Crystal structure and computational study of an oxo-bridged bis-titanium(III) complex

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The solid-state structure of the new compound μ-oxido-bis[dichloridotris(tetrahydrofuran-κO)titanium(III)], [$Ti_2Cl_4O(C_4H_8O)_6$], at 150 K has been determined. The crystal has monoclinic ($C2/c$) symmetry and the complex features C_2 symmetry about the bridging O atom. Positional disorder is evident in one of the three tetrahydrofuran environments. A post-Hartree–Fock computational analysis indicates that the complex has nearly degenerate triplet and singlet spin states, with the former favoured slightly by ca 2 kJ mol^{-1}.

1. Introduction

Molecular titanium oxo species are numerous, with the vast majority featuring the metal in the +4 oxidation state. In addition to their diverse structural chemistry, they can have varying applications, such as for CO_2 sorption (Hong & Chun, 2013) or as precursors to ceramics (Boyle *et al.*, 2002) and polyoxometalates (Ishimoto *et al.*, 2015). Amongst structurally characterized dititanium(IV) clusters with bridging oxo groups, supporting ligands include cyclopentadienyl (Luo *et al.*, 2009) and salen [N,N'-ethylenebis(salicylimine)] ligands (Aoyama *et al.*, 1988) or, in some cases, simply solvent molecules (Strel'tsova *et al.*, 1988; Mahrwald *et al.*, 2001). Given the highly oxophilic nature of titanium, in many cases these species arise from the unexpected oxidation and/or hydrolysis of a monometallic precursor complex (Crestani *et al.*, 2013; Barroso *et al.*, 2013).

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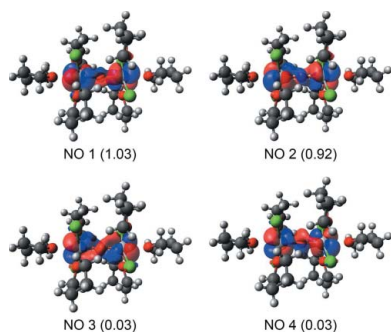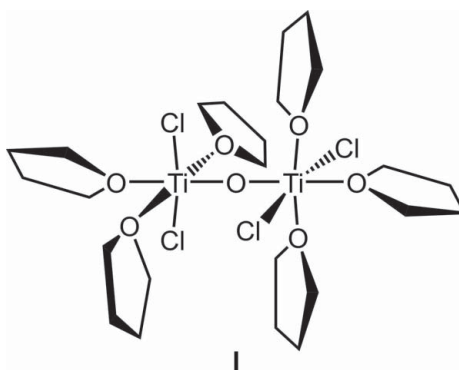
Reports of Ti^{III} analogues with this motif are rare, though titanium(III) compounds have many practical applications, including as components in heterogeneous Ziegler–Natta alkene polymerization catalysts (Ziegler *et al.*, 1955; Natta *et al.*, 1955), and as reagents/catalyts in various organic transformations (Rosales *et al.*, 2015). Herein we report the first instance of a structurally characterized dititanium(III) oxychloride molecule, [{$TiCl_2(THF)_3$}$_2(\mu$-O)] (**1**), presenting a structural analysis and computational modelling.

NO 1 (1.03) NO 2 (0.92)

NO 3 (0.03) NO 4 (0.03)

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Table 1
Experimental details.

Crystal data	
Chemical formula	[Ti₂Cl₄O(C₄H₈O)₆]
M_r	686.22
Crystal system, space group	Monoclinic, $C2/c$
Temperature (K)	150
a, b, c (Å)	19.1347 (5), 9.1227 (3), 18.7937 (5)
β (°)	102.092 (2)
V (Å³)	3207.84 (16)
Z	4
Radiation type	Mo $K\alpha$
μ (mm⁻¹)	0.87
Crystal size (mm)	0.33 × 0.33 × 0.28
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Numerical (*SADABS*; Bruker, 2016)
T_{min}, T_{max}	0.562, 0.678
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	25791, 4461, 3244
R_{int}	0.068
$(\sin\theta/\lambda)_{max}$ (Å⁻¹)	0.695
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.073, 0.138, 1.13
No. of reflections	4461
No. of parameters	182
No. of restraints	10
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}, \Delta\rho_{min}$ (e Å⁻³)	0.57, −0.41

Computer programs: *SAINT* (Bruker, 2016), *APEX2* (Bruker, 2016), *SHELXT2018* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b) and *OLEX2* (Dolomanov *et al.*, 2009).

2. Experimental

2.1. Synthesis and crystallization

Manipulations were conducted under an inert atmosphere of argon using standard Schlenk techniques. Tetrahydrofuran (THF) and hexanes were dried using a solvent purification system, and stored in PTFE-stoppered flasks over activated 4 Å molecular sieves. The complex [TiCl₃(THF)₃] was obtained from Strem and used as received. The compound 1,3-di-*tert*-butylimidazolin-2-ylidene (SI'Bu) was prepared according to a reported procedure (Denk *et al.*, 1997).

The title compound (**1**) was prepared in an attempt to synthesize an N-heterocyclic carbene-ligated derivative of this Ti^{III} complex. Complex **1** was obtained from an equimolar solution of [TiCl₃(THF)₃] and SI'Bu in THF layered with hexanes and stored at 5 °C. After several weeks, a single red crystal was observed to form, which was used in subsequent diffraction studies.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms were placed in calculated positions (C—H = 0.99 Å) and refined according to a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$. One THF ligand in the asymmetric unit showed signs of positional disorder and was modelled as a two-part *ca* 70:30 anisotropic mixture, with C—O and C—C distances restrained to obtain reasonable geometries.

3. Results and discussion

A single crystal of the new complex [{TiCl₂(THF)₃}₂(μ-O)] (**1**) was obtained unexpectedly from a solution of the well-known Ti^{III} salt [TiCl₃(THF)₃]. Presumably, adventitious moisture caused a partial hydrolysis of this complex. Compound **1** is the first reported bimetallic dichloridotitanium(III) complex bridged by an oxo ligand. A pyridine-substituted bromide complex, [{TiBr₂(py)₃(μ-O)}₂], has been reported previously (Troyanov *et al.*, 1990).

The asymmetric unit of complex **1** contains one {TiCl₂-(THF)₃O} moiety with the oxo ligand sitting on a twofold rotational axis. Thus, the complex has ideal C_2 symmetry. The titanium centres feature distorted octahedral coordination, with the chloride ligands on each metal *trans*, leaving the THF and oxo ligands in an approximate square plane. The THF ligands exhibit twist conformations. The two Cl—Ti—Cl units are staggered when viewed down the Ti—O—Ti axis. As in the precursor compound [TiCl₃(THF)₃], the THF ligands are meridionally coordinated. The overall molecular structure is depicted in Fig. 1 and the packing within the unit cell is shown in Fig. 2.

The Ti—O(oxo) distances are 1.8091 (7) Å, while the Ti—O(THF) distances range from 2.142 (3) to 2.229 (3) Å, with the longest distance observed for the THF ligand *trans* to the strongly donating oxo group. The Ti—Cl distances are 2.4398 (12) and 2.4482 (12) Å. The O—Ti—O—Ti—O fragment containing the THF ligands *trans* to the oxo group is nearly linear, with O—Ti—O and Ti—O—Ti bond angles of 179.21 (13) and 179.1 (3)°, respectively. The ligands *cis* to the oxo group are bent away from it, with O—Ti—*X* angles in the range 95.20 (13)–97.47 (9)°. No significant intermolecular interactions were identified in the crystal structure.

Compared to the analogous ligand values in [TiCl₃(THF)₃] (Handlovič *et al.*, 1981), the Ti—Cl distances in complex **1** are elongated by *ca* 4% [*cf.* 2.341 (3)–2.360 (3) Å] and the Ti—O
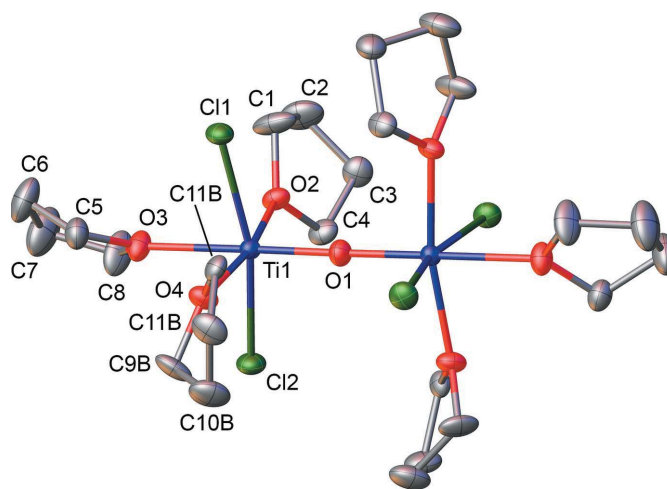
Figure 1
Displacement ellipsoid plot (50% probability level) of complex **1**. C atoms with the suffix '*B*' illustrate one part of a two-part anisotropic disorder model. Symmetry-equivalent atoms (unlabelled) are generated by the operator ($-x + 1, y, -z + \frac{3}{2}$). H atoms have been omitted for clarity.
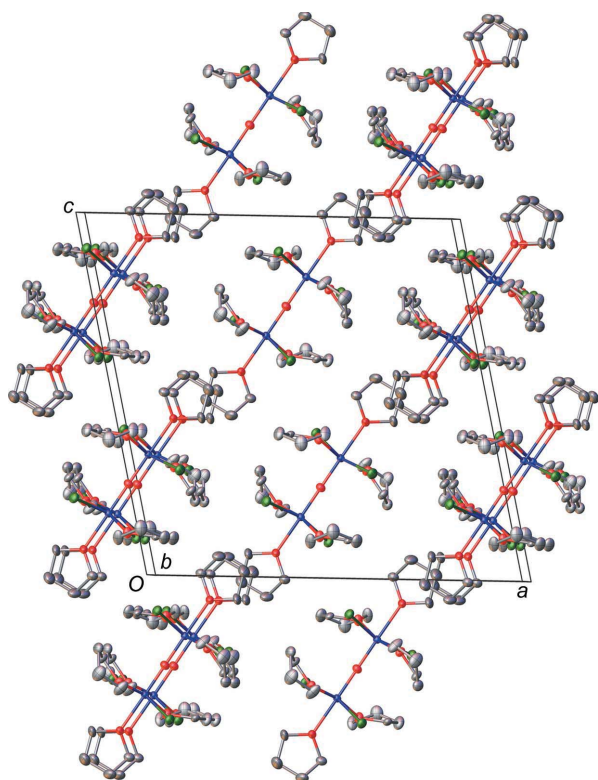
Figure 2
The packing diagram for complex **1**.

distances are longer by 2% [*cf.* 2.084 (7)–2.181 (6) Å]. This may be reasonably ascribed to a combination of the steric influence of the two adjacent octahedral coordination environments, as well as the presence of a strongly electron-donating oxo ligand.

The related titanium(IV) complex [{TiCl$_3$(THF)$_2$(μ-O)}$_2$] (Strel'tsova *et al.*, 1988; Mahrwald *et al.*, 2001) features a similar structure. It also crystallizes in the space group $C2/c$ with C_2 molecular symmetry. The three chloride ligands on the metal centres form *mer* arrangements, which are twisted relative to each other when viewed down the Ti—O—Ti direction. Compared to the title complex, the metal–ligand bond distances are shortened by *ca* 1 and 6% for Ti—O [1.7845 (6)–2.164 (2) Å] and Ti—Cl [2.281 (1)–2.3089 (8) Å], respectively, in keeping with the higher oxidation state in this Ti^{IV} derivative. The structure of the isomorphous zirconium(IV) complex [{ZrCl$_3$(THF)$_2$(μ-O)}$_2$] has also been reported (Guan *et al.*, 1999). A trimetallic Ti^{IV} analogue, [TiCl$_2$(μ-O)]$_3$, has been observed to crystallize in two different stereoisomeric forms (Gritzo *et al.*, 2004; Zhang *et al.*, 2014).

The vanadium(III) complex [{VCl$_2$(THF)$_3$}$_2$(μ-O)] (Chandrasekhar & Bird, 1984) is isomorphous with complex **1**. In that case, the authors surmised that an initially formed V^{II} species was oxidized by adventitious oxygen before forming the bimetallic complex. In this vanadium complex, the metal–ligand distances are *ca* 2% shorter for chloride [2.384 (6)–2.390 (6) Å] and μ-oxo [1.769 (5) Å], and *ca* 1% elonged for the THF ligands [2.16 (1)–2.26 (1) Å], compared to complex **1**.

Since complex **1** features two adjacent Ti^{III} (d^1) centres, there is the question of magnetic coupling between the two. Some experimental measurements on molecules containing the [Ti^{III}—O—Ti^{III}] fragment have been reported previously. For the putative complex [L_2Ti$_2$Cl$_4$O] (L = 1,4,7-trimethyl-1,4,7-triazacyclononane), a temperature-independent magnetic moment of 1.72 μ_B per Ti centre indicated paramagnetic behaviour, *i.e.* uncoupled spins, in the range 90–298 K (Bodner *et al.*, 1990). Two related pseudohalide complexes [L_2Ti$_2$X$_4$O] (X = NCO or NCS) showed weak antiferromagnetic coupling, with the magnetic moment decreasing significantly from ambient temperature values of ∼1.7 to 1.12–1.15 μ_B below 30 K (Jeske *et al.*, 1994).

The title complex was analysed with density functional and multireference post-Hartree–Fock methods using the *ORCA* electronic structure package (Version 4.2.1; Neese *et al.*, 2020). The geometries of the complex in the lowest singlet and triplet electronic states were optimized with the TPSSh density functional (Staroverov *et al.*, 2003) and the def2-TZVP basis set (Weigend & Ahlrichs, 2005; Hellweg *et al.*, 2007). The optimized geometries and energies of the triplet and broken-symmetry (unrestricted) singlet states were found to be nearly equivalent, with a difference in electronic energy of 0.2 kJ mol^{-1} and an r.m.s. deviation with respect to the atomic coordinates of 0.002 Å. Therefore, subsequent calculations were performed on the TPSSh/def2-TZVP optimized triplet structure.

Taking the active electrons to be the unpaired α electrons and the active orbitals to be the occupied open-shell orbitals and two unoccupied orbitals, the (2,4) complete–active space self-consistent field (CASSCF) wave function was determined with the same basis set. The resulting natural orbitals and their occupancies are shown in Fig. 3. The CASSCF energies were improved by applying fully internally contracted second-order N-electron valence state perturbation theory (FIC-NEVPT2;
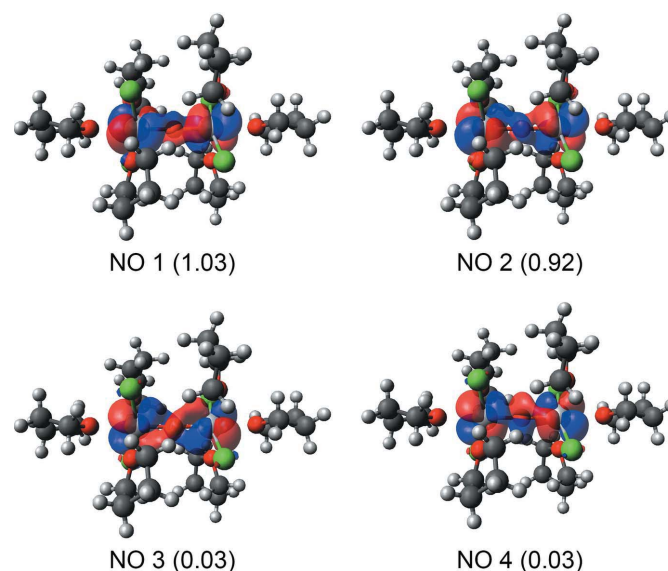

Figure 3
Natural orbitals (NOs) with occupancies shown in parenthesis for complex **1** at the (2,4)-CASSCF/def2-TZVP level.

Angeli *et al.*, 2001*a*,*b*, 2002). The FIC-NEVPT2 energies, for the (2,4)-CASSCF reference, of the singlet and triplet states are nearly equivalent. The triplet is predicted to be lower in energy than the singlet, by 2.4 kJ mol^{-1}. These findings are thus generally consistent with previously discussed experimental, as well as prior configuration interaction (CI) studies (Fink *et al.*, 1994), which indicate no strong coupling of electron spins in linear [Ti^{III}—O—Ti^{III}] systems. One difference is the finding that the triplet state is slightly more stable in complex **1**, which would predict ferromagnetic coupling at low temperatures.

Experimental confirmation of the magnetic behaviour of **1**, along with other spectroscopic properties, will require further study on additional quantities of the complex. An intentional synthesis should be possible *via* controlled hydrolysis of the precursor [TiCl$_3$(THF)$_3$].

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Computing details

Data collection: *SAINT* (Bruker, 2016); cell refinement: *APEX2* (Bruker, 2016); data reduction: *SAINT* (Bruker, 2016); program(s) used to solve structure: SHELXT2018 (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov *et al.*, 2009); software used to prepare material for publication: OLEX2 (Dolomanov *et al.*, 2009).

***μ*-Oxido-bis[dichloridotris(tetrahydrofuran-*κO*)titanium(III)]**

Crystal data

$[Ti_2Cl_4O(C_4H_8O)_6]$	$F(000) = 1440$
$M_r = 686.22$	$D_x = 1.421$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 19.1347$ (5) Å	Cell parameters from 9986 reflections
$b = 9.1227$ (3) Å	$\theta = 2.5–29.6°$
$c = 18.7937$ (5) Å	$\mu = 0.87$ mm^{-1}
$\beta = 102.092$ (2)°	$T = 150$ K
$V = 3207.84$ (16) Å^3	Block, clear light red
$Z = 4$	$0.33 \times 0.33 \times 0.28$ mm

Data collection

Bruker APEXII CCD diffractometer	4461 independent reflections
φ and ω scans	3244 reflections with $I > 2\sigma(I)$
Absorption correction: numerical (SADABS; Bruker, 2016)	$R_{int} = 0.068$
	$\theta_{max} = 29.6°$, $\theta_{min} = 2.5°$
$T_{min} = 0.562$, $T_{max} = 0.678$	$h = -21 \rightarrow 25$
25791 measured reflections	$k = -11 \rightarrow 12$
	$l = -25 \rightarrow 26$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + 30.5697P]$
$R[F^2 > 2\sigma(F^2)] = 0.073$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.138$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.13$	$\Delta\rho_{max} = 0.57$ e Å^{-3}
4461 reflections	$\Delta\rho_{min} = -0.41$ e Å^{-3}
182 parameters	Extinction correction: SHELXT2018
10 restraints	(Sheldrick, 2015a),
Hydrogen site location: inferred from neighbouring sites	$Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
	Extinction coefficient: 0.00039 (7)

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{iso}*/U_{eq}$	Occ. (<1)
Ti1	0.43130 (4)	0.55202 (7)	0.66762 (4)	0.01715 (16)	
Cl1	0.48830 (5)	0.37747 (11)	0.59944 (5)	0.0254 (2)	
Cl2	0.35094 (6)	0.72586 (11)	0.70921 (6)	0.0283 (2)	
O1	0.500000	0.5536 (5)	0.750000	0.0249 (8)	
O2	0.37164 (15)	0.3758 (3)	0.70116 (15)	0.0231 (6)	
O3	0.34579 (14)	0.5523 (4)	0.56683 (14)	0.0277 (6)	
C1	0.3783 (3)	0.2223 (5)	0.6840 (3)	0.0441 (13)	
H1A	0.428225	0.188668	0.700561	0.052*	
H1B	0.363459	0.205566	0.630934	0.052*	
C2	0.3295 (3)	0.1431 (6)	0.7241 (3)	0.0481 (14)	
H2A	0.344622	0.040137	0.734186	0.057*	
H2B	0.279355	0.145037	0.696499	0.057*	
C3	0.3384 (2)	0.2311 (5)	0.7932 (3)	0.0324 (10)	
H3A	0.383188	0.204980	0.827718	0.038*	
H3B	0.297459	0.216653	0.817106	0.038*	
C4	0.3409 (2)	0.3859 (5)	0.7659 (2)	0.0278 (9)	
H4A	0.292234	0.428372	0.753550	0.033*	
H4B	0.371007	0.448157	0.803364	0.033*	
C5	0.3560 (2)	0.5794 (5)	0.4940 (2)	0.0325 (10)	
H5A	0.403410	0.544106	0.488285	0.038*	
H5B	0.352068	0.685421	0.482495	0.038*	
C6	0.2973 (3)	0.4953 (7)	0.4456 (3)	0.0513 (15)	
H6A	0.283008	0.542792	0.397404	0.061*	
H6B	0.312242	0.393259	0.438912	0.061*	
C7	0.2381 (3)	0.4994 (9)	0.4857 (3)	0.0617 (18)	
H7A	0.205144	0.581543	0.468189	0.074*	
H7B	0.210670	0.406647	0.478715	0.074*	
C8	0.2718 (2)	0.5198 (7)	0.5631 (3)	0.0475 (14)	
H8A	0.248572	0.601541	0.584008	0.056*	
H8B	0.266981	0.429577	0.590949	0.056*	
O4A	0.47581 (15)	0.7265 (3)	0.61486 (16)	0.0256 (6)	0.305 (10)
C9A	0.4666 (11)	0.8798 (15)	0.6335 (10)	0.037 (2)	0.305 (10)
H9AA	0.490493	0.901398	0.684430	0.044*	0.305 (10)
H9AB	0.415424	0.906631	0.625989	0.044*	0.305 (10)
C10A	0.5028 (10)	0.9567 (17)	0.5800 (12)	0.046 (2)	0.305 (10)
H10A	0.471578	0.958661	0.530799	0.055*	0.305 (10)
H10B	0.515873	1.058390	0.595679	0.055*	0.305 (10)
C11A	0.5679 (11)	0.866 (3)	0.5809 (18)	0.038 (3)	0.305 (10)
H11A	0.607203	0.893953	0.621795	0.045*	0.305 (10)

H11B	0.584567	0.875524	0.534694	0.045*	0.305 (10)
C12A	0.5431 (12)	0.711 (2)	0.591 (2)	0.023 (2)	0.305 (10)
H12A	0.535634	0.656542	0.543999	0.027*	0.305 (10)
H12B	0.578690	0.657804	0.627323	0.027*	0.305 (10)
O4B	0.47581 (15)	0.7265 (3)	0.61486 (16)	0.0256 (6)	0.695 (10)
C9B	0.4520 (4)	0.8769 (7)	0.6009 (5)	0.037 (2)	0.695 (10)
H9BA	0.414616	0.902429	0.628045	0.044*	0.695 (10)
H9BB	0.433408	0.893978	0.548355	0.044*	0.695 (10)
C10B	0.5197 (4)	0.9630 (8)	0.6284 (6)	0.046 (2)	0.695 (10)
H10C	0.516303	1.062613	0.607030	0.055*	0.695 (10)
H10D	0.530015	0.971064	0.682082	0.055*	0.695 (10)
C11B	0.5756 (5)	0.8740 (11)	0.6031 (6)	0.038 (3)	0.695 (10)
H11C	0.622887	0.886866	0.636076	0.045*	0.695 (10)
H11D	0.579341	0.902179	0.553189	0.045*	0.695 (10)
C12B	0.5498 (4)	0.7179 (10)	0.6051 (7)	0.023 (2)	0.695 (10)
H12C	0.551874	0.666786	0.559096	0.027*	0.695 (10)
H12D	0.579946	0.663704	0.645962	0.027*	0.695 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ti1	0.0167 (3)	0.0163 (3)	0.0178 (3)	0.0004 (3)	0.0021 (2)	−0.0008 (3)
Cl1	0.0277 (5)	0.0219 (5)	0.0287 (5)	0.0048 (4)	0.0107 (4)	−0.0014 (4)
Cl2	0.0296 (5)	0.0248 (5)	0.0323 (5)	0.0067 (4)	0.0103 (4)	−0.0038 (4)
O1	0.022 (2)	0.028 (2)	0.0226 (19)	0.000	0.0002 (15)	0.000
O2	0.0273 (15)	0.0185 (14)	0.0259 (14)	−0.0053 (11)	0.0108 (12)	−0.0033 (11)
O3	0.0183 (14)	0.0435 (18)	0.0207 (14)	0.0014 (13)	0.0033 (11)	−0.0041 (13)
C1	0.068 (4)	0.021 (2)	0.055 (3)	−0.010 (2)	0.040 (3)	−0.012 (2)
C2	0.059 (4)	0.027 (3)	0.065 (4)	−0.014 (2)	0.028 (3)	−0.007 (2)
C3	0.031 (2)	0.031 (2)	0.035 (2)	−0.0086 (19)	0.0091 (19)	0.0018 (19)
C4	0.032 (2)	0.029 (2)	0.027 (2)	−0.0024 (18)	0.0164 (18)	−0.0025 (17)
C5	0.032 (2)	0.040 (3)	0.024 (2)	0.002 (2)	0.0020 (17)	0.0023 (19)
C6	0.048 (3)	0.078 (4)	0.026 (2)	−0.019 (3)	0.004 (2)	−0.011 (3)
C7	0.034 (3)	0.105 (5)	0.043 (3)	−0.012 (3)	0.000 (2)	−0.017 (3)
C8	0.017 (2)	0.089 (4)	0.034 (3)	−0.007 (2)	0.0015 (18)	−0.008 (3)
O4A	0.0231 (15)	0.0179 (14)	0.0363 (17)	−0.0006 (11)	0.0075 (12)	0.0034 (12)
C9A	0.031 (4)	0.020 (3)	0.060 (6)	0.009 (2)	0.012 (4)	0.017 (4)
C10A	0.046 (4)	0.021 (3)	0.070 (6)	−0.004 (3)	0.013 (4)	0.000 (4)
C11A	0.037 (3)	0.030 (3)	0.050 (8)	−0.005 (2)	0.017 (4)	0.012 (4)
C12A	0.024 (3)	0.029 (2)	0.016 (6)	−0.001 (2)	0.007 (3)	−0.004 (3)
O4B	0.0231 (15)	0.0179 (14)	0.0363 (17)	−0.0006 (11)	0.0075 (12)	0.0034 (12)
C9B	0.031 (4)	0.020 (3)	0.060 (6)	0.009 (2)	0.012 (4)	0.017 (4)
C10B	0.046 (4)	0.021 (3)	0.070 (6)	−0.004 (3)	0.013 (4)	0.000 (4)
C11B	0.037 (3)	0.030 (3)	0.050 (8)	−0.005 (2)	0.017 (4)	0.012 (4)
C12B	0.024 (3)	0.029 (2)	0.016 (6)	−0.001 (2)	0.007 (3)	−0.004 (3)

Geometric parameters (Å, º)

Ti1—Cl1	2.4398 (12)	C7—C8	1.474 (7)
Ti1—Cl2	2.4482 (12)	C8—H8A	0.9900
Ti1—O1	1.8091 (7)	C8—H8B	0.9900
Ti1—O2	2.142 (3)	O4A—C9A	1.462 (14)
Ti1—O3	2.229 (3)	O4A—C12A	1.460 (14)
Ti1—O4A	2.144 (3)	C9A—H9AA	0.9900
Ti1—O4B	2.144 (3)	C9A—H9AB	0.9900
O2—C1	1.448 (5)	C9A—C10A	1.509 (16)
O2—C4	1.462 (4)	C10A—H10A	0.9900
O3—C5	1.444 (5)	C10A—H10B	0.9900
O3—C8	1.434 (5)	C10A—C11A	1.496 (16)
C1—H1A	0.9900	C11A—H11A	0.9900
C1—H1B	0.9900	C11A—H11B	0.9900
C1—C2	1.502 (7)	C11A—C12A	1.511 (15)
C2—H2A	0.9900	C12A—H12A	0.9900
C2—H2B	0.9900	C12A—H12B	0.9900
C2—C3	1.505 (7)	O4B—C9B	1.452 (7)
C3—H3A	0.9900	O4B—C12B	1.468 (7)
C3—H3B	0.9900	C9B—H9BA	0.9900
C3—C4	1.506 (6)	C9B—H9BB	0.9900
C4—H4A	0.9900	C9B—C10B	1.510 (9)
C4—H4B	0.9900	C10B—H10C	0.9900
C5—H5A	0.9900	C10B—H10D	0.9900
C5—H5B	0.9900	C10B—C11B	1.497 (9)
C5—C6	1.499 (6)	C11B—H11C	0.9900
C6—H6A	0.9900	C11B—H11D	0.9900
C6—H6B	0.9900	C11B—C12B	1.510 (8)
C6—C7	1.487 (7)	C12B—H12C	0.9900
C7—H7A	0.9900	C12B—H12D	0.9900
C7—H7B	0.9900		
Cl1—Ti1—Cl2	165.98 (5)	H7A—C7—H7B	108.7
O1—Ti1—Cl1	97.47 (9)	C8—C7—C6	106.3 (4)
O1—Ti1—Cl2	96.55 (9)	C8—C7—H7A	110.5
O1—Ti1—O2	95.20 (13)	C8—C7—H7B	110.5
O1—Ti1—O3	179.21 (13)	O3—C8—C7	107.3 (4)
O1—Ti1—O4A	95.86 (13)	O3—C8—H8A	110.3
O1—Ti1—O4B	95.86 (13)	O3—C8—H8B	110.3
O2—Ti1—Cl1	89.38 (8)	C7—C8—H8A	110.3
O2—Ti1—Cl2	89.04 (8)	C7—C8—H8B	110.3
O2—Ti1—O3	84.79 (11)	H8A—C8—H8B	108.5
O2—Ti1—O4A	168.93 (11)	C9A—O4A—Ti1	121.3 (7)
O2—Ti1—O4B	168.93 (11)	C12A—O4A—Ti1	122.3 (10)
O3—Ti1—Cl1	83.32 (8)	C12A—O4A—C9A	109.1 (11)
O3—Ti1—Cl2	82.67 (8)	O4A—C9A—H9AA	111.6
O4A—Ti1—Cl1	88.68 (8)	O4A—C9A—H9AB	111.6

O4A—Ti1—Cl2	90.21 (8)	O4A—C9A—C10A	100.9 (11)
O4A—Ti1—O3	84.16 (11)	H9AA—C9A—H9AB	109.4
O4B—Ti1—Cl1	88.68 (8)	C10A—C9A—H9AA	111.6
O4B—Ti1—Cl2	90.21 (8)	C10A—C9A—H9AB	111.6
O4B—Ti1—O3	84.16 (11)	C9A—C10A—H10A	111.1
Ti1—O1—Ti1[i]	179.1 (3)	C9A—C10A—H10B	111.1
C1—O2—Ti1	125.7 (2)	H10A—C10A—H10B	109.0
C1—O2—C4	108.4 (3)	C11A—C10A—C9A	103.4 (13)
C4—O2—Ti1	122.0 (2)	C11A—C10A—H10A	111.1
C5—O3—Ti1	125.8 (2)	C11A—C10A—H10B	111.1
C8—O3—Ti1	125.6 (3)	C10A—C11A—H11A	111.0
C8—O3—C5	108.5 (3)	C10A—C11A—H11B	111.0
O2—C1—H1A	110.7	C10A—C11A—C12A	103.7 (13)
O2—C1—H1B	110.7	H11A—C11A—H11B	109.0
O2—C1—C2	105.1 (4)	C12A—C11A—H11A	111.0
H1A—C1—H1B	108.8	C12A—C11A—H11B	111.0
C2—C1—H1A	110.7	O4A—C12A—C11A	105.5 (12)
C2—C1—H1B	110.7	O4A—C12A—H12A	110.6
C1—C2—H2A	111.4	O4A—C12A—H12B	110.6
C1—C2—H2B	111.4	C11A—C12A—H12A	110.6
C1—C2—C3	101.9 (4)	C11A—C12A—H12B	110.6
H2A—C2—H2B	109.3	H12A—C12A—H12B	108.8
C3—C2—H2A	111.4	C9B—O4B—Ti1	130.2 (4)
C3—C2—H2B	111.4	C9B—O4B—C12B	107.6 (5)
C2—C3—H3A	111.3	C12B—O4B—Ti1	120.4 (4)
C2—C3—H3B	111.3	O4B—C9B—H9BA	111.3
C2—C3—C4	102.3 (4)	O4B—C9B—H9BB	111.3
H3A—C3—H3B	109.2	O4B—C9B—C10B	102.5 (5)
C4—C3—H3A	111.3	H9BA—C9B—H9BB	109.2
C4—C3—H3B	111.3	C10B—C9B—H9BA	111.3
O2—C4—C3	105.7 (3)	C10B—C9B—H9BB	111.3
O2—C4—H4A	110.6	C9B—C10B—H10C	111.1
O2—C4—H4B	110.6	C9B—C10B—H10D	111.1
C3—C4—H4A	110.6	H10C—C10B—H10D	109.1
C3—C4—H4B	110.6	C11B—C10B—C9B	103.2 (6)
H4A—C4—H4B	108.7	C11B—C10B—H10C	111.1
O3—C5—H5A	110.8	C11B—C10B—H10D	111.1
O3—C5—H5B	110.8	C10B—C11B—H11C	110.9
O3—C5—C6	104.7 (4)	C10B—C11B—H11D	110.9
H5A—C5—H5B	108.9	C10B—C11B—C12B	104.2 (6)
C6—C5—H5A	110.8	H11C—C11B—H11D	108.9
C6—C5—H5B	110.8	C12B—C11B—H11C	110.9
C5—C6—H6A	111.1	C12B—C11B—H11D	110.9
C5—C6—H6B	111.1	O4B—C12B—C11B	106.3 (6)
H6A—C6—H6B	109.0	O4B—C12B—H12C	110.5
C7—C6—C5	103.5 (4)	O4B—C12B—H12D	110.5
C7—C6—H6A	111.1	C11B—C12B—H12C	110.5
C7—C6—H6B	111.1	C11B—C12B—H12D	110.5

| C6—C7—H7A | 110.5 | H12C—C12B—H12D | 108.7 |
| C6—C7—H7B | 110.5 | | |

Symmetry code: (i) −*x*+1, *y*, −*z*+3/2.