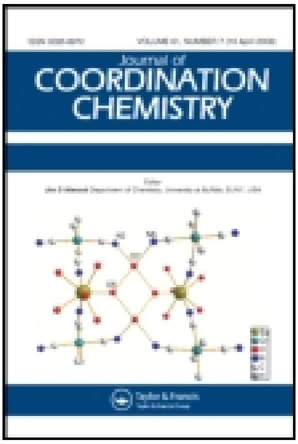

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Unexpected formation, X-ray structure, and characterization of the triangular $[Ti_3O(OMe)_6(\eta^5-C_5H_5)_3](I_3)$ complex from hydrolysis and methanolysis of $[Ti(\eta^5-C_5H_5)_2I_2]$

Theocharis C. Stamatatos [a] , Spyros P. Perlepes [b] , Manolis J. Manos [c] , Anastasios J. Tasiopoulos [c] & Nikolaos Klouras [b]

[a] Department of General and Inorganic Chemistry, Faculty of Chemistry , Aristotle University of Thessaloniki , P.O. Box 135, 54124 Thessaloniki, Greece

[b] Department of Chemistry , University of Patras , 26500 Patras, Greece

[c] Department of Chemistry , University of Cyprus , 1678 Nicosia, Cyprus

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Unexpected formation, X-ray structure, and characterization of the triangular $[Ti_3O(OMe)_6(\eta^5\text{-}C_5H_5)_3](I_3)$ complex from hydrolysis and methanolysis of $[Ti(\eta^5\text{-}C_5H_5)_2I_2]$

THEOCHARIS C. STAMATATOS†, SPYROS P. PERLEPES‡, MANOLIS J. MANOS§, ANASTASIOS J. TASIOPOULOS§ and NIKOLAOS KLOURAS*‡

†Department of General and Inorganic Chemistry, Faculty of Chemistry, Aristotle University of Thessaloniki, P.O. Box 135, 54124 Thessaloniki, Greece
‡Department of Chemistry, University of Patras, 26500 Patras, Greece
§Department of Chemistry, University of Cyprus, 1678 Nicosia, Cyprus

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A convenient route has been developed for the formation of $[Ti^{IV}_3O(OMe)_6(\eta^5\text{-}C_5H_5)_3](I_3)$ (**2**) involving methanolysis (and possibly hydrolysis) of species derived from titanocene diiodide, $[Ti^{IV}(\eta^5\text{-}C_5H_5)_2I_2]$ (**1**), under aerobic conditions. Single-crystal X-ray crystallography reveals that the cation of **2** consists of three Ti^{IV}'s in a triangular arrangement bridged by a central μ_3-oxide; the latter lies 0.686 Å out of the Ti_3 plane. Each edge of the triangle is bridged by oxygen of $\eta^1:\mu$-MeO^-. Terminal ligation is provided by three methoxide and three cyclopentadienyl groups. All Ti^{IV} centers are five-coordinate in an extremely distorted geometry. IR and electronic data are discussed in terms of the known structure and coordination modes of O^{2-}, MeO^-, and η^5-$C_5H_5^-$. A proposal for the mechanism of the unexpected formation of the triiodide (I_3^-) counteranion that is present in the crystal structure of **2** is also provided.

Keywords: Tris(cyclopentadienyl)hexamethoxido-oxidotrititanium(IV) triiodide; Bis(η^5-cyclopentadienyl)diiodotitanium(IV); Triangular titanium(IV) complexes; Methanolysis route; Crystal structures; Reactivity studies

1. Introduction

Titanium presents a wide variety of applications in multidisciplinary fields of materials and life sciences, the latter including biology, pharmacology, and bioinorganic chemistry [1–5]. From the materials science perspective, several titanium(IV) alkoxides and aryloxides are excellent precursors to ceramic materials and catalysts in organic chemistry, respectively [6–9]. For biological and pharmaceutical aspects of titanium chemistry, the main goals remain to increase the variety of potential antitumor drugs, which may lead to higher activities, attack of different types of tumor cells, better solubility, and lower toxicity [10]. Titanium comes in contact with both low and high molecular mass ligands, which gradually induce its solubilization [3, 5].

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*Corresponding author. Email: n.klouras@chemistry.upatras.gr

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Therefore, further studies on the coordination chemistry of this metal and on the reactivity of its complexes are topics of interest.

Titanocene dihalides, $[Ti(\eta^5\text{-}C_5H_5)_2X_2]$ ($X = F$, Cl, Br, I; $C_5H_5^- = Cp^-$), are among the most widely studied titanium(IV) compounds. Reasons for this interest are varied, but mainly include the fact that such complexes belong to a relatively new class of small hydrophobic organometallic anticancer agents that exhibit antitumor activities against cancer cell lines, such as leukemias P388 and L1210, B16 melanoma, and also against human colon, renal, and lung carcinomas transplanted into athymic mice [11–14]. Titanocene dichloride, $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$, which has a quasi-tetrahedral structure, is the main starting material for much of the chemistry of Ti^{IV} [1]. Reactions of $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ with a wide variety of bidentate chelating ligands have been explored over the last 40 years, leading to new coordination chemistry for this class of compounds with interesting structural features and exciting properties [15–18].

The fluoride-, bromide-, and iodide-analogs of titanocene dichloride were prepared by some of us [19, 20] and others [21], and we have pursued the reactivity of all four compounds with chelating or bridging polydentate ligands, as a means of obtaining new, structurally unprecedented complexes [22–24]. For example, reaction of $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ and 2,6-bis(3,5-dimethylpyrazolyl-1-yl)pyridine (bdmpp) in Me_2CO proceeded with complete substitution of the cyclopentadienyl ligands and afforded $[Ti^{IV}Cl_2(O_2)(bdmpp)]$ containing the side-on (η^2) O_2^{2-} group [24].

As part of a broad research program to investigate the reactivity of $[Ti^{IV}(\eta^5\text{-}C_5H_5)_2X_2]$ ($X =$ halide groups) with or without ancillary chelating/bridging organic ligands, and under convenient synthetic conditions, this report contains our initial research in the latter area. In particular, we describe our discoveries from the "dissolution" of $[Ti^{IV}(\eta^5\text{-}C_5H_5)_2I_2]$ (**1**) in various alcoholic media under aerobic conditions. The starting material has a formal 16-electron configuration and is quite labile toward iodide substitution by other groups that will satisfy the requirement for a stable 18-electron configuration [25]. The reaction of **1** with MeOH and H_2O has surprisingly led to the new, trinuclear $[Ti_3^{IV}O(OMe)_6(\eta^5\text{-}C_5H_5)_3](I_3)$ (**2**) compound possessing a triangular, oxide-centered topology. The single-crystal X-ray structure of **2**, its spectroscopic characterization, and a proposed mechanism for the unexpected formation of triiodide anion (I_3^-) are herein described.

2. Experimental

2.1. *Materials and spectroscopic measurements*

All manipulations were performed under aerobic conditions using chemicals as received, unless otherwise stated. Reagents and solvents were purchased from commercial sources, and were purified (where necessary) and dried before use by standard procedures. The starting $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ was synthesized under an argon atmosphere using dried THF by the method of Wilkinson and Birmingham [26] and recrystallized from boiling toluene.

Microanalyses (C, H, and N) were performed by the in-house facilities at the University of Patras using an EA 1108 Carlo Erba analyser. IR spectra (4000–450 cm^{-1}) were recorded on a Perkin-Elmer 16 PC FT-spectrometer using samples prepared as

KBr pellets. The solid-state (diffuse reflectance) spectrum in the 300–800 nm range was recorded on a Varian Cary 3 spectrometer equipped with an integration sphere; the sample was diluted with spectroscopic grade MgO.

2.2. *Syntheses*

2.2.1. Synthesis of $[Ti(\eta^5\text{-}C_5H_5)_2I_2]$ (1). A solution of NaI (3.74 g, 25.0 mmol) in reagent grade Me_2CO (40 mL) was added to a stirred solution of $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$ (1.50 g, 6.0 mmol) in the same solvent (100 mL). The initial light-red color of the solution rapidly changed to dark red. The mixture was refluxed under argon for 1 h, during which time the color of the solution changed to dark purple. The resulting suspension was evaporated to dryness under reduced pressure and the red-brown residue redissolved in $CHCl_3$ (50 mL), in a Soxhlet apparatus, to give a dark red solution. Evaporation of the latter under reduced pressure gave a dark red microcrystalline product, which was stored in the dark under argon. The identity of the product was confirmed by elemental analyses, and IR spectroscopic comparison with authentic material [21]. Yield: 2.32 g (88% based on the available Ti^{IV}); $T_{dec} > 307°C$. Anal. Calcd for $C_{10}H_{10}TiI_2$ (%): C, 27.81; H, 2.33. Found (%): C, 28.13; H, 2.29. Diagnostic IR bands (KBr pellet, cm^{-1}): 3092s, 1436s, 1366w, 1128w, 1012s, 866sh, 860m, 818vs.

2.2.2. Synthesis of $[Ti_3O(OMe)_6(\eta^5\text{-}C_5H_5)_3](I_3)$ (2). Freshly prepared **1** (0.15 g, 0.35 mmol) was added in portions in boiling MeOH (25 mL). The resulting dark red suspension was stirred at room temperature for 40 min, during which all solid dissolved and the color of the solution changed to orange. Slow cooling of the final solution afforded, within 1 h, X-ray quality red needle-like crystals of **2**. The crystals were collected by filtration, washed with cold MeOH (2 × 2 mL) and Et_2O (2 × 3 mL), and dried in air. Yield: 0.04 g (36% based on the available Ti^{IV}). Anal. Calcd for $C_{21}H_{33}Ti_3O_7I_3$ (%): C, 26.67; H, 3.52. Found (%): C, 26.91; H, 3.36. IR data (KBr pellet, cm^{-1}): 3454mb, 2908m, 2810m, 1638m, 1436m, 1098vs, 1050s, 1020m, 834vs, 816m, 632vs, 598s, 566m, 498m, 428w.

2.3. *Single-crystal X-ray crystallography*

Data for **2** were collected on an Oxford Diffraction SuperNova Dual diffractometer (equipped with a Sapphire CCD area detector) at 100 K using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). A suitable, needle-shaped crystal was attached to a glass fiber using silicone grease. An initial search for reciprocal space revealed a monoclinic cell for **2**; the choice of space group $P2_1/c$ was confirmed by the subsequent solution and refinement of the structure. Cell parameters were refined using 9136 reflections. Data (513 frames) were collected using the ω-scan method (0.75° frame width). The structure was solved by direct methods using SIR92 [27] and refined by full-matrix least-squares on F^2 with SHELXL-97 [28]. The non-H atoms were treated anisotropically. All hydrogens were placed in calculated, ideal positions, and refined as riding on their respective carbons. The programs used were CRYSALIS CCD [29] for data collection, CRYSALIS RED [29] for cell and data refinement, WINGX [30] for crystallographic calculations, and MERCURY [31] and DIAMOND [32] for molecular graphics. Important crystal data and parameters for data collection and refinement are listed in table 1.

3. Results and discussion

3.1. *Synthetic comments and spectroscopic discussion*

Our group has had a longstanding interest in the synthesis, characterization, and biological activity of metallocene dihalides, $[M(\eta^5\text{-}C_5H_5)_2X_2]$ (M = Ti, V, Nb, Mo, Re; X = halide ligand; $C_5H_5^- = Cp^-$), as well as their chemical reactivity with either chelating or bridging polydentate organic ligands as a means of preparing new, structurally interesting complexes. For example, we have just reported the last member, the fluoro derivative, of the $[Ti(\eta^5\text{-}C_5H_5)_2X_2]$ family of complexes [19]. More recently, we investigated the reactions between $[M(\eta^5\text{-}C_5H_5)_2Cl_2]$ (M = Ti, Zr, Hf) and the polydentate chelating/bridging ligand pyridine-2,6-dicarboxylic acid (dipicolinic acid; dipicH$_2$), which afforded a family of complexes, $[M(\eta^5\text{-}C_5H_5)_2(\text{dipic})]$ [33].

$[Ti(\eta^5\text{-}C_5H_5)_2I_2]$ (**1**) was first prepared from its bromide analog in acetone by adding excess KI [26a]. It was also prepared accidentally in a form suitable for single-crystal

Table 1. Crystallographic data for **2**.

Parameter	**2**
Empirical formula	$C_{21}H_{33}Ti_3I_3O_7$
Formula weight (g mol^{-1})	921.87
Crystal size (mm)	0.18 × 0.05 × 0.02
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	9.7936(2)
b	15.6118(4)
c	19.6096(4)
α	90
β	90.951(2)
γ	90
Volume (Å^3), Z	2997.81(12), 4
ρ_{calc} (g cm^{-3})	2.043
Radiation, λ (Å)	Mo-Kα, 0.71073
Temperature (K)	100(2)
μ (mm^{-1})	3.904
F(000)	1760
θ range (°)	2.96–26.49
Index ranges (°)	$-12 \le h \le 12$; $-19 \le k \le 15$; $-24 \le l \le 24$
Data collected/unique (R_{int})	14332/6209 (0.0453)
Data with $I > 2\sigma(I)$	4987
Goodness-of-fit on F^2	1.066
R_1 ($I > 2\sigma(I)$)^a	0.0546
wR_2 ($I > 2\sigma(I)$)^b	0.1376
$(\Delta\rho)_{max}/(\Delta\rho)_{min}$ (e Å^{-3})	2.423/ − 1.693

$^a R_1 = \Sigma(|F_o| - |F_c|)/\Sigma(|F_o|)$.
$^b wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

X-ray crystallography by Shur [21] in 2006 as a by-product of the reaction between $[Ti(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_5H_4B(C_6F_5)_3\}]$ and $CH_3CH_2CH_2I$ under argon. Instead of following the above literature methods, we decided to perform the convenient metathesis reaction between the known, chloro analog, $[Ti(\eta^5\text{-}C_5H_5)_2Cl_2]$, and excess NaI in refluxing Me_2CO under argon; recrystallization of the crude product from $CHCl_3$ afforded **1** as a red microcrystalline solid in yields as high as ~90%. Since this route gives the starting material in yields higher than those reported by Wilkinson and Birmingham [26a] who used $[Ti(\eta^5\text{-}C_5H_5)_2Br_2]$ and KI, we have presented this preparation in detail in Section 2.2. Our preparation of **1** involves the reaction represented by equation (1):

$$\left[Ti\left(\eta^5 - C_5H_5\right)_2Cl_2\right] + 2NaI \xrightarrow{Me_2CO/CHCl_3} \left[Ti\left(\eta^5 - C_5H_5\right)_2I_2\right] + 2NaCl \qquad (1)$$

With the identity and high-yield synthesis of **1** established, we undertook the challenge of using **1** as a starting material to new polynuclear species, with or without additional chelating/bridging organic ligand. This work deals with the latter approach, and particularly with the hydrolysis/alcoholysis of **1** under ambient conditions. We initially explored reactions of **1** with MeOH at temperatures as high as 60°C (near the boiling point of the solvent) in order to enhance the solubility of the mononuclear compound. We noticed a gradual color change of the solution from dark red to orange over a period of ~40–50 min, with the latter color remaining stable even after a period of 24 h, clearly indicating the occurrence of a new chemical reaction. Slow evaporation of the resulting solution at room temperature readily afforded red needle-like, X-ray quality crystals of the trinuclear complex $[Ti_3O(OMe)_6(\eta^5\text{-}C_5H_5)_3](I_3)$ (**2**) in yields as high as 36% based on Ti.

We were surprised to see that the product is a new triangular, μ_3-oxido centered, cationic Ti^{IV} complex also bearing six methoxides and three cyclopentadienyls, as well as a triiodide counteranion (vide infra). The reaction is unusual and complicated; thus, we cannot offer a precise reaction mechanism which can safely describe the formation of **2**. As with many reactions in higher oxidation state transition metal cluster chemistry, the resulting solution likely contains a mixture of species in equilibrium, and what crystallizes out is determined by the relative solubilities, the nature of counterions, the percentage of humidity, the lattice energies, and related factors. It should be mentioned at this point that the reaction does not take place in anhydrous MeOH under argon or any other kind of inert atmosphere. Thus, the process of the reaction clearly demands the presence of an alcoholic medium which contains appreciable amounts of H_2O (aqueous-based media) and atmospheric O_2.

Taking into account these two factors, we offer a possible reaction mechanism for the unexpected formation of the triiodide group (I_3^-) as counteranion in the crystal structure of **2** (vide infra). The mechanism is based on equations (2)–(4).

$$\left[Ti\left(\eta^5\text{-}C_5H_5\right)_2I_2\right] \overset{H_2O}{\longrightarrow} \left[Ti\left(\eta^5\text{-}C_5H_5\right)_2(H_2O)_2\right]^{2+} + 2I^-, \qquad (2)$$

$$4I^- + O_2 \rightleftharpoons 2I_2 + 2O^{2-}, \qquad (3)$$

$$I^- + I_2 \rightleftharpoons I_3^-. \qquad (4)$$

The first step (equation (2)) represents the replacement of the labile iodo ligands by aqua groups in **1** and the subsequent formation of $[Ti(\eta^5\text{-}C_5H_5)_2(H_2O)_2]^{2+}$ cations and

I^- anions in the solution. This is a known reaction found and described for titanocene dihalides, $[Ti(\eta^5\text{-}C_5H_5)_2X_2]$ (X = F, Cl, Br, I), when these are exposed to aqueous media under aerobic conditions [34]. The required amounts of H_2O for the process are clearly contained in the MeOH solvent (reagent grade). Parallel replacement of iodo ligands by MeOH groups cannot be ruled out. The formation of $[Ti(\eta^5\text{-}C_5H_5)_2(MeOH)_2]^{2+}$ in solution lowers the pK_a of MeOH and activates it for deprotonation (methanolysis). The second step (equation (3)) may consist of air oxidation of iodides (I^-) to elemental iodine (I_2) from atmospheric O_2, with the concomitant reduction of the latter to yield the oxido group (O^{2-}). Further, the O^{2-} ions could potentially have the role of proton acceptors to facilitate deprotonation of the MeOH groups and/or the role of the bridging ligand to favor the formation of the triangle. Of course, such a role could also be played by the released cyclopentadienyl ions. Finally, the third step (equation (4)) includes the *in situ* generation of triiodide anions (I_3^-) from the well-known reaction between iodide and iodine.

Compound **2** is a stable solid at room temperature, and non-sensitive toward air and moisture. It is sparingly soluble in dimethylformamide and dimethylsulfoxide, and insoluble in almost all common organic solvents such as chloroform, benzene, and toluene. Simplified preparations of **2** can be represented by equations (5) or (6). Equation (5) denotes a simple methanolysis route, whereas equation (6) represents a mixed hydrolysis/methanolysis process. Since **2** is not formed using absolute MeOH, we believe that the O^{2-} ligand derives from H_2O that is present in the solvent, and thus both hydrolysis and methanolysis are involved in the formation of the triangular cluster.

$$6[Ti(\eta^5\text{-}C_5H_5)_2I_2] + O_2 + 12MeOH \rightarrow 2[Ti_3O(OMe)_6(\eta^5\text{-}C_5H_5)_3](I_3) + 6C_5H_6 + 6HI, \quad (5)$$

$$6\left[Ti\left(\eta^5\text{-}C_5H_5\right)_2I_2\right] + O_2 + 2H_2O + 12MeOH \rightarrow 2\left[Ti_3O(OMe)_6\left(\eta^5\text{-}C_5H_5\right)_3\right](I_3) + 6C_5H_6 + 6HI + 2H_2O. \quad (6)$$

In a next synthetic step we wondered if the ethoxido, or any other alkoxido, analog of **2** could be prepared by employing a similar reaction, i.e., the "dissolution" of **1** in EtOH or any other alcoholic medium. Unfortunately, we were not able to isolate any material other than insoluble amorphous precipitates that were probably Ti oxides. This is likely due to a combination of factors including the different acidity, bulkiness, and H_2O amount of EtOH and related alcohols compared with the corresponding parameters of MeOH.

The IR spectra of π-bonded cyclopentadienyl metal complexes have been studied [35–37]. In the IR spectrum of **2** the bands at 2908, 1436, 1020, 834/816, and 632 cm^{-1} can be assigned [35–37] to $\nu(CH)$, $\nu(CC)$, $\delta(CH)$, $\pi(CH)$, and $\delta(CCC)$, respectively. A strong band at 598 cm^{-1} is also present in the IR spectrum of **2**; this band is absent from the spectrum of **1** and can be assigned [36] to a vibration involving a Ti^{IV}–O^{2-} stretch.

The solid-state electronic spectrum of **2** is featureless beyond 500 nm, due to the fact that Ti^{IV} has no d electrons. The band at ~430 nm can be reasonably attributed to an O^{2-} to Ti^{IV} charge-transfer (LMCT) transition [5, 38].

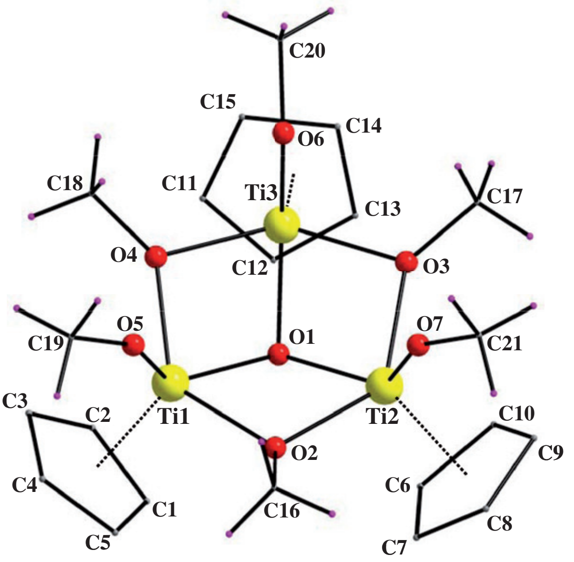

Figure 1. Labeled PovRay representation of the cation of **2** with the atom-numbering scheme. Color scheme: Ti^{IV} – yellow; O – red; C – gray; H – purple.

3.2. *Description of structure*

The molecular structure and a crystal packing diagram of **2** are shown in figures 1 and 2, respectively. Selected interatomic distances and angles are listed in table 2.

Complex **2** crystallizes in the monoclinic space group $P2_1/c$. The crystal structure of **2** consists of $[Ti_3O(OMe)_6(Cp)_3]^+$ (figure 1) and I_3^-. The cation consists of three Ti^{IV}'s in a triangular arrangement bridged by a central μ_3-oxide [O(1)]. Each edge of the Ti$_3$ triangle is bridged by alkoxide [O(2), O(3), and O(4)] of an $\eta^1:\mu$-MeO$^-$. The centroids (Cp, Cp$'$, and Cp$''$) of the three Cp$^-$ rings formally occupy one terminal coordination site around each metal ion. Five-coordination at each Ti^{IV} center is completed by a terminal η^1-MeO$^-$ group [O(5), O(6), and O(7)]. The coordination geometry about all three Ti^{IV}'s is extremely distorted and can be described either as distorted square pyramidal (quasi-square pyramidal) or as distorted trigonal bipyramidal (quasi-trigonal bipyramidal). Adopting the former view, the apical sites for all three Ti^{IV} centers are occupied by the centroids of the Cp$^-$ rings, while in the latter description O(2) and O(4) for Ti(1), O(2) and O(3) for Ti(2), and O(3) and O(4) for Ti(3) define the axial sites. The Ti $\cdots$ Ti separations are almost equal [3.160(2)–3.176(2) Å]; the triangle is thus scalene and almost equilateral within the usual 3σ criterion. The oxidation states of titaniums are +4 by charge balance considerations and inspection of Ti–O bond distances, and confirmed quantitatively by bond valence sum (BVS) calculations; these gave values of 3.73–3.76 for **2** [39, 40]. BVS calculations also confirm that the central oxygen is O^{2-}, giving a value of 2.04 for O(1), and all six bridging and terminal MeO$^-$ groups are deprotonated, giving values in the range of 1.98–2.06 for O(3–7) of **2** [39, 40].

The central oxide O(1) of **2** is 0.686 Å above the Ti$_3$ plane on the same side as the cyclopentadienyl groups, and the three Ti–O^{2-} bonds are equal [1.951(5)–1.958(5) Å] and comparable with those reported for other complexes containing the

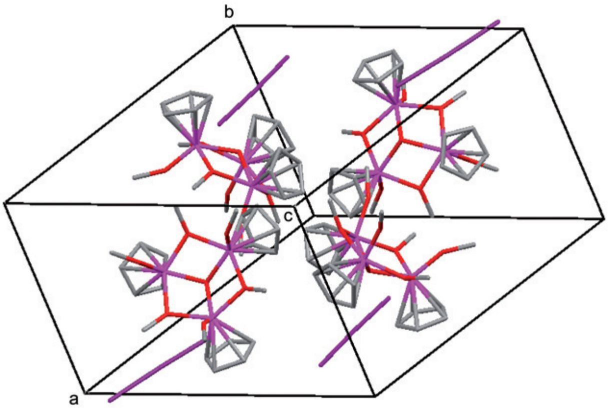

Figure 2. Drawing of the crystal packing of **2**.

Table 2. Selected interatomic distances (Å) and angles (°) for **2**.[a]

Ti(1)–O(1)	1.951(5)	Ti(2)–C(10)	2.367(8)
Ti(1)–O(2)	2.023(5)	Ti(2)–Cp′	2.038
Ti(1)–O(4)	2.021(5)	Ti(3)–O(1)	1.954(5)
Ti(1)–O(5)	1.799(5)	Ti(3)–O(3)	2.014(5)
Ti(1)–C(1)	2.361(7)	Ti(3)–O(4)	2.030(5)
Ti(1)–C(2)	2.351(8)	Ti(3)–O(6)	1.801(5)
Ti(1)–C(3)	2.343(7)	Ti(3)–C(11)	2.369(9)
Ti(1)–C(4)	2.363(7)	Ti(3)–C(12)	2.364(9)
Ti(1)–C(5)	2.375(7)	Ti(3)–C(13)	2.365(8)
Ti(1)–Cp	2.041	Ti(3)–C(14)	2.362(8)
Ti(2)–O(1)	1.958(5)	Ti(3)–C(15)	2.356(8)
Ti(2)–O(2)	2.040(5)	Ti(3)–Cp″	2.040
Ti(2)–O(3)	2.034(5)	I(1)–I(2)	2.8882(8)
Ti(2)–O(7)	1.789(5)	I(2)–I(3)	2.9526(7)
Ti(2)–C(6)	2.356(7)	Ti(1) . . . Ti(2)	3.173(2)
Ti(2)–C(7)	2.360(7)	Ti(1) . . . Ti(3)	3.176(2)
Ti(2)–C(8)	2.360(7)	Ti(2) . . . Ti(3)	3.160(2)
Ti(2)–C(9)	2.364(7)		
Ti(1)–O(1)–Ti(2)	108.5(2)	O(2)–Ti(2)–O(3)	133.8(2)
Ti(1)–O(1)–Ti(3)	108.8(2)	O(2)–Ti(2)–O(7)	90.2(2)
Ti(2)–O(1)–Ti(3)	107.8(2)	O(2)–Ti(2)–Cp′	110.98
Ti(1)–O(2)–Ti(2)	102.7(2)	O(3)–Ti(2)–O(7)	90.0(2)
Ti(1)–O(4)–Ti(3)	103.3(2)	O(3)–Ti(2)–Cp′	110.68
Ti(2)–O(3)–Ti(3)	102.6(2)	O(7)–Ti(2)–Cp′	114.85
O(1)–Ti(1)–O(2)	72.7(2)	O(1)–Ti(3)–O(3)	72.8(2)
O(1)–Ti(1)–O(4)	72.5(2)	O(1)–Ti(3)–O(4)	72.2(2)
O(1)–Ti(1)–O(5)	130.9(2)	O(1)–Ti(3)–O(6)	129.3(2)
O(1)–Ti(1)–Cp	113.51	O(1)–Ti(3)–Cp″	116.74
O(2)–Ti(1)–O(4)	132.4(2)	O(3)–Ti(3)–O(4)	133.3(2)
O(2)–Ti(1)–O(5)	89.5(2)	O(3)–Ti(3)–O(6)	90.0(2)
O(2)–Ti(1)–Cp	112.23	O(3)–Ti(3)–Cp″	111.26
O(4)–Ti(1)–O(5)	89.4(2)	O(4)–Ti(3)–O(6)	88.9(2)
O(4)–Ti(1)–Cp	110.96	O(4)–Ti(3)–Cp″	111.72
O(5)–Ti(1)–Cp	115.50	O(6)–Ti(3)–Cp″	113.92
O(1)–Ti(2)–O(2)	72.2(2)	I(1)–I(2)–I(3)	176.49(3)
O(1)–Ti(2)–O(3)	72.3(2)	Ti(1) . . . Ti(2) . . . Ti(3)	60.20(4)
O(1)–Ti(2)–O(7)	129.2(2)	Ti(2) . . . Ti(3) . . . Ti(1)	60.10(4)
O(1)–Ti(2)–Cp′	115.90	Ti(3) . . . Ti(1) . . . Ti(2)	59.71(4)

[a] Cp, Cp′, and Cp″ are the centroids for the cyclopentadienyl rings C(1)C(2)C(3)C(4)C(5), C(6)C(7)C(8)C(9)C(10), and C(11)C(12)C(13)C(14)C(15), respectively.

$\{Ti_3^{IV}(\mu_3\text{-}O)\}^{10+}$ core [8, 41]. The Ti–O^{2-}–Ti angles are equal, in the range 107.8(2)–108.8(2)° [8, 41]. The Ti_3O_3 ring, comprising three Ti^{IV} ions and three oxygens from bridging MeO^-, is not planar; Ti(1), Ti(2), and Ti(3) deviate 0.162, 0.116, and 0.138 Å from the Ti_3O_3 best-mean-plane, all three pointing toward μ_3-O^{2-}. Furthermore, O(2), O(3), and O(4) deviate 0.139, 0.119, and 0.158 Å from the Ti_3O_3 best-mean-plane, in the direction toward the terminal MeO^- groups. The Cp^- rings are planar. The five Ti–C distances of each cyclopentadienyl group range from 2.343(7) to 2.375(7) Å, establishing a distinct *pentahapto* coordination mode for each Cp^- in **2**. The mean Ti-C bond distances [2.359 Å (for Cp), 2.361 Å (for Cp′), and 2.363 Å (for Cp″)] are in agreement with the corresponding values of other cyclopentadienyltitanium(IV) complexes [19–21, 26]. C–C bond lengths in the cyclopentadienyl rings of **2** with average values of 1.389 Å (for Cp) and 1.403 Å (for Cp′ and Cp″) are within the usual range reported for organometallic complexes containing Cp^- [19–21, 26]. Moreover, the I(1)–I(2) and I(2)–I(3) separations of 2.888 and 2.953 Å, respectively, and the I(1)–I(2)–I(3) bond angle of 176.5° are normal for an isolated, almost linear, triiodide (I_3^-) [42].

Complex **2** joins a small family of structurally characterized Ti^{IV} complexes with an oxide-centered triangular topology [8, 41], and it is only the second member of this family in which the edges of the triangle are bridged by methoxide groups [41a]. Finally, **2** joins a handful of titanium(IV) complexes bearing I_3^- as counterion [42b,c]. Despite the commonly found triangular topology in Ti^{IV}/oxido/alkoxido cluster chemistry, **2** is only the second example of such a species bearing cyclopentadienyl groups as terminal ligands [41a].

4. Concluding comments and perspectives

The main aspect of this work is the discovery of a convenient synthetic route for the formation of an organometallic Ti^{IV} complex based on a simple hydrolysis/alcoholysis reaction of $[Ti(\eta^5\text{-}C_5H_5)_2X_2]$ (X = halide ligand). Half-titanocene complexes have been shown previously [43] to react with H_2O giving oxido-bridged dinuclear compounds without requiring the addition of external organic ligand. We have shown in this work that $[Ti(\eta^5\text{-}C_5H_5)_2I_2]$ reacts, and not simply dissolves and recrystallizes as was initially anticipated, with H_2O and MeOH under aerobic conditions leading to $[Ti_3^{IV}O(OMe)_6(\eta^5\text{-}C_5H_5)_3](I_3)$ (**2**). It seems that the formation of Ti^{IV}–O^{2-}–Ti^{IV} bridges is a general trend of titanocene chemistry in H_2O-containing organic solvents. Compound **2** has been fully characterized by single-crystal X-ray crystallography and IR and electronic spectroscopies, and found to possess a triangular arrangement of three Ti^{IV} centers bridged by oxide and methoxide groups. From a synthetic viewpoint, we have further developed [44] the use of convenient (i.e., aerobic reactions, aqueous-based media) synthetic conditions for the preparation of Group 4 metal complexes with mixed cyclopentadienyl/oxide/alkoxide ligation, this time without employing a chelating/bridging organic group. This opens the door for reactions of the $[M^{IV}(\eta^5\text{-}C_5H_4R)_2X_2]$ (M = Ti, Zr, Hf; R = H, Me, $SiMe_3$, ...; X = halide) complexes with a great variety of alcoholic media. Further, we are intending to investigate the catalytic activity of **2** for reactions such as ethylene polymerization [43]. Experiments on these projects are currently in progress in our laboratories.

Supplementary material

CCDC 812032 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44)1223-336033; or E-mail: deposit@ccdc.cam.ac.uk

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