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Hexakis(μ-acetato-κ^2O,O')hexaisopropoxyhexa-μ_3-oxo-hexatitanium

Ruohong Sui,[a] P. A. Charpentier,[a] A. S. Rizkalla[a] and M. C. Jennings[b]*

[a]Department of Chemical and Biochemical Engineering, The University of Western Ontario, London, Ontario, Canada N6A 5B9, and [b]Department of Chemistry, The University of Western Ontario, London, Ontario, Canada N6A 5B7

Correspondence e-mail: mjenning@uwo.ca

Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.016 Å
Disorder in main residue
R factor = 0.076
wR factor = 0.195
Data-to-parameter ratio = 14.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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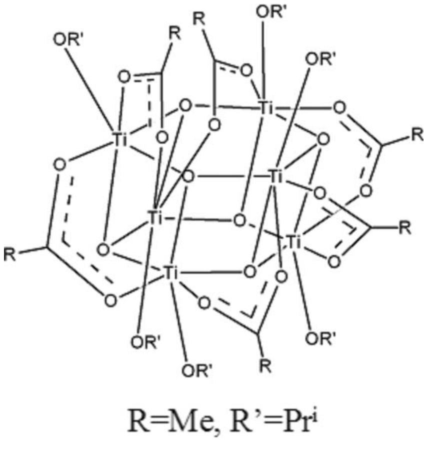
The title compound, $[Ti_6(C_2H_3O_2)_6(C_3H_7O)_6O_6]$, was prepared by the stoichiometric reaction of acetic acid with titanium isopropoxide in supercritical CO_2. There are two independent half-molecules in the asymmetric unit. The symmetry-complete hexaprismatic molecules are centrosymmetric.

Comment

TiO_2 nanomaterials are of great interest for energy conversion and photocatalysis since the discovery of their ability to photoelectrolyse water and generate hydrogen (Fujishima & Honda, 1972). One of the challenges during the sol–gel process used to produce TiO_2 nanostructures is the control of the activity of Ti^{IV} precursors. Before the sol–gel process was developed, acetic acid was widely used to stabilize Ti^{IV} by forming Ti–acetate coordination bonds (Sanchez *et al.*, 1988). The crystal structures of a variety of carboxylic-acid-modified titanium alkoxides are known. Numerous molecular shapes of titanium oxocarboxylates have been found, including four distinct shapes for hexatitanium complexes (Rammal *et al.*, 2002).



R=Me, R'=Pr^i

(I)

An examination of solely acetic-acid-modified hexatitanium isopropoxide complexes has produced three of the four possible shapes; a hexaprismane shape for the title compound, (I), has already been predicted by spectroscopic means (Papiernik *et al.*, 1998), and X-ray crystallography has confirmed a rutilane shape for $[Ti_6(\mu_3\text{-O})_2(\mu_2\text{-O})_2(\mu_2\text{-OPr}^i)_2(\text{OPr}^i)_6(\mu_2\text{-OAc})_8]$, (II) (Laaziz *et al.*, 1990) and a bitricyclane shape for $[Ti_6(\mu_3\text{-O})_2(\mu_2\text{-O})_2(\mu_2\text{-OPr}^i)_6(\text{OPr}^i)_6(\mu_2\text{-OAc})_4]$, (III) (Doeuff *et al.*, 1989). Each of the

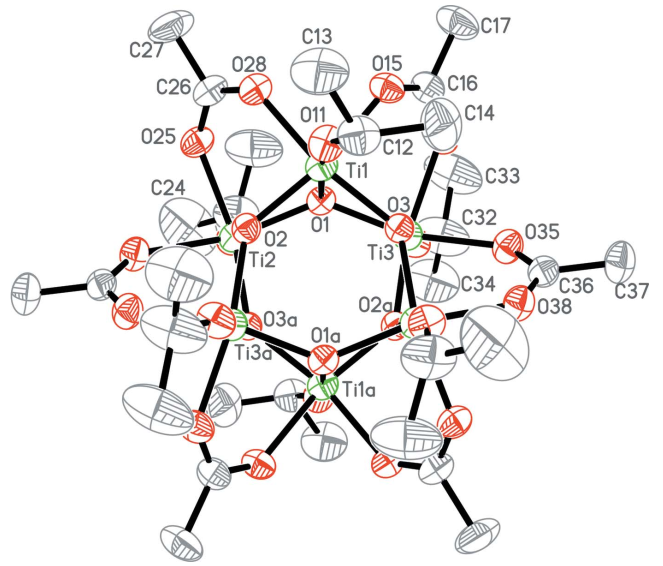


Figure 1
The molecular structure of one of the independent molecules of (I), showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity. Atoms labelled with the suffix 'a' are related by the symmetry code $(1 - x, 1 - y, -z)$.

above complexes was prepared using conventional solvent methods.

The direct sol–gel process in supercritical CO_2 ($scCO_2$) has the potential to produce new and interesting materials. For example, SiO_2 aerogel was prepared by reacting silicon alkoxide with formic acid (Loy *et al.*, 1997; Sui *et al.*, 2004), TiO_2 nanoparticles were synthesized using titanium alkoxide, water and a surfactant (Lim *et al.*, 2004), crystalline metal oxides were obtained by controlled hydrolysis and condensation of alkoxides (Jensen *et al.*, 2005), and TiO_2 nanofibres were produced by polycondensation of acetic acid with titanium oxide in a 3.5–5.5:1 ratio (Sui *et al.*, 2005).

We have prepared acetic-acid-modified titanium(IV) isopropoxide (I) in $scCO_2$ by lowering the acid ratio to 1.33:1. Two types of crystals were produced. Yellow blocks were found to be the same as structure (II) (Laaziz *et al.*, 1990) and colourless plates gave spectroscopic data consistent with the structure of (I) (Papiernik *et al.*, 1998), indicating a hexaprismane type complex. We have fully characterized (I) by single-crystal X-ray crystallography. The X-ray crystal structure, coupled with the spectroscopic data (IR and NMR), is crucial in understanding the chemistry and, consequently, the evolution of nanostructures during the direct sol–gel process in a supercritical fluid.

The hexaprismatic structure obtained for (I) has been observed in other single-crystal structures: $[Ti_6(\mu_3\text{-}O)_6(\mu_2\text{-}O_2CR)_6(OR')_6]$, with $R = H$ and $R' = Pr^i$ (Boyle *et al.*, 1998), $R = C_6H_4OPh$ and $R' = Et$ (Papiernik *et al.*, 1998), $R = CHCl_2$ and $R' = Pr^i$ (Pandy *et al.*, 2000), and $R = CH_2Ph$ and $R' = Pr^i$ (Rammal *et al.*, 2002). The title structure contains two independent molecules, the asymmetric unit being two half-molecules. The complete molecules are generated by inversion centres. Fig. 1 shows the molecular structure of one of the two independent molecules.

The core structure consists of two six-membered rings of alternating Ti and O atoms in an eclipsed configuration. These irregular hexagons are linked through Ti—O bonds. The Ti—O—Ti angles are in the range 134.8 (3)–135.5 (3)° and the O—Ti—O angles are in the range 101.4 (2)–102.0 (2)°. The hydridization of the μ_3-oxo groups is closer to sp^3 than sp^2 (average sum of angles = 336.5°). The two hexagons are further linked through bridging acetate ligands. Each Ti atom possesses a terminal isopropyl ligand and two of the bridging acetate ligands, in addition to the three oxo ligands. Thus, the titanium centres are distorted octahedra. The bonds and angles are typical for these hexaprismatic polyhedra.

Experimental

The synthesis of the materials was carried out in a 10 ml stainless view cell equipped with a temperature controller (Fuji) and a pressure display (Omega). CO_2 was pumped into the view cell using a syringe pump (ISCO). A check valve was used to prevent backflow of CO_2 into the pump. The *in situ* FT–IR incorporated with the autoclave is explained more fully elsewhere (Sui *et al.*, 2004). Acetic acid (0.273 g, 99.7%, Aldrich) and titanium isopropoxide (1 g, 97%, Aldrich) were quickly inserted into the 10 ml view cell. This was followed by addition of 6000 psi CO_2 (99.99%, BOC Canada) at 313 K and mixing using a magnetic stirrer. The stirring was stopped after 8 h. Crystals were observed to form in the view cell after 15 d. The crystals were washed with CO_2 (200 ml) at 6000 psi at a flow rate of 0.5 ml min^{-1} (temperature 313 K). The CO_2 was vented.

Crystal data

$[Ti_6(C_2H_3O_2)_6(C_3H_7O)_6O_6]$
$M_r = 1092.18$
Triclinic, $P\bar{1}$
$a = 10.2466\ (14)$ Å
$b = 12.2908\ (12)$ Å
$c = 20.225\ (3)$ Å
$\alpha = 89.861\ (8)^\circ$
$\beta = 83.883\ (6)^\circ$
$\gamma = 75.461\ (7)^\circ$
$V = 2450.7\ (5)$ Å^3

$Z = 2$
$D_x = 1.480$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 20933 reflections
$\theta = 1.7$–25.0°
$\mu = 1.01$ mm^{-1}
$T = 298\ (2)$ K
Plate, colourless
$0.20 \times 0.17 \times 0.05$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer
φ scans, and ω scans with κ offsets
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.811$, $T_{max} = 0.949$
13625 measured reflections

7905 independent reflections
2994 reflections with $I > 2\sigma(I)$
$R_{int} = 0.091$
$\theta_{max} = 25.0^\circ$
$h = -12 \rightarrow 12$
$k = -14 \rightarrow 14$
$l = -19 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.076$
$wR(F^2) = 0.195$
$S = 0.96$
7905 reflections
560 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0734P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.40$ e Å^{-3}

All the crystals were thin plates and even though the best possible crystal was selected, it gave weak diffraction data. This, in conjuction with the data set being only 91% complete to 25° in 2θ, has lowered the precision of the structure. All H atoms were positioned geometrically and constrained as riding atoms, with C—H = 0.96 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms, and C—H = 0.98 Å and

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$U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C) for methine H atoms. One of the isopropyl units was modelled as disordered over two sites with refined occupancies of 0.447 (19) and 0.553 (19). The following four bond lengths of the disordered group were restrained to be similar: C52—C53*A*, C52—C54*A*, C52—C53*B* and C52—C54*B*.

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*.

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