

The new polynuclear titanium(IV) complex $[(\text{Cp}^*\text{TiCl})(\mu\text{-O})_2(\text{Cp}^*\text{Ti})_2(\mu\text{-O})(\mu\text{-O})_2]_2\text{Ti}$ (Cp^* is $\eta^5\text{-C}_5\text{Me}_5$)

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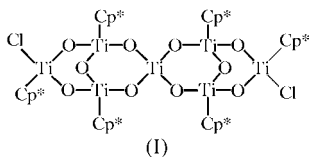
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A new polynuclear titanium(IV) complex, dichlorodeca- μ_2 -oxo-hexakis(pentamethylcyclopentadienyl)hexatitanium(IV), $[\text{Ti}_6(\text{C}_{10}\text{H}_{15})_6\text{Cl}_2\text{O}_{10}]$, has been synthesized by hydrolysis of a titanium complex bearing an *N*-(2-hydroxy-3,5-dimethylbenzyl)diethanolamine Mannich ligand. The molecule has two O-bridged Ti_3O_3 rings linked to two similar rings through a tetrahedrally O-coordinated Ti atom. All Ti atoms except the central one are coordinated to pentamethylcyclopentadienyl (Cp^*) ligands. The Cp^* ligands are arranged with approximate $\bar{3}$ symmetry with respect to the Ti/O/Cl core.

Comment

In recent years, organometallic oxides have attracted considerable interest as hydrocarbon-soluble models for metal oxide surfaces and thus help to provide a basic understanding of catalyst-to-support interactions in heterogeneous catalytic processes (Bottomley, 1992; Pop & Müller, 1991; Bottomley & Sutin, 1988; Day & Klemperer, 1985). Previously, chain and ring polyhedral organotitanoxanes with frameworks have



been well established, starting from $[\text{Cp}^*\text{TiCl}_3]$ (Cp^* is $\eta^5\text{-C}_5\text{H}_5\text{-}n\text{R}_n$, R is Me, SiMe_3 or $t\text{Bu}$, and $n = 0, 1, 2, 3, 4, 5$) (Pilar *et al.*, 1995; Carofiglio *et al.*, 1992; Babcock *et al.*, 1987). However, few organotitanoxanes have been obtained from other complexes. Hence, our work has been aimed at synthesizing new polynuclear organotitanoxanes starting from some complicated complexes. We report here the synthesis and crystal structure of the first such species, $[(\text{Cp}^*\text{TiCl})(\mu\text{-O})_2(\text{Cp}^*\text{Ti})_2(\mu\text{-O})(\mu\text{-O})_2]_2\text{Ti}$ (Cp^* is $\eta^5\text{-C}_5\text{Me}_5$), (I).

The Ti/O/Cl core of (I), which consists of four fused Ti_3O_3 rings, is illustrated in Fig. 1. In the complete molecule (Fig. 2),

all the Ti atoms are in an approximately tetrahedral environment, with atoms Ti1–Ti6 being coordinated to $\eta^5\text{-Cp}^*$ in a three-legged piano-stool configuration. The Ti atoms are in three distinct stereochemical environments: Ti7 is coordinated to four bridging O atoms (O_b), Ti2, Ti3, Ti5 and Ti6 are coordinated by three O_b atoms plus $\eta^5\text{-Cp}^*$, and Ti1 and Ti4 are coordinated by two O_b atoms, one Cl atom and one $\eta^5\text{-Cp}^*$ ligand.

The ranges of the Ti–O and Ti–Cl bond lengths (Table 1) are 1.8–2.2 and 2.2–2.5 Å, respectively, which are in the normal ranges. However, the Ti–O distances for Ti atoms bonded to Cl and for Ti7 are somewhat shorter than those found for Ti bonded to three O_b atoms. The atoms of the individual $\eta^5\text{-Cp}^*$ molecules are coplanar.

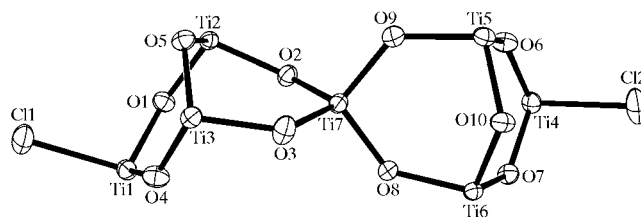


Figure 1

The Ti/O/Cl core of (I). The b axis is approximately horizontal. Displacement ellipsoids are shown at the 50% probability level. The $\eta^5\text{-Cp}^*$ ligands have been omitted.

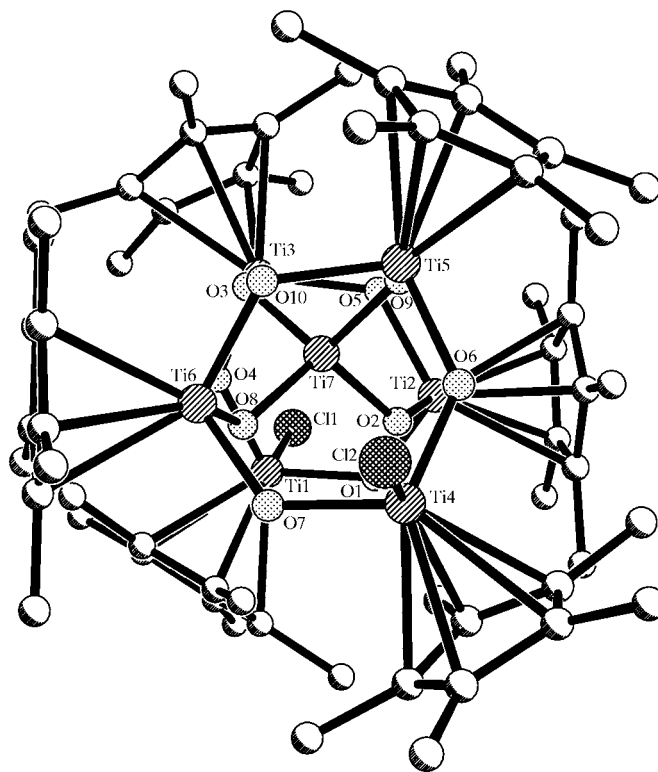


Figure 2

The structure of (I), viewed parallel to b and along the pseudo- $\bar{3}$ axis. Hatched, cross-hatched, stippled and open circles represent Ti, Cl, O and C atoms, respectively.

When viewed along the *b* axis, the entire molecule gives a pseudo-hexagonal impression in projection (Fig. 2). The two six-membered core rings, Ti1/Ti2/Ti3/O1/O4/O5 and Ti4/Ti5/Ti6/O6/O7/O10, are in an almost eclipsed conformation but with Ti over O, and the η^5 -Cp* ligands are arranged with approximate $\bar{3}$ symmetry with respect to the Ti/O/Cl core. There is a distance of 9.057 (1) Å between atoms Ti1 and Ti4.

Experimental

Reaction of the titanium complex bearing the *N*-(3,5-dimethyl-2-hydroxybenzyl)diethanolamine Mannich base with an excess of 1.5 *M* aqueous NH₄OH in toluene for 3 d at ambient temperature, followed by filtration to remove NH₄Cl, drying over Na₂SO₄, elution through a basic alumina chromatography column and removal of the solvent under reduced pressure, yielded yellow crystals of (I) in 58% yield.

Crystal data

[Ti₆(C₁₀H₁₅)₆Cl₂O₁₀]
M_r = 1377.52
 Monoclinic, *P*₂₁/*n*
a = 11.4724 (14) Å
b = 29.713 (4) Å
c = 19.495 (2) Å
 β = 92.090 (2)°
V = 6641.0 (14) Å³
Z = 4

D_x = 1.378 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 5764 reflections
 θ = 2.5–25.9°
 μ = 0.93 mm⁻¹
T = 293 (2) K
 Prismatic, pale yellow
 0.28 × 0.26 × 0.10 mm

Data collection

Bruker CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SHELXTL*; Bruker, 1997)
T_{min} = 0.781, *T_{max}* = 0.917
 37338 measured reflections

13061 independent reflections
 10417 reflections with *I* > 2σ(*I*)
R_{int} = 0.026
 θ_{max} = 26.1°
h = -13 → 14
k = -33 → 36
l = -24 → 13

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.043
wR (*F*²) = 0.121
S = 1.02
 13061 reflections
 741 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0707P)^2 + 2.2925P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.025$
 $\Delta\rho_{\text{max}} = 0.44 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.24 \text{ e \AA}^{-3}$

H atoms were placed geometrically and refined with fixed individual displacement parameters [*U_{iso}*(H) = 1.5*U_{eq}*(C)] using a riding model, with C–H = 0.96 Å.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT-NT* (Bruker, 2003); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

Table 1

Selected geometric parameters (Å, °).

Ti1–O1	1.8049 (18)	Ti4–C31	2.379 (3)
Ti1–O4	1.8073 (19)	Ti5–O10	1.8334 (18)
Ti1–Cl1	2.2919 (9)	Ti5–O6	1.844 (2)
Ti2–O5	1.8401 (18)	Ti5–O9	1.8485 (19)
Ti2–O1	1.8461 (19)	Ti6–O10	1.8374 (18)
Ti2–O2	1.8492 (18)	Ti6–O7	1.8389 (18)
Ti3–O5	1.8331 (17)	Ti6–O8	1.8572 (17)
Ti3–O4	1.844 (2)	Ti7–O8	1.8091 (18)
Ti3–O3	1.8454 (19)	Ti7–O9	1.811 (2)
Ti4–O7	1.8095 (18)	Ti7–O2	1.8157 (18)
Ti4–O6	1.814 (2)	Ti7–O3	1.8167 (19)
Ti4–Cl2	2.2914 (10)		
O1–Ti1–O4	103.85 (9)	O6–Ti4–C35	98.25 (11)
O1–Ti1–Cl1	102.67 (7)	Cl2–Ti4–C31	122.84 (9)
O1–Ti2–O2	102.69 (9)	O2–Ti7–O3	106.26 (8)
O7–Ti4–O6	104.44 (8)	Ti7–O3–Ti3	128.29 (10)
O7–Ti4–Cl2	101.01 (7)	Ti3–O5–Ti2	121.26 (10)
O6–Ti4–Cl2	104.93 (8)		

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1483). Services for accessing these data are described at the back of the journal.

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