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Structure of an Organotitanoxane Containing a Tetrahedral Ti_4O_6 Cage, $C_{40}H_{60}O_6Ti_4$

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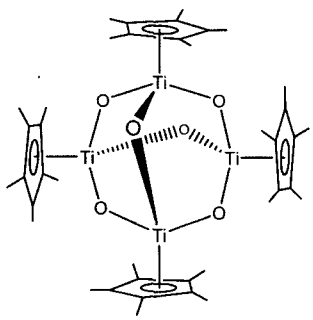
Abstract

The crystal structure of the title compound has been analyzed by single crystal X-ray diffraction method. The compound crystallized in the triclinic space group $P\bar{1}$ with a=11.300(6) Å, b=11.301(6) Å, c=18.716(10) Å, α=82.833(10)°, β= 83.042(11)°, γ= 66.139(10)°, V=2162(2) Å^3, Z=2 and R1=0.661 for 10578 unique reflections. The four C_5Me_5 planar groups form a tetrahedron with a mean dihedral angle 70.92(9)° among them and the Ti_4O_6 cage sits at the center of the tetrahedron. Each Ti atom in the Ti_4O_6 cage is bonded by three bridging oxygen atoms and coordinated by a C_5Me_5 ligand with a mean distance 2.067 Å from Ti atoms to the centroids of the four five-membered rings. Two oxygen atoms facing each other in Ti_4O_6 cage are 4.051(3) Å away in average.

1. Introduction

In the process of the synthesis of pentamethylcyclophentadienyl-(2-phenyl phenoxy) titanium dichloride by the reaction of trichlorophentamethyl cyclophetadienyl titanium with 2-phenyl phenoxy lithium salt at ambient temperature, good single crystals were obtained and so we collected its intensity of a whole sphere of reciprocal space with a resolution of 0.75 Å and then solved the structure. Unexpectedly, however, the $C_{40}H_{60}O_6Ti_4$ was obtained. The synthetic mechanism of (I) is not clear, but the study of the mechanism is in progress in our group.



(I)

The structure of (I) was already elucidated by Babcock, Day and Klemperer in 1987.[1] Here we report a far more detailed structural result of (I) than previous one.[1]

2. Experimental Section

2-1. Collection and reduction of X-ray diffraction data

The same routine processes for the data collection and reduction of X-ray diffraction data carried out by Kim and others[2] were faithfully followed and only difference was that a complete sphere of intensity data was collected because the title compound belonged to the triclinic system.

The X-ray diffraction data were collected on a Bruker SMART diffractometer[3,4] with 1 K CCD area detector using graphite-monochromated MoKα radiation (λ=0.71073 Å) at 233 K.

2-2. Structure solution and refinement

The structure was solved by direct methods and subsequent Fourier synthesis with the space group $P\bar{1}$; it was refined by full-matrix least-squares on F^2 using reflections with $I>2\sigma$.[5] Anisotropic displacement parameters were assigned to all non-hydrogen atoms and the C6, C7, C8, C9, C10, C26 and C30

Table 1. Crystal data and structure refinement for (I)

Empirical formula	$C_{40}H_{60}O_6Ti_4$
Formula weight	828.48
Temperature	233(2) K
Wavelength	0.71073 Å
Crystal system, space group	triclinic, $P\bar{1}$
Unit cell dimensions	a=11.300(6) Å alpha=82.833(10) deg. b=11.302(6) Å beta=83.042(11) deg. c=18.716(10) Å gamma=66.139(10) deg.
Volume	2162(2) $Å^3$
Z, Calculated density	2, 1.272 Mg/m^3
Absorption coefficient	0.752 mm^{-1}
F(000)	872
Crystal size	0.25×0.20×0.13 mm
Theta range for data collection	1.10 to 28.28 deg.
Limiting indices	-15<=h<=15, -14<=k<=14, -24<=l<=24
Reflections collected/unique	29069/10578 [R(int)=0.1013]
Completeness to theta=28.28	98.6%
Max. and min. transmission	0.9079 and 0.8366
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	10578/0/452
Goodness-of-fit on F^2	1.002
Final R indices [I>2sigma(I)]	R1=0.0661, wR2=0.1588
R indices (all data)	R1=0.1784, wR2=0.2245
Extinction coefficient	0.0005(5)
Largest diff. peak and hole	0.589 and -0.555 $eÅ^{-3}$

atoms of the C_5Me_5 groups in the periphery have abnormally large thermal parameters due to the librational and rotational disorder (see Table 2).

All methyl hydrogen atoms were placed in idealized position riding on each parent atom with an isotropic displacement parameter $1.5U_{eq}$(C). Final difference electron density map showed no features of chemical significance, with highest peak 0.59 $eÅ^{-3}$ at 0.97 Å from H6A and -0.56 $eÅ^{-3}$ at 0.88 Å from Ti4. The crystallographic data, final conventional agreement indexes and other structure refinement parameters are listed in Table 1. Final atomic coordinates and the equivalent isotropic thermal parameters are given in Table 2. Table 3 shows selected bond lengths and angles. All average values given in this paper are calculated by the program AVERESD.[6]

3. Results and Discussion

A molecule consists of a Ti_4O_6 cage besieged by four C_5Me_5 planar groups tetrahedrally (see Fig. 1, 2, 3, and 4).

In the Ti_4O_6 cage as shown in Figs. 1, 2, 3 and Table 3, the coordination geometry at each Ti atom is pseudo-tetrahedral with three sites being occupied by bridging oxygen atoms and the remaining site by a π-bonded C_5Me_5 ligand, which is exactly same as that of the previous paper published by Babcock *et al.*[1]

The Ti-O bond distances vary from 1.837(3) Å of Ti1-O5 to 1.859(4) Å of Ti4-O6 with an average length 1.844(1) Å, and the O-Ti-O angles from 101.37(15)° of O4-Ti2-O5 to 102.32(16)° of O4-Ti1-O6 with an average angle 101.93(44)° which is significantly smaller than the tetrahedral angle 109.47° probably due to the accommodation of the large and planar C_5Me_5 ligand. The average O-O distance is 2.864(1) Å.

These values are scarcely different from the reported average Ti-O distance 1.837(3) Å and average O-Ti-O angle 101.9(1)°.[1]

The Ti-O-Ti angles are in the range 122.52(18)°-123.39(17)° with an average value 123.02(7)° and the average Ti-Ti distance 3.241(1) Å is 0.377 Å

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($A^2 \times 10^3$) for (I). U(eq) is defined as one third of the trace of the orthogonalized Uij tensor

	x	y	z	U(eq)
Ti(1)	8208(1)	5012(1)	2536(1)	31(1)
Ti(2)	9524(1)	7120(1)	2293(1)	29(1)
Ti(3)	6698(1)	7864(1)	1731(1)	30(1)
Ti(4)	7029(1)	7558(1)	3446(1)	32(1)
O(1)	8298(3)	7952(3)	1636(2)	31(1)
O(2)	8596(3)	7675(3)	3156(2)	35(1)
O(3)	6101(3)	8343(3)	2655(2)	34(1)
O(4)	7143(3)	6085(3)	1848(2)	34(1)
O(5)	9629(3)	5437(3)	2350(2)	33(1)
O(6)	7430(3)	5812(3)	3368(2)	36(1)
C(1)	7109(7)	7691(10)	4681(3)	74(3)
C(2)	6659(10)	8984(9)	4358(4)	83(3)
C(3)	5185(7)	8156(10)	4301(4)	70(2)
C(4)	5436(8)	9244(7)	4125(3)	68(2)
C(5)	6157(9)	7229(7)	4651(3)	67(2)
C(6)	4561(12)	10506(10)	3740(5)	194(8)
C(7)	7358(15)	9891(13)	4286(6)	226(10)
C(8)	3995(10)	7982(15)	4133(6)	187(7)
C(9)	8408(10)	6949(16)	5015(5)	228(10)
C(10)	6257(15)	5891(10)	4951(5)	184(7)
C(11)	11218(6)	7248(7)	1435(3)	50(2)
C(12)	11809(5)	6252(6)	1950(4)	49(2)
C(13)	11610(5)	6809(7)	2619(3)	49(2)
C(14)	10902(5)	8167(6)	2498(3)	47(2)
C(15)	10660(5)	8433(6)	1764(4)	51(2)
C(16)	11186(7)	7096(10)	651(4)	91(3)
C(17)	12549(7)	4847(7)	1836(5)	92(3)
C(18)	12052(8)	6105(9)	3345(4)	98(3)
C(19)	10500(8)	9165(8)	3049(5)	94(3)
C(20)	9950(7)	9757(8)	1392(5)	96(3)
C(21)	6302(6)	9221(7)	627(3)	53(2)
C(22)	6149(5)	8086(7)	520(3)	49(2)
C(23)	5082(5)	8044(6)	974(3)	46(2)
C(24)	4575(5)	9154(6)	1371(3)	47(2)
C(25)	5333(6)	9888(6)	1156(4)	52(2)
C(26)	7295(8)	9692(10)	231(4)	106(3)
C(27)	6980(8)	7049(9)	20(4)	97(3)
C(28)	4546(7)	7001(7)	1024(5)	83(3)
C(29)	3417(6)	9488(8)	1926(4)	85(3)
C(30)	5154(9)	11133(7)	1480(5)	104(3)
C(31)	8522(6)	2957(5)	3199(3)	47(2)
C(32)	7492(6)	3264(5)	2756(3)	46(2)
C(33)	8011(6)	3267(6)	2022(3)	48(2)
C(34)	9336(6)	2984(5)	2025(3)	47(2)
C(35)	9659(6)	2781(5)	2755(3)	44(1)
C(36)	8416(8)	2823(7)	4020(3)	74(2)
C(37)	6085(7)	3589(7)	3001(5)	81(2)
C(38)	7291(8)	3488(7)	1363(4)	79(2)
C(39)	10259(7)	2950(6)	1371(4)	66(2)
C(40)	10972(6)	2466(6)	3007(4)	68(2)

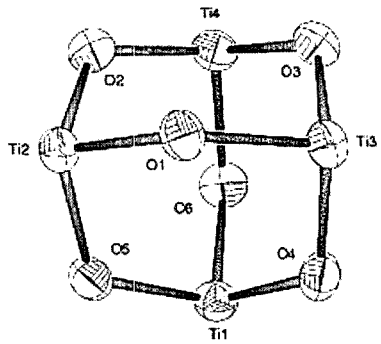


Fig. 1. ORTEP representation[7] and numbering scheme for tetrahedral Ti_4O_6 cage.

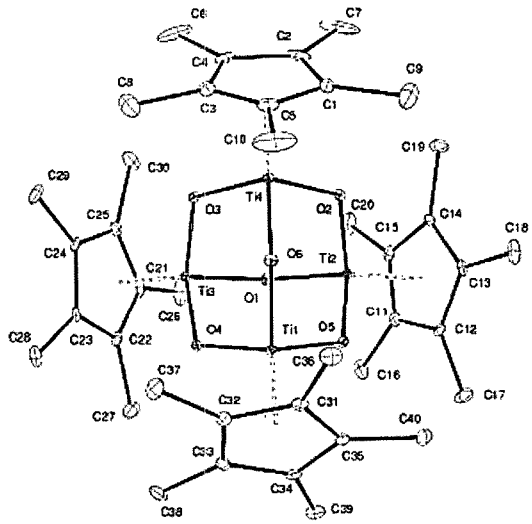


Fig. 2. ORTEP drawing[7] of the molecule with numbering scheme embossing the tetrahedral Ti_4O_6 cage. The coordinative links of titanium atoms to four C_5Me_5 ligands are indicated by dotted lines and sixty hydrogen atoms of methyl groups are omitted. Thermal ellipsoids are scaled to 10% probability.

longer than the average O-O distance 2.864(1) Å.

The mean O-O distance of the three pairs of vis-a-vis oxygen atoms, O1-O6, O2-O4, and O3-O5, in Ti_4O_6 cage is 4.051(3) Å and, as can be seen in Fig. 1, each of the four six-membered (-Ti-O-)$_3$ rings in the cage has a chair configuration.

As can be seen from complete molecules viewed along two different directions shown in Fig. 2 and 3, and its steroview given in Fig. 4, the four C_5Me_5 groups having a tetrahedron structure surround the

Table 3. Selected bond lengths [Å] and angles [deg] for (I)

Ti(1)-O(5)	1.837(3)	Ti(1)-O(4)	1.839(4)	Ti(1)-O(6)	1.842(4)
Ti(1)-C(34)	2.383(5)	Ti(1)-C(32)	2.396(5)	Ti(1)-C(33)	2.397(6)
Ti(1)-C(35)	2.403(6)	Ti(1)-C(31)	2.404(5)	Ti(1)-Ti(2)	3.2447(18)
Ti(1)-Ti(4)	3.2451(18)	Ti(1)-Ti(3)	3.2454(18)	Ti(2)-O(1)	1.840(3)
Ti(2)-O(2)	1.847(4)	Ti(2)-O(5)	1.848(4)	Ti(2)-C(13)	2.382(6)
Ti(2)-C(11)	2.385(5)	Ti(2)-C(15)	2.387(6)	Ti(2)-C(14)	2.391(5)
Ti(2)-C(12)	2.397(5)	Ti(2)-Ti(3)	3.231(2)	Ti(2)-Ti(4)	3.2423(18)
Ti(3)-O(1)	1.837(3)	Ti(3)-O(3)	1.844(3)	Ti(3)-O(4)	1.855(4)
Ti(3)-C(23)	2.374(5)	Ti(3)-C(24)	2.377(5)	Ti(3)-C(22)	2.378(6)
Ti(3)-C(21)	2.387(6)	Ti(3)-C(25)	2.388(6)	Ti(3)-Ti(4)	3.237(2)
Ti(4)-O(3)	1.837(4)	Ti(4)-O(2)	1.840(4)	Ti(4)-O(6)	1.859(4)
Ti(4)-C(1)	2.350(6)	Ti(4)-C(2)	2.376(6)	Ti(4)-C(3)	2.383(6)
Ti(4)-C(5)	2.397(6)	Ti(4)-C(4)	2.400(6)		
Ti(4)-O(3)-Ti(3)	123.18(18)	Ti(1)-O(4)-Ti(3)	122.91(18)		
Ti(1)-O(5)-Ti(2)	123.39(17)	Ti(1)-O(6)-Ti(4)	122.52(18)		

O(5)-Ti(1)-O(4)	101.58(15)	O(5)-Ti(1)-O(6)	102.10(15)
O(4)-Ti(1)-O(6)	102.32(16)	O(1)-Ti(2)-O(2)	102.15(16)
O(1)-Ti(2)-O(5)	101.93(15)	O(2)-Ti(2)-O(5)	101.37(15)
O(1)-Ti(3)-O(3)	101.93(15)	O(1)-Ti(3)-O(4)	101.78(15)
O(3)-Ti(3)-O(4)	102.16(15)	O(3)-Ti(4)-O(2)	101.83(16)
O(3)-Ti(4)-O(6)	102.19(16)	O(2)-Ti(4)-O(6)	101.79(15)
Ti(3)-O(1)-Ti(2)	122.95(18)	Ti(4)-O(2)-Ti(2)	123.15(19)
Ti(4)-O(3)-Ti(3)	123.18(18)	Ti(1)-O(4)-Ti(3)	122.91(18)
Ti(1)-O(5)-Ti(2)	123.39(17)	Ti(1)-O(6)-Ti(4)	122.52(18)

tetrahedral Ti_4O_6 core.

The average ring C-C distance is 1.403(2) Å in the five-membered rings and the average ring-to-methyl C-C distance is 1.512(2) Å.

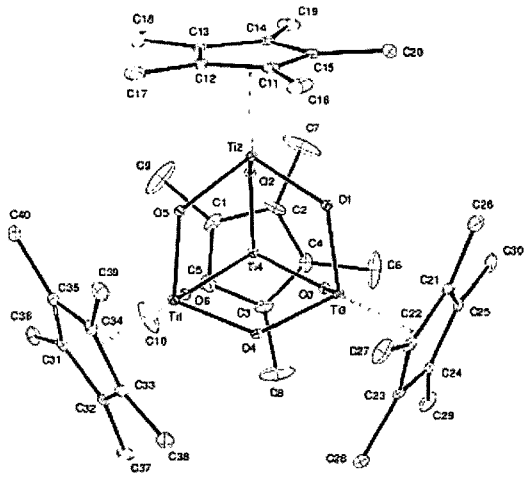


Fig. 3. Four C_5Me_5 groups form a tetrahedron having the Ti_4O_6 cage at center.

Ti-C (pentagon) distances are ranging from 2.350(6) Å of Ti4-C1 to 2.404(5) Å of Ti1-C31 with a mean length 2.386(1) Å and the average distance from Ti atoms to the centroids of the four five-membered rings is 2.067 Å.

All these values are very similar to the average Ti-C distance 2.378(5), average ring C-C distance 1.392(8) and ring-to-methyl C-C distance 1.504(10) reported already by Babcock *et al.*[1]

The four five-membered rings of four C_5Me_5

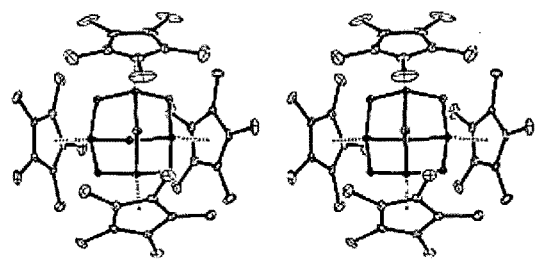


Fig. 4. Steroview of a molecule with anisotropic thermal ellipsoids drawn at their 10% probability level.

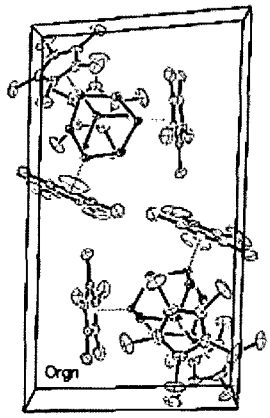


Fig. 5. The ORTEP drawing[7] of two molecules in a unit cell viewed along [100]. Hydrogen atoms are omitted for clarity. Origin, lower left; b-axis, horizontal; c-axis, vertical.

groups are planar within 0.014(4) Å and they are coordinating to four titanium atoms in Ti_4O_6 groups with an average dihedral angle 70.92(9)°.

Two molecules in the packing diagram of Fig. 5 are related by an inversion symmetry and no intermolecular contact less than 3.769 Å in the molecular packing indicates that the molecules are held together only by van der Waals force.

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