Synthesis and Structure of an Organotitanoxane Containing a Tetrahedral Ti_4O_6 Cage, $[(\eta^5\text{-}C_5Me_5)Ti]_4O_6$

L. M. Babcock,[a] **V. W. Day,**[b]* **and W. G. Klemperer**[a]*

[a] *Department of Chemistry and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801, U.S.A.*
[b] *Crystalytics Company, Lincoln, Nebraska 68501, U.S.A.*

Base hydrolysis of $(\eta^5\text{-}C_5Me_5)TiCl_3$ in toluene yields $[(\eta^5\text{-}C_5Me_5)Ti]_4O_6$ which, according to *X*-ray structural analysis, has an adamantane-like cage structure with a tetrahedral $Ti^{IV}{}_4O_6$ core.

The family of polyhedral organosiloxanes $(RSiO_{3/2})_n$ is well established,[1] but no corresponding organotitanoxane cage compounds are known. Since chain and ring organotitanoxanes with $Ti^{IV}{}_2O$ (ref. 2), $Ti^{IV}{}_3O_3$ (ref. 3), and $Ti^{IV}{}_4O_4$ (ref. 4) frameworks as well as mixed-valence cages $L_6Ti_6O_{8\text{-}x}Cl_x$ (ref. 5) ($L = \eta^5\text{-}C_5H_5$, $\eta^5\text{-}MeC_5H_4$; $x = 0,2,4$) are known to be stable, organotitanoxane cages with $Ti^{IV}{}_nO_{3n/2}$ frameworks are expected to be stable species. We report here the synthesis and structure of the first such species, $[(\eta^5\text{-}C_5Me_5)Ti]_4O_6$.

Reaction of $(\eta^5\text{-}C_5Me_5)TiCl_3$[6] with excess of 1.5 M aqueous NH_4OH in toluene for three days at ambient temperature followed by filtration to remove NH_4Cl, drying over Na_2SO_4, elution through a basic alumina chromatography column, and removal of solvent under reduced pressure yields yellow, crystalline $[(\eta^5\text{-}C_5Me_5)Ti]_4O_6$ in 65% yield.† The course of

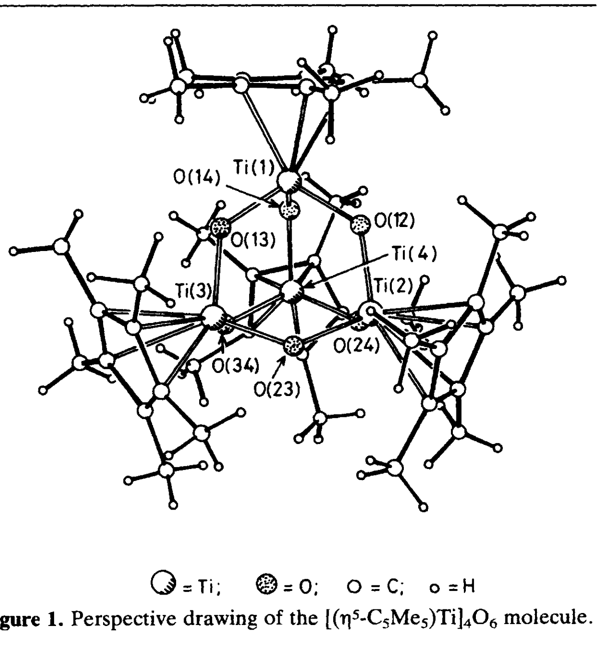

Figure 1. Perspective drawing of the $[(\eta^5\text{-}C_5Me_5)Ti]_4O_6$ molecule.

---

† $[(\eta^5\text{-}C_5Me_5)Ti]_4O_6$: satisfactory elemental analyses (C,H,Ti) were obtained; ^1H n.m.r. ($CDCl_3$, 300 MHz, rel. to Me_4Si) δ 1.973(s); $^{13}C\{^1H\}$ n.m.r. ($CDCl_3$, 75.48 MHz, rel. to Me_4Si) δ 11.37 (s, C_5Me_5), 121.47 (s, C_5Me_5); ^{17}O n.m.r. (0.02 M $CHCl_3$, 22 °C, 33.92 MHz, rel. to tap water) δ 645 p.p.m. (s, 42 Hz full width at half maximum); i.r. (mineral oil) ν(Ti–O–Ti) 780 cm^{-1}; *m/z* (field desorption) 828.

$(\eta^5\text{-}C_5Me_5)TiCl_3$ hydrolysis is very dependent upon reaction conditions.[7] Hydrolysis in refluxing acetone, for example, yields $[(\eta^5\text{-}C_5Me_5)TiCl(\mu\text{-}O)]_3$,‡ the chloro analogue of a known compound, $[(\eta^5\text{-}C_5Me_5)TiCH_3(\mu\text{-}O)]_3$.[3a]

X-Ray structural analysis of crystalline $[(\eta^5\text{-}C_5Me_5)Ti]_4O_6$, obtained from toluene solution, revealed the presence of an adamantane-like cage molecule with a tetrahedral Ti_4O_6 core (see Figure 1).§ The Ti_4O_6 cage approximates quite closely its maximum possible point group symmetry of T_d. The Cg–Ti,¶ Cg–O, and Ti–O distances average** 1.978 (—,4,5,4), 2.018 (—,2,6,6), and 1.837 (3,4,12,12) Å, respectively; the Ti–Cg–Ti, Ti–O–Ti, and O–Ti–O angles average 109.5(—,1,3,6), 123.0(1,2,4,6), and 101.9(1,2,6,12)°, respectively. The two types of O–Cg–O angles average 90.0(—,1,3,12) and 179.9(—,0,1,3)°, respectively. Each of the six-membered $(\text{–Ti–O–})_3$ rings in the cage exists in a chair configuration.

The co-ordination geometry at each Ti^{IV} atom is pseudo-tetrahedral with three sites being occupied by bridging oxygen atoms and the remaining site by a π-bonded $\eta^5\text{-}C_5Me_5$ ligand; Ti–C, ring C–C, and ring-to-methyl C–C distances average 2.378(5,10,25,20), 1.392(8,23,72,20), and 1.504(10,12,48,20) Å, respectively. The Ti–Cp distances and Cp–Ti–O angles average 2.062(—,5,10,4) Å and 116.2(—,7,12,12)°, respectively. Thus the metrical parameters for the Ti^{IV} co-ordination sphere in $[(\eta^5\text{-}C_5Me_5)Ti]_4O_6$ are similar to those previously observed for Ti in chain and ring organotitanoxanes.[2–4]

We acknowledge the National Science Foundation for partial support of this work. L. M. B. was supported by the U.S. Department of Energy, Division of Materials Science, under Contract DE-AC02-76ER01198. Field desorption mass spectra were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois, supported in part by a grant from the National Institute of General Medical Sciences (GM27029).

Received, 19th January 1987; Com. 064

---

‡ $[(\eta^5\text{-}C_5Me_5)TiCl(\mu\text{-}O)]_3$: satisfactory elemental analyses (C,H,Ti,Cl); ^1H n.m.r. ($CDCl_3$, 300 MHz, rel. to Me_4Si) δ 2.122 (s, 30H), 2.098 (s, 15H); ^{13}C {^1H} n.m.r. ($CDCl_3$, 75.48 MHz, rel. to Me_4Si) δ 12.11 (s, 5C, $C_5\textit{Me}_5$), 12.40 (s, 10C, $C_5\textit{Me}_5$), 128.22 (s, 10C, $\textit{C}_5Me_5$), 128.90 (s, 5C, $\textit{C}_5Me_5$); i.r. (mineral oil) ν(Ti–O–Ti) 780 cm^{-1}; *m/z* (field desorption) 704.

§ *Crystal data:* $C_{40}H_{60}O_6Ti_4$, *M* = 828.5, triclinic, space group $P\bar{1}\text{–}C_i$, *a* = 11.355(3), *b* = 12.347(3), *c* = 18.694(4) Å, α = 89.91(2), β = 96.87(2), γ = 123.36(2)°; *U* = 2167(1) $Å^3$; *Z* = 2; D_c = 1.27 g/cm^3; $\mu(Mo\text{-}K_{\bar{\alpha}})_{calc.} = 0.74\ mm^{-1}$; 9926 unique data having $2\theta(Mo\text{-}K_{\bar{\alpha}}) < 55°$ were collected on a Nicolet $P\bar{1}$ autodiffractometer using graphite monochromated $Mo\text{-}K_{\bar{\alpha}}$ radiation (λ = 0.71073 Å) and full (1.2° wide) ω scans. The intensity data were corrected empirically for variable absorption effects and the structure was solved using (SHELXTL) 'direct methods' techniques. The resulting structural parameters have been refined using counter-weighted cascade block-diagonal least-squares techniques to $R = 0.051$ and $R_w = 0.069$ for 7004 independent absorption-corrected reflections having $I > 3\sigma(I)$. These refinement cycles employed anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for the hydrogen atoms of the methyl groups which were refined as rigid rotors with idealized sp^3 hybridization and a C–H bond length of 0.96 Å.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

¶ Cg is used to represent the centre-of-gravity for the Ti_4O_6 cage; Cp(1)—Cp(4) represents the centre-of-gravity for the five-membered rings of the four independent C_5Me_5 ligands.

** The first number in parentheses following an averaged value of a bond length or angle is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements which are included in the averaged value.

References

1 M. G. Voronkov and V. I. Lavrent'yev, *Top. Curr. Chem.*, 1982, **102**, 199; V. W. Day, W. G. Klemperer, V. V. Mainz, and D. M. Millar, *J. Am. Chem. Soc.*, 1985, **107**, 8262.

2 U. Thewalt and B. Kebbel, *J. Organomet. Chem.*, 1978, **150**, 59; U. Thewalt and D. Schomburg, *ibid.*, 1977, **127**, 169; R. D. Gorsich, *J. Am. Chem. Soc.*, 1960, **82**, 4211; P. Corradini and G. Allegra, *ibid.*, 1959, **81**, 5510.

3 (a) S. G. Blanco, M. P. G. Sal, S. M. Carreras, M. Mena, P. Royo, and R. Serrano, *J. Chem. Soc., Chem. Commun.*, 1986, 1572; (b) H. Köpf, S. Grabowski, and R. Voigtländer, *J. Organomet. Chem.*, 1981, **216**, 185.

4 J. L. Petersen, *Inorg. Chem.*, 1980, **19**, 181; A. C. Skapski and P. G. H. Troughton, *Acta Crystallogr., Sect. B*, 1970, **26**, 716.

5 A. Roth, C. Floriani, A. Chiesi-Villa, and C. Guastini, *J. Am. Chem. Soc.*, 1986, **108**, 6832; F. Bottomley, D. F. Drummond, G. O. Egharevba, and P. S. White, *Organometallics*, 1986, **5**, 1620; J. C. Huffman, J. G. Stone, W. C. Krusell, and K. G. Caulton, *J. Am. Chem. Soc.*, 1977, **99**, 5829.

6 J. Blenkers, H. J. de Liefde Meijer, and J. H. Teuben, *J. Organomet. Chem.*, 1981, **218**, 383.

7 H. Röhl, E. Lange, T. Gössl, and G. Roth, *Angew. Chem., Int. Ed. Engl.*, 1962, **1**, 117; H. Röhl, E. Lange, and W. Eversmann, Ger. Pat. 1 153 366, 1963.