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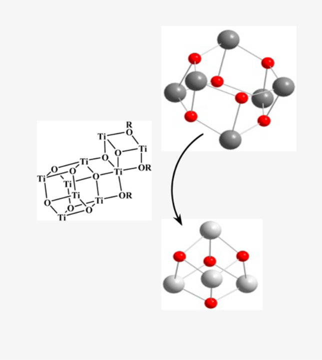
The Structural Conversion of Multinuclear Titanium(IV) μ-Oxo-complexes

Aleksandra Radtke, Piotr Piszczek,* Tadeusz Muzioł, and Andrzej Wojtczak

Nicolaus Copernicus University, Faculty of Chemistry, ul. Gagarina 7, 87-100 Toruń, Poland

Supporting Information

ABSTRACT: For the first time we report the structural conversion processes of hexanuclear μ-oxo-Ti(IV) complexes into tetranuclear ones. Single-crystal X-ray diffraction studies reveal that metastable hexanuclear μ-oxo complexes ($[Ti_6O_6(O^tBu)(O_2CR')_6]$) are formed in the first stage of reactions between $[Ti(O^tBu)_4]$ and branched carboxylic acids R′COOH (R′ = $C(Me)_2Et$, $CH_2{}^tBu$, ^tBu). In the next stage they convert into tetranuclear μ-oxo-Ti(IV) complexes of the formula $[Ti_4O_4(O^tBu)_4(O_2CR')_4]$. Spectroscopic investigations (^{13}C NMR, IR, and MS) proved that the conversion of hexanuclear clusters relies on the attachment of smaller units (e.g., $[Ti_3O(O^tBu)_8(O_2CR')_2]$ or $[Ti_4O_2(O^tBu)_6(O_2CR')_6]$) and intermediate species formation (e.g., $[Ti_9O_8(O^tBu)_{14}(O_2CR')_6]$). The decomposition of intermediate systems in the next reaction stage leads to the formation of tetranuclear clusters. The type of solvent used in the synthesis of multinuclear oxo-Ti(IV) complexes is an important factor, which influences the kind of clusters formed.



INTRODUCTION

Research on the synthesis and properties of multinuclear titanium(IV) μ-oxo-complexes, which was carried out in recent years, revealed their great potential for production of materials based on titanium dioxide. The use of these compounds enables the control of the precursor reactivity in sol−gel processes, the control of the structure of nanocrystalline TiO_2 films in CVD methods, and tuning of the hybrid interfaces for the preparation of inorganic−organic hybrid materials based on $\{Ti_a(\mu_i\text{-}O)_b\}$ (i = 2, 3, 4) cores.[1−5] Multinuclear titanium(IV) μ-oxo-alkoxo-carboxylate complexes of the general formula $[Ti_aO_b(OR)_c(O_2CR')_{4a-2b-c}]$, which are formed in reactions of titanium alkoxides ($Ti(OR)_4$ with organic acids (R′COOH) using a 1:1 ratio, are particularly interesting.[6−10] There are two possible mechanisms enabling the formation of carboxylate-substituted Ti(IV) oxo-clusters. One of these mechanisms assumes that the controlled growth of oxo clusters follows the slow *in situ* formation of water molecules (during the esterification process) and hydrolysis of alkoxide ligands. According to the second mechanism, oxo bridges are produced in the nonhydrolytic process.[2,11−18] Though the general synthesis scheme of these compounds has been discussed in detail in earlier reports, problems associated with understanding the mechanisms of formation of multinuclear Ti(IV) complexes with controlled structure of $\{Ti_a(\mu_i\text{-}O)_b\}$ core remain unsolved. Clear understanding of this process would enable the formation of precursors containing well-defined core structure, which is crucial for the production of inorganic−organic hybrid materials, as well as for titanium dioxide ceramic coatings of strictly defined polycrystalline structure.[2,4,5,9,16−18] Earlier reports revealed that major factors affecting the self-limiting growth of carboxylate-substituted oxo-clusters are the presence of two different anionic ligands (−OR and $-O_2CR'$) in the coordination sphere of the central ion, their different capabilities to balance the metal charge, and the metal coordination number.[19−21] Schubert suggested that the possible route for the stepwise assembly of larger titanium oxo-clusters is preceded by the formation of small units (preunits), for example, $[Ti_3O(OR)_8(O_2CR')_2]$ or $[Ti_4O_2(OR)_6(O_2CR')_6]$. Analyzing the reaction pathway of $Ti(O^iBu)_4$ with branched organic acids (R′COOH, R′ = ^tBu, $CH_2{}^tBu$, $C(Me)_2Et$), we have found that the structurally stable μ-oxo-Ti(IV) complexes containing $\{Ti_6(\mu_3\text{-}O)_6\}$ cores were obtained by the conversion of previously formed metastable intermediate systems.[10] That process has not been investigated in detail yet, although the knowledge about its course can be important for the synthesis of materials containing $\{Ti_a(\mu_i\text{-}O)_b\}$ skeletons with well-defined structure. To find the details of structural conversion processes of multinuclear oxo-Ti(IV) complexes, we investigated the pathways of the reaction of $[Ti(O^tBu)_4]$ with branched carboxylic acids R′COOH (R′ = $C(Me)_2Et$, $CH_2{}^tBu$, ^tBu). Results of our work are presented and discussed in this paper.

EXPERIMENTAL SECTION

General Remarks. Synthesized complexes were characterized using elemental analyses, IR, and NMR spectroscopy methods. Elemental analyses of C and H were performed using Vario MACRO CHN ELEMENTAR analyzer. The Ti% was gravimetrically determined as TiO_2, according to the Meth−Cohn et al. method.[22] Infrared (IR) spectra were recorded on PerkinElmer Spectrum 2000 spectrometer within range of 400−4000 cm^{-1} with a medium slit width and peak resolution of 4.0 cm^{-1}. The crystals were studied as a powder dispersed in the KBr pellet. Variable-temperature IR (VT IR) spectra of crystalline powders were registered using SPECAC

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Table 1. Crystal Systems and Space Group Symmetries for Complexes 1−4 and 6

complex	crystal system	space-group	*a* [Å]	*b* [Å]	*c* [Å]	*α* [deg]	*β* [deg]	*γ* [deg]	*R* indices (used data) [$I > 2\sigma(I)$]
(**1**)	cubic	$Pa\bar{3}$	20.5595(2)	20.5595(2)	20.5595(2)				$R1^a = 0.0855$, $wR2^b = 0.2051$
(**2**)	orthorhombic	*Pnma*	20.2877(10)	23.6297(12)	11.5533(6)				$R1^a = 0.0554$, $wR2^b = 0.1430$
(**3**)	rhombohedral	$R\bar{3}c$	19.1601(5)	19.1601(5)	19.1601(5)	58.004(2)	58.004(2)	58.004(2)	$R1^a = 0.0518$, $wR2^b = 0.1496$
(**4**)	orthorhombic	*Pnma*	18.2573(4)	16.2919(5)	20.8348(5)				$R1^a = 0.0532$, $wR2^b = 0.1651$
(**6**)	monoclinic	$P2_1/m$	12.962(3)	16.979(3)	13.317(3)		104.16(3)		$R1 = 0.0761$, $wR2 = 0.2220$

$^aR1 = \sum||F_0| - |F_c||/\sum|F_0|$. $^bwR2 = \{[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]\}^{1/2}$.

temperature variable cell. Solid-state ^{13}C NMR spectra were registered on Bruker AMX 300. The solution ^{13}C NMR spectra ($CDCl_3$) were recorded using a 5 mm solution probe on Varian Gemini 2000. Mass spectra of synthesized complexes (**1**)−(**6**) were recorded at the temperature range of 423−593 K with an MS AMD-604, MASPEC system using the electron ionization (EI) method. Additionally complexes (5)−(7) were studied with electrospray ionization mass spectrometry (ESI-MS) method, using Mass AB Sciex typ QStar XL MS-MS spectrometer. Very poor solubility of these compounds in organic solvents and very low signal intensity caused the use of the MCA scanning mode (summing of 100 scans).

Synthesis. All operations were conducted under argon atmosphere using standard Schlenk methods. Before use solvents were dried and then distilled under Ar. Reagents $Ti(O^tBu)_4$ and organic acids (R′COOH; R′ = ^{t}Bu, $CH_2{}^tBu$, C(Me)Et) were used as received from Aldrich. The solution of organic acid in toluene (14.69 mmol of acid in 4 mL of the solvent) was added dropwise to the solution of $Ti(O^tBu)_4$ (14.69 mmol) in ^{t}BuOH/toluene mixture (4 mL, 1:1) and stirred for 24 h.

$[Ti_6O_6(O^tBu)_6(O_2CC(Me)_2Et)_6]\cdot C_7H_8$ (1) and $[Ti_4O_4(O^tBu)_4(O_2CC(Me)_2Et)_4]$ (2). Crystals were grown by slow evaporation of the reaction mixture (0.17 g of $Et(Me)_2CCOOH$ and 0.5 g of $Ti(O^tBu)_4$) under Ar atmosphere in the glovebox. The colorless crystals of (**1**) were obtained after 2 d. Leaving the crystals in the mother liquor for next 3 d led to the formation of crystals of (**2**). Yield = 77%.

Compound (**1**). Elem. anal. for $Ti_6O_{24}C_{67}H_{128}$, calcd: Ti 17.93%, C 50.14%, H 7.98%; found: Ti 18.11%, C 50.30%, H 8.12%; ^{13}C NMR (solid state, 295 K, δ[ppm]): 9.51 CH_3(Et), 25.64, 25.90 CH_2(Et), 30.68, 31.57 $CH_3(C(Me)_2)$, 43.24 $C(C(Me)_2)$, 185.35, 186.57 C(COO), 34.77, 36.21 $CH_3(^tBu)$, 84.78, 86.16 $C(^tBu)$, 126.36, C_5H_6, 21.43 CH_3(toluene); ^{13}C NMR ($CDCl_3$, 295 K, δ[ppm]): 9.30 CH_3(Et), 25.06, CH_2(Et), 30.98, $CH_3(C(Me)_2)$, 43.76 $C(C(Me)_2)$, 186.00 C(COO), 34.60 $CH_3(^tBu)$, 85.13 $C(^tBu)$.

Compound (**2**). Elem. anal. for $Ti_4O_{16}C_{40}H_{80}$, calcd: Ti 19.02%, C 47.64%, H 7.94%; found: Ti 19.28%, C 47.91%, H 8.06%; ^{13}C NMR (solid state, 295 K, δ[ppm]): 9.49 CH_3(Et), 24.80, 25.30 CH_2(Et), 30.80, 31.24 $CH_3(C(Me)_2)$, 43.74 $C(C(Me)_2)$, 183.50, 185.34, 186.00 C(COO), 34.78, 36.28 $CH_3(^tBu)$, 84.70, 86.44 $C(^tBu)$; ^{13}C NMR ($CDCl_3$, 295 K, δ[ppm]): 9.24 CH_3(Et), 25.01, CH_2(Et), 30.98, $CH_3(C(Me)_2)$, 43.70 $C(C(Me)_2)$, 186.83 C(COO), 34.65 $CH_3(^tBu)$, 85.19 $C(^tBu)$.

$[Ti_6O_6(O^tBu)_6(O_2CCH_2{}^tBu)_6]\cdot 1.5\ C_7H_8$ (3) and $[Ti_4O_4(O^tBu)_4(O_2CCH_2{}^tBu)_4]\cdot 0.5\ C_7H_8$ (4). Crystals were grown by slow evaporation of the reaction mixture (0.17 g of $^tBuCH_2CCOOH$, 0.5 g of $Ti(O^tBu)_4$) under Ar atmosphere in the glovebox. The colorless crystals of (**3**) were obtained after 3 d. Leaving the crystals in the mother liquor for next 2 d led to the formation of crystals of (**4**). Yield = 79%.

Compound (**3**). Elem. anal. for $Ti_6O_{24}C_{70.5}H_{132}$, calcd: Ti 17.40%, C 51.28%, H 7.99%; found: Ti 17.15%, C 51.39%, H 8.06%; ^{13}C NMR (solid state, 295 K, δ[ppm]): 50.00 CH_2, 29.34, 29.70 $CH_3(^tBu)$, 32.67 $C(^tBu)$, 187.70, 188.02 C(COO), 30.99 $CH_3(^tBu)$, 84.21, 84.96 $C(^tBu)$, 127.88, 128.18 C_5H_6, 21.12 CH_3(toluene); ^{13}C NMR ($CDCl_3$, 295 K, δ[ppm]): 50.20 CH_2, 29.40 $CH_3(^tBu)$, 31.47 $C(^tBu)$, 181.80 C(COO), 31.25 $CH_3(^tBu)$, 84.98 $C(^tBu)$, 128.23, 129.00 C_5H_6, 21.15 CH_3(toluene).

Compound (**4**). Elem. anal. for $Ti_4O_{16}C_{43.5}H_{84}$, calcd: Ti 18.17%, C 49.53%, H 7.96%; found: Ti 18.28%, C 49.77%, H 8.13%; ^{13}C NMR (solid state, 295 K, δ[ppm]): 50.32 CH_2, 29.47, 29.72, 30.46 $CH_3(^tBu)$, 32.35 $C(^tBu)$, 181.15, 182.66, 187.79 C(COO), 31.01 $CH_3(^tBu)$, 84.40, 85.06 $C(^tBu)$, 128.08, 128.38 C_5H_6, 21.54 CH_3(toluene); ^{13}C NMR ($CDCl_3$, 295 K, δ[ppm]): 50.55 CH_2, 29.98 $CH_3(^tBu)$, 31.22 $C(^tBu)$, 181.81 C(COO), 31.15 $CH_3(^tBu)$, 85.70 $C(^tBu)$, 128.22, 129.02 C_5H_6, 21.44 CH_3(toluene).

Compound (5) and $[Ti_4O_4(O^tBu)_4(O_2C^tBu)_4]\cdot 0.5\ C_7H_8$ (6). Crystals were grown by slow evaporation of the reaction mixture (0.15 g of ^{t}BuCOOH, 0.5 g of $Ti(O^tBu)_4$) under Ar atmosphere in the glovebox. The crystalline powder of (**5**) was obtained after 3 d. Leaving the crystalline powder in the mother liquor for next 2 d led to the formation of crystals of (**6**). Yield = 74%.

Compound (**5**). Elem. anal. for $Ti_9O_{34}C_{86}H_{180}$, calcd: Ti 19.74%, C 47.16%, H 8.22%; found: Ti 20.02%, C 47.3%, H 7.99%; ^{13}C NMR (solid state, 295 K, δ[ppm]): 28.10, 28.30, 31.29. $CH_3(^tBu)$, 39.40, 40.6 $C(^tBu)$, 183.67, 185.06, 186.60, 187.60 C(COO), 78.20, 85.00 $C(^tBu)$, ^{13}C NMR ($CDCl_3$, 295 K, δ[ppm]): 27.42, 31.18 $CH_3(^tBu)$, 38.86 $C(^tBu)$, 185.10 C(COO), 85.00 $C(^tBu)$.

Compound (**6**). Elem. anal. for $Ti_4O_{16}C_{36}H_{72}$, calcd: Ti 20.13%, C 45.40%, H 7.57%; found: Ti 20.36%, C 45.66%, H 7.79%; ^{13}C NMR (solid state, 295 K, δ[ppm]): 27.77, 31.29 $CH_3(^tBu)$, 38.95, 39.55 $C(^tBu)$, 183.67, 185.06, 186.54 C(COO), 83.91, 85.24 $C(^tBu)$, 125.90, 129.20, C_5H_6, 21.15 CH_3(toluene); ^{13}C NMR ($CDCl_3$, 295 K, δ[ppm]): 27.42, 31.23 $CH_3(^tBu)$, 38.86 $C(^tBu)$, 183.95 C(COO), 85.75 $C(^tBu)$, 126.29, 129.21, C_5H_6, 22.42 CH_3(toluene).

Compound (**7**). To obtain crystals of the complex (**5**) with good quality, an attempt was made to synthesize of this compound by another method. The solution of 2,2-dimethylpropionate acid in toluene (14.69 mmol of acid in 4 mL of the solvent) was added dropwise to the solution of $Ti(O^tBu)_4$ (14.69 mmol) in toluene (4 mL) and stirred for 24 h. Crystals were grown by slow evaporation of the reaction mixture (0.15 g of ^{t}BuCOOH, 0.5 g of $Ti(O^tBu)_4$) under Ar atmosphere in the glovebox. The colorless crystals of (**7**) were obtained after 7 days. Yield = 82%.

Elem. anal. for $Ti_6O_{24}C_{48}H_{108}$, calcd: Ti 21.24%, C 42.48%, H 7.96%; found: Ti 21.44%, C 42.60%, H 7.77%; ^{13}C NMR (solid state, 295 K, δ[ppm]): 26.62, 29.29 $CH_3(^tBu)$, 38.85, 39.61 $C(^tBu)$, 183.08, 184.00 C(COO), 81.46, 86.66 $C(^tBu)$; ^{13}C NMR ($CDCl_3$, 295 K, δ[ppm]): 27.41, 31.15 $CH_3(^tBu)$, 38.88 $C(^tBu)$, 183.99 C(COO), 85.78 $C(^tBu)$).

X-ray Crystallographic Study. Diffraction data of the titanium complexes were collected on Oxford Sapphire with CCD area detector.[23] The space groups were assigned based on the systematic absences. All structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 with SHELXL-2013 program.[24] The numerical absorption correction was applied for all crystals (RED171 package of programs, Oxford Diffraction, 2000[23]). Basic crystal data can be found in Table 1, and detailed data are presented in Table S1 in the Supporting Information.

■ RESULTS AND DISCUSSION

Synthesis and Structure Characterization. Studied oxo-Ti(IV) complexes were synthesized in the 1:1 reactions between titanium *tert*-butoxide ($Ti(O^tBu)_4$) and selected branched carboxylic acids, at room temperature, and in argon atmosphere, with procedure consistent with the earlier reports.[6−10] A mixture of toluene and *tert*-BuOH (1:1) was used as the solvent, in accordance to our previous experience with the stabilization of intermediate structures.[10] Because of the possibility of the structural conversion of solid products, the formation of crystals was monitored using IR spectroscopy. First colorless crystals were isolated after 2 to 3 d from reaction mixtures of titanium *tert*-butoxide and appropriate acids: R′COOH; R′ = C(Me)$_2$Et, CH$_2{}^t$Bu, and ^{t}Bu. Isolated solid products (crystals, crystalline powders) were marked as complexes (**1**), (**3**), and (**5**), respectively. The obtained crystals were kept in the reaction mixture for the next few days. Repetition of spectroscopic studies of crystalline products after the next 2 to 3 d revealed that other types of oxo-Ti(IV) complexes were formed, and these compounds were marked as (**2**), (**4**), and (**6**), respectively. The synthesized complexes are stable in air and poorly soluble in organic solvents. Good quality single crystals of (**1**), (**3**), (**2**), (**4**), and (**6**) allowed the X-ray crystal structure determination of their structure. Unfortunately, the quality of complex (**5**) crystals was poor, and therefore its structure has been defined based only on the spectral data analysis. To improve the complex (**5**) crystal quality, the reaction between Ti(O^{t}Bu)$_4$ and ^{t}BuCOOH were carried out in pure toluene as a solvent. Also in this case, the quality of isolated crystals of (**7**) was unsuitable for determination of their structure using the single-crystal X-ray diffraction method.

The initial stage of the synthesis procedure resulted in the formation of hexanuclear μ-oxo-Ti(IV) complexes of formulas $[Ti_6O_6(O^tBu)_6(O_2CC(Me)_2Et)_6]\cdot$toluene (**1**) and $[Ti_6O_6(O^tBu)_6(O_2CCH_2{}^tBu)_6]\cdot$1.5toluene (**3**). The single-crystal X-ray diffraction studies of (**1**) and (**3**) proved that their structures consist of hexanuclear $\{Ti_6(\mu_3\text{-}O)_6\}$ skeletons, arranged into two Ti_3O_3 faces bridged by six *syn*−*syn* carboxylate groups and six terminal alkoxide ligands. Geometry of these skeletons is similar to structures described previously for hexanuclear μ_3-oxo-Ti(IV) complexes.[6−10] Detailed structural data for (**1**) and (**3**) are summarized in Supporting Information (Figure S1 and Table S2). Complexes (**2**), (**4**), and (**6**) form cubane-like structures of formulas: $[Ti_4O_4(O^tBu)_4(O_2CC(Me)_2Et)_4]$ (**2**), $[Ti_4O_4(O^tBu)_4(O_2CCH_2{}^tBu)_4]\cdot$0.5toluene (**4**), and $[Ti_4O_4(O^tBu)_4(O_2C^tBu)_4]\cdot$0.5toluene (**6**). The central part of their molecules consists of tetranuclear $\{Ti_4(\mu_3\text{-}O)_4\}$ skeletons stabilized by four *syn*−*syn* carboxylate groups and four terminal *tert*-butoxide ligands (Figure 1). According to earlier reports, a similar type of structure was obtained only in a direct reaction of Ti(OR)$_4$ (R = ^{i}Pr, Bu, Ph, and ^{t}Bu) with R′COOH (R′ = Co$_3$C(CO)$_9$ and ^{i}Pr) acids.[25]

All titanium atoms in compounds (**2**), (**4**), and (**6**) are six-coordinated, and they have an octahedral coordination sphere consisting of three oxoanions, two carboxylates, and one O^{t}Bu ligand. The $\{Ti_4(\mu_3\text{-}O_4)\}$ core forms a tetragonally distorted cube with alternately arranged Ti and O atoms organized into Ti_2O_2 faces, linked by four carboxylate groups. The titanium oxide bonds formed by atoms belonging to the same Ti_2O_2 faces range from 1.915(2) to 1.9225(19) Å (**2**), 1.9161(18)−1.9213(19) Å (**4**), and 1.9139(19)−1.925(2) Å (**6**). Distances between Ti and O atoms belonging to different polyhedron faces are significantly longer, and the values are 2.086(3)−2.097(2), 2.0946(19)−2.104(3), and 2.072(3)−2.106(3) Å for (**2**), (**4**), and (**6**), respectively. In the $\{Ti_4(\mu_3\text{-}O)_4\}$ core of these complexes, the Ti−Ti distances corresponding to the diagonal of rectangular Ti_2O_2 faces are close to 2.90 Å, while Ti−Ti distances between atoms belonging to different faces are close to 3.02 Å. Titanium atoms of two polyhedron faces described above are linked by four carboxylate groups forming *syn*−*syn* asymmetrical bridges (Supporting Information, Table S2). Terminal alkoxide ligands form the shortest Ti−O bonds, being in the range from 1.746(2) to 1.772(3) Å (Table S2).

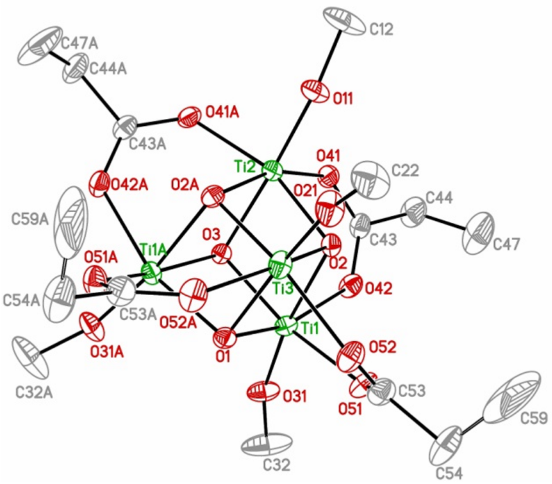


Figure 1. Structure of $[Ti_4O_4(O^tBu)_4(O_2CC(Me)_2Et)_4]\cdot$0.5toluene (**2**). For clarity, CH$_3$ groups, H atoms, and toluene molecules are omitted.

Crystal structure determination of two structurally different solid products as a result of the Ti(O^{t}Bu)$_4$ reactions with branched acids allowed the comparison of the geometry of $\{Ti_a(\mu_3\text{-}O)_b\}$ clusters formed before and after the conversion. Both $\{Ti_6-(\mu_3\text{-}O)_6\}$ and $\{Ti_4-(\mu_3\text{-}O)_4\}$ cores can be described as cuboids with hexagonal or square basis, respectively, and with rectangular side faces. Titanium atoms occupying opposite nodes of the side faces are linked by carboxylate bridges. Comparison reveals that the major differences between two types of clusters are Ti−(μ_3-O)−Ti and (μ_3-O)−Ti−(μ_3-O) angles, and they strongly affect other parameters. In the $\{Ti_4-(\mu_3\text{-}O)_4\}$ core, these angles should be close to 90°, and in fact they range from 97.04(9) to 98.51(13) and from 81.01(9) to 82.51(9)°, respectively. For $\{Ti_6-(\mu_3\text{-}O)_6\}$ cores, these angles should be close to 90° for rectangular and 120° for hexagonal faces. In the reported structures they are 99.52(7)−100.74(15) and 77.19(14)−78.09(7)°, respectively, for rectangular faces, while in the hexagonal faces they are 134.91(9)−135.2(2) and 101.54(19)−101.85(9)°, respectively. These valence angles strongly affect Ti−Ti distances. For the $\{Ti_6-(\mu_3\text{-}O)_6\}$ core, Ti−Ti distances between Ti_3O_3 faces are much shorter (close to 3.12 Å) than between titanium atoms belonging to the same face (∼3.50 Å). Contrary to the $\{Ti_4-(\mu_3\text{-}O)_4\}$ distorted cube, Ti−Ti distances between Ti_2O_2 faces are shorter (∼2.90 Å) than those within the faces (∼3.02 Å). Therefore, in the $\{Ti_4-(\mu_3\text{-}O)_4\}$ type of cluster, the difference between Ti−Ti distances for atoms belonging to the same or different Ti_2O_2 faces is only 0.12 Å, whereas in the $\{Ti_6-(\mu_3\text{-}O)_6\}$ core it is 0.4 Å. Generally we noticed the significant shortening of Ti−Ti distances resulting from the conversion of the $\{Ti_6-(\mu_3\text{-}O)_6\}$ into $\{Ti_4-(\mu_3\text{-}O)_4\}$ cluster. It is 0.1 Å (3.12 vs 3.02 Å) for distances between Ti_aO_a faces, but it decreases approximately by 0.6 Å for intraface distances (3.50 vs 2.90 Å). Hence, it should be expected that the character of interactions between titanium atoms in clusters composed of the smaller $\{Ti_a-(\mu_3\text{-}$

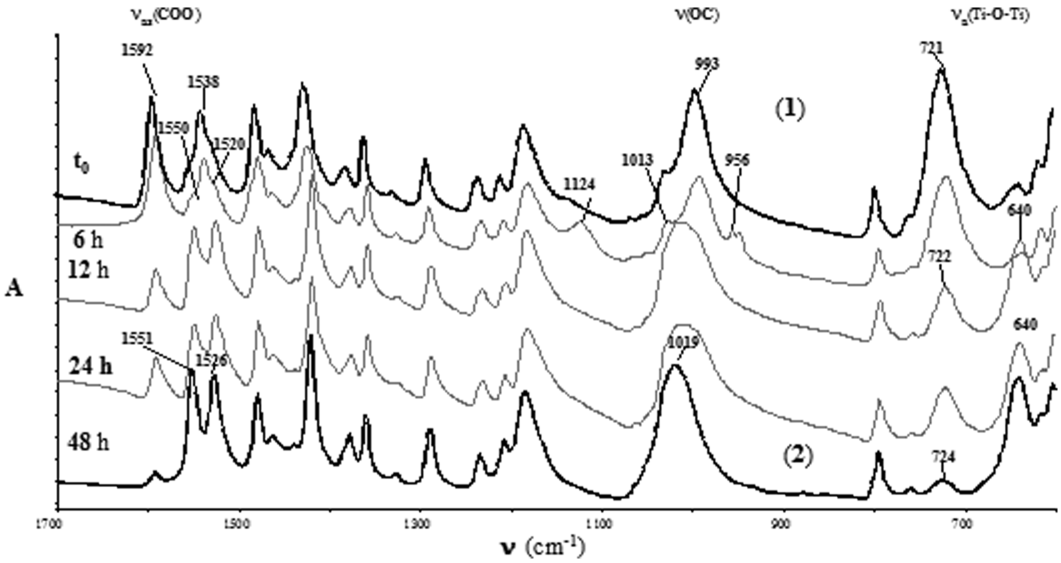


Figure 2. IR spectra illustrate the structural conversion of (**1**) to (**2**) as a function of time.

Table 2. Positions of Absorption Bands Detected between 400 and 1700 cm^{-1} in IR Spectra of Complexes (1)−(6)

Modes	Wavenumbers (cm^{-1})						
	(1)	**(2)**	**(3)**	**(4)**	**(5)**	**(6)**	**(7)**
ν_{as}(COO)	1592(m)	*1591*(vw)	1600(m)	*1598* (w)	1588(m)		1594(m)
		1551(m)		1555 (m)	*1568*(m)	1545(m)	
	1538(m)	1526(m)	1538(m)	1532 (m)	1533(m)	1521(m)	1540(m)
ν_s(COO) + δ(CH_3,CH_2)	1478(m)	1478(m)	1479(m)	1477(w)	1484(s)	1484(m)	1486(m)
	1463(w)	1462(w)	1464(w)	1449(m)			
	1425(s)	1420(s)	1426(m)	1412(s)	1431(s)	1425(s)	1433(s)
ν(^{t}C) + ν(OC) + δ(Ti-O-C)	1233(m)	1224(m)	1234(m)	1233(m)	1229(s)	1227(m)	1233(m)
	1208(m)	1207(m)					
	1182(m)	1184(s)	1185(s)	1184(m)	1183(m)	1185(m)	1184(w)
				1146(w)	*1089*(m)		
	1027(w)	1019(s)	1014(w)	1028(w)	*1030*(m)	1013(s)	
	993(s)		998(s)	1006(m)	1008(m)		1002(m)
ν_a(Ti-O-Ti)	721(s)	724(w)	721(s)	716(w)	741(m)	730(vw)	728(m)
							682(m)
	636(w)	640(m)	636(w)	640(m)	*665*(m)	642(m)	
	613(w)			616(s)			
					608(s)		608(s)
ν_{as}(Ti-OR)		603(m)		600(s)		606(s)	
	599(w)	565(m)	599(m)	524(w)		566(m)	
			565(w)				
δ(OOC)	496(w)	499(w)	496(w)	494(w)	491(w)	497(w)	493(m)
	464(w)	469(w)	450(w)	448(w)	468(w)		468(w)
	433(w)	430(w)	415(w)	415(w)	442(m)	436(m)	442(m)

O)$_b$} skeletons (as in the case of {Ti_4−(μ_3-O)$_4$}) is much more metallic than it is in the cluster containing the larger cores, that is, {Ti_6−(μ_3-O)$_6$}. These changes in the size of titanium-oxo cores should also affect the length of bonds between metal ions and oxo bridges, carboxylate bridges, and alkoxide ligands. Comparison of (**1**), (**3**) and (**2**), (**4**) revealed the slight differences in the length of Ti−O bonds between Ti_3O_3 and Ti_2O_2 faces (~2.17−2.19 Å for (**1**), (**3**) and ~2.09−2.10 Å for (**2**), (**4**)). Analysis of Ti−OOCR′ distances indicates that they are slightly shorter in tetranuclear clusters, while no significant differences were found for Ti−OR distances (Supporting Information, Table S2).

The results of structural studies revealed that Ti−Ti and Ti−O distances, which were found in clusters containing {Ti_4(μ_3-O)$_4$} cores, are shorter than analogical distances in the structure of hexanuclear complexes. Analysis of these data indicates the higher stability of the tetranuclear complex in comparison to the hexanuclear one, which is consistent with synthesis results.

Spectral Characterization. ^{13}C NMR spectra of complexes (**1**)−(**4**) and (**6**) are in good agreement with the crystallographic data (Experimental Section). They indicate the clear differences between two received types of complexes. The detection of four carbon signals of COO groups at 183.67, 185.06, 186.60, 187.60 ppm and two carbon signals of alkoxide ligands 78.80, 85.00 ppm in the NMR spectrum of (**5**) revealed that the structure of this compound is different from other complexes. Analysis of these data suggests that in the structure of (**5**), carboxylate groups form four different types of COO bridges, which may differ in symmetry of C−O or O−Ti bonds. Moreover, the detection of two peaks assigned to carbon atoms of −OR groups indicates that alkoxide groups are differently coordinated; that is, as the terminal ligands (signal at 85.00 ppm) and bridging one (signal at 78.80 ppm).

The use of different IR spectrophotometry methods enabled the study of the following problems: (a) spectral differences between structurally well-defined hexanuclear and tetranuclear systems, (b) the determination of the possible structure of complexes (**5**) and (**7**), and (c) mechanism of potential structural conversion.

The noticeable changes in the position of bands, assigned to stretching vibrations of Ti–O–Ti bridges, carboxylate bridges, and terminal alkoxide ligands, observed in vibrational spectra of complexes (**1**), (**3**) and (**2**), (**4**), are caused by significant differences in their structure. In spectra of (**1**) and (**3**), ν_a(Ti–O–Ti) bands (s)/(m) were found at 721 cm^{-1},[6,9,10,26] while in spectra of (**2**) and (**4**) they were detected at 616–640 cm^{-1} (Table 2). A significant shift of ν_a(Ti–O–Ti) bands toward lower frequencies, in spectra of (**2**) and (**4**) in comparison to (**1**) and (**3**), can be explained as a result of decrease of Ti–Ti distances and changes in the length of Ti–O bonds between Ti_2O_2 faces inside of the $\{Ti_4-(\mu_3\text{-}O)_4\}$ skeleton (Supporting Information, Table S2). These differences also affect the strength and the symmetry of interactions of carboxylate bridges, which is confirmed by the shift of ν_{as}(COO) bands toward lower frequencies. Corresponding ν_{as}(COO) bands were found in spectra of (**1**) and (**3**) at 1592–1600 cm^{-1} (m) and 1538 cm^{-1}(m) and at 1551–1555 cm^{-1} (m) and 1526–1532 cm^{-1} (m) in spectra of (**2**) and (**4**). Slight differences in the position of ν(OC) bands, which appear between 990 and 1020 cm^{-1} in spectra of (**1**), (**3**) as well as (**2**), (**4**), reflect the minor differences in lengths of Ti–OR bonds in their structure. Detection of bands at 643 cm^{-1} (m) (ν_a(Ti–O–Ti)), 1014 cm^{-1} (s) (ν(OC)), and 1524, 1549 cm^{-1} (m) (ν_{as}(COO)) in the spectrum of (**6**) (similarly as in spectra of (**2**) and (**4**)), confirms the formation of tetranuclear oxo-Ti(IV) complex.

Poor quality of isolated crystals of (**5**) and (**7**) caused that the structure of these complexes could not be determined based on single-crystal diffraction data; however, significant differences between IR spectra of hexa- and tetranuclear oxo-Ti(IV) complexes enabled the structure identification (Table 2, Figure 3). The sequence of bands at 742 cm^{-1} (ν_a(Ti–O–Ti)), 998–1030 cm^{-1} (ν(OC)), and 1536, 1590 cm^{-1} (ν_{as}(COO)), which was found in the spectrum of (**7**), indicates that clusters $[Ti_6O_6(O^tBu)_6(O_2C^tBu)_6]$ were formed. Analysis of spectral data revealed that 1:1 reaction of $Ti(O^tBu)_4$ with ^tBuCOOH in pure toluene proceeds with the formation of hexanuclear oxo-Ti(IV) complex without its conversion up to tetranuclear cluster.

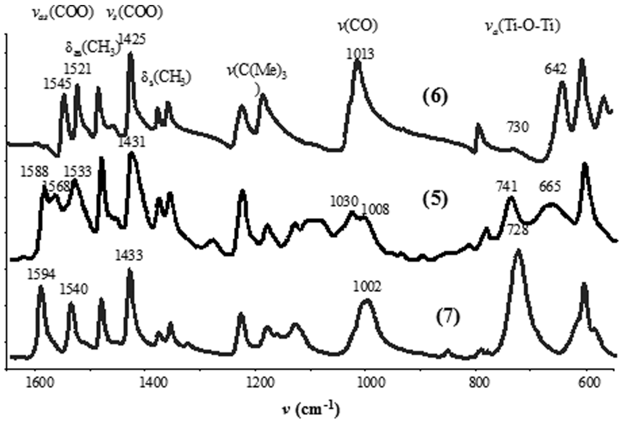


Figure 3. IR spectra of crystalline products formed during the reaction of $Ti(O^tBu)_4$ with ^tBuCOOH; $[Ti_6O_6(O^tBu)_6(O_2C^tBu)_6]$ (**7**), $[Ti_9O_8(O^tBu)_{14}(O_2C^tBu)_6]$ (**5**), $[T_4O_4(O^tBu)_4(O_2C^tBu)_4]$ (**6**).

The spectral identification of the complex (**5**) structure is more complicated. Analysis of data presented in Table 2 revealed the unique spectrum of this compound, in comparison to (**1**)–(**4**) and (**6**), (**7**), pointing out that another type of the structure was formed. Bands that were found at 1533 and 1588 cm^{-1} (m) (ν_{as}(COO)), 1008 cm^{-1} (m) (ν(CO)), and 741 cm^{-1} (m) (ν_a(Ti–O–Ti)) confirmed the presence of hexanuclear Ti(IV) oxo-carboxo-alkoxide systems in the structure of (**5**).[6–10,26] However, the appearance of bands at 1568(m), 1089 (m), 1030 (m), and 675 (m), 664 (m) cm^{-1}, which were assigned to ν_{as}(COO), ν(CO), and ν_a(Ti–O–Ti) vibrations, respectively, indicates that a new type of the cluster was formed. (Table 2, Figure 3). An inspection of crystallization processes under a microscope exhibited that only one type of crystal/crystal powder was formed in mother liquor, which transforms in bulk during the longer period. Therefore, products isolated in the first step of the reaction between $Ti(O^tBu)_4$ and ^tBuCOOH (using the mixture of toluene and ^tBuOH as a solvent) should not be regarded as a mixture of two crystalline forms but as a single entity. To identify the structure of (**5**), we can assume that hydrolysis and condensation processes, which proceed in the reaction mixture, cause the attachment of smaller units (e.g., $[Ti_3O(O^tBu)_8(O_2CR')_2]$ or $[Ti_4O_2(O^tBu)_6(O_2CR')_6]$) to hexanuclear clusters.[18] In this way, the metastable intermediate clusters are formed. The decomposition of above species leads to the formation of tetranuclear complexes, in the next stage of the reaction.

Steric effects seem to justify the formation of the more stable intermediate system (**5**) than $[Ti_6(\mu_3\text{-}O)_6(O^tBu)_6(O_2C^tBu)_6]$ (when the mixture of toluene and ^tBuOH was used), as in the case of (**1**) and (**3**). In hexanuclear clusters, the carboxylate moieties are positioned every 60° around the $\{Ti_6-(\mu_3\text{-}O)_6\}$ core, while for the tetranuclear cores this angle is 90°. Therefore, the steric hindrance caused by the presence of bulky *tert*-butyl groups in the immediate environment of $\{Ti_6-(\mu_3\text{-}O)_6\}$ skeletons seem to be the main factor causing the instability of hexanuclear clusters. It is interesting that weak/very weak bands at 716–724 and 1591–1598 cm^{-1} are also found in spectra of tetranuclear complexes (**2**) and (**4**) (Table 2). It suggests that the conversion processes of (**1**) and (**3**) can also proceed through the formation of the intermediate systems. However, their stability is considerably lower than in the case of (**5**). To study this problem, IR spectra of crystal/crystalline powder (**1**) and (**3**), isolated from the mother liquor every 6 h, were recorded. To avoid the contact of the isolated crystals or crystalline powder with the air/moisture, their extraction and IR spectra registration were carried out in an Ar atmosphere. Figure 2 presents spectral changes, which were found for solid reaction products isolated within 48 h from the time of the appearance of first solid species in the 1:1 mixture of $Ti(O^tBu)_4$ with $Et(Me)_2CCOOH$. Analysis of these data confirms that the hexanuclear complex (**1**) is the main solid product, which is formed in the first stage of this reaction (t = 0). However, beside bands that enable the identification of the complex containing the $\{Ti_6(\mu_3\text{-}O)_6\}$ cores (1538, 1592, 993, and 721 cm^{-1}), also bands at 1520, 1550 cm^{-1} (ν_{as}(COO), 1027 cm^{-1} (ν(OC)), and 636 cm^{-1} (ν_a(Ti–O–Ti)) were found. Moreover, after 6 h we noticed the appearance of bands at 956 and 1124 cm^{-1}, similar to the spectrum of (**5**). This would confirm the high reactivity of the formed hexanuclear clusters, which in mother liquor undergo the further reactions

Table 3. Results of ESI-MS Studies of Complexes (5), (6), and (7)

(5)			(6)			(7)		
fragmentation ion	relative intensity	m/z	fragmentation ion	relative intensity	m/z	fragmentation ion	relative intensity	m/z
			$[Ti_9O_7(O^tBu)_{14}(O_2C^tBu)_6]^+$	2	2172			
$[Ti_8O_9(O^tBu)_9(O_2C^tBu)_6]^+$	>2	1791	$[Ti_8O_7(O^tBu)_{12}(O_2C^tBu)_4]^+$	>2	1776			
$[Ti_6O_5(O^tBu)_{15}(O_2C^tBu)]^+$	>2	1564	$[Ti_7O_8(O^tBu)_{10}(O_2C^tBu)_5]^+$	2	1699			
$[Ti_7O_6(O^tBu)_6(O_2C^tBu)_6]^+$	11	1476						
$[Ti_7O_5(O^tBu)_7(O_2C^tBu)_5]^+$	13	1432						
						$[Ti_6O_3(O^tBu)_{14}(O_2C^tBu)_2]^+$	2	1560
						$[Ti_6O_7(O^tBu)_{13}(O_2C^tBu)]^+$	11	1450
$[Ti_6O_5(O^tBu)_7(O_2C^tBu)_5]^+$	25	1384				$[Ti_6O_6(O^tBu)_6(O_2C^tBu)_6]^+$	36	1428
$[Ti_5O_3(O^tBu)_{12}(O_2C^tBu)_2]^+$	38	1366				$[Ti_6O_3(O^tBu)_{12}(O_2C^tBu)_2]^+$	15	1414
$[Ti_6O_6(O^tBu)_9(O_2C^tBu)_3]^+$	52	1344				$[Ti_6O_6(O^tBu)_5(O_2C^tBu)_6]^+$	29	1355
$[Ti_6O_5(O^tBu)_7(O_2C^tBu)_4]^+$	100	1283				$[Ti_6O_4(O^tBu)_8(O_2C^tBu)_4]^+$	11	1340
$[Ti_6O_5(O^tBu)_8(O_2C^tBu)_3]^+$	5	1255				$[Ti_6O_6(O^tBu)_4(O_2C^tBu)_6]^+$	3	1282
						$[Ti_5O_4(O^tBu)_5(O_2C^tBu)_6]^+$	7	1275
						$[Ti_5O_3(O^tBu)_7(O_2C^tBu)_4]^+$	18	1203
						$[Ti_5O_7(O^tBu)_4(O_2C^tBu)_5]^+$	>2	1149
			$[Ti_5O_8(O^tBu)_3(O_2C^tBu)_4]^+$	3	991	$[Ti_5O_6(O^tBu)_4(O_2C^tBu)_5]^+$	5	1133
			$[Ti_5O_7(O^tBu)_3(O_2C^tBu)_4]^+$	25	975	$[Ti_4O_2(O^tBu)_{10}(O_2C^tBu)]^+$	>2	1055
						$[Ti_5O_6(O^tBu)_2(O_2C^tBu)_5]^+$	69	987
$[Ti_4O_3(O^tBu)_7(O_2C^tBu)_2]^+$	3	953	$[Ti_4O_4(O^tBu)_4(O_2C^tBu)_4]^+$	100	952	$[Ti_5O_6(O^tBu)_3(O_2C^tBu)_4]^+$	100	959
			$[Ti_4O_4(O^tBu)_3(O_2C^tBu)_4]^+$	10	879	$[Ti_5O_6(O^tBu)_4(O_2C^tBu)_3]^+$	20	931
			$[Ti_4O_4(O^tBu)_4(O_2C^tBu)_3]^+$	>2	851	$[Ti_5O_6(O^tBu)_5(O_2C^tBu)_2]^+$	2	903
			$[Ti_4O_5(O^tBu)(O_2C^tBu)_4]^+$	>2	749			
$[Ti_3O_4(O^tBu)_2(O_2C^tBu)_4]^+$	3	758	$[Ti_4O_5(O^tBu)_2(O_2C^tBu)_3]^+$	>2	721	$[Ti_5O_6(O^tBu)_7]^+$	5	847
$[Ti_3O_2(O^tBu)_5(O_2C^tBu)_2]^+$	10	743				$[Ti_7O_8(O^tBu)_5]^+$	23	829
$[Ti_3O(O^tBu)_5(O_2C^tBu)_2]^+$	6	727	$[Ti_4O_6(O_2C^tBu)_4]^+$	>2	692	$[Ti_3O_4(O^tBu)_2(O_2C^tBu)_4]^+$	4	758
$[Ti_3O(O^tBu)_3(O_2C^tBu)_3]^+$	27	682	$[Ti_4O_5(O^tBu)_4(O_2C^tBu)]^+$	>2	665	$[Ti_4O_7(O^tBu)_3(O_2C^tBu)_2]^+$	7	725
$[Ti_2O_2(O^tBu)_6(O_2C^tBu)]^+$	47	667				$[Ti_4O_5(O^tBu)_3(O_2C^tBu)_2]^+$	9	693
$[Ti_4O_2(O^tBu)_3(O_2C^tBu)_2]^+$	10	645	$[Ti_3O(O^tBu)_2(O_2C^tBu)_3]^+$	>2	609	$[Ti_4O_3(O^tBu)_2(O_2C^tBu)_3]^+$	2	689
$[Ti_3(O^tBu)_5(O_2C^tBu)_4]^+$	28	610	$[Ti_3O(O^tBu)_5]^+$	>2	525	$[Ti_4O_5(O^tBu)_3]^+$	2	637

with formation of the intermediate system. In case of (**1**) this intermediate complex is unstable, and after 12 h it decomposes with the formation of tetrameric clusters (**2**). After 48 h the final structure (**2**) is formed (corresponding bands appear at 1526, 1551, 1019, and 640 cm^{-1}). However, the presence of very weak bands at 724 and 1591 cm^{-1} indicate the remains of the intermediate system. Similar spectral transition effects were noted in spectra of complex (**3**), for which crystals were isolated from the reaction mixture every 6 h during 2 d.

To establish the composition of complexes (**5**) and (**7**), mass spectrometry analysis (electron ionization mass spectrometry (EI MS) and electrospray mass spectrometry (ESMS)) was carried out. Results of these studies are presented in Table 3 and Supporting Information, Table S3. Analysis of these data revealed that fragmentation of parent clusters occurs by the detachment of alkoxide or carboxylate ligands and also $[TiO(O^tBu)_2]$ (m/z = 210), $[TiO(O_2CR')_2]$ (m/z = 266/294), and $[Ti(O^tBu)_4]$ (m/z = 340) fragments, analogous to these reported in refs 27 and 28. Fragmentation results in a family of species, which possess the similar multinuclear titanium oxide cores ($\{Ti_aO_b\}$) and which are produced by fragmentation of larger clusters and/or during many other processes, for example, ligand exchange or elimination of ester, ether, or R′ groups of OOCR′.

Comparison of EI MS spectra of complexes (**1**), (**3**), and (**5**) showed that species containing $\{T_6O_6\}$ cores, which are formed by detachment of alkoxide or carboxylate ligands, correspond to a main fragment family (Supporting Information, Table S3). It confirms that fragments composed of $\{Ti_6O_6\}$ cores form the basis of the cluster of (**5**) structure, which is consistent with results of IR spectral analysis. Further fragmentation of these species, which is mainly the elimination of $[TiO(O^tBu)_2]$, $[TiO(O_2CR')_2]$ species leads to the production of fragments containing cores of $\{Ti_4O_4\}$ type ((**1**), (**5**)) and $\{Ti_5O_b\}$ (b = 3, 5; (**3**)). The last family of species includes fragmentation ions containing $\{Ti_aO_b\}$ (a = 2, 3; b = 1−4) cores, which are formed by the loss of the following fragments: $Ti(O^tBu)_4$, TiO_2, $^tBuO_2C^tBu$, and O^tBu_2. A similar fragmentation pathway was also found in previously studied mass spectra of $[Ti_6O_6(OR)_6(OOCR')_6]$ complexes.[9,28] However, spectra of complexes (**5**) and (**3**) revealed also several peaks of very low intensity at m/z = 1971, 1914, 1655, 1654, and 1468, which were assigned to such fragmentation species as $[Ti_9O_8(O^tBu)_{14}(O_2CCH_2{}^tBu)_3(OOC)]^+$, $[Ti_9O_8(O^tBu)_{13}(O_2C^tBu)_4]^+$, $[Ti_7O_7(O^tBu)_{11}(O_2C^tBu)_4]^+$, $[Ti_7O_8(O^tBu)_{10}(O_2CCH_2{}^tBu)_4]^+$, and $[Ti_7O_9(O^tBu)_8(O_2C^tBu)_4]^+$ (Supporting Information, Table S3). The appearance of these fragments suggests that they are produced by fragmentation of clusters, which cores are composed of more than six titanium atoms. That is consistent with results of IR spectroscopic studies, which suggest the creation of the intermediate cluster as a result of a combination of hexanuclear clusters with the small units. In the case of (**5**) these types of clusters were isolated as a metastable crystalline powder, but for (**1**) and (**3**) they were formed during the conversion processes. Considering the results of EI MS and IR studies the general formula of this type of cluster can be proposed as $[Ti_9O_8(O^tBu)_{14}(O_2CR')_6]$.

To confirm the above data, we decided to make additional analyses of complexes (**5**), (**6**), and (**7**) using ESI-MS method. Despite the poor solubility of studied complexes in water and organic acids, the positive ion mass spectra of these compounds dissolved in dry tetrahydrofuran were collected with the cone voltage settings of 60 V. Results of these investigations are presented in Table 3.

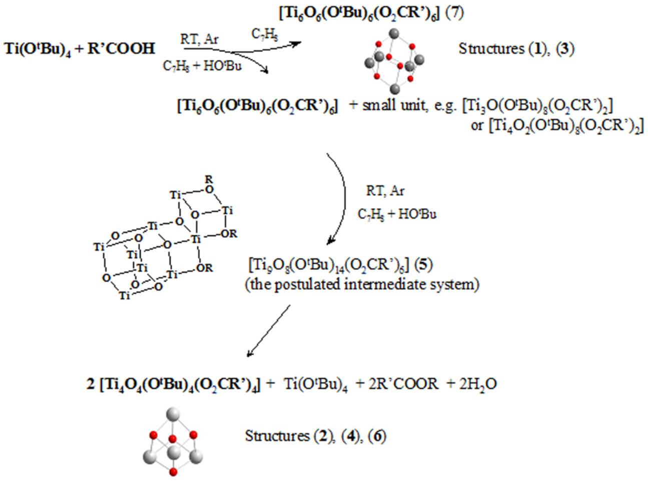
The fragmentation of postulated clusters $[Ti_9O_8(O^tBu)_{14}(O_2CR')_6]$ (**5**) leads to the production of two main groups of species, that is, multinuclear ions composed of $\{Ti_6O_b\}$ (b = 5, 6) cores and $\{Ti_aO_b\}$ (a = 2, 3; b = 1−4). It suggests that clusters of the general formula $[Ti_3O(O^tBu)_8(O_2CR')_2]$ or $[Ti_4O_2(O^tBu)_8(O_2CR')_2]$ (small units[18]) are combined to $\{Ti_6(\mu_3\text{-}O)_6\}$ skeletons during their transformation into the stable tetranuclear species. In the ESI-MS spectrum of (**6**) the main group of fragmentation ions is produced by the fragmentation of $[Ti_4O_4(O^tBu)_4(O_2C^tBu)_4]$ clusters (m/z = 952). Peaks, which were found at m/z = 991 ($[Ti_5O_8(O^tBu)_3(O_2C^tBu)_4]^+$) and 975 ($[Ti_5O_7(O^tBu)_3(O_2C^tBu)_4]^+$) and signals of very low intensity (2 or >2) at m/z = 2172, 1776, 1699, 609, 525 (Table 3), can be assigned to species produced during the fragmentation of the intermediate system (**5**), whose residues were present in the studied sample of complex (**6**). Similar conclusions can be derived from IR spectra of tetranuclear complexes (**2**), (**4**), and (**6**). The ESI-MS studies confirm that structure of complex (**7**) is composed of hexanuclear clusters $[Ti_6O_6(O^tBu)_6(O_2C^tBu)_6]$. The intense peaks, which were detected in the spectrum of this compound, were assigned to the cluster $[Ti_6O_6(O^tBu)_6(O_2C^tBu)_6]$ and species produced by its fragmentation, for example, $[Ti_6O_6(O^tBu)_5(O_2C^tBu)_6]^+$, $[Ti_6O_6(O^tBu)_6(O_2C^tBu)_6]^+$, $[Ti_5O_6(O^tBu)_3(O_2C^tBu)_4]^+$, and $[Ti_5O_6(O^tBu)_4(O_2C^tBu)_3]^+$ (Table 3).

Structural Conversion of Hexanuclear μ-Oxotitanium(IV) Complexes. On the basis of the results of structural and spectroscopic studies, we decided to propose a potential mechanism of the structural transitions, which were noted during reactions of $Ti(O^tBu)_4$ with organic acids (R′COOH; R′ = $C(Me)_2Et$, $CH_2{}^tBu$, and ^tBu) in 1:1 molar ratio (Scheme 1). Understanding of these processes is particularly important for the fabrication of hybrid materials based on titanium oxo-skeletons with well-defined structure.

Assuming that the stepwise assembly of large clusters is the result of smaller units attachment (e.g., $[Ti_3O(O^tBu)_8(O_2CR')_2]$ or $[Ti_4O_2(O^tBu)_8(O_2CR')_2]$[18]) note that the first crystalline products of reactions mentioned above are hexanuclear clusters $[Ti_6O_6(O^tBu)_6(O_2CR')_6]$, as proved by structural studies of complexes (**1**) and (**3**). The type of solvent used in these reactions has an important effect on the structure of formed clusters. The use of pure toluene in the reaction of titanium *tert*-butoxide with ^{t}BuCOOH leads to the formation of the structurally stable hexanuclear complex (**7**) (which has been proved by IR and ESI-MS spectral analysis). In contrast, complex (**5**), of a different type of structure, is produced when the toluene/^{t}BuOH mixture is used. Moreover, the use of this mixture as a solvent leads to the conversion of hexanuclear complexes (**1**) and (**3**) to tetranuclear compounds (**2**), (**4**), and (**6**).

Results of spectroscopic studies (IR, MS) revealed that the conversion of clusters proceeds with the production of the intermediate system. Its stability is usually very low; however the steric effects caused this type of cluster to be isolated from the reaction mixture of $Ti(O^tBu)_4$ with ^{t}BuCOOH as the complex (**5**) (Figure 3). The structural uniqueness of (**5**) was confirmed by ^{13}C NMR and IR spectroscopic investigations (poor quality of the isolated crystals did not allow for the determination of their structure by single-crystal X-ray diffraction). Analysis of spectral data suggests that cluster (**5**) is formed by the attachment of small units (e.g., $[Ti_3O(O^tBu)_8(O_2CR')_2]$ or $[Ti_4O_2(O^tBu)_8(O_2CR')_2]$) to species composed of $\{Ti_6(\mu_3\text{-}O)_6\}$ cores (Scheme 1). Considering results of MS studies, the general formula of complex (**5**) can be presented as $[Ti_9O_8(O^tBu)_{14}(O_2CR')_6]$. Further conversion of this system leads to the production of clusters containing $\{Ti_4(\mu_3\text{-}O)_4\}$ cores.

Scheme 1. Scheme of the Proposed Structural Conversion of $[Ti_6O_6(O^tBu)_6(O_2CR')_6]$ (1), (3) into $[T_4O_4(O^tBu)_4(O_2CR')_4]$ (2), (4), (6) by the Metastable Intermediate System (5)



■ CONCLUSIONS

Results of our investigations proved the conversion of hexanuclear cluster $[Ti_6O_6(O^tBu)_6(O_2CR')_6]$ into tetranuclear complex $[Ti_4O_4(O^tBu)_4(O_2CR')_4]$. This type of conversion can be used as an additional path in the scheme of possible routes for the stepwise assembly of large clusters starting from small units, given by Schubert.[18]

Analysis of X-ray diffraction and spectral data proved that the conversion of $[Ti_6O_6(O^tBu)_6(O_2CR')_6]$ clusters proceeds by formation of the intermediate system of the postulated formula $[Ti_9O_8(O^tBu)_{14}(O_2CR')_6]$. According to spectral data this intermediate system is a result of the attachment of smaller units by complexes composed of $\{Ti_6(\mu_3\text{-}O)_6\}$ cores, produced in the first stage of reactions between $Ti(O^tBu)_4$ and appropriate organic acids (R′COOH; R′ = $C(Me)_2Et$, $CH_2{}^tBu$, ^tBu). Moreover, the important influence of the solvent on the structure and stability of formed clusters has been shown.

Knowing the conversion mechanism of multinuclear oxo-Ti(IV) complexes, it becomes possible to control the synthesis of materials with desired structure of $\{Ti_a(\mu_3\text{-}O)_b\}$ (a = b = 4, 6) cores.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic data, including structures in CIF files, selected bond lengths and angles of complexes **1**−**4** and **6**, MS-EI data pertaining to complexes **1**, **3**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org. The CCDC entries 896697, 896698, 896695, 896696, and 922540 contain the supplementary crystallographic data for compounds **1**−**4** and **6**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: piszczek@chem.umk.pl.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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