

# Carboxylate-substituted Ti(IV) oxo clusters with a Ti<sub>3</sub>O core

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## ARTICLE INFO

### Article history:

Received 27 October 2017

Accepted 25 November 2017

Available online 26 November 2017

### Keywords:

Metal oxo clusters

Titanium compounds

Carboxylate ligands

X-ray structure analyses

## ABSTRACT

Ti<sub>3</sub>O(OiPr)<sub>6</sub>(OOC-adamantyl)<sub>4</sub> and Ti<sub>3</sub>O<sub>2</sub>(OiPr)<sub>3</sub>(OOCPh<sub>3</sub>)<sub>5</sub> were obtained from the reaction of Ti(OiPr)<sub>4</sub> with adamantylcarboxylic or triphenylacetic acid, respectively. The structures of both are based on a central Ti<sub>3</sub>O unit, which is substituted by different numbers of bridging carboxylate ligands and, in the case of the adamantyl derivative, also a chelating one.

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## 1. Introduction

The Ti<sub>3</sub>O unit, where a μ<sub>3</sub>-oxygen ion connects three titanium atoms, is a wide-spread building block in Ti(IV) oxo clusters of higher nuclearity, such as oxo-alkoxo clusters [1,2] or many carboxylate- [3] and phosphonate-decorated [4] derivatives thereof. This is not too surprising, if one bears in mind that formation of the cluster cores is governed by the same structural criteria than that of the TiO<sub>2</sub> modifications rutile and anatase with μ<sub>3</sub>-oxygen atoms.

Given the importance of the Ti<sub>3</sub>O building block in clusters of higher nuclearity, it is rather surprising that only few trinuclear Ti<sup>IV</sup> oxo compounds are known. This article deals with compounds in which the Ti atoms are only coordinated by oxygen atoms, but nevertheless [(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>Ti<sub>3</sub>O(OMe)<sub>6</sub>]<sup>+</sup> [5,6], and [Ti<sub>3</sub>O(S<sub>2</sub>)<sub>3</sub>Cl<sub>6</sub>]<sup>2-</sup> [7] should be mentioned. Partial hydrolysis of Ti(OR)<sub>4</sub> mostly results in clusters of higher nuclearity, and only a few Ti<sub>3</sub> alkoxo derivatives were isolated and structurally characterized. The Ti/O core of the parent compound, Ti<sub>3</sub>O(OR)<sub>10</sub> [1,8], is approximately C<sub>3</sub>-symmetric, the Ti<sub>3</sub> triangle being capped by both a pyramidal μ<sub>3</sub>-O and a μ<sub>3</sub>-OR group, and each Ti-Ti edge bridged by a μ<sub>2</sub>-OR. The remaining six OR groups are terminal (two at each Ti atom). This structure is retained in Ti<sub>3</sub>O(OiPr)<sub>7</sub>[Me<sub>2</sub>C(O)CH=C(O)CH<sub>2</sub>C(O)Me<sub>2</sub>], where the three oxygen atoms of the enolate form of 2,6-dimethylhept-3-en-2,4,6-triol occupy the positions of two terminal OR and the μ<sub>3</sub>-OR [9,10]. The structures of Ti<sub>3</sub>O(OR)<sub>8</sub>(OOCR')<sub>2</sub> (R = OiPr, R' = Ph [11]; R = CH<sub>2</sub>CMe<sub>3</sub>, R' = H or Me [12]) are variations of the Ti<sub>3</sub>O(OR)<sub>10</sub> structure, as one μ<sub>2</sub>-OR and the μ<sub>3</sub>-OR are

both replaced by bridging OOCR' ligands. Since bridging R'COO ligands occupy one coordination site less than μ<sub>3</sub>-OR, one Ti atom in Ti<sub>3</sub>O(OR)<sub>8</sub>(OOCR')<sub>2</sub> is five-coordinate. Contrary to Ti<sub>3</sub>O(OR)<sub>10</sub>, the μ<sub>3</sub>-O is approximately in plane with the three Ti atoms. Two isomers of this structure exist: one (for R' = Ph and H) in which the two R'COO ligands bridge different Ti-Ti edges, and one (for R' = Me) where both bridge the same Ti-Ti edge.

Reaction of Ti(OR)<sub>4</sub> with carboxylic acids results in the formation of carboxylate-substituted oxo clusters. In such reactions, partial substitution of the OR groups by carboxylate ligands and generation of water or oxo groups through ester formation between the carboxylic acid and eliminated alcohol compete with each other. The relative rates of both reactions are influenced by a number of parameters [3]. The obtained oxo clusters are thus characterized by the degree of substitution (RCOO/Ti ratio) and the degree of condensation (O/Ti ratio). Ti<sub>3</sub>O(OR)<sub>8</sub>(OOCR')<sub>2</sub> clusters, with the lowest O/Ti ratio (0.33), were only obtained until present upon reaction of carboxylic acids with Ti(OCH<sub>2</sub>CMe<sub>3</sub>)<sub>4</sub>, containing the bulky neopentyl groups [12] (the phenyl derivative [11] was obtained by another route). Less bulky OR groups always resulted in clusters with a higher nuclearity and a higher O/Ti ratio [3]. We now report that with bulky carboxylic acids, Ti<sub>3</sub>O clusters are formed as well, with variations of the previously observed structures.

## 2. Results and discussion

Reaction of Ti(OiPr)<sub>4</sub> with 1.75 M equivalents of adamantylcarboxylic acid (Ad-COOH) in THF resulted in the formation of Ti<sub>3</sub>O(OiPr)<sub>6</sub>(OOC-Ad)<sub>4</sub> (**1**), the crystal structure of which contains two very similar molecules in the asymmetric unit. The high

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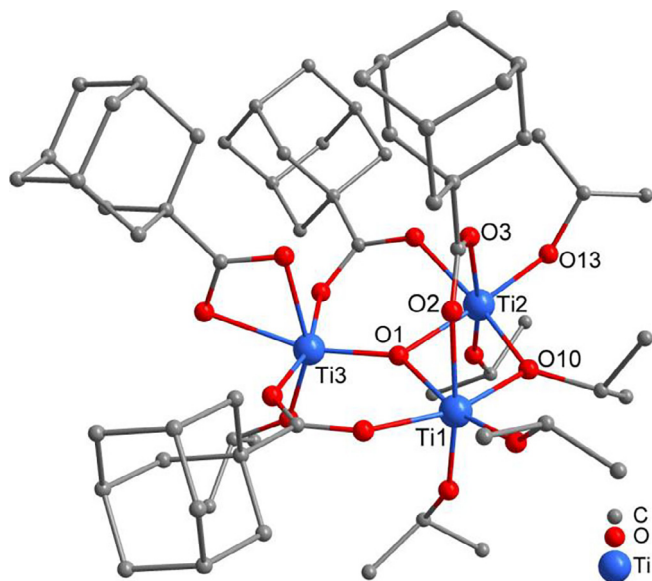


Fig. 1. Molecular structure of  $\text{Ti}_3\text{O}(\text{OiPr})_6(\text{OOC-Ad})_4$  (**1**).

degree of substitution (at a low O/Ti ratio) is very surprising, especially for a bulky carboxylate ligand.

The structure of **1** (Fig. 1) is derived from that of  $\text{Ti}_3\text{O}(\text{OiPr})_8(\text{OOCPh})_2$  [11] and  $\text{Ti}_3\text{O}(\text{OCH}_2\text{CMe}_3)_8(\text{OOCH})_2$  [12] in a way that a second OR-bridge in the reference compounds is replaced by a carboxylate ligand. Additionally, one terminal OR group of the previously 5-coordinate Ti atom is replaced by a chelating OOC-Ad ligand, which thus becomes 6-coordinate. Chelating OOCR ligands are very rare in Ti(IV) chemistry. Each Ti atom in **1** is 6-coordinate: both Ti1 and Ti2 are coordinated by the  $\mu_3$ -O, two bridging OOC-Ad, one  $\mu_2$ -OiPr and two terminal OiPr, while Ti3 is coordinated by the  $\mu_3$ -O, two bridging OOC-Ad, one chelating OOC-Ad and only one terminal OiPr. Because of the OiPr bridge, the Ti1–Ti2 distance (3.18 Å) is much shorter than Ti2–Ti3 (3.51 Å) and Ti1–Ti3 (3.57 Å). The  $\mu_3$ -O (O1), is strongly shifted towards Ti3 (Ti1–O1 2.101(1), Ti2–O1 2.086(1), Ti3–O1 1.800(1) Å; similar for the second molecule in the asymmetric unit). The Ti3–O1 distance is in fact in the typical range of Ti– $\mu_2$ O distances (see below for compound **2**), while Ti1–O1 and Ti2–O1 are longer than typical Ti– $\mu_3$ O distances in undistorted  $\text{Ti}_3\text{O}$  units (1.95–2.00 Å [1,9]). The distortion of the  $\text{Ti}_3\text{O}$  triangle is also reflected in the Ti–O1–Ti bond angles (Ti1–O1–Ti2 98.66(5), Ti1–O1–Ti3 132.55(6), Ti2–O1–Ti3 128.70(6)°; sum 359.91°).

When ester formation is sluggish because of low reactivity of an acid or an alcohol, cluster formation is also retarded. We found previously, that in such cases addition of acetic acid is very helpful, because the relatively faster formation of acetic acid esters delivers the oxo groups for cluster formation [4,13]. To this end, reaction of  $\text{Ti}(\text{OiPr})_4$  with 2 M equivalents of triphenylacetic acid was performed in the presence of 2 M equivalents of acetic acid.  $\text{Ti}_3\text{O}_2(\text{OiPr})_3(\text{OOC-CPh}_3)_5$  (**2**) was obtained under these conditions (note that the clusters do not contain acetate ligands).

The structure of **2** (Fig. 2) is another modification of the  $\text{Ti}_3\text{O}$  motif. Surprisingly, both the O/Ti and the RCOO/Ti ratio are higher than in **1** and the  $\text{Ti}_3\text{O}(\text{OR})_8(\text{OOCR}')_2$  clusters. The higher O/Ti ratio can be rationalized by the easier formation of water due to the presence of acetic acid. Five bridging OOC-CPh<sub>3</sub> groups surround the  $\text{Ti}_3\text{O}$  triangle in **2**; the Ti1–Ti2 edge is additionally bridged by a  $\mu_2$ -O. The sixth coordination site at each Ti atom is occupied by a terminal OiPr group. The structure of **2** is very much related to the so-called basic carboxylates of +III metals, such as  $[\text{Fe}_3\text{O}(\text{OOCR})_6\text{L}_3]^+$ , where each M–M edge is bridged by two

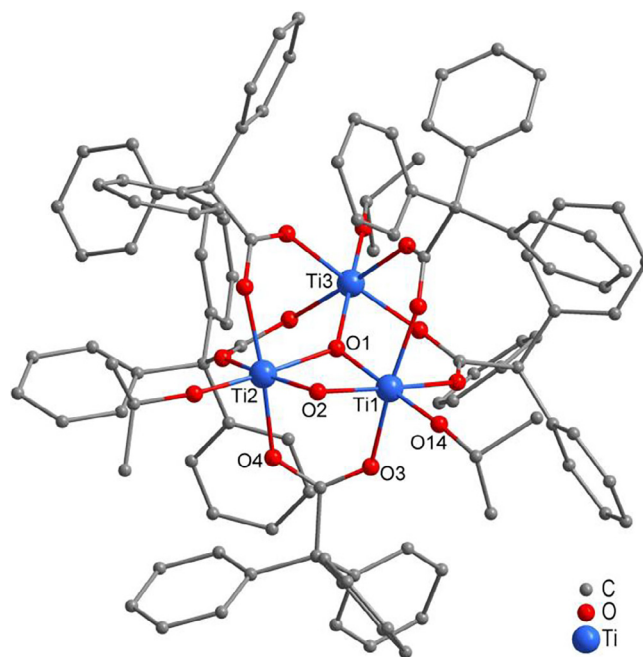


Fig. 2. Molecular structure of  $\text{Ti}_3\text{O}_2(\text{OiPr})_3(\text{OOCCPh}_3)_5$  (**2**).

carboxylate ligands and neutral ligands L complement the coordination sphere of the metal atoms.

The  $\mu_3$ -O (O1), is slightly shifted towards Ti3 (Ti1–O1 2.001(2), Ti2–O1 1.979(2), Ti3–O1 1.896(2) Å). Note that the Ti1–O1 and Ti2–O1 distances are significantly shorter and the Ti3–O1 distance longer than in **1** which is most likely due to the different ligand sphere. This distortion of the  $\text{Ti}_3\text{O}$  triangle and the (non-crystallographic) mirror symmetry of the Ti/O core are also reflected in the Ti–O1–Ti bond angles (Ti1–O1–Ti2 93.22(7), Ti1–O1–Ti3 130.80(9), Ti2–O1–Ti3 130.66(9)°; sum 354.68°). The Ti–O bond lengths of the  $\mu_2$ -oxygen O2 (Ti1–O2 1.845(2), Ti2–O2 1.837(2) Å) are typical for such arrangements. For example, the Ti–O distances in the “titanyl carboxylates”  $\text{Ti}_8(\mu_2\text{-O}_8)(\text{OOCR})_{16}$  are in the range 1.75–1.85 Å [14]. Compared with the latter compounds, the Ti1–O2–Ti2 bond angle (103.51(9)°) in **2** is fairly acute.

### 3. Conclusions

The large structural variety of Ti(IV) oxo/alkoxo clusters results from a wide range of nuclearities, different O/Ti ratios and different degrees of substitution by organic ligands. Among them, trinuclear compounds with a central  $\text{Ti}_3\text{O}$  unit are rare, and  $\text{Ti}_3\text{O}(\text{OR})_8(\text{OOCR}')_2$  was the only type of carboxylate-substituted  $\text{Ti}_3\text{O}$  clusters isolated until present. This is surprising, because  $\text{Ti}_3\text{O}$  units are very common building blocks in higher-nuclearity clusters. The structures reported in this article demonstrate a much larger structural variability of the ligand sphere around  $\text{Ti}_3\text{O}$  units than anticipated. More than two edge-bridging carboxylate ligands can be accommodated, and even a rare chelating carboxylate ligand was observed (in **1**). In fact, the structure of  $\text{Ti}_3\text{O}_2(\text{OiPr})_3(\text{OOCCPh}_3)_5$  (**2**) is a close structural analogy to the well-known  $[\text{M}_3\text{O}(\text{OOCR})_6\text{L}_3]^+$  compounds of +III metals.

Two reactions compete with each other when carboxylate-substituted metal oxo clusters are formed by reaction of metal alkoxides with carboxylic acids, viz. substitution of OR groups by carboxylate ligands and ester formation which generates water. The relative rate of both reactions has a large influence on the composition of the obtained clusters (assuming that hydrolysis of M–OR groups is fast). The results presented in this article show that

steric effects also play a major role. We have previously postulated that larger clusters could be formed by expansion of the cluster core starting from  $Ti_3O$  clusters [3]. This is supported by the finding that bulky ligands, such as bulky carboxylate ligands (this work) or bulky OR groups [12], result in stable  $Ti_3O$  clusters, i.e. they probably inhibit attachment of additional Ti-containing units and thus cluster growth.

#### 4. Experimental

All experiments were carried out under Ar atmosphere using standard Schlenk techniques.  $Ti(OiPr)_4$  was obtained from ABCR. All solvents used for NMR spectroscopy (Eurisotop) were degassed prior to use and stored over molecular sieve.  $^1H$  and  $^{13}C$  solution NMR spectra were recorded on a Bruker AVANCE 250 (250.13 MHz [ $^1H$ ], 62.86 MHz [ $^{13}C$ ]) equipped with a 5-mm inverse-broad-band probe head and a z-gradient unit.

##### 4.1. $Ti_3O(OiPr)_6(OOC-Ad)_4 \cdot 0.5 THF$ (**1**)

Adamantylcarboxylic acid (678 mg, 3.76 mmol) was suspended in 2 ml of THF and 620  $\mu$ l (2.14 mmol) of  $Ti(OiPr)_4$  were added. A clear solution was obtained after stirring, from which crystals of **1** were formed after 16 weeks. Yield 470 mg (52%).  $^1H$  NMR ( $CD_2Cl_2$ )  $\delta$  = 1.17–1.44 (m, 36H,  $CH_3$ ), 1.61–1.76 (br, 24H,  $CH_2$ ), 1.82–1.95 (br, m, 24H,  $CH_2$ ), 1.95–2.05 (br, 12H, CH), 4.75 (m, 1H, CH), 4.93 (m, 3H, CH), 5.08 (m, 1H, CH), 5.32 (m, 1H, CH) ppm.  $^{13}C$  NMR ( $CD_2Cl_2$ )  $\delta$  = 23.34, 24.41, 24.75, 24.87, 25.11, 25.16, 25.54 ( $CH_3$ ), 27.86, 28.12, 28.22, 28.32, 28.51, 28.67 ( $CH_2$ ), 36.38, 36.66, 36.81 (CH), 37.00 ( $CH_2$ ), 37.81 (CH), 38.80, 38.96, 39.12, 39.16, 39.29, 39.36 ( $CH_2$ ), 40.35, 40.98, 41.25, 41.45 (C-COO), 77.46, 77.85, 78.72, 78.77, 78.97 ( $CH_{iPr}$ ), 182.83, 183.35, 184.83, 185.29 (COO) ppm (signals partially overlapping).

##### 4.2. $Ti_3O_2(OiPr)_3(OOCCPh_3)_5 \cdot CH_2Cl_2$ (**2**)

$Ti(OiPr)_4$  (158.4  $\mu$ l, 0.55 mmol) was added to a suspension of 315 mg (1.09 mmol) of triphenylacetic acid in 3 ml of 2-propanol. 62.5  $\mu$ l (1.09 mmol) of acetic acid were added to the obtained suspension. Since no clear solution was achieved after heating, 2 ml of  $CH_2Cl_2$  were added. Crystals of **2** were obtained from the then clear solution after 4 months. Yield 270 mg (82%).  $^1H$  NMR ( $C_6D_6$ )  $\delta$  = 0.74 (d,  $J$  = 6.09 Hz, 6H,  $CH_3$ ), 0.90 (d,  $J$  = 6.09 Hz, 6H,  $CH_3$ ), 0.92 (d,  $J$  = 5.94 Hz, 6H,  $CH_3$ ), 3.82 (m,  $J$  = 6.09 Hz, 1H, CH), 4.62 (m, 2H, CH), 7.09–7.33 (m, 57H,  $CH_{arom}$ ), 7.39–7.64 (m, 18H,  $CH_{arom}$ ) ppm.  $^{13}C$  NMR ( $C_6D_6$ )  $\delta$  = 23.58, 24.18, 24.25 ( $CH_3$ ), 68.63, 69.13, 69.41 (C-Ph), 79.38, 79.52 ( $CH_{iPr}$ ), 126.63, 127.50, 130.90, 131.10, 131.19 ( $CH_{arom}$ ), 143.29, 144.19, 144.41 (C- $C_{arom}$ ), 181.08, 181.34, 185.44 (COO) ppm (some signals of the aromatic region overlap with the solvent signal).

##### 4.3. X-ray structure analyses

Crystallographic data were collected on a Bruker AXS SMART APEX II four-circle diffractometer with  $\kappa$ -geometry using  $MoK_{\alpha}$  ( $\lambda$  = 0.71073 Å) radiation. The data were corrected for polarization and Lorentz effects, and an empirical absorption correction (SADABS) was employed. The cell dimensions were refined with all unique reflections. SAINT PLUS software (Bruker Analytical X-ray Instruments, 2007) was used to integrate the frames. Symmetry was then checked with the program PLATON [15].

The structures were solved by charge flipping (JANA2006). Refinement was performed by the full-matrix least-squares method based on  $F^2$  (SHELXL97) with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in

**Table 1**

Crystal data, data collection parameters and refinement details.

	<b>1</b> · 0.5 THF	<b>2</b> · $CH_2Cl_2$
Empirical formula	$C_{64}H_{106}O_{15.5}Ti_3$	$C_{110}H_{98}Cl_2O_{15}Ti_3$
$M_r$	1267.2	1874.5
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
$a$ (Å)	22.9659(9)	15.093(1)
$b$ (Å)	23.0489(9)	24.913(3)
$c$ (Å)	25.350(1)	24.777(3)
$\alpha$ (°)	90	90
$\beta$ (°)	103.813(2)	97.736(4)
$\gamma$ (°)	90	90
$V$ (Å <sup>3</sup> )	13030.9(9)	9231(2)
$Z$	8	4
$D_x$ (g·cm <sup>-3</sup> )	1.292	1.349
$T$ (K)	100	100
$\mu$ (mm <sup>-1</sup> )	0.423	0.379
Crystal size (mm)	0.4 × 0.4 × 0.3	0.6 × 0.5 × 0.4
No. measd, indep, obs. refl.	503074, 39867,	171490, 18625,
( $I > 2\sigma(I)$ )	27534	13707
$R_{int}$	0.0528	0.065
$\theta_{max}$ (°)	30.54	26.28
$R[F^2 > 2\sigma(F)]$ , $\omega R(F^2)$ , $S$	0.0495, 0.127, 1.030	0.048, 0.118, 1.041
No. of parameters	1947	1226
Weighting scheme <sup>a</sup>	$w = 0.0686$ , $y = 9.6749$	$w = 0.0605$ , $y = 10.6792$
$\delta\rho_{max}$ , $\delta\rho_{min}$ (e Å <sup>-3</sup> )	1.040, -0.894	1.153, -0.841

<sup>a</sup>  $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$ , where  $P = (F_o^2 + 2F_c^2)/3$ .

calculated positions and refined riding with the corresponding atom. Part of the adamantyl and OiPr groups in **1** and the  $CH_2Cl_2$  molecule in **2** were disordered. Crystal data, data collection parameters and refinement details are listed in Table 1.

CCDC-1574861 (**1**) and -4862 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

#### Acknowledgments

This work was supported by the Austrian Science Fund (FWF), Austria (project P22536). The authors thank the X-ray Center of Vienna University of Technology for its support.

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