum transmission factors of 0.864 and 0.904 (Krause *et al.*, 2015). The displacement ellipsoids were drawn at the 50% probability level. The data were merged to form a set of 4968 independent data with $R(\text{int}) = 0.0582$ and a coverage of 99.6%. The monoclinic space group *P21/c* was determined by systematic absences and statistical tests and verified by subsequent refinement. The structure was solved by direct methods and refined by full-matrix least-squares methods on F^2 .

A total of 379 parameters were refined against 4968 data to give $wR(F^2) = 0.1229$ and $S = 0.984$ for weights of $w = 1/[s^2(F^2) + (0.0900 P)^2 + 0.4000 P]$, where $P = [F_o^2 + 2F_c^2]/3$. The final $R(F)$ was 0.0420 for the 3934 observed, $[F > 4 \sigma(F)]$, data. The largest shift/s.u. was 0.001 in the final refinement cycle. The final difference map had maxima and minima of 0.564 and -0.707 e \AA^{-3} , respectively. The X-ray crystallographic data has been submitted to the Cambridge Structural Database.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Ti1	0.23757 (3)	0.27877 (4)	0.52659 (2)	0.01242 (14)
Cl1	0.08372 (4)	0.29034 (6)	0.54994 (3)	0.01954 (17)
F1	0.00839 (14)	0.35382 (17)	0.35953 (10)	0.0471 (5)
F2	-0.04629 (13)	0.20602 (18)	0.27930 (10)	0.0453 (5)
F3	0.09556 (14)	0.29234 (17)	0.29047 (10)	0.0440 (5)
F4	0.01723 (15)	-0.03175 (17)	0.33302 (11)	0.0519 (5)
F5	0.13441 (15)	0.04539 (17)	0.29625 (10)	0.0468 (5)
F6	0.17015 (15)	-0.03587 (15)	0.40541 (10)	0.0452 (5)
F7	0.11586 (12)	-0.03793 (16)	0.54016 (10)	0.0399 (4)
F8	0.18142 (16)	-0.14042 (17)	0.64284 (12)	0.0559 (6)
F9	0.26588 (13)	-0.11180 (16)	0.56607 (10)	0.0388 (4)
F10	0.30104 (16)	-0.0130 (2)	0.76008 (10)	0.0593 (6)
F11	0.40387 (12)	-0.02103 (17)	0.69618 (9)	0.0378 (4)
F12	0.36859 (14)	0.15502 (18)	0.73564 (9)	0.0432 (5)
F13	0.35957 (13)	0.19588 (17)	0.37698 (9)	0.0366 (4)
F14	0.50952 (14)	0.12417 (18)	0.42146 (10)	0.0458 (5)
F15	0.48170 (14)	0.32223 (16)	0.42168 (10)	0.0411 (5)
F16	0.59612 (12)	0.12469 (18)	0.57080 (10)	0.0455 (5)
F17	0.57008 (12)	0.32210 (17)	0.57630 (10)	0.0419 (5)
F18	0.51019 (12)	0.19529 (17)	0.63939 (9)	0.0371 (4)
O1	0.17872 (12)	0.20501 (15)	0.43429 (9)	0.0173 (4)
O2	0.27198 (12)	0.13877 (15)	0.58666 (9)	0.0166 (4)
O3	0.36457 (12)	0.29014 (15)	0.51504 (9)	0.0151 (4)
O4	0.21035 (12)	0.45446 (15)	0.47342 (9)	0.0159 (4)
O5	0.29344 (12)	0.40218 (15)	0.62214 (9)	0.0171 (4)
C1	0.0363 (2)	0.2527 (3)	0.32909 (16)	0.0317 (7)

C2	0.08771 (19)	0.1580 (2)	0.39018 (14)	0.0202 (6)
H2	0.044296	0.144049	0.422740	0.024*
C3	0.1030 (2)	0.0337 (3)	0.35594 (15)	0.0288 (6)
C4	0.2017 (2)	-0.0576 (3)	0.59623 (17)	0.0303 (7)
C5	0.24189 (19)	0.0646 (2)	0.63554 (14)	0.0199 (5)
H5	0.186717	0.108028	0.648787	0.024*
C6	0.3300 (2)	0.0457 (3)	0.70725 (15)	0.0313 (7)
C7	0.4460 (2)	0.2102 (3)	0.43168 (16)	0.0273 (6)
C8	0.43050 (18)	0.1979 (2)	0.50863 (14)	0.0175 (5)
H8	0.400039	0.114424	0.511673	0.021*
C9	0.5278 (2)	0.2099 (3)	0.57390 (16)	0.0268 (6)
C10	0.24761 (19)	0.4840 (2)	0.41010 (13)	0.0188 (5)
H10A	0.236777	0.412906	0.374522	0.023*
H10B	0.320045	0.504382	0.428445	0.023*
C11	0.1864 (2)	0.5961 (3)	0.37291 (15)	0.0265 (6)
H11A	0.224154	0.649274	0.347877	0.032*
H11B	0.122329	0.570331	0.335365	0.032*
C12	0.1688 (2)	0.6630 (2)	0.43848 (17)	0.0300 (7)
H12A	0.111163	0.720959	0.421247	0.036*
H12B	0.229079	0.710321	0.467785	0.036*
C13	0.14695 (19)	0.5575 (2)	0.48432 (15)	0.0216 (6)
H13A	0.165042	0.580831	0.538235	0.026*
H13B	0.075085	0.534296	0.465743	0.026*
C14	0.2531 (2)	0.4263 (2)	0.68441 (14)	0.0231 (6)
H14A	0.249614	0.348035	0.711704	0.028*
H14B	0.185126	0.463146	0.665311	0.028*
C15	0.3259 (2)	0.5172 (3)	0.73536 (15)	0.0318 (7)
H15A	0.380907	0.472747	0.773328	0.038*
H15B	0.291513	0.572981	0.761594	0.038*
C16	0.3651 (2)	0.5899 (2)	0.68097 (15)	0.0251 (6)
H16A	0.316295	0.653889	0.653447	0.030*
H16B	0.429902	0.630870	0.707385	0.030*
C17	0.3776 (2)	0.4884 (2)	0.62865 (15)	0.0232 (6)
H17A	0.373852	0.523353	0.578781	0.028*
H17B	0.442781	0.445263	0.650081	0.028*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ti1	0.0111 (2)	0.0140 (2)	0.0132 (2)	-0.00076 (17)	0.00517 (17)	-0.00024 (16)
Cl1	0.0143 (3)	0.0214 (3)	0.0259 (3)	0.0006 (2)	0.0107 (2)	0.0000 (2)
F1	0.0429 (11)	0.0381 (11)	0.0425 (11)	0.0130 (9)	-0.0119 (8)	-0.0046 (8)
F2	0.0299 (10)	0.0628 (13)	0.0295 (10)	-0.0096 (9)	-0.0101 (8)	-0.0069 (8)
F3	0.0456 (11)	0.0488 (11)	0.0298 (10)	-0.0120 (9)	0.0006 (8)	0.0149 (8)
F4	0.0522 (12)	0.0423 (11)	0.0631 (13)	-0.0302 (9)	0.0209 (10)	-0.0288 (10)
F5	0.0657 (13)	0.0502 (11)	0.0363 (10)	-0.0055 (10)	0.0330 (10)	-0.0131 (8)
F6	0.0642 (13)	0.0223 (9)	0.0449 (11)	0.0018 (9)	0.0112 (10)	-0.0043 (8)
F7	0.0256 (9)	0.0321 (9)	0.0574 (12)	-0.0083 (7)	0.0067 (8)	-0.0050 (8)

F8	0.0612 (14)	0.0343 (11)	0.0819 (15)	-0.0082 (9)	0.0363 (12)	0.0256 (10)
F9	0.0375 (10)	0.0265 (9)	0.0547 (11)	0.0036 (8)	0.0179 (9)	-0.0098 (8)
F10	0.0682 (14)	0.0882 (16)	0.0290 (10)	0.0156 (12)	0.0262 (10)	0.0328 (10)
F11	0.0312 (9)	0.0471 (10)	0.0331 (9)	0.0189 (8)	0.0075 (7)	0.0064 (8)
F12	0.0429 (11)	0.0536 (12)	0.0249 (9)	0.0086 (9)	-0.0010 (8)	-0.0104 (8)
F13	0.0334 (10)	0.0552 (11)	0.0233 (9)	0.0023 (8)	0.0119 (7)	-0.0096 (7)
F14	0.0409 (11)	0.0554 (12)	0.0523 (11)	0.0145 (9)	0.0308 (9)	-0.0093 (9)
F15	0.0510 (11)	0.0441 (10)	0.0401 (10)	-0.0119 (9)	0.0312 (9)	0.0063 (8)
F16	0.0226 (9)	0.0588 (12)	0.0538 (11)	0.0240 (9)	0.0105 (8)	0.0113 (9)
F17	0.0224 (9)	0.0459 (11)	0.0508 (11)	-0.0150 (8)	0.0020 (8)	0.0025 (8)
F18	0.0258 (9)	0.0573 (11)	0.0252 (9)	0.0060 (8)	0.0038 (7)	0.0129 (8)
O1	0.0151 (9)	0.0205 (9)	0.0149 (9)	-0.0023 (7)	0.0026 (7)	-0.0015 (7)
O2	0.0160 (9)	0.0189 (9)	0.0182 (9)	-0.0005 (7)	0.0100 (7)	0.0025 (7)
O3	0.0145 (9)	0.0159 (9)	0.0154 (9)	0.0019 (7)	0.0055 (7)	0.0002 (6)
O4	0.0179 (9)	0.0159 (9)	0.0165 (9)	0.0024 (7)	0.0089 (7)	0.0015 (7)
O5	0.0179 (9)	0.0212 (9)	0.0150 (8)	-0.0067 (7)	0.0089 (7)	-0.0047 (7)
C1	0.0273 (16)	0.0362 (16)	0.0238 (15)	-0.0039 (13)	-0.0030 (12)	-0.0035 (13)
C2	0.0185 (13)	0.0249 (14)	0.0170 (13)	-0.0078 (11)	0.0051 (10)	-0.0052 (10)
C3	0.0326 (16)	0.0287 (15)	0.0253 (15)	-0.0100 (13)	0.0093 (12)	-0.0051 (12)
C4	0.0306 (16)	0.0211 (14)	0.0435 (17)	-0.0014 (12)	0.0180 (14)	0.0070 (12)
C5	0.0215 (13)	0.0213 (13)	0.0224 (13)	0.0044 (11)	0.0147 (11)	0.0066 (10)
C6	0.0379 (17)	0.0380 (17)	0.0222 (14)	0.0124 (14)	0.0156 (13)	0.0098 (13)
C7	0.0248 (15)	0.0317 (16)	0.0315 (16)	0.0007 (12)	0.0176 (13)	-0.0045 (12)
C8	0.0142 (12)	0.0157 (12)	0.0255 (14)	0.0006 (10)	0.0106 (10)	0.0026 (10)
C9	0.0193 (14)	0.0307 (16)	0.0317 (16)	0.0046 (12)	0.0099 (12)	0.0060 (12)
C10	0.0212 (13)	0.0208 (13)	0.0183 (13)	-0.0003 (11)	0.0115 (10)	0.0060 (10)
C11	0.0253 (15)	0.0259 (14)	0.0288 (15)	0.0022 (12)	0.0092 (12)	0.0108 (11)
C12	0.0298 (16)	0.0181 (14)	0.0465 (18)	0.0029 (12)	0.0184 (14)	0.0063 (12)
C13	0.0228 (14)	0.0155 (13)	0.0301 (14)	0.0068 (11)	0.0133 (11)	0.0009 (10)
C14	0.0289 (15)	0.0278 (14)	0.0179 (13)	-0.0037 (12)	0.0150 (11)	-0.0047 (11)
C15	0.0375 (17)	0.0373 (17)	0.0227 (14)	-0.0121 (14)	0.0123 (13)	-0.0117 (12)
C16	0.0271 (15)	0.0220 (14)	0.0247 (14)	-0.0065 (12)	0.0059 (11)	-0.0053 (11)
C17	0.0223 (14)	0.0260 (14)	0.0235 (14)	-0.0113 (11)	0.0106 (11)	-0.0058 (11)

Geometric parameters (Å, °)

Ti1—O1	1.8386 (17)	C1—C2	1.526 (4)
Ti1—O2	1.8426 (17)	C2—C3	1.521 (4)
Ti1—O3	1.8679 (17)	C2—H2	1.0000
Ti1—O4	2.1043 (17)	C4—C5	1.518 (4)
Ti1—O5	2.1593 (17)	C5—C6	1.523 (4)
Ti1—Cl1	2.3399 (9)	C5—H5	1.0000
F1—C1	1.338 (3)	C7—C8	1.527 (4)
F2—C1	1.334 (3)	C8—C9	1.523 (4)
F3—C1	1.332 (4)	C8—H8	1.0000
F4—C3	1.341 (3)	C10—C11	1.511 (4)
F5—C3	1.330 (3)	C10—H10A	0.9900
F6—C3	1.322 (3)	C10—H10B	0.9900

F7—C4	1.341 (3)	C11—C12	1.506 (4)
F8—C4	1.335 (3)	C11—H11A	0.9900
F9—C4	1.338 (3)	C11—H11B	0.9900
F10—C6	1.338 (3)	C12—C13	1.506 (4)
F11—C6	1.329 (3)	C12—H12A	0.9900
F12—C6	1.327 (4)	C12—H12B	0.9900
F13—C7	1.326 (3)	C13—H13A	0.9900
F14—C7	1.337 (3)	C13—H13B	0.9900
F15—C7	1.335 (3)	C14—C15	1.511 (4)
F16—C9	1.338 (3)	C14—H14A	0.9900
F17—C9	1.334 (3)	C14—H14B	0.9900
F18—C9	1.333 (3)	C15—C16	1.515 (4)
O1—C2	1.379 (3)	C15—H15A	0.9900
O2—C5	1.374 (3)	C15—H15B	0.9900
O3—C8	1.384 (3)	C16—C17	1.509 (4)
O4—C13	1.472 (3)	C16—H16A	0.9900
O4—C10	1.472 (3)	C16—H16B	0.9900
O5—C14	1.469 (3)	C17—H17A	0.9900
O5—C17	1.475 (3)	C17—H17B	0.9900
O1—Ti1—O2	100.14 (8)	F13—C7—C8	110.3 (2)
O1—Ti1—O3	94.69 (7)	F15—C7—C8	112.4 (2)
O2—Ti1—O3	92.72 (7)	F14—C7—C8	112.1 (2)
O1—Ti1—O4	88.84 (7)	O3—C8—C9	109.0 (2)
O2—Ti1—O4	170.98 (7)	O3—C8—C7	108.6 (2)
O3—Ti1—O4	85.68 (7)	C9—C8—C7	112.8 (2)
O1—Ti1—O5	167.56 (7)	O3—C8—H8	108.8
O2—Ti1—O5	92.10 (7)	C9—C8—H8	108.8
O3—Ti1—O5	86.87 (7)	C7—C8—H8	108.8
O4—Ti1—O5	78.95 (6)	F18—C9—F17	106.6 (2)
O1—Ti1—C11	91.72 (6)	F18—C9—F16	107.7 (2)
O2—Ti1—C11	90.52 (5)	F17—C9—F16	107.3 (2)
O3—Ti1—C11	172.19 (6)	F18—C9—C8	110.2 (2)
O4—Ti1—C11	90.02 (5)	F17—C9—C8	112.3 (2)
O5—Ti1—C11	85.92 (5)	F16—C9—C8	112.5 (2)
C2—O1—Ti1	140.75 (15)	O4—C10—C11	104.20 (19)
C5—O2—Ti1	142.97 (15)	O4—C10—H10A	110.9
C8—O3—Ti1	130.80 (15)	C11—C10—H10A	110.9
C13—O4—C10	109.58 (17)	O4—C10—H10B	110.9
C13—O4—Ti1	129.17 (14)	C11—C10—H10B	110.9
C10—O4—Ti1	120.92 (13)	H10A—C10—H10B	108.9
C14—O5—C17	108.95 (17)	C12—C11—C10	102.6 (2)
C14—O5—Ti1	129.22 (14)	C12—C11—H11A	111.2
C17—O5—Ti1	121.54 (13)	C10—C11—H11A	111.2
F3—C1—F2	107.2 (2)	C12—C11—H11B	111.2
F3—C1—F1	106.9 (2)	C10—C11—H11B	111.2
F2—C1—F1	107.0 (2)	H11A—C11—H11B	109.2
F3—C1—C2	112.9 (2)	C11—C12—C13	102.9 (2)

F2—C1—C2	112.0 (2)	C11—C12—H12A	111.2
F1—C1—C2	110.6 (2)	C13—C12—H12A	111.2
O1—C2—C3	110.1 (2)	C11—C12—H12B	111.2
O1—C2—C1	109.6 (2)	C13—C12—H12B	111.2
C3—C2—C1	111.2 (2)	H12A—C12—H12B	109.1
O1—C2—H2	108.6	O4—C13—C12	104.0 (2)
C3—C2—H2	108.6	O4—C13—H13A	111.0
C1—C2—H2	108.6	C12—C13—H13A	111.0
F6—C3—F5	106.6 (2)	O4—C13—H13B	111.0
F6—C3—F4	107.4 (2)	C12—C13—H13B	111.0
F5—C3—F4	106.5 (2)	H13A—C13—H13B	109.0
F6—C3—C2	111.3 (2)	O5—C14—C15	105.0 (2)
F5—C3—C2	113.5 (2)	O5—C14—H14A	110.7
F4—C3—C2	111.1 (2)	C15—C14—H14A	110.7
F9—C4—F8	107.4 (2)	O5—C14—H14B	110.7
F9—C4—F7	107.4 (2)	C15—C14—H14B	110.7
F8—C4—F7	106.8 (2)	H14A—C14—H14B	108.8
F9—C4—C5	112.3 (2)	C14—C15—C16	103.0 (2)
F8—C4—C5	112.3 (2)	C14—C15—H15A	111.2
F7—C4—C5	110.3 (2)	C16—C15—H15A	111.2
O2—C5—C4	108.8 (2)	C14—C15—H15B	111.2
O2—C5—C6	109.0 (2)	C16—C15—H15B	111.2
C4—C5—C6	112.7 (2)	H15A—C15—H15B	109.1
O2—C5—H5	108.8	C17—C16—C15	101.9 (2)
C4—C5—H5	108.8	C17—C16—H16A	111.4
C6—C5—H5	108.8	C15—C16—H16A	111.4
F12—C6—F11	107.2 (2)	C17—C16—H16B	111.4
F12—C6—F10	107.5 (2)	C15—C16—H16B	111.4
F11—C6—F10	107.3 (2)	H16A—C16—H16B	109.2
F12—C6—C5	110.5 (2)	O5—C17—C16	104.4 (2)
F11—C6—C5	113.0 (2)	O5—C17—H17A	110.9
F10—C6—C5	111.1 (2)	C16—C17—H17A	110.9
F13—C7—F15	106.8 (2)	O5—C17—H17B	110.9
F13—C7—F14	107.5 (2)	C16—C17—H17B	110.9
F15—C7—F14	107.5 (2)	H17A—C17—H17B	108.9
O2—Ti1—O1—C2	85.1 (2)	O2—C5—C6—F12	53.2 (3)
O3—Ti1—O1—C2	178.7 (2)	C4—C5—C6—F12	174.1 (2)
O4—Ti1—O1—C2	-95.8 (2)	O2—C5—C6—F11	-67.0 (3)
O5—Ti1—O1—C2	-84.6 (4)	C4—C5—C6—F11	53.9 (3)
C11—Ti1—O1—C2	-5.8 (2)	O2—C5—C6—F10	172.4 (2)
O1—Ti1—O2—C5	-99.1 (3)	C4—C5—C6—F10	-66.8 (3)
O3—Ti1—O2—C5	165.7 (3)	Ti1—O3—C8—C9	-119.1 (2)
O5—Ti1—O2—C5	78.7 (3)	Ti1—O3—C8—C7	117.6 (2)
C11—Ti1—O2—C5	-7.2 (3)	F13—C7—C8—O3	-60.6 (3)
O1—Ti1—O3—C8	-64.4 (2)	F15—C7—C8—O3	58.5 (3)
O2—Ti1—O3—C8	36.0 (2)	F14—C7—C8—O3	179.7 (2)
O4—Ti1—O3—C8	-152.9 (2)	F13—C7—C8—C9	178.4 (2)

O5—Ti1—O3—C8	128.0 (2)	F15—C7—C8—C9	-62.5 (3)
Ti1—O1—C2—C3	-135.4 (2)	F14—C7—C8—C9	58.7 (3)
Ti1—O1—C2—C1	102.0 (3)	O3—C8—C9—F18	60.8 (3)
F3—C1—C2—O1	51.3 (3)	C7—C8—C9—F18	-178.4 (2)
F2—C1—C2—O1	172.5 (2)	O3—C8—C9—F17	-57.8 (3)
F1—C1—C2—O1	-68.3 (3)	C7—C8—C9—F17	62.9 (3)
F3—C1—C2—C3	-70.6 (3)	O3—C8—C9—F16	-179.0 (2)
F2—C1—C2—C3	50.5 (3)	C7—C8—C9—F16	-58.2 (3)
F1—C1—C2—C3	169.7 (2)	C13—O4—C10—C11	-11.7 (3)
O1—C2—C3—F6	41.1 (3)	Ti1—O4—C10—C11	162.37 (15)
C1—C2—C3—F6	162.8 (2)	O4—C10—C11—C12	32.5 (3)
O1—C2—C3—F5	-79.2 (3)	C10—C11—C12—C13	-41.1 (3)
C1—C2—C3—F5	42.4 (3)	C10—O4—C13—C12	-13.9 (3)
O1—C2—C3—F4	160.8 (2)	Ti1—O4—C13—C12	172.74 (16)
C1—C2—C3—F4	-77.6 (3)	C11—C12—C13—O4	33.9 (3)
Ti1—O2—C5—C4	106.6 (3)	C17—O5—C14—C15	-8.2 (3)
Ti1—O2—C5—C6	-130.1 (2)	Ti1—O5—C14—C15	177.99 (17)
F9—C4—C5—O2	51.7 (3)	O5—C14—C15—C16	30.3 (3)
F8—C4—C5—O2	172.9 (2)	C14—C15—C16—C17	-40.6 (3)
F7—C4—C5—O2	-68.0 (3)	C14—O5—C17—C16	-17.4 (3)
F9—C4—C5—C6	-69.3 (3)	Ti1—O5—C17—C16	157.00 (16)
F8—C4—C5—C6	51.9 (3)	C15—C16—C17—O5	35.7 (3)
F7—C4—C5—C6	171.0 (2)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C2—H2 \cdots C11	1.00	2.75	3.321 (3)	117
C5—H5 \cdots C11	1.00	2.76	3.329 (3)	117
C10—H10A \cdots F3	0.99	2.47	3.278 (3)	139
C10—H10B \cdots F17 ⁱ	0.99	2.43	3.243 (3)	139
C11—H11B \cdots F2 ⁱⁱ	0.99	2.53	3.132 (3)	119
C12—H12A \cdots C11 ⁱⁱⁱ	0.99	2.96	3.657 (3)	129
C12—H12B \cdots F9 ^{iv}	0.99	2.58	3.361 (3)	136
C13—H13B \cdots C11 ⁱⁱⁱ	0.99	2.86	3.500 (3)	123
C14—H14A \cdots F12	0.99	2.61	3.315 (3)	129
C17—H17A \cdots F15 ⁱ	0.99	2.62	3.174 (3)	116
C17—H17A \cdots O4	0.99	2.61	3.124 (3)	112

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x, y+1/2, -z+1/2$; (iii) $-x, -y+1, -z+1$; (iv) $x, y+1, z$.