Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Decakis(μ_2-acetato-κ^2O:O')bis(μ_2-isopropoxy-κ^2O:O)tetraisopropoxytetra-μ_3-oxo-tetratitaniumdizirconium

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Received 17 August 2007; accepted 23 August 2007

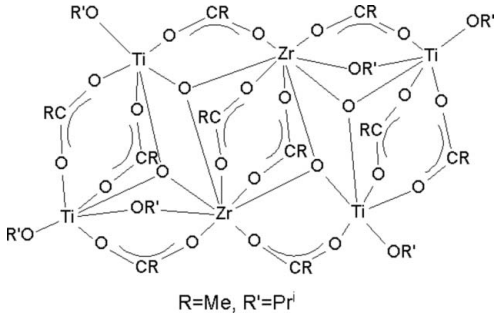
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.008 Å; disorder in main residue; R factor = 0.043; wR factor = 0.116; data-to-parameter ratio = 14.8.

The title complex, $[Ti_4Zr_2(C_2H_3O_2)_{10}(C_3H_7O)_6O_4]$, was prepared in supercritical CO_2. The molecule lies on a crystallographic inversion center. The metallic core contains two Zr atoms each coordinated by eight O atoms in a distorted square-antiprismatic geometry and four Ti atoms in distorted octahedral coordination geometries. The overall metallic core conformation can be described as 'raft'-style since all six metal atoms and four bridging O atoms form an approximately planar arrangement. One of the unique terminal isopropoxide ligands is disordered over two sites with equal occupancies.

Related literature

For background information, see: Durr *et al.* (2006); Fujishima & Honda (1972); Laaziz *et al.* (1992); Lee *et al.* (2006); Mihaiu *et al.* (2007); Ohtani *et al.* (1997); Pal *et al.* (2007); Sui *et al.* (2004, 2005, 2006). The only other two published crystal structures of hexametallic Zr—Ti metal cluster compounds (Moraru *et al.*, 2001) are also triclinic with Z = 1. These both form 'raft'- style complexes as opposed to the numerous forms observed with pure Ti_6 or Zr_6 complexes.

For related literature, see: Allen (2002); Hernandez-Alonso *et al.* (2006); Kitiyanan *et al.* (2006).



R=Me, R'=Pr^i

Experimental

Crystal data

$[Ti_4Zr_2(C_2H_3O_2)_{10}(C_3H_7O)_6O_4]$
M_r = 1383.00
Triclinic, $P\overline{1}$
a = 10.1178 (4) Å
b = 11.9884 (5) Å
c = 12.3722 (4) Å
α = 94.713 (2)°
β = 90.775 (2)°
γ = 105.608 (2)°
V = 1439.48 (9) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.96 mm^{-1}
T = 296 (2) K
0.20 × 0.07 × 0.04 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.832, T_{max} = 0.969
15521 measured reflections
5064 independent reflections
4164 reflections with $I > 2\sigma(I)$
R_{int} = 0.053

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.116
S = 1.04
5064 reflections
343 parameters
28 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.62 e Å^{-3}

Data collection: *COLLECT* (Nonius, 2001); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 2001); software used to prepare material for publication: *SHELXTL/PC*.

The authors thank the Canadian Natural Science and Engineering Research Council (NSERC), and the Materials and Manufacturing Ontario Emerging Materials Program (MMO-EMK) for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2485).

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supplementary materials

Acta Cryst. (2007). E**63**, m2429-m2430 [**doi:10.1107/S1600536807041694**]

Decakis(μ_2-acetato-κ^2O:O')bis(μ_2-isopropoxy-κ^2O:O)tetraisopropoxytetra-μ_3-oxo-tetratitaniumdizirconium

R. A. Lucky, R. Sui, P. A. Charpentier and M. C. Jennings

Comment

Titanium dioxide (TiO_2) nanomaterials have been widely used as photocatalysts, optical coatings and electrodes in solar cells for numerous reasons. They possess favorable opto-electrical properties, and further, they are inexpensive, chemically stable and non-toxic. This field was pioneered by Fujishima & Honda (1972) with their work on the photo–induced splitting of water in the suspensions of micrometer sized titania. The performance depends on some important properties such as surface area, crystal size, thermal stability and quantum efficiency (Ohtani *et al.*, 1997; Pal *et al.*, 2007). These properties depend highly on both the synthesis method, and the subsequent thermal treatment technique, *i.e.* calcination.

In some cases, doping with a second metal has been found to be very effective in improving the properties of TiO_2. Zirconia has been reported as one of the most suitable dopants to enhance the thermal stability and activity of TiO_2 nanomaterials (Hernandez-Alonso *et al.*, 2006; Durr *et al.*, 2006; Kitiyanan *et al.*, 2006). Binary metal oxides are synthesized by the Sol-Gel process because it has the ability to produce large scale homogeneous multicomponent metal oxides with lower cost and milder operating conditions compared to the CVD sputtering method (Mihaiu *et al.*, 2007). Laaziz *et al.* (1992) produced Ti—Zr metal oxide crystals using a 1:1 molar ratio of titanium and zirconium precursors by acetic acid modified Sol-gel process in n-propanol. The resulting crystal structure was $Zr_6Ti_3(OPr)_{16}(OAc)_8O_6$.

The Sol-gel process in supercritical carbon dioxide ($ScCO_2$) has the potential to produce new and high quality materials. SiO_2 aerogel (Sui *et al.*, 2004), ZrO_2 monolith (Sui *et al.*, 2006), and TiO_2 nanofibers (Sui *et al.*, 2005) were produced by poly condensation of acetic acid with respective alkoxide and amorphous ZrO_2 by a reverse microemulsion process (Lee *et al.*, 2006). To the best of our knowledge, no one has produced binary metal oxide single crystals in supercritical CO_2. It is important to investigate the single-crystal structure of binary metal alkoxides to understand the chemistry and the mechanism of nanostructure formation during the Sol-gel process in $ScCO_2$.

Towards this end we attempted to synthesize an acetic-acid-modified Ti—Zr propoxide in $ScCO_2$ using an acid:alkoxide ratio of 1.33:1. This yielded colourless plates which were fully characterized by single-crystal X-ray crystallography. The results of the study revealed a "raft" style hexanuclear mixed metal complex, $Ti_4Zr_2(\mu_3\text{-}O)_4(\mu\text{-}O_2CCH_3)_{10}(\mu\text{-}O^iPr)_2(O^iPr)_4$, see Scheme. The molecule resided on a centre of symmetry, so only half of the molecule comprises the asymmetric unit. One of the terminal isopropoxide ligands is disordered and was modelled isotropically in equal ratios.

The core of the heterometallic structure consists of two Zr atoms and four Ti atoms linked by triply-bridging O atoms. The compound is also linked together *via* 10 bridging acetate ligands, 2 bridging isopropoxide ligands with the coordination completed by 4 isopropoxide ligands (Fig. 1). The titanium centers are surrounded by a distorted octahedron of O atoms, which is typical, as is the higher coordination number observed for the zirconium centers, in this case, 8. The μ_3-oxo groups appear to be sp^2 hybridized (average sum of angles = 352.0°).

Metal pure Titanium or Zirconium hexametallic species have been known to form prismatic hexagons, or octahedrons or "raft" style complexes. A search of the CSD V5.28 (Allen, 2002) revealed only two other hexametallic Zr—Ti metal clusters and they were both "raft" style. The crystal structures of the two complexes $Ti_2Zr_4(\mu_3\text{-}O)_4(\mu\text{-}O_2CC(CH_3)(CH_2))_{10}(\mu\text{-}O^nBu)_2(O_2CC(CH_3)\ (CH_2))_4$and $Ti_4Zr_2(\mu_3\text{-}O)_4(\mu\text{-}O_2CC(CH_3)(CH_2))_{10}\ (\mu\text{-}O^nBu)_2(O^nBu)_4$ were determined by Moraru *et al.* (2001). As with the title compound both of these complexes crystallize in space group P-1 with $Z = 1$.

Experimental

The synthesis of single crystals in $scCO_2$ was carried out in a 10 ml stainless steel view cell connected to a syringe pump (ISCO 260DM) for pumping CO_2. A check valve (HIP) was used to prevent possible back flow from the view cell. The temperature and pressure in the view cell were measured and controlled by means of a T-type thermocouple (Omega), a heating tape, a temperature controller (Omega) and a pressure transducer (Omega). 2 ml (6.6 mmol) of titanium (IV) isopropoxide (reagent grade 97%), 0.325 ml (0.73 mmol) zirconium (IV) propoxide (reagent grade 90%) and 0.55 ml (9.8 mmol) of 99.7% acetic acid were quickly placed in the view cell, followed by addition of CO_2 (insrument grade 99.99%) to 5000 PSI pressure and 313 K temperature. A magnetic stirrer was used for mixing the reaction. Colorless crystals started to appear after 15 days and after 30 days the material was washed continuously using $ScCO_2$ at a controlled flow rate of approximately 0.5 ml/min, followed by controlled venting. The synthesized material was kept under an Argon atmosphere until ready for the X-ray diffraction experiment.

Refinement

One of the isopropoxide units was modelled as disordered over two sites with occpuncies of 0.50/0.50. The following two bond lengths of the disordered moiety were restrained to be similar: O31—C32A, O31—C32B. The following four bond lengths of the disordered moiety were restrained to be similar: C32A—C33A, C32A—C34A, C32B—C33B, C32B—C34B. Soft restraints were applied to the isotropic displacement parameters of the disordered moiety. C32A and C32B had their displacement parameters restrained to be equal. The disorder has resulted in larger than normal displacment ellipsoids for the atoms involved.

All H atoms were positioned geometrically and constrained as riding atoms with C—H = 0.98Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for methyne H atoms and C—H = 0.96Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms.

Figures

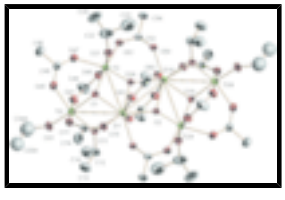

Fig. 1. The molecular structure of the title ccompound with 30% probability displacement ellipsoids and the atom labelling scheme. H atoms are omitted for clarity. Atoms labelled with the suffix 'a' are related by the symmetry operator $(1 - x, 2 - y, 2 - z)$.

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Crystal data

$[Ti_4Zr_2(C_2H_3O_2)_{10}(C_3H_7O)_6O_4]$	$Z = 1$
$M_r = 1383.00$	$F_{000} = 708$
Triclinic, $P\overline{1}$	$D_x = 1.595$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation λ = 0.71073 Å
$a = 10.1178$ (4) Å	Cell parameters from 10310 reflections
$b = 11.9884$ (5) Å	θ = 2.0–27.5º
$c = 12.3722$ (4) Å	μ = 0.96 mm^{-1}
α = 94.713 (2)º	$T = 296$ (2) K
β = 90.775 (2)º	Plate, colourless
γ = 105.608 (2)º	0.20 × 0.07 × 0.04 mm
$V = 1439.48$ (9) Å^3	

Data collection

Nonius KappaCCD diffractometer	5064 independent reflections
Radiation source: fine-focus sealed tube	4164 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.053$
$T = 296(2)$ K	$\theta_{max} = 25.0$º
φ scans, and ω scans with κ offsets	$\theta_{min} = 2.6$º
Absorption correction: multi-scan (SORTAV; Blessing, 1995)	$h = -12 \rightarrow 12$
$T_{min} = 0.832$, $T_{max} = 0.969$	$k = -14 \rightarrow 12$
15521 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.043$	H-atom parameters constrained
$wR(F^2) = 0.116$	$w = 1/[\sigma^2(F_o^2) + (0.0533P)^2 + 1.8365P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.002$
5064 reflections	$\Delta\rho_{max} = 0.45$ e Å^{-3}
343 parameters	$\Delta\rho_{min} = -0.62$ e Å^{-3}
28 restraints	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

Special details

Experimental. Absorption correction: multi-scan from symmetry-related measurements (*SORTAV*; Blessing, 1995)

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}	Occ. (<1)
Zr1	0.36683 (4)	0.91306 (3)	0.91786 (3)	0.03491 (13)	
Ti2	0.64206 (7)	0.97018 (6)	0.79062 (5)	0.03841 (19)	
Ti3	0.35561 (8)	0.74024 (7)	0.69502 (6)	0.0452 (2)	
O1	0.4534 (3)	0.8919 (2)	0.7651 (2)	0.0392 (6)	
O2	0.4157 (3)	1.0079 (2)	1.07191 (19)	0.0371 (6)	
O11	0.2824 (3)	0.7274 (2)	0.8373 (2)	0.0447 (7)	
C12	0.1925 (5)	0.6317 (4)	0.8897 (5)	0.0681 (14)	
H12A	0.1869	0.6599	0.9656	0.082*	
C13	0.0541 (6)	0.6062 (6)	0.8399 (6)	0.094 (2)	
H13A	0.0256	0.6765	0.8414	0.141*	
H13B	−0.0086	0.5508	0.8797	0.141*	
H13C	0.0546	0.5746	0.7661	0.141*	
C14	0.2513 (7)	0.5290 (5)	0.8899 (6)	0.0912 (19)	
H14A	0.2558	0.4975	0.8166	0.137*	
H14B	0.1936	0.4707	0.9301	0.137*	
H14C	0.3419	0.5534	0.9232	0.137*	
O21	0.6591 (3)	1.1083 (3)	0.7418 (2)	0.0527 (7)	
C22	0.7334 (8)	1.2032 (6)	0.6853 (6)	0.103 (2)	
H22A	0.6695	1.2203	0.6330	0.123*	
C23	0.7868 (12)	1.3112 (6)	0.7649 (9)	0.184 (5)	
H23A	0.7423	1.2986	0.8326	0.276*	
H23B	0.7674	1.3769	0.7355	0.276*	
H23C	0.8841	1.3258	0.7767	0.276*	
C24	0.8473 (10)	1.1835 (7)	0.6272 (7)	0.154 (4)	
H24A	0.9241	1.1931	0.6769	0.231*	
H24B	0.8717	1.2382	0.5735	0.231*	
H24C	0.8227	1.1059	0.5922	0.231*	
O31	0.2771 (3)	0.6024 (3)	0.6257 (3)	0.0611 (9)	
C32A	0.261 (2)	0.5116 (17)	0.5429 (16)	0.143 (4)*	0.50
H32A	0.3207	0.5464	0.4857	0.172*	0.50
C33A	0.129 (2)	0.479 (2)	0.4949 (19)	0.179 (9)*	0.50

H33A	0.1226	0.4167	0.4391	0.269*	0.50
H33B	0.1110	0.5440	0.4637	0.269*	0.50
H33C	0.0635	0.4528	0.5489	0.269*	0.50
C34A	0.324 (3)	0.425 (2)	0.581 (2)	0.204 (11)*	0.50
H34A	0.2740	0.3493	0.5503	0.306*	0.50
H34B	0.3224	0.4283	0.6586	0.306*	0.50
H34C	0.4176	0.4417	0.5589	0.306*	0.50
C32B	0.292 (3)	0.5001 (15)	0.5687 (16)	0.143 (4)*	0.50
H32B	0.3791	0.4910	0.5965	0.172*	0.50
C33B	0.308 (3)	0.507 (2)	0.4565 (18)	0.207 (11)*	0.50
H33D	0.2603	0.5596	0.4314	0.310*	0.50
H33E	0.2716	0.4313	0.4190	0.310*	0.50
H33F	0.4041	0.5348	0.4426	0.310*	0.50
C34B	0.191 (3)	0.396 (2)	0.592 (2)	0.190 (10)*	0.50
H34D	0.1753	0.3399	0.5303	0.286*	0.50
H34E	0.1060	0.4141	0.6096	0.286*	0.50
H34F	0.2227	0.3643	0.6532	0.286*	0.50
O41	0.5140 (3)	0.6760 (3)	0.7397 (3)	0.0548 (8)	
C42	0.6246 (4)	0.7114 (4)	0.7958 (4)	0.0492 (10)	
O43	0.6846 (3)	0.8148 (3)	0.8253 (2)	0.0506 (7)	
C44	0.6887 (6)	0.6198 (5)	0.8282 (5)	0.0821 (17)	
H44A	0.7317	0.5920	0.7669	0.123*	
H44B	0.6192	0.5565	0.8529	0.123*	
H44C	0.7563	0.6522	0.8855	0.123*	
O45	0.4674 (3)	0.7947 (3)	0.5625 (2)	0.0590 (8)	
C46	0.5882 (5)	0.8594 (4)	0.5547 (3)	0.0559 (12)	
O47	0.6705 (3)	0.9047 (3)	0.6325 (2)	0.0561 (8)	
C48	0.6347 (7)	0.8837 (6)	0.4403 (4)	0.092 (2)	
H48A	0.6134	0.9531	0.4212	0.138*	
H48B	0.5880	0.8194	0.3900	0.138*	
H48C	0.7320	0.8940	0.4376	0.138*	
O51	0.8441 (3)	1.0276 (3)	0.8471 (2)	0.0480 (7)	
C52	0.8950 (4)	1.0991 (4)	0.9271 (3)	0.0419 (9)	
O53	0.8269 (3)	1.1369 (2)	0.9984 (2)	0.0473 (7)	
C54	1.0481 (4)	1.1436 (5)	0.9367 (4)	0.0637 (13)	
H54A	1.0757	1.2222	0.9171	0.096*	
H54B	1.0883	1.0956	0.8890	0.096*	
H54C	1.0785	1.1415	1.0102	0.096*	
O61	0.3775 (3)	1.0931 (2)	0.8858 (2)	0.0441 (6)	
C62	0.4569 (4)	1.1892 (4)	0.9196 (3)	0.0455 (10)	
O63	0.5568 (3)	1.2066 (2)	0.9872 (2)	0.0440 (6)	
C64	0.4300 (6)	1.2946 (4)	0.8765 (5)	0.0711 (15)	
H64A	0.4652	1.3027	0.8050	0.107*	
H64B	0.4747	1.3624	0.9236	0.107*	
H64C	0.3330	1.2861	0.8733	0.107*	
O71	0.2073 (3)	0.8079 (3)	0.6488 (2)	0.0528 (7)	
C72	0.1513 (4)	0.8744 (4)	0.7072 (3)	0.0485 (10)	
O73	0.1912 (3)	0.9176 (3)	0.7996 (2)	0.0482 (7)	
C74	0.0268 (6)	0.8987 (6)	0.6578 (4)	0.0774 (16)	

H74A	−0.0505	0.8318	0.6598	0.116*
H74B	0.0433	0.9156	0.5839	0.116*
H74C	0.0079	0.9642	0.6981	0.116*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Zr1	0.0278 (2)	0.0345 (2)	0.0407 (2)	0.00664 (15)	0.00253 (14)	−0.00048 (15)
Ti2	0.0311 (4)	0.0410 (4)	0.0416 (4)	0.0078 (3)	0.0053 (3)	0.0010 (3)
Ti3	0.0373 (4)	0.0457 (4)	0.0488 (4)	0.0087 (3)	0.0006 (3)	−0.0089 (3)
O1	0.0357 (14)	0.0403 (15)	0.0412 (14)	0.0111 (12)	0.0015 (11)	−0.0001 (11)
O2	0.0323 (14)	0.0365 (14)	0.0415 (14)	0.0087 (11)	0.0033 (11)	−0.0007 (11)
O11	0.0389 (15)	0.0359 (15)	0.0532 (16)	0.0013 (12)	0.0056 (12)	−0.0029 (12)
C12	0.067 (3)	0.048 (3)	0.082 (3)	0.004 (2)	0.013 (3)	−0.001 (2)
C13	0.061 (4)	0.092 (5)	0.119 (5)	0.003 (3)	0.003 (3)	0.004 (4)
C14	0.104 (5)	0.057 (3)	0.116 (5)	0.025 (3)	0.011 (4)	0.021 (3)
O21	0.0484 (18)	0.0498 (18)	0.0569 (17)	0.0051 (14)	0.0066 (14)	0.0129 (14)
C22	0.093 (5)	0.096 (5)	0.120 (5)	0.010 (4)	0.019 (4)	0.056 (4)
C23	0.246 (13)	0.058 (5)	0.215 (11)	−0.018 (6)	0.118 (10)	−0.001 (6)
C24	0.185 (9)	0.118 (7)	0.135 (7)	−0.010 (6)	0.096 (7)	0.025 (5)
O31	0.0553 (19)	0.0532 (19)	0.0669 (19)	0.0098 (15)	−0.0031 (15)	−0.0225 (16)
O41	0.0447 (18)	0.0458 (17)	0.073 (2)	0.0145 (14)	−0.0017 (15)	−0.0080 (15)
C42	0.041 (2)	0.049 (3)	0.059 (3)	0.017 (2)	0.005 (2)	−0.001 (2)
O43	0.0428 (17)	0.0445 (17)	0.0647 (18)	0.0145 (14)	−0.0024 (14)	−0.0029 (14)
C44	0.066 (4)	0.054 (3)	0.129 (5)	0.023 (3)	−0.020 (3)	0.004 (3)
O45	0.053 (2)	0.071 (2)	0.0470 (17)	0.0109 (17)	0.0053 (14)	−0.0115 (15)
C46	0.050 (3)	0.071 (3)	0.045 (2)	0.015 (2)	0.008 (2)	−0.002 (2)
O47	0.0444 (17)	0.069 (2)	0.0493 (17)	0.0102 (15)	0.0078 (14)	−0.0079 (15)
C48	0.089 (4)	0.122 (5)	0.050 (3)	0.003 (4)	0.015 (3)	0.000 (3)
O51	0.0301 (14)	0.0549 (18)	0.0551 (17)	0.0074 (13)	0.0056 (12)	−0.0044 (14)
C52	0.032 (2)	0.046 (2)	0.048 (2)	0.0086 (18)	0.0056 (17)	0.0084 (19)
O53	0.0322 (15)	0.0510 (17)	0.0533 (16)	0.0043 (13)	0.0090 (12)	−0.0055 (13)
C54	0.032 (2)	0.074 (3)	0.079 (3)	0.007 (2)	0.006 (2)	−0.006 (3)
O61	0.0384 (15)	0.0399 (16)	0.0531 (16)	0.0092 (13)	−0.0041 (12)	0.0043 (13)
C62	0.037 (2)	0.042 (2)	0.058 (2)	0.0116 (19)	0.0029 (19)	0.0052 (19)
O63	0.0375 (16)	0.0341 (15)	0.0577 (17)	0.0057 (12)	−0.0008 (13)	0.0025 (12)
C64	0.068 (3)	0.047 (3)	0.098 (4)	0.013 (2)	−0.020 (3)	0.017 (3)
O71	0.0431 (17)	0.063 (2)	0.0517 (17)	0.0163 (15)	−0.0039 (13)	−0.0047 (15)
C72	0.037 (2)	0.056 (3)	0.051 (2)	0.013 (2)	−0.0019 (19)	−0.003 (2)
O73	0.0354 (15)	0.0535 (18)	0.0557 (17)	0.0151 (13)	−0.0042 (13)	−0.0050 (14)
C74	0.059 (3)	0.109 (5)	0.072 (3)	0.042 (3)	−0.013 (3)	−0.008 (3)

Geometric parameters (Å, °)

Zr1—O2	2.118 (2)	C32A—H32A	0.9800
Zr1—O1	2.118 (2)	C33A—H33A	0.9600
Zr1—O2^{i}	2.147 (3)	C33A—H33B	0.9600
Zr1—O53^{i}	2.191 (3)	C33A—H33C	0.9600

Zr1—O61	2.201 (3)	C34A—H34A	0.9600
Zr1—O63^{i}	2.210 (3)	C34A—H34B	0.9600
Zr1—O11	2.295 (3)	C34A—H34C	0.9600
Zr1—O73	2.301 (3)	C32B—C33B	1.406 (16)
Zr1—Ti2	3.1578 (8)	C32B—C34B	1.441 (16)
Zr1—Ti3	3.2913 (8)	C32B—H32B	0.9800
Zr1—Zr1^{i}	3.4454 (7)	C33B—H33D	0.9600
Ti2—O21	1.775 (3)	C33B—H33E	0.9600
Ti2—O2^{i}	1.827 (2)	C33B—H33F	0.9600
Ti2—O1	1.896 (3)	C34B—H34D	0.9600
Ti2—O51	2.065 (3)	C34B—H34E	0.9600
Ti2—O43	2.097 (3)	C34B—H34F	0.9600
Ti2—O47	2.100 (3)	O41—C42	1.261 (5)
Ti3—O31	1.772 (3)	C42—O43	1.247 (5)
Ti3—O11	1.921 (3)	C42—C44	1.495 (6)
Ti3—O1	1.946 (3)	C44—H44A	0.9600
Ti3—O71	1.986 (3)	C44—H44B	0.9600
Ti3—O41	2.044 (3)	C44—H44C	0.9600
Ti3—O45	2.055 (3)	O45—C46	1.268 (6)
O2—Ti2^{i}	1.827 (2)	C46—O47	1.251 (5)
O2—Zr1^{i}	2.147 (3)	C46—C48	1.524 (7)
O11—C12	1.462 (6)	C48—H48A	0.9600
C12—C13	1.466 (8)	C48—H48B	0.9600
C12—C14	1.505 (7)	C48—H48C	0.9600
C12—H12A	0.9800	O51—C52	1.261 (5)
C13—H13A	0.9600	C52—O53	1.255 (5)
C13—H13B	0.9600	C52—C54	1.496 (6)
C13—H13C	0.9600	O53—Zr1^{i}	2.191 (3)
C14—H14A	0.9600	C54—H54A	0.9600
C14—H14B	0.9600	C54—H54B	0.9600
C14—H14C	0.9600	C54—H54C	0.9600
O21—C22	1.426 (7)	O61—C62	1.250 (5)
C22—C24	1.428 (10)	C62—O63	1.265 (5)
C22—C23	1.529 (11)	C62—C64	1.498 (6)
C22—H22A	0.9800	O63—Zr1^{i}	2.210 (3)
C23—H23A	0.9600	C64—H64A	0.9600
C23—H23B	0.9600	C64—H64B	0.9600
C23—H23C	0.9600	C64—H64C	0.9600
C24—H24A	0.9600	O71—C72	1.279 (5)
C24—H24B	0.9600	C72—O73	1.231 (5)
C24—H24C	0.9600	C72—C74	1.500 (6)
O31—C32A	1.407 (14)	C74—H74A	0.9600
O31—C32B	1.408 (15)	C74—H74B	0.9600
C32A—C33A	1.396 (15)	C74—H74C	0.9600
C32A—C34A	1.456 (16)		
O2—Zr1—O1	140.96 (10)	C12—C13—H13A	109.5
O2—Zr1—O2^{i}	72.20 (11)	C12—C13—H13B	109.5

O1—Zr1—O2^{i}	69.68 (10)	H13A—C13—H13B	109.5
O2—Zr1—O53^{i}	76.97 (10)	C12—C13—H13C	109.5
O1—Zr1—O53^{i}	141.85 (10)	H13A—C13—H13C	109.5
O2^{i}—Zr1—O53^{i}	148.21 (10)	H13B—C13—H13C	109.5
O2—Zr1—O61	75.99 (10)	C12—C14—H14A	109.5
O1—Zr1—O61	88.40 (10)	C12—C14—H14B	109.5
O2^{i}—Zr1—O61	78.44 (10)	H14A—C14—H14B	109.5
O53^{i}—Zr1—O61	101.67 (11)	C12—C14—H14C	109.5
O2—Zr1—O63^{i}	77.27 (10)	H14A—C14—H14C	109.5
O1—Zr1—O63^{i}	102.10 (10)	H14B—C14—H14C	109.5
O2^{i}—Zr1—O63^{i}	77.47 (10)	C22—O21—Ti2	150.7 (4)
O53^{i}—Zr1—O63^{i}	88.45 (11)	O21—C22—C24	115.2 (6)
O61—Zr1—O63^{i}	148.32 (10)	O21—C22—C23	109.8 (6)
O2—Zr1—O11	141.88 (10)	C24—C22—C23	107.9 (7)
O1—Zr1—O11	68.41 (10)	O21—C22—H22A	107.9
O2^{i}—Zr1—O11	119.81 (9)	C24—C22—H22A	107.9
O53^{i}—Zr1—O11	80.96 (10)	C23—C22—H22A	107.9
O61—Zr1—O11	139.47 (10)	C22—C23—H23A	109.5
O63^{i}—Zr1—O11	71.41 (10)	C22—C23—H23B	109.5
O2—Zr1—O73	126.31 (9)	H23A—C23—H23B	109.5
O1—Zr1—O73	78.02 (10)	C22—C23—H23C	109.5
O2^{i}—Zr1—O73	134.51 (10)	H23A—C23—H23C	109.5
O53^{i}—Zr1—O73	71.69 (11)	H23B—C23—H23C	109.5
O61—Zr1—O73	69.29 (10)	C22—C24—H24A	109.5
O63^{i}—Zr1—O73	141.88 (10)	C22—C24—H24B	109.5
O11—Zr1—O73	73.50 (10)	H24A—C24—H24B	109.5
O2—Zr1—Ti2	105.70 (7)	C22—C24—H24C	109.5
O1—Zr1—Ti2	35.70 (7)	H24A—C24—H24C	109.5
O2^{i}—Zr1—Ti2	33.99 (6)	H24B—C24—H24C	109.5
O53^{i}—Zr1—Ti2	176.67 (7)	C32A—O31—Ti3	155.7 (11)
O61—Zr1—Ti2	81.03 (7)	C32B—O31—Ti3	148.6 (11)
O63^{i}—Zr1—Ti2	90.22 (7)	C33A—C32A—O31	112.0 (17)
O11—Zr1—Ti2	95.72 (7)	C33A—C32A—C34A	121 (2)
O73—Zr1—Ti2	107.73 (7)	O31—C32A—C34A	108.5 (16)
O2—Zr1—Ti3	165.63 (7)	C33A—C32A—H32A	104.6
O1—Zr1—Ti3	34.20 (7)	O31—C32A—H32A	104.6
O2^{i}—Zr1—Ti3	98.04 (6)	C34A—C32A—H32A	104.6
O53^{i}—Zr1—Ti3	110.59 (7)	C33B—C32B—O31	114.6 (18)
O61—Zr1—Ti3	113.07 (7)	C33B—C32B—C34B	112 (2)
O63^{i}—Zr1—Ti3	90.48 (7)	O31—C32B—C34B	114.2 (19)
O11—Zr1—Ti3	34.77 (7)	C33B—C32B—H32B	104.8
O73—Zr1—Ti3	68.06 (7)	O31—C32B—H32B	104.8
Ti2—Zr1—Ti3	66.362 (19)	C34B—C32B—H32B	104.8
O2—Zr1—Zr1^{i}	36.38 (7)	C32B—C33B—H33D	109.5

O1—Zr1—Zr1^{i}	105.14 (7)	C32B—C33B—H33E	109.5
O2^{i}—Zr1—Zr1^{i}	35.82 (6)	H33D—C33B—H33E	109.5
O53^{i}—Zr1—Zr1^{i}	113.02 (7)	C32B—C33B—H33F	109.5
O61—Zr1—Zr1^{i}	74.12 (7)	H33D—C33B—H33F	109.5
O63^{i}—Zr1—Zr1^{i}	74.30 (7)	H33E—C33B—H33F	109.5
O11—Zr1—Zr1^{i}	142.49 (7)	C32B—C34B—H34D	109.5
O73—Zr1—Zr1^{i}	143.19 (7)	C32B—C34B—H34E	109.5
Ti2—Zr1—Zr1^{i}	69.503 (17)	H34D—C34B—H34E	109.5
Ti3—Zr1—Zr1^{i}	133.05 (2)	C32B—C34B—H34F	109.5
O21—Ti2—O2^{i}	101.96 (13)	H34D—C34B—H34F	109.5
O21—Ti2—O1	104.06 (13)	H34E—C34B—H34F	109.5
O2^{i}—Ti2—O1	81.71 (11)	C42—O41—Ti3	137.5 (3)
O21—Ti2—O51	88.72 (13)	O43—C42—O41	125.9 (4)
O2^{i}—Ti2—O51	90.22 (11)	O43—C42—C44	117.9 (4)
O1—Ti2—O51	166.02 (12)	O41—C42—C44	116.2 (4)
O21—Ti2—O43	161.19 (13)	C42—O43—Ti2	131.3 (3)
O2^{i}—Ti2—O43	91.35 (12)	C42—C44—H44A	109.5
O1—Ti2—O43	90.87 (12)	C42—C44—H44B	109.5
O51—Ti2—O43	77.87 (12)	H44A—C44—H44B	109.5
O21—Ti2—O47	88.87 (13)	C42—C44—H44C	109.5
O2^{i}—Ti2—O47	165.51 (13)	H44A—C44—H44C	109.5
O1—Ti2—O47	86.37 (11)	H44B—C44—H44C	109.5
O51—Ti2—O47	99.72 (11)	C46—O45—Ti3	131.7 (3)
O43—Ti2—O47	80.58 (12)	O47—C46—O45	125.6 (4)
O21—Ti2—Zr1	106.25 (10)	O47—C46—C48	118.0 (5)
O2^{i}—Ti2—Zr1	41.05 (8)	O45—C46—C48	116.4 (4)
O1—Ti2—Zr1	40.69 (7)	C46—O47—Ti2	132.3 (3)
O51—Ti2—Zr1	130.54 (8)	C46—C48—H48A	109.5
O43—Ti2—Zr1	92.52 (8)	C46—C48—H48B	109.5
O47—Ti2—Zr1	126.75 (9)	H48A—C48—H48B	109.5
O31—Ti3—O11	103.45 (14)	C46—C48—H48C	109.5
O31—Ti3—O1	175.91 (13)	H48A—C48—H48C	109.5
O11—Ti3—O1	79.97 (11)	H48B—C48—H48C	109.5
O31—Ti3—O71	93.18 (14)	C52—O51—Ti2	128.7 (2)
O11—Ti3—O71	90.21 (12)	O53—C52—O51	125.0 (4)
O1—Ti3—O71	89.02 (12)	O53—C52—C54	117.7 (4)
O31—Ti3—O41	88.12 (14)	O51—C52—C54	117.4 (4)
O11—Ti3—O41	91.42 (13)	C52—O53—Zr1^{i}	141.7 (3)
O1—Ti3—O41	89.57 (11)	C52—C54—H54A	109.5
O71—Ti3—O41	177.63 (14)	C52—C54—H54B	109.5
O31—Ti3—O45	91.71 (14)	H54A—C54—H54B	109.5
O11—Ti3—O45	164.65 (12)	C52—C54—H54C	109.5
O1—Ti3—O45	84.79 (12)	H54A—C54—H54C	109.5
O71—Ti3—O45	91.39 (13)	H54B—C54—H54C	109.5
O41—Ti3—O45	86.59 (13)	C62—O61—Zr1	133.0 (3)
O31—Ti3—Zr1	146.00 (11)	O61—C62—O63	126.6 (4)

O11—Ti3—Zr1	42.94 (8)	O61—C62—C64	116.6 (4)
O1—Ti3—Zr1	37.72 (8)	O63—C62—C64	116.7 (4)
O71—Ti3—Zr1	83.70 (8)	C62—O63—Zr1^{i}	131.9 (3)
O41—Ti3—Zr1	96.33 (8)	C62—C64—H64A	109.5
O45—Ti3—Zr1	122.15 (9)	C62—C64—H64B	109.5
Ti2—O1—Ti3	133.57 (14)	H64A—C64—H64B	109.5
Ti2—O1—Zr1	103.61 (11)	C62—C64—H64C	109.5
Ti3—O1—Zr1	108.08 (12)	H64A—C64—H64C	109.5
Ti2^{i}—O2—Zr1	145.76 (14)	H64B—C64—H64C	109.5
Ti2^{i}—O2—Zr1^{i}	104.95 (12)	C72—O71—Ti3	127.0 (3)
Zr1—O2—Zr1^{i}	107.80 (10)	O73—C72—O71	124.9 (4)
C12—O11—Ti3	133.3 (3)	O73—C72—C74	118.9 (4)
C12—O11—Zr1	124.4 (3)	O71—C72—C74	116.3 (4)
Ti3—O11—Zr1	102.28 (12)	C72—O73—Zr1	135.7 (3)
O11—C12—C13	108.6 (5)	C72—C74—H74A	109.5
O11—C12—C14	111.8 (4)	C72—C74—H74B	109.5
C13—C12—C14	114.9 (5)	H74A—C74—H74B	109.5
O11—C12—H12A	107.1	C72—C74—H74C	109.5
C13—C12—H12A	107.1	H74A—C74—H74C	109.5
C14—C12—H12A	107.1	H74B—C74—H74C	109.5
O2—Zr1—Ti2—O21	−79.65 (13)	O61—Zr1—O2—Ti2^{i}	115.4 (3)
O1—Zr1—Ti2—O21	92.81 (16)	O63^{i}—Zr1—O2—Ti2^{i}	−81.7 (2)
O2^{i}—Zr1—Ti2—O21	−89.65 (16)	O11—Zr1—O2—Ti2^{i}	−46.6 (3)
O61—Zr1—Ti2—O21	−7.05 (12)	O73—Zr1—O2—Ti2^{i}	64.9 (3)
O63^{i}—Zr1—Ti2—O21	−156.47 (12)	Ti2—Zr1—O2—Ti2^{i}	−168.3 (2)
O11—Zr1—Ti2—O21	132.19 (13)	Ti3—Zr1—O2—Ti2^{i}	−113.8 (3)
O73—Zr1—Ti2—O21	57.72 (13)	Zr1^{i}—Zr1—O2—Ti2^{i}	−162.5 (3)
Ti3—Zr1—Ti2—O21	113.10 (11)	O1—Zr1—O2—Zr1^{i}	−12.8 (2)
Zr1^{i}—Zr1—Ti2—O21	−83.35 (10)	O2^{i}—Zr1—O2—Zr1^{i}	0.0
O2—Zr1—Ti2—O2^{i}	10.00 (19)	O53^{i}—Zr1—O2—Zr1^{i}	172.10 (14)
O1—Zr1—Ti2—O2^{i}	−177.54 (17)	O61—Zr1—O2—Zr1^{i}	−82.13 (12)
O61—Zr1—Ti2—O2^{i}	82.60 (14)	O63^{i}—Zr1—O2—Zr1^{i}	80.74 (12)
O63^{i}—Zr1—Ti2—O2^{i}	−66.83 (14)	O11—Zr1—O2—Zr1^{i}	115.89 (15)
O11—Zr1—Ti2—O2^{i}	−138.16 (14)	O73—Zr1—O2—Zr1^{i}	−132.66 (12)
O73—Zr1—Ti2—O2^{i}	147.37 (14)	Ti2—Zr1—O2—Zr1^{i}	−5.85 (11)
Ti3—Zr1—Ti2—O2^{i}	−157.25 (12)	Ti3—Zr1—O2—Zr1^{i}	48.7 (4)
Zr1^{i}—Zr1—Ti2—O2^{i}	6.30 (12)	O31—Ti3—O11—C12	4.4 (4)
O2—Zr1—Ti2—O1	−172.46 (14)	O1—Ti3—O11—C12	−173.3 (4)
O2^{i}—Zr1—Ti2—O1	177.54 (17)	O71—Ti3—O11—C12	97.7 (4)
O61—Zr1—Ti2—O1	−99.86 (14)	O41—Ti3—O11—C12	−84.0 (4)
O63^{i}—Zr1—Ti2—O1	110.72 (14)	O45—Ti3—O11—C12	−166.3 (5)
O11—Zr1—Ti2—O1	39.39 (14)	Zr1—Ti3—O11—C12	178.2 (4)
O73—Zr1—Ti2—O1	−35.09 (14)	O31—Ti3—O11—Zr1	−173.82 (13)
Ti3—Zr1—Ti2—O1	20.29 (12)	O1—Ti3—O11—Zr1	8.46 (11)

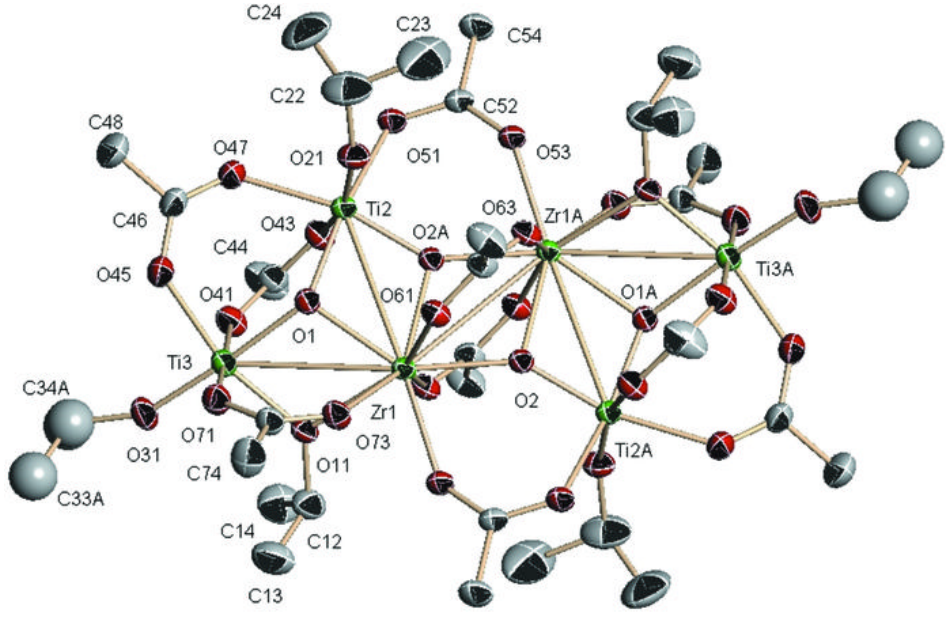
Zr1^{i}—Zr1—Ti2—O1	−176.16 (12)	O71—Ti3—O11—Zr1	−80.51 (13)
O2—Zr1—Ti2—O51	22.99 (14)	O41—Ti3—O11—Zr1	97.77 (12)
O1—Zr1—Ti2—O51	−164.56 (17)	O45—Ti3—O11—Zr1	15.5 (5)
O2^{i}—Zr1—Ti2—O51	12.99 (16)	O2—Zr1—O11—C12	25.2 (4)
O61—Zr1—Ti2—O51	95.59 (13)	O1—Zr1—O11—C12	173.3 (3)
O63^{i}—Zr1—Ti2—O51	−53.84 (13)	O2^{i}—Zr1—O11—C12	124.4 (3)
O11—Zr1—Ti2—O51	−125.17 (13)	O53^{i}—Zr1—O11—C12	−29.8 (3)
O73—Zr1—Ti2—O51	160.35 (14)	O61—Zr1—O11—C12	−127.3 (3)
Ti3—Zr1—Ti2—O51	−144.27 (12)	O63^{i}—Zr1—O11—C12	61.6 (3)
Zr1^{i}—Zr1—Ti2—O51	19.28 (11)	O73—Zr1—O11—C12	−103.3 (3)
O2—Zr1—Ti2—O43	99.15 (11)	Ti2—Zr1—O11—C12	149.9 (3)
O1—Zr1—Ti2—O43	−88.39 (15)	Ti3—Zr1—O11—C12	−178.4 (4)
O2^{i}—Zr1—Ti2—O43	89.15 (14)	Zr1^{i}—Zr1—O11—C12	86.5 (3)
O61—Zr1—Ti2—O43	171.75 (10)	O2—Zr1—O11—Ti3	−156.34 (12)
O63^{i}—Zr1—Ti2—O43	22.33 (11)	O1—Zr1—O11—Ti3	−8.23 (10)
O11—Zr1—Ti2—O43	−49.01 (11)	O2^{i}—Zr1—O11—Ti3	−57.16 (15)
O73—Zr1—Ti2—O43	−123.48 (11)	O53^{i}—Zr1—O11—Ti3	148.59 (14)
Ti3—Zr1—Ti2—O43	−68.10 (8)	O61—Zr1—O11—Ti3	51.2 (2)
Zr1^{i}—Zr1—Ti2—O43	95.45 (8)	O63^{i}—Zr1—O11—Ti3	−120.00 (14)
O2—Zr1—Ti2—O47	179.28 (14)	O73—Zr1—O11—Ti3	75.13 (12)
O1—Zr1—Ti2—O47	−8.27 (16)	Ti2—Zr1—O11—Ti3	−31.70 (11)
O2^{i}—Zr1—Ti2—O47	169.28 (17)	Zr1^{i}—Zr1—O11—Ti3	−95.12 (14)
O61—Zr1—Ti2—O47	−108.12 (14)	Ti3—O11—C12—C13	−69.9 (5)
O63^{i}—Zr1—Ti2—O47	102.45 (14)	Zr1—O11—C12—C13	108.0 (4)
O11—Zr1—Ti2—O47	31.12 (14)	Ti3—O11—C12—C14	57.9 (6)
O73—Zr1—Ti2—O47	−43.36 (14)	Zr1—O11—C12—C14	−124.2 (4)
Ti3—Zr1—Ti2—O47	12.02 (12)	O2^{i}—Ti2—O21—C22	136.2 (8)
Zr1^{i}—Zr1—Ti2—O47	175.57 (12)	O1—Ti2—O21—C22	−139.5 (8)
O2—Zr1—Ti3—O31	97.2 (4)	O51—Ti2—O21—C22	46.3 (8)
O1—Zr1—Ti3—O31	177.1 (2)	O43—Ti2—O21—C22	2.1 (10)
O2^{i}—Zr1—Ti3—O31	143.4 (2)	O47—Ti2—O21—C22	−53.5 (8)
O53^{i}—Zr1—Ti3—O31	−22.6 (2)	Zr1—Ti2—O21—C22	178.4 (8)
O61—Zr1—Ti3—O31	−135.8 (2)	Ti2—O21—C22—C24	10.0 (13)
O63^{i}—Zr1—Ti3—O31	66.0 (2)	Ti2—O21—C22—C23	−112.1 (9)
O11—Zr1—Ti3—O31	10.8 (2)	O11—Ti3—O31—C32A	−162 (2)
O73—Zr1—Ti3—O31	−81.7 (2)	O71—Ti3—O31—C32A	107 (2)
Ti2—Zr1—Ti3—O31	156.0 (2)	O41—Ti3—O31—C32A	−71 (2)
Zr1^{i}—Zr1—Ti3—O31	134.7 (2)	O45—Ti3—O31—C32A	15 (2)
O2—Zr1—Ti3—O11	86.4 (3)	Zr1—Ti3—O31—C32A	−170 (2)
O1—Zr1—Ti3—O11	166.30 (17)	O11—Ti3—O31—C32B	−121.0 (18)
O2^{i}—Zr1—Ti3—O11	132.58 (14)	O71—Ti3—O31—C32B	148.0 (18)
O53^{i}—Zr1—Ti3—O11	−33.36 (15)	O41—Ti3—O31—C32B	−30.0 (18)
O61—Zr1—Ti3—O11	−146.61 (15)	O45—Ti3—O31—C32B	56.5 (18)
O63^{i}—Zr1—Ti3—O11	55.17 (14)	Zr1—Ti3—O31—C32B	−128.6 (18)

O73—Zr1—Ti3—O11	−92.48 (15)	C32B—O31—C32A—C33A	144 (6)
Ti2—Zr1—Ti3—O11	145.19 (13)	Ti3—O31—C32A—C33A	−127 (2)
Zr1^{i}—Zr1—Ti3—O11	123.92 (13)	C32B—O31—C32A—C34A	8(4)
O2—Zr1—Ti3—O1	−79.9 (3)	Ti3—O31—C32A—C34A	97 (3)
O2^{i}—Zr1—Ti3—O1	−33.71 (14)	C32A—O31—C32B—C33B	41 (4)
O53^{i}—Zr1—Ti3—O1	160.35 (15)	Ti3—O31—C32B—C33B	−87 (3)
O61—Zr1—Ti3—O1	47.09 (14)	C32A—O31—C32B—C34B	−90 (5)
O63^{i}—Zr1—Ti3—O1	−111.13 (14)	Ti3—O31—C32B—C34B	141.8 (16)
O11—Zr1—Ti3—O1	−166.30 (17)	O31—Ti3—O41—C42	−178.2 (5)
O73—Zr1—Ti3—O1	101.22 (15)	O11—Ti3—O41—C42	−74.8 (5)
Ti2—Zr1—Ti3—O1	−21.10 (12)	O1—Ti3—O41—C42	5.2 (5)
Zr1^{i}—Zr1—Ti3—O1	−42.38 (13)	O45—Ti3—O41—C42	90.0 (5)
O2—Zr1—Ti3—O71	−176.5 (3)	Zr1—Ti3—O41—C42	−32.0 (5)
O1—Zr1—Ti3—O71	−96.58 (16)	Ti3—O41—C42—O43	−16.3 (8)
O2^{i}—Zr1—Ti3—O71	−130.29 (12)	Ti3—O41—C42—C44	164.2 (4)
O53^{i}—Zr1—Ti3—O71	63.77 (13)	O41—C42—O43—Ti2	−4.4 (7)
O61—Zr1—Ti3—O71	−49.49 (12)	C44—C42—O43—Ti2	175.1 (3)
O63^{i}—Zr1—Ti3—O71	152.29 (12)	O21—Ti2—O43—C42	−117.0 (5)
O11—Zr1—Ti3—O71	97.12 (16)	O2^{i}—Ti2—O43—C42	107.6 (4)
O73—Zr1—Ti3—O71	4.64 (12)	O1—Ti2—O43—C42	25.9 (4)
Ti2—Zr1—Ti3—O71	−117.68 (10)	O51—Ti2—O43—C42	−162.4 (4)
Zr1^{i}—Zr1—Ti3—O71	−138.96 (10)	O47—Ti2—O43—C42	−60.3 (4)
O2—Zr1—Ti3—O41	1.1 (3)	Zr1—Ti2—O43—C42	66.6 (4)
O1—Zr1—Ti3—O41	81.03 (15)	O31—Ti3—O45—C46	−144.2 (4)
O2^{i}—Zr1—Ti3—O41	47.32 (12)	O11—Ti3—O45—C46	26.7 (8)
O53^{i}—Zr1—Ti3—O41	−118.62 (13)	O1—Ti3—O45—C46	33.7 (4)
O61—Zr1—Ti3—O41	128.13 (12)	O71—Ti3—O45—C46	122.6 (4)
O63^{i}—Zr1—Ti3—O41	−30.09 (12)	O41—Ti3—O45—C46	−56.2 (4)
O11—Zr1—Ti3—O41	−85.26 (15)	Zr1—Ti3—O45—C46	39.1 (5)
O73—Zr1—Ti3—O41	−177.74 (13)	Ti3—O45—C46—O47	1.5 (8)
Ti2—Zr1—Ti3—O41	59.93 (9)	Ti3—O45—C46—C48	−178.0 (4)
Zr1^{i}—Zr1—Ti3—O41	38.65 (10)	O45—C46—O47—Ti2	−34.4 (8)
O2—Zr1—Ti3—O45	−88.8 (3)	C48—C46—O47—Ti2	145.1 (4)
O1—Zr1—Ti3—O45	−8.91 (16)	O21—Ti2—O47—C46	−89.8 (5)
O2^{i}—Zr1—Ti3—O45	−42.62 (13)	O2^{i}—Ti2—O47—C46	49.0 (8)
O53^{i}—Zr1—Ti3—O45	151.44 (14)	O1—Ti2—O47—C46	14.3 (4)
O61—Zr1—Ti3—O45	38.18 (14)	O51—Ti2—O47—C46	−178.4 (4)
O63^{i}—Zr1—Ti3—O45	−120.03 (13)	O43—Ti2—O47—C46	105.8 (5)
O11—Zr1—Ti3—O45	−175.20 (17)	Zr1—Ti2—O47—C46	19.7 (5)
O73—Zr1—Ti3—O45	92.32 (14)	O21—Ti2—O51—C52	72.6 (4)
Ti2—Zr1—Ti3—O45	−30.01 (11)	O2^{i}—Ti2—O51—C52	−29.3 (4)
Zr1^{i}—Zr1—Ti3—O45	−51.29 (12)	O1—Ti2—O51—C52	−83.8 (6)
O21—Ti2—O1—Ti3	129.2 (2)	O43—Ti2—O51—C52	−120.6 (4)
O2^{i}—Ti2—O1—Ti3	−130.5 (2)	O47—Ti2—O51—C52	161.3 (3)
O51—Ti2—O1—Ti3	−75.2 (5)	Zr1—Ti2—O51—C52	−37.8 (4)

O43—Ti2—O1—Ti3	−39.3 (2)	Ti2—O51—C52—O53	11.2 (6)
O47—Ti2—O1—Ti3	41.2 (2)	Ti2—O51—C52—C54	−167.8 (3)
Zr1—Ti2—O1—Ti3	−132.1 (3)	O51—C52—O53—Zr1^{i}	30.5 (7)
O21—Ti2—O1—Zr1	−98.70 (14)	C54—C52—O53—Zr1^{i}	−150.5 (4)
O2^{i}—Ti2—O1—Zr1	1.63 (11)	O2—Zr1—O61—C62	40.7 (4)
O51—Ti2—O1—Zr1	56.9 (5)	O1—Zr1—O61—C62	−103.2 (4)
O43—Ti2—O1—Zr1	92.86 (12)	O2^{i}—Zr1—O61—C62	−33.6 (4)
O47—Ti2—O1—Zr1	173.37 (13)	O53^{i}—Zr1—O61—C62	113.9 (4)
O11—Ti3—O1—Ti2	121.3 (2)	O63^{i}—Zr1—O61—C62	7.5 (5)
O71—Ti3—O1—Ti2	−148.3 (2)	O11—Zr1—O61—C62	−156.4 (3)
O41—Ti3—O1—Ti2	29.8 (2)	O73—Zr1—O61—C62	179.0 (4)
O45—Ti3—O1—Ti2	−56.9 (2)	Ti2—Zr1—O61—C62	−68.1 (4)
Zr1—Ti3—O1—Ti2	130.7 (3)	Ti3—Zr1—O61—C62	−127.5 (3)
O11—Ti3—O1—Zr1	−9.43 (12)	Zr1^{i}—Zr1—O61—C62	3.0 (3)
O71—Ti3—O1—Zr1	80.95 (13)	Zr1—O61—C62—O63	−1.3 (7)
O41—Ti3—O1—Zr1	−100.95 (13)	Zr1—O61—C62—C64	179.4 (3)
O45—Ti3—O1—Zr1	172.44 (14)	O61—C62—O63—Zr1^{i}	−3.5 (6)
O2—Zr1—O1—Ti2	11.6 (2)	C64—C62—O63—Zr1^{i}	175.7 (3)
O2^{i}—Zr1—O1—Ti2	−1.46 (10)	O31—Ti3—O71—C72	137.7 (4)
O53^{i}—Zr1—O1—Ti2	−176.23 (13)	O11—Ti3—O71—C72	34.3 (4)
O61—Zr1—O1—Ti2	76.80 (12)	O1—Ti3—O71—C72	−45.7 (4)
O63^{i}—Zr1—O1—Ti2	−73.05 (13)	O45—Ti3—O71—C72	−130.5 (4)
O11—Zr1—O1—Ti2	−137.23 (14)	Zr1—Ti3—O71—C72	−8.3 (4)
O73—Zr1—O1—Ti2	145.96 (13)	Ti3—O71—C72—O73	8.2 (7)
Ti3—Zr1—O1—Ti2	−145.59 (19)	Ti3—O71—C72—C74	−170.9 (4)
Zr1^{i}—Zr1—O1—Ti2	3.73 (12)	O71—C72—O73—Zr1	0.2 (7)
O2—Zr1—O1—Ti3	157.16 (12)	C74—C72—O73—Zr1	179.2 (4)
O2^{i}—Zr1—O1—Ti3	144.13 (14)	O2—Zr1—O73—C72	175.9 (4)
O53^{i}—Zr1—O1—Ti3	−30.6 (2)	O1—Zr1—O73—C72	29.9 (4)
O61—Zr1—O1—Ti3	−137.61 (12)	O2^{i}—Zr1—O73—C72	75.0 (4)
O63^{i}—Zr1—O1—Ti3	72.54 (13)	O53^{i}—Zr1—O73—C72	−126.6 (4)
O11—Zr1—O1—Ti3	8.36 (11)	O61—Zr1—O73—C72	122.7 (4)
O73—Zr1—O1—Ti3	−68.45 (12)	O63^{i}—Zr1—O73—C72	−64.5 (5)
Ti2—Zr1—O1—Ti3	145.59 (19)	O11—Zr1—O73—C72	−40.9 (4)
Zr1^{i}—Zr1—O1—Ti3	149.32 (9)	Ti2—Zr1—O73—C72	50.0 (4)
O1—Zr1—O2—Ti2^{i}	−175.29 (19)	Ti3—Zr1—O73—C72	−4.4 (4)
O2^{i}—Zr1—O2—Ti2^{i}	−162.5 (3)	Zr1^{i}—Zr1—O73—C72	129.2 (4)
O53^{i}—Zr1—O2—Ti2^{i}	9.6 (2)		

Symmetry codes: (i) −*x*+1, −*y*+2, −*z*+2.

Fig. 1


C24
C23
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Ti2
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C44
O45
O41
O61
O1A
Ti3A
O1
Ti3
C34A
Zr1
O2
O71
O73
O31
Ti2A
C74
O11
C33A
C14
C12
C13