

## The conversion of multinuclear $\mu$ -oxo titanium(IV) species in the reaction of $\text{Ti}(\text{O}^i\text{Bu})_4$ with branched organic acids; results of structural and spectroscopic studies

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### Abstract

Crystalline materials have been synthesized in reactions of titanium(IV) isobutoxide with branched organic acids ( $\text{HOOCR}'$ ,  $\text{R}' = \text{C}(\text{CH}_3)_2\text{Et}$ ,  $^i\text{Bu}$ ,  $\text{CH}_2^i\text{Bu}$ ) in the molar ratio 1:1 at room temperature under Ar atmosphere. Particular attention has been paid on the structural and spectral characterization of metastable intermediate complexes of general formulas:  $[\text{Ti}_7\text{O}_9(\text{O}^i\text{Bu})_4(\text{HO}^i\text{Bu})(\text{OOC}(\text{CH}_3)_2\text{Et})_6]_2$  (**1**) and  $[\text{Ti}_6\text{O}_5(\text{O}^i\text{Bu})_6(\text{OOC}^i\text{Bu})_8]$  (**3**), and their conversion towards more structurally stable compounds  $[\text{Ti}_6\text{O}_6(\text{O}^i\text{Bu})_6(\text{OOC}(\text{Me})_2\text{Et})_6]$  (**2**) and  $[\text{Ti}_6\text{O}_6(\text{H}_2\text{O})_2(\text{O}^i\text{Bu})_6(\text{OOC}^i\text{Bu})_6]$  (**4**). The hexanuclear structure of (**5**) ( $[\text{Ti}_6\text{O}_6(\text{O}^i\text{Bu})_6(\text{OOCCH}_2^i\text{Bu})_6]$ ) has been postulated on the basis of IR and  $^{13}\text{C}$  NMR spectroscopic data analysis. The possible reaction pathways which may occur during the formation above mentioned compounds are also discussed.

**Keywords:** Multinuclear  $\mu$ -oxo titanium(IV) complexes; Cluster conversion; Crystal structures; IR; NMR.

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## 1 Introduction

The interest of metal alkoxides ( $M(OR)_4$ ;  $M = Si, Ti, Zr$ ) reactions with bidentate ligands, e.g.  $\beta$ -diketonates, carboxylates or sulfonates, is caused by the necessity of the moderation of metal alkoxides extremely high reactivity towards nucleophilic reagents [1-5]. The application of metal alkoxides, especially  $Ti(OR)_4$ , as precursors in sol-gel, chemical vapor deposition (CVD), and atomic layer deposition (ALD) techniques, which are usually used in the fabrication of titanium oxide containing ceramics or titanium dioxide nanoparticle layers, is limited [6-15]. Simultaneously above mentioned reactions enable the formation of organically modified transition-metal oxide clusters during organic-inorganic hybrid materials synthesis [16,17].

Multinuclear  $\mu$ -oxo titanium alkoxo carboxylate complexes of the general formula  $[Ti_aO_b(OR)_i(OOCR')_{4a-2b-i}]$  are the final products of titanium(IV) alkoxides reaction with carboxylic acids [2,3,18-20]. Complexes containing hexanuclear  $\mu_3$ -oxo Ti(IV) cores ( $\{Ti_6-(\mu_3-O)_6\}$ ) were isolated and structurally characterized from 1:1 mixtures of  $Ti(OR)_4$  ( $R = Et, iPr, CH_2^tBu$ ) and  $HOOCR'$  ( $R' = H, Me, CH_2^tBu, Ph, PhOC_6H_4$ ) [3,18,20]. The same compounds were synthesized in reactions of  $Ti(OR)_4$  ( $R = iPr, Bu, and Si(Me)_3$ ) with branched organic acids ( $HOOCR'$ ;  $R' = ^tBu, CH_2^tBu, C(Me)_2Et$ ) [21-24]. Hexanuclear systems mentioned above were formed by the conversion of the earlier obtained unstable intermediate species; it has been proved by spectral data investigations. Unfortunately, the crystallographic structures of intermediate species have not been solved because the quality of isolated crystals was very poor. Multinuclear oxo Ti(IV) complex conversion towards the hexanuclear system was also observed by Papiernik et.al. [20]. According to this report, the  $[Ti_6O_4(OEt)_8(OOCMe)_8]$  complex has been isolated from the 1:1 reaction mixture of  $Ti(OEt)_4$  with acetic acid in toluene. The further heating of the reaction mixture led to the elimination

of esters and the conversion of  $[\text{Ti}_6\text{O}_4(\text{OEt})_8(\text{OOCMe})_8]$  into  $[\text{Ti}_6\text{O}_6(\text{OEt})_6(\text{OOCMe})_6]$ . Schubert proposed, based on literature reports, the scheme of the reaction pathway from the small units (e.g.  $[\text{Ti}_3\text{O}(\text{OR})_8(\text{OOCR}')_2]$ ) by intermediate systems up to  $[\text{Ti}_6\text{O}_6(\text{OEt})_6(\text{OOCMe})_6]$  [3]. The exact recognition of these reactions pathway has a fundamental importance for synthesis of new materials, in which the structure of  $\{\text{Ti}_x(\mu_i\text{-O})_y\}$  clusters have to be precisely controlled. This paper deals with the structural and spectral characterization of multinuclear  $\mu$ -oxo titanium(IV) complexes synthesized in 1:1 reactions of titanium(IV) tetraisobutoxide with 2,2-dimethylpropionic acid, 2,2-dimethylbutyric acid, and 3,3-dimethylbutyric acid. Titanium(IV) tetraisobutoxide was selected taking into consideration its ability to the formation of more structural stable intermediate species in comparison to the other titanium alkoxides (e.g.  $\text{Ti}(\text{OR})_4$ ;  $\text{R} = \text{Et}, ^i\text{Pr}, \text{Bu}$ ).

## 2 Experimental part

### 2.1 General procedures

All reactions of titanium isobutoxide ( $\text{Ti}(\text{O}^i\text{Bu})_4$ ) with the following carboxylic acids:  $\text{R}'\text{COOH}$ ;  $\text{R}' = ^i\text{Bu}, \text{C}(\text{CH}_3)_2\text{Et}, \text{CH}_2^i\text{Bu}$  were carried out as it was reported in detail for  $[\text{Ti}_6\text{O}_6(\text{OR})_6(\text{OOC}^i\text{Bu})_6]$  ( $\text{R} = ^i\text{Pr}, \text{Bu}, \text{SiMe}_3$ ) [21,24]. The % Ti was gravimetrically determined as  $\text{TiO}_2$ , according to the Meth-Cohn et al. method [25]. Synthesized complexes were characterized using IR and NMR spectroscopy methods. Infrared (IR) spectra were recorded on Perkin Elmer Spectrum 2000 spectrometer within range  $400\text{-}4000\text{ cm}^{-1}$  with a medium slit width and peak resolution of  $4,0\text{ cm}^{-1}$ . The crystals were studied as a powder dispersed in the KBr pellet. Solid-state  $^{13}\text{C}$  NMR spectra were registered on Bruker AMX 300. Solution  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra ( $\text{CDCl}_3$ ) were recorded using a 5 mm solution probe on Varian Gemini 2000.

## 2.2 Characterization data

[Ti<sub>7</sub>O<sub>9</sub>(O<sup>i</sup>Bu)<sub>4</sub>(HO<sup>i</sup>Bu)(OOCC(CH<sub>3</sub>)<sub>2</sub>Et)<sub>6</sub>]<sub>2</sub> (**1**): Anal. Calculated for Ti<sub>14</sub>O<sub>52</sub>C<sub>112</sub>H<sub>224</sub>: Ti, 21.85%, C, 43.80%; H, 7.23%; Found: Ti, 21.42%, C, 44.01%; H, 7.25%.

[Ti<sub>6</sub>O<sub>6</sub>(O<sup>i</sup>Bu)<sub>6</sub>(OOCC(CH<sub>3</sub>)<sub>2</sub>Et)<sub>6</sub>] (**2**): Yield: 77%. Anal. Calculated for Ti<sub>6</sub>O<sub>24</sub>C<sub>60</sub>H<sub>120</sub>: Ti, 19.02%, C, 47.64%; H, 7.94%; Found: Ti, 19.27%, C, 47.28%; H, 7.91%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 295 K, δ [ppm]): 0.83 (triplet, *J*<sub>H-H</sub> = 7 Hz, CH<sub>3</sub> (Et)), 0.97 (doublet, *J*<sub>H-H</sub> = 6 Hz, CH<sub>3</sub> (<sup>i</sup>Bu)), 1.08 (singlet, CH<sub>3</sub> (C(CH<sub>3</sub>)<sub>2</sub>Et)), 1.45-1.54 (multiplets, CH (<sup>i</sup>Bu)), 2.14 (septet, *J*<sub>H-H</sub> = 6 Hz, CH<sub>2</sub> (Et)), 4.38 (doublet, *J*<sub>H-H</sub> = 6 Hz, CH<sub>2</sub> (<sup>i</sup>Bu)).

[Ti<sub>6</sub>O<sub>5</sub>(O<sup>i</sup>Bu)<sub>8</sub>(OOC<sup>t</sup>Bu)<sub>6</sub>] (**3**): Anal. Calculated for: Ti<sub>6</sub>O<sub>27</sub>C<sub>64</sub>H<sub>126</sub>: Ti, 18.42%, C, 25.65%; H, 8.18%; Found: Ti, 18.28%, C, 25.42%; H, 8.12%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 295 K, δ [ppm]): 0.95 (doublet, *J*<sub>H-H</sub> = 6 Hz, CH<sub>3</sub> (<sup>i</sup>Bu)), 1.01 (doublet, *J*<sub>H-H</sub> = 6 Hz, CH<sub>3</sub> (<sup>t</sup>Bu)), 1.14 (singlet, CH (<sup>i</sup>Bu)), 4.41 (doublet, *J*<sub>H-H</sub> = 6 Hz, CH<sub>2</sub> (<sup>i</sup>Bu)).

[Ti<sub>6</sub>O<sub>6</sub>(H<sub>2</sub>O)<sub>2</sub>(O<sup>i</sup>Bu)<sub>6</sub>(OOC<sup>t</sup>Bu)<sub>6</sub>] (**4**): Yield: 60%. Anal. Calculated for Ti<sub>6</sub>O<sub>26</sub>C<sub>54</sub>H<sub>112</sub>: Ti, 19.63%, C, 44.28%; H, 7.65%; Found: Ti, 19.87%, C, 44.26%; H, 7.88%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 295 K, δ [ppm]): 1.00 (doublet, *J*<sub>H-H</sub> = 6 Hz, CH<sub>3</sub> (<sup>i</sup>Bu)), 1.13 (singlet, CH<sub>3</sub> (<sup>t</sup>Bu)), 2.05 (septet, *J*<sub>H-H</sub> = 6 Hz, CH (<sup>i</sup>Bu)), 3.47 (broad singlet, HDO), 4.40 (doublet, *J*<sub>H-H</sub> = 6 Hz, CH<sub>2</sub> (<sup>i</sup>Bu)).

[Ti<sub>6</sub>O<sub>6</sub>(O<sup>i</sup>Bu)<sub>6</sub>(OOCCH<sub>2</sub><sup>t</sup>Bu)<sub>6</sub>] (**5**): Yield: 82%. Anal. Calculated for Ti<sub>6</sub>O<sub>26</sub>C<sub>54</sub>H<sub>112</sub>: Ti, 19.63%, C, 44.28%; H, 7.65%; Found: Ti, 19.52%, C, 44.22%; H, 7.73%. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, 295 K, δ [ppm]): 0.95 (doublet, *J*<sub>H-H</sub> = 6 Hz, CH<sub>3</sub> (<sup>i</sup>Bu)), 1.02 (singlet, CH<sub>3</sub> (<sup>t</sup>Bu)), 2.08 (singlet, CH<sub>2</sub> (<sup>t</sup>Bu)), 1.37 (doublet, *J*<sub>H-H</sub> = 6 Hz, CH (<sup>i</sup>Bu)), 4.42 (doublet, *J*<sub>H-H</sub> = 6 Hz, CH<sub>2</sub> (<sup>i</sup>Bu)).

## 2.3 X-ray crystallographic analysis

Diffraction data of (**1**)-(4) complexes were collected at 293 K with ω-2θ method using Oxford Sapphire diffractometer with CCD area detector, Mo Kα radiation λ = 0.71073 Å [26].

All structures were solved by direct methods and refined by full-matrix least-squares techniques on  $F^2$  with SHELXL program [27]. The numerical absorption correction was applied for all crystals (RED171 package of programs, Oxford Diffraction, 2000) [26].

In **(1)** and **(4)** all heavy atoms were refined with anisotropic thermal displacement parameters, whereas for **(2)** and **(3)** some carbon atoms of partially occupied O<sup>i</sup>Bu group were refined isotropically. Positions of hydrogen atoms attached to carbon atoms were assigned to calculated positions, and refined with isotropic thermal displacement parameters fixed to a value, which is 20 or 50% higher than those of the corresponding carbon atoms. For some carboxylate groups and O<sup>i</sup>Bu ligands, thermal disorder was observed and alternative conformations were proposed. Due to the quality of the data and instability of the structure, several positional and thermal restraints were applied (DFIX, DANG, ISOR, EADP and DELU) mainly on <sup>i</sup>BuO groups but also on carboxylate anions. There is lack of several carbon and hydrogen atoms for partially occupied conformations in the final model of **(1)**-**(3)** and both hydrogen atoms of O7 water molecule in the final model of **(4)**. All figures were prepared in DIAMOND [28] and Mercury2.3 [29]. The results of the refinement need some comments as at least for **(3)** and **(4)** structures the refinement finished at quite high R values. Despite many efforts we do not manage to get better results. Due to the quality of these data sets (high  $R_{\text{int}}$  values in the high resolution shells and low value of  $I/\sigma(I)$  dropping even below 1) a cut off for the resolution was imposed at 1.0 and 1.1 Å for **(3)** and **(4)**, respectively. Moreover, for **(3)** the crystal was twinned and/or partially preserved previous form. Twinning was detected by ROTAX program [30] and the found matrix was applied to SHELXL, which significantly improved a quality of the difference electron density map. The synthesis of **(4)** and data collection for it was repeated several times at room temperature and at 100 K. Surprisingly, even at low temperature, which usually helps to improve the quality of the model, and for good data sets with  $R_{\text{int}} = 4\text{-}5\%$ , we did not obtain a better model with lower



R1 and wR2 values. Moreover, these trials got stuck in approximately 15-16%. The compounds reported in this paper revealed very weak intermolecular interactions and many disordered groups. In general, the core was stable, whereas other parts showed enhanced thermal displacement parameters. The conversion effect has influence on the quality reduction of crystallographic data. This process led to the crystallization of a mixture of different structural forms. Analysis of spectral data proved that conversion effects appear just after formation of the crystal and therefore studying only one form is very difficult. The final models are not quite adjusted to crystallographic data, and therefore the solving and refinement of these structures is a great challenge. Due to high thermal parameters and disorders present in all four structures also hydrogen positions suffer and their reliability is limited.

Data collection and structure refinement parameters are given in Table 1. Crystal data of (1)-(4) complexes have been deposited with CCDC (deposition number CCDC 856417 (1), 856418 (2), 856419 (3), and 856420 (4)).

### 3 Results and Discussion

Crystalline materials were synthesized in the reaction of titanium(IV) tetraisobutoxide with the branched organic acids (HOOCR'; R' = <sup>t</sup>Bu, CH<sub>2</sub><sup>t</sup>Bu, C(CH<sub>3</sub>)<sub>2</sub>Et) at room temperature under argon atmosphere using 1:1 molar ratio (Ti : ligand). The slow evaporation of the reaction mixture under argon atmosphere leads to the formation of single colorless crystals, after 5-7 days. Crystals (possessing a suitable quality for the X-ray single-crystal diffraction measurements) were isolated and their crystallographic and spectral (IR, NMR) studies have been carried out. Structural investigations were repeated after 10-14 and 25-30 days. Table 1 lists details of X-ray data collection for (1)-(4) complexes, moreover selected bond distances and angles of studied compounds are presented in supplementary Table 5 and Table 6.

The poor quality of complex (5) crystals made impossible to solve the crystallographic structure, and therefore it has been determined on the basis of the spectral data analysis.

### 3.1 Multinuclear Ti(IV) complexes synthesized in the 1:1 reaction of $\text{Ti}(\text{O}^i\text{Bu})_4$ with $\text{HOOC}(\text{CH}_3)_2\text{Et}$

The colorless crystals of complex (1) have been isolated after 5 days of slow evaporation of the reaction mixture (1:1 molar ratio,  $\text{Ti}(\text{O}^i\text{Bu})_4/\text{HOOC}(\text{CH}_3)_2\text{Et}$ , toluene) under the argon atmosphere at room temperature. X-ray diffraction studies showed that the structure of (1) consists of dimeric units of the general formula  $[\text{Ti}_7\text{O}_9(\text{O}^i\text{Bu})_4(\text{HO}^i\text{Bu})(\text{OCC}(\text{CH}_3)_2\text{Et})_6]_2$  formed around the inversion center. The dimeric skeletons are composed of hexanuclear  $\mu_3$ -oxo titanium(IV) cores ( $\{\text{Ti}_6-(\mu_3\text{-O})_6\}$  (Ti1-Ti6, O1-O6)) stabilized by six *syn-syn* carboxylate bridges (C13,O11,O12 – C63,O61,O62) and three terminal alkoxide ligands (O71, O81, O91). Hexanuclear cores are linked by three oxygen atoms belonging to oxo bridges of  $\{[\text{Ti}_2(\mu\text{-O})_6(\text{HO}^i\text{Bu})_2(\mu\text{-O}^i\text{Bu})_2]\}$  fragments (Fig. 1). All titanium atoms occur in slightly distorted octahedral environment in three different surroundings. Ti4, Ti5, Ti6 atoms are coordinated by two oxygen atoms of carboxylic groups, three  $\mu_3$ -oxo bridges and one terminal  $\text{O}^i\text{Bu}$  ligand. Whereas Ti1, Ti2, Ti3 atoms are surrounded by two oxygen atoms of carboxylic groups, three  $\mu_3$ -oxo and one  $\mu$ -oxo (O7-O9) bridges. Each of two Ti7 atoms of the  $\{[\text{Ti}_2(\mu\text{-O})_6(\text{HO}^i\text{Bu})_2(\mu\text{-O}^i\text{Bu})_2]\}$  fragment is surrounded by oxygen atoms of three  $\mu$ -oxo (O7-O9) bridges, two  $\mu\text{-O}^i\text{Bu}$  (O101) bridges, and one adducted  $\text{HO}^i\text{Bu}$  (O111) molecule.  $\text{Ti}\cdots\text{Ti}$  distances (Ti1-Ti6) vary from 3.0892(12) Å up to 3.5259(13) Å, whereas  $\text{Ti7}\cdots\text{Ti7}$  distances are about 3.2104(17) Å (Fig. 1). Simultaneously distances between Ti7 and Ti1-Ti3 atoms change in the range 3.3243(13)-3.3418(13) Å. The lengths of Ti-O bonds vary between 1.865(4)-1.927(4) Å and 2.079(3)-2.222(4) Å in the case of Ti-( $\mu_3$ -O) bridges and 1.777(3)-1.887(3) Å of Ti-( $\mu$ -O) bridges. The hexanuclear Ti-O half units are stabilized by six

asymmetric, carboxylate *syn-syn* bridges ( $\mu$ -OOCR). The shorter bond lengths change in the range 2.025(4)–2.053(4) Å and the longer ones 2.059(4)–2.099(4) Å. The length of Ti–O<sup>i</sup>Bu bonds change from 1.753(4)–1.770(4) Å, for terminal ligands of {Ti<sub>6</sub>-( $\mu$ <sub>3</sub>-O)<sub>6</sub>} cores, up to 2.015(3), 2.029(3) Å of Ti-( $\mu$ -O<sup>i</sup>Bu) bridges of {[Ti<sub>2</sub>( $\mu$ -O)<sub>6</sub>(HO<sup>i</sup>Bu)<sub>2</sub>( $\mu$ -O<sup>i</sup>Bu)<sub>2</sub>]} species. For adducted alcohol molecules the length of Ti–O bonds amounted 2.202(4) Å. Ti-( $\mu$ <sub>3</sub>-O)-Ti angles change into two ranges: the first one from 98.22(15)° to 103.77(15)° for three atoms belonging to different titanium-oxide levels and the second one from 128.99(17)° to 136.9(2)° for the corresponding atoms of the same Ti<sub>3</sub>-O<sub>3</sub> levels of {Ti<sub>6</sub>-( $\mu$ <sub>3</sub>-O)<sub>6</sub>} cores. The values of Ti7-( $\mu$ -O)-Ti (Ti1, Ti2, Ti3) angles change in the range 129.90(18)–130.49(19), whereas alkoxide ligand bridges form Ti7-O101-Ti7(-x,-y,-z+1) angle of 105.09(14)°.

The conversion of (1) towards the hexanuclear Ti(IV) complex (2), of the general formula [Ti<sub>6</sub>O<sub>6</sub>(O<sup>i</sup>Bu)<sub>6</sub>(OCC(Me)<sub>2</sub>Et)<sub>6</sub>], after next 7 days of the crystallization process, has been observed (Fig. 2). X-ray diffraction studies proved the formation of hexameric structure surrounding the inversion center with [Ti<sub>3</sub>O<sub>3</sub>(O<sup>i</sup>Bu)<sub>3</sub>(OCC(Me)<sub>2</sub>Et)<sub>3</sub>] moiety in the asymmetric unit. This structure is analogical to complexes synthesized in the reaction Ti(OR)<sub>4</sub> (R = <sup>i</sup>Pr, Bu, Si(CH<sub>3</sub>)<sub>3</sub>) with 2,2-dimethylpropionic acid [21,23,24]. According to these data all titanium atoms are found in slightly distorted octahedral environment with three  $\mu$ <sub>3</sub>-oxygen atoms, two carboxylate groups and single O<sup>i</sup>Bu ligand forming a coordination sphere. The Ti–O distances in  $\mu$ <sub>3</sub>-oxide bridges change in the range 1.868(4)–1.904(4) Å and 2.134(4)–2.169(4) Å, and they are similar to analogous distances of hexanuclear Ti(IV) complexes described in the earlier reports [21,23,24]. Also in this case {Ti<sub>6</sub>-( $\mu$ <sub>3</sub>-O)<sub>6</sub>} core is stabilized by six asymmetric *syn-syn* carboxylate bridges (length of Ti–O bonds: 2.039(5)–2.062(5) Å for shorter and 2.070(5)–2.082(5) Å for longer) and six terminal alkoxo ligands (length of Ti–O





bonds: 1.753(5)-1.771(4) Å). Metal-oxide distances mentioned above are comparable with similar distances of  $[\text{Ti}_6\text{O}_6(\text{OR})_6(\text{OOC}^i\text{Bu})_6]$  ( $\text{R} = {}^i\text{Pr}, \text{Bu}, \text{Si}(\text{CH}_3)_3$ ) complexes [21,23,24].

Complexes **(1)** and **(2)** were characterized using IR spectroscopy and obtained results are listed in Table 2. Since both **(1)** and **(2)** possess  $\text{OCC}(\text{Me})_2\text{Et}$ ,  $\text{O}^i\text{Bu}$  ligands and  $\mu_3$ -oxo bridges, therefore to identify these complexes structure, the following absorption bands were used: (a) stretching modes of coordinated carboxylic groups ( $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$ ), (b) stretching vibrations of coordinated alkoxides groups ( $\nu(\text{OR})$ ), and (c) stretching modes of nonlinear oxo bridges ( $\nu_{\text{a}}(\text{Ti-O-Ti})$ ). In spectra of **(1)** and **(2)**, the bands attributed to symmetric ( $\nu_{\text{s}}$ ) and asymmetric ( $\nu_{\text{as}}$ ) stretching vibrations of COO groups were detected in the range 1426-1478  $\text{cm}^{-1}$  and 1531-1585  $\text{cm}^{-1}$  respectively (Table 2). Values of  $\Delta(\nu_{\text{as}} - \nu_{\text{s}})$  parameters 107 and 105  $\text{cm}^{-1}$  are typical for *syn-syn* bidentate COO bridges [21, 31]. The detection of the composite band between 1052 and 1133  $\text{cm}^{-1}$ , assigned to  $\nu(\text{CO})$  vibrations of alkoxides groups proves the presence of coordinated isobutoxide ligands in the structures of **(1)** and **(2)**. Detection of the  $\nu(\text{CO})$  band component at 1083  $\text{cm}^{-1}$ , and also very weak and broad  $\nu(\text{OH})$  band at 3448  $\text{cm}^{-1}$  confirms the presence of adducted alcohol molecules in the structure of **(1)**. The intense bands, which were found at 741 and 742  $\text{cm}^{-1}$  in spectra of **(1)** and **(2)** respectively have been attributed to  $\nu_{\text{a}}(\text{Ti-O-Ti})$  vibrations of nonlinear oxo bridges [31].

Analysis of  $^{13}\text{C}$  NMR spectra of **(1)** and **(2)** in solid phase revealed the lack of significant differences in chemical shift of carboxylate carbon resonance signals (Table 3). Signals, which were found at  $\delta = 184.61$  ppm (**(1)**) and 184.67 ppm (**(2)**) have been assigned to equivalent carboxylate group of  $\text{OCC}(\text{CH}_3)_2\text{Et}$  ligands, which stabilize  $\{\text{Ti}_6(\mu_3\text{-O})_6\}$  cores. Splitted resonance signals of  $\text{CH}({}^i\text{Bu})$ ,  $\text{CH}_2({}^i\text{Bu})$ , and  $\text{CH}_3({}^i\text{Bu})$  groups carbon atoms, detected in  $^{13}\text{C}$  NMR spectra of **(1)**, have been attributed to the presence of both isobutoxide ligands and

isobutyl alcohol in the structure of this complex. The low structural stability of (1) in the solution caused that the significant differences in  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of this complex and (2) were not found.

### 3.2 Multinuclear Ti(IV) complexes obtained in the 1:1 reaction of $\text{Ti}(\text{O}^i\text{Bu})_4$ with $\text{HOOC}^i\text{Bu}$

The slow evaporation of the 1:1 mixture of titanium tetrabutoxide with 2,2-dimethyl propionic acid in toluene under the inert atmosphere leads to the separation of colourless single crystals after 5 days. Formation of the complex (3), with general formula  $[\text{Ti}_6\text{O}_5(\text{O}^i\text{Bu})_6(\text{OOC}^i\text{Bu})_8]$ , has been proved by analysis of X-ray diffraction data, collected at 293 K (Table 1). The structure of (3) consists of two titanium(IV) triangle units ( $\{\text{Ti}_3-(\mu_3\text{-O})\}$ ) formed by three titanium atoms (Ti1, Ti2, Ti4 and Ti3, Ti5 Ti6) linked by  $\mu_3$ -oxo bridges (O1 and O2) (Fig. 3). These simple units are stabilized by the  $\mu$ -alkoxo bridge (O121 and O141), three bidentately coordinated OOC<sup>i</sup>Bu groups (O41, O71, O81 and O31, O51, O61), and two terminal O<sup>i</sup>Bu ligands (O91, O111 and O101, O131).  $\{\text{Ti}_3-(\mu_3\text{-O})\}$  units are connected by three  $\mu$ -oxo bridges (O3, O4, O5) and two *syn-syn* carboxylate ones (O11 and O21) (Fig. 3). The angles between different triangle units formed by metal atoms amount  $14.55(13)^\circ$  between Ti1-Ti2-Ti4 and Ti1-Ti4-Ti6 planes,  $59.90(10)^\circ$  between Ti1-Ti4-Ti6 and Ti1-Ti6-Ti5, and  $14.96(18)^\circ$  between Ti1-Ti6-Ti5 and Ti3-Ti5-Ti6. Oxygen atoms O1 and O2 are slightly shifted from the plane of Ti1-Ti2-Ti4 (0.110(9) Å) and Ti3-Ti5-Ti6 (-0.096(10) Å). The Ti1 $\cdots$ Ti6 distance (3.248(4) Å) is 0.15 Å longer than Ti $\cdots$ Ti distances between different  $\text{Ti}_3\text{-O}_3$  levels of  $\{\text{Ti}_6(\mu_3\text{-O})_6\}$  core in (2). Two other distances between triangle units Ti1 $\cdots$ Ti5 and Ti4 $\cdots$ Ti6 amount 3.351(4) and 3.320(4) Å respectively and there are 0.15 Å shorter than Ti $\cdots$ Ti distances in the same level of the  $\{\text{Ti}_6(\mu_3\text{-O})_6\}$  core. In the structure of (3), two long Ti $\cdots$ Ti distances, ranging from 3.464(4) to 3.481(4) Å, and one short (3.113(4)

Å and 3.145(4) Å) are very similar to these found in the  $\{\text{Ti}_6(\mu_3\text{-O})_6\}$  core of (2). This fact suggests that discussed triangle units may take part in the formation of  $\{\text{Ti}_6(\mu_3\text{-O})_6\}$  skeletons and can be considered as precursors of such cores. The differences in  $\text{Ti}\cdots\text{Ti}$  distances are associated with the values of  $\text{Ti-O-Ti}$  angles, and shortest  $\text{Ti}\cdots\text{Ti}$  distances correspond to the smallest angles observed around  $\mu_3$ -oxo O1 and O2 atoms. Two other angles around these atoms are much bigger ranging from 126.1(5) to 130.5(5)°. They correspond to the longer distances between titanium atoms. Values of  $\text{Ti}(\mu\text{-O})\text{-Ti}$  angles (O3, O4 and O5) are similar and amount 132.9(6), 133.3(7) and 127.8(5)°, respectively. Moreover  $\text{Ti-O-Ti}$  angles, which are 100.8(4) and 103.0(5)° were found for  $\mu\text{-O}^i\text{Bu}$  bridges (Fig. 3).

The length of titanium-oxo bonds depends on the type of Ti atoms and its positions in the triangle unit. Analysis of  $\text{Ti}(\mu_3\text{-O})$  distances in the triangle confirmed the formation of two shorter bonds (e.g. 1.849(10) and 1.973(9) Å for Ti1 and Ti2) and the longer one (e.g. 2.046(10) Å for Ti4) similarly to analogical distances, which were found in the hexanuclear structure of (2). However, in this last complex the transformation is completed and differences between shorter and longer bonds are more distinctive. The lengths of  $\text{Ti}(\mu\text{-O})$  distances change from 1.766(12) to 1.862(9) Å. All carboxylate groups form asymmetric *syn-syn* bridges, which lengths change from 1.962(11) to 2.127(14) Å. The shortest  $\text{Ti-O}(\text{OOC}^i\text{Bu})$  bonds (< 2 Å) were found for external Ti2 and Ti3 atoms, whereas the longest ones (2.063(13)-2.127(14) Å) were detected for Ti1 and Ti6 atoms. Analysis of  $\text{Ti-O}^i\text{Bu}$  distances revealed that non-bridging  $\text{O}^i\text{Bu}$  groups form shortest bonds (1.761(12)-1.809(13) Å), whereas the lengths of  $\text{Ti}(\mu\text{-O}^i\text{Bu})$  bonds is lengthened in the range 0.10-0.15 Å. Simultaneously, a significant asymmetry of  $\text{Ti-O}$  bonds (exceeding 0.20 Å) were detected for bridging  $\text{O}^i\text{Bu}$  ligands. In this case the shorter metal-oxide distances amounted 1.870(12),

1.940(10) Å, whereas the longer ones 2.104(11), 2.138(10) Å, for Ti-( $\mu$ -O141<sup>i</sup>Bu) and Ti-( $\mu$ -O121<sup>i</sup>Bu) respectively.

The formation of alkoxide bridges in the structure of **(3)** and the structure of triangle units suggests its possible future conversion to hexanuclear system, similarly as in the case of **(1)**. Therefore, the X-ray diffraction studies have been repeated for single crystals isolated after the next 7 days from the reaction mixture. Obtained results proved the structural conversion of **(3)** (monoclinic, *C*2) into the complex **(4)** (triclinic, *P*-1). The final model represents classical {Ti<sub>6</sub>( $\mu$ <sub>3</sub>-O<sub>6</sub>)} core with additional water molecules above and below the upper and lower base, respectively. In the asymmetric unit [Ti<sub>3</sub>O<sub>3</sub>(H<sub>2</sub>O)(O<sup>i</sup>Bu)<sub>3</sub>(OOC<sup>t</sup>Bu)<sub>3</sub>] moiety was found with all atoms in general positions. It is positioned around the inversion center. All titanium atoms are surrounded by seven oxygen atoms descended from: (a) three  $\mu$ <sub>3</sub>-oxo bridges, (b) two carboxylate groups, (c) single O<sup>i</sup>Bu ligand, and (d) water molecule. Water molecules (O<sub>w</sub>) were found at significantly larger Ti-O distances (Ti<sub>3</sub>-O<sub>w</sub> = 2.240(13), Ti<sub>1</sub>-O<sub>w</sub> = 2.357(16) and Ti<sub>2</sub>-O<sub>w</sub> = 2.550(11) Å). Surprisingly, this molecule is not equally distant from all three Ti atoms, the distances differ enormously and the biggest values can be even considered as semi-coordination. Moreover, higher thermal displacement factor of O<sub>w</sub> (O7) atom reveals that it is less stable than other  $\mu$ <sub>3</sub>-O atoms. Therefore, we supposed that this is transient structure, which was effectively caught during conversion, however the future studies revealed that this is the final structure with loosely bound water molecule trapped between alkoxide chains, which hamper its dissociation. This water molecule is shifted 1.24 Å from the {Ti<sub>3</sub>-O<sub>3</sub>} plane. The formation of {Ti<sub>6</sub>( $\mu$ <sub>3</sub>-O)<sub>6</sub>} skeleton causes that Ti···Ti distances are longer (3.535(5)-3.582(6) Å) than in the case of **(2)**. The shorter Ti···Ti distances (2.992(5)-3.049(6) Å) and longer Ti-( $\mu$ <sub>3</sub>-O) bonds (2.124(9)-2.196(9) Å) were found between different {Ti<sub>3</sub>-O<sub>3</sub>} levels. Analysis of Ti-O<sup>i</sup>Bu distances confirmed the formation of the shortest bonds in the range

1.807(10)-1.839(11) Å. Asymmetric *syn-syn* carboxylate bridges link metal atoms descended from two different levels with distances ranging from 2.035(13) to 2.100(14) Å. However, due to significant root-mean-square values (much bigger than found for {Ti<sub>6</sub>(μ<sub>3</sub>-O)<sub>6</sub>} cores of (2) and (1)) these distances are within an experimental error. Problems with the exact solution of complex (4) structure caused that low temperature single-crystal diffraction studies (123 K) have been also carried out. Obtained results revealed significant differences in the unit cell parameters of crystals studied at 123 and 303 K (Table 4). The decrease of the unit cell along “a” axis from 12.050(2) Å to 10.948(2) Å and change of the γ angle value from 105.33(3)° to 102.41(1)° at 303 and 123 K, respectively, was observed. Analysis of the low temperature X-ray diffraction data showed the lack of significant differences in the length of metal-oxide bonds of the {Ti<sub>6</sub>(μ<sub>3</sub>-O)<sub>6</sub>} skeleton, and clear changes of Ti-O<sub>w</sub> bond lengths (Table 4). Moreover results of these studies revealed changes in the length of Ti-O<sub>w</sub> bonds, which are associated with the increase of the Ti<sup>3</sup>-O<sup>i</sup>Bu distance (1.807(10) Å (303 K), 1.895(14) Å (123 K)) and with the decrease of Ti<sup>1</sup>-O<sup>i</sup>Bu and Ti<sup>2</sup>-O<sup>i</sup>Bu distances (1.839(11), 1.829(14) Å (303 K) – 1.795(15), 1.812(14) Å (123 K)).

Differences between the structures of (3) and (4) have found confirmation in their IR spectra (Table 2). The composed interactions of bidentate carboxylate bridges in the structure of (3) caused the splitting of bands assigned to the asymmetric COO stretching modes ( $\nu_{\text{as}}(\text{COO})$  - 1591, 1557, 1539 cm<sup>-1</sup>). It may be effected by the coupling of the asymmetric carboxylate bridge vibrations, which stabilize two distorted {Ti<sub>3</sub>-(μ<sub>3</sub>-O)} cores and two carboxylate groups linked these cores. In the spectrum of (4) only two bands assigned to  $\nu_{\text{as}}(\text{COO})$  modes at 1587, 1584 cm<sup>-1</sup> have been detected. A similar spectral effect was found in IR spectra of these multinuclear oxo Ti(IV) alkoxide carboxylate complexes, in which hexanuclear {Ti<sub>6</sub>-(μ<sub>3</sub>-O)<sub>6</sub>} cores were stabilized by *syn-syn* carboxylate bridges [21-24]. Differences between titanium-oxide cores of (3) and (4) caused significant changes in the position and splitting of

Ti-O-Ti asymmetric bridge bands, detected between 710 and 790  $\text{cm}^{-1}$  (Table 2) [21-24]. The coordination of water molecules in the structure of (4) has been confirmed by the detection of very weak bands  $\nu(\text{OH})$  at 3400-3600  $\text{cm}^{-1}$  and  $\delta(\text{H}_2\text{O})$  at 1619  $\text{cm}^{-1}$  of this complex IR spectrum.

The temperature dependence of (4) structural transitions were studied using variable temperature IR spectroscopy between 98 and 523 K. Analysis of X-ray diffraction data collected at 123 K and at 303 K showed significant changes in the strength of metal-water and metal-alkoxide interactions with the decrease of temperature. Very low intensity of absorption bands descending from stretching and bending vibrations of water molecules caused that temperature transitions in the structure of (4) were determined on the basis of  $\nu(\text{CO})$  frequency dependence versus temperature (Fig. 5). According to this dependency, a significant phase transition between 143 and 253 K was found.  $\nu(\text{CO})$  band shifts toward the lower frequencies, which were observed in this temperature region, may be explained by the changes in the strength of Ti-O<sup>i</sup>Bu and Ti-water interactions (Table 4). Between 253 and 313 K the structure of (4) was stable but above 313 K the next transition, connected with the partial decomposition of this complex, was observed [24].

Analysis of  $^{13}\text{C}$  NMR spectra of (3) and (4) complexes revealed the clear differences in the chemical shift and splitting of carbon resonance signals (Table 3). The formation of two types of carboxylate bridges in the structure of (3) (bridged Ti atoms in  $\{\text{Ti}_3-(\mu_3\text{-O})\}$  triangles and linked two  $\{\text{Ti}_3-(\mu_3\text{-O})\}$  triangles) led to two sets of resonance lines located at  $\delta = 183.41$ , 187.14 ppm in the solid state  $^{13}\text{C}$  NMR spectrum. One signal at  $\delta = 184.26$  ppm in the spectrum of (4) indicates the formation of the equivalent carboxylate bridges, similarly as in the case of (2). Above mentioned structural differences between (3) and (4) influence also on the chemical shift and splitting of carbon atom resonance signals of 2,2-methylpropane and

methyl-1-propane groups (Table 3). In order to determine the structural stability of (3) and (4) in solutions, the  $^{13}\text{C}$  NMR spectra of crystals dissolved in  $\text{CDCl}_3$  have been studied (Table 3). Analysis of (3)  $^{13}\text{C}$  NMR spectra showed clear differences in position and splitting of carbon atom signals of  $\text{OOC}^t\text{Bu}$  and  $\text{O}^i\text{Bu}$  ligands, which may be caused by structural changes of this complex. The chemical shifts of well-resolved signals, due to the carbon atoms of isobutoxy and 2,2-dimethylpropionate groups, which were detected in the  $^{13}\text{C}$  NMR spectrum of (4) in  $\text{CDCl}_3$  solution are similar to those found in the solid state spectrum (Table 3). These results suggest that the crystal structure of (4) is generally preserved when solvated in a solvent.  $^1\text{H}$  NMR spectrum of (4) in  $\text{CDCl}_3$  solution exhibits proton peaks due to  $-\text{CH}$ ,  $-\text{CH}_2$ , and  $-\text{CH}_3$  groups of  $\text{O}^i\text{Bu}$  and  $\text{OOC}^t\text{Bu}$  ligands (Experimental Part). A broad-weak peak, which was found at  $\delta = 3.47$  ppm is characteristic for protons of HDO confirming the presence of water molecule in the structure of this complex.

### 3.3 Multinuclear Ti(IV) complexes obtained in the 1:1 reaction of $\text{Ti}(\text{O}^i\text{Bu})_4$ with $\text{HOOCCH}_2^t\text{Bu}$

Slow evaporation of the reaction mixture at inert atmosphere led to the separation, , of the colorless crystalline powder or small crystals after 5-7 days. Unfortunately, the poor quality of these crystals (in spite of the multiple crystallization experiments) caused that the crystallographic structure of (5) has not been solved. Therefore the possible structure of (5) has been proposed on the basis of IR and NMR spectroscopic studies.

Absorption bands, which were found at 1538, 1589  $\text{cm}^{-1}$  and 1416, 1456  $\text{cm}^{-1}$  in IR spectra of this compound have been attributed to  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  modes of asymmetric *syn-syn* carboxylate groups (Table 2). The position of  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  modes and their splitting, are similar to these, which were found in spectra of (2), (4), and previously studied Ti(IV) complexes containing  $\{\text{Ti}_6-(\mu_3\text{-O})_6\}$  skeletons [21-24,32]. Values of  $\Delta(\nu_{\text{as}} - \nu_{\text{s}})$  parameter, 122 and 149  $\text{cm}^{-1}$ , indicate on the formation the *syn-syn* carboxylate bridges,



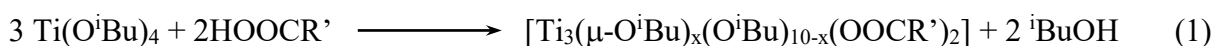
which stabilize hexanuclear  $\mu$ -oxo titanium(IV) cores. Spectral similarities for bands registered in ranges 1046-1135  $\text{cm}^{-1}$  and 717-743  $\text{cm}^{-1}$  between (**5**) and other hexanuclear Ti(IV) complexes were also observed (Table 2). Bands, which were found in above mentioned ranges have been assigned to the C-O stretching vibration ( $\nu(\text{CO})$ ) of terminal O<sup>i</sup>Bu ligands and Ti-O stretching modes ( $\nu_a(\text{TiOTi})$ ) of nonlinear Ti-O-Ti oxo bridges respectively [21,24,31]. Especially important is the detection of two  $\nu_a(\text{Ti-O-Ti})$  bands at 717 and 743  $\text{cm}^{-1}$ . A similar spectral effect, which was observed in spectra of  $[\text{Ti}_6\text{O}_6(\text{OSi}(\text{CH}_3)_3)_6(\text{OOCR}')_6]$  ( $\text{R}' = \text{}^i\text{Bu}, \text{CH}_2^i\text{Bu}, \text{C}(\text{CH}_3)_2\text{Et}$ ) has been explained by the differences in the length of Ti-O bonds of  $[\text{Ti}_3-(\mu_3\text{-O})_3]$  levels, and the mutual “twisting” of these levels in the  $\{\text{Ti}_6-(\mu_3\text{-O})_6\}$  core [24]. According to these reports, the appearance of the splitting  $\nu_a(\text{Ti-O-Ti})$  band at 717 and 743  $\text{cm}^{-1}$  in the spectrum of (**5**) suggests the formation of the analogical type of the  $\{\text{Ti}_6-(\mu_3\text{-O})_6\}$  skeleton.

The structure of (**5**) has been also characterized by  $^{13}\text{C}$  NMR spectroscopy in the solid state. Analysis of data presented in Table 3 exhibits typical chemical shift of resonance signals attributed to carbon atoms of  $\text{OOCCH}_2^i\text{Bu}$  and O<sup>i</sup>Bu ligands coordinated with Ti(IV) ions of  $\{\text{Ti}_6-(\mu_3\text{-O})_6\}$  cores ((**2**), (**4**), [24]). Single signal of the carboxylate carbon at  $\delta = 179,97$  ppm suggests the lack of significant differences in the strength of Ti-OOC bonds, which stabilize  $\{\text{Ti}_6-(\mu_3\text{-O})_6\}$  cores. Simultaneously, the type of the carboxylate ligand influences on the chemical shift of carboxylate carbon signals in  $^{13}\text{C}$  NMR spectra of (**5**) ( $\delta = 179,97$  ppm) and (**2**) ( $\delta = 183,67$  ppm). Analysis of  $^{13}\text{C}$  NMR spectra of (**5**) in  $\text{CDCl}_3$  solution (Table 3) revealed the lack of significant changes in the structure of this complex in the solid phase and solution. Spectral characterization of (**5**) suggests that the main product of the  $\text{Ti}(\text{O}^i\text{Bu})_4$  reaction with  $\text{HOOCCH}_2^i\text{Bu}$  acid is the hexanuclear  $\mu$ -oxo Ti(IV) complex of the general formula  $[\text{Ti}_6\text{O}_6(\text{O}^i\text{Bu})_6(\text{OOCCH}_2^i\text{Bu})_6]$ .

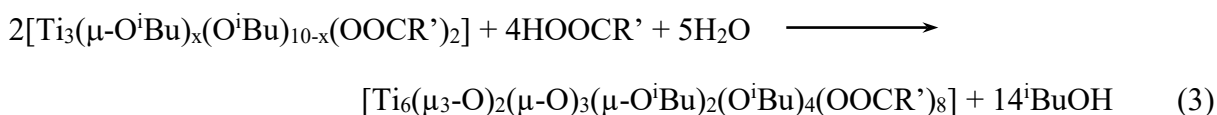
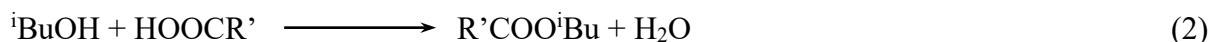


### 3.4. Discussion

In order to explain the complicated pathway of titanium(IV) tetraisobutoxide reactions with branched organic acids, the tendency of titanium alkoxides to the formation of oligomers containing bridging positions ( $[\text{Ti}_a(\mu_n\text{-OR})_x(\text{OR})_{4a-x}]$ ;  $n = 2, 3$ ) should be considered [33-35]. Therefore, we assumed, that in the first stage of  $\text{Ti}(\text{O}^i\text{Bu})_4$  reactions with  $\text{HOOCR}'$  ( $\text{R}' = \text{C}(\text{CH}_3)_2\text{Et}, ^i\text{Bu}, \text{CH}_2^i\text{Bu}$ ) simple units are formed (eqn. 1) [3]. The base unit is composed of three titanium atoms linked by alkoxides bridges, stabilized by carboxylate bridges and terminal isobutoxides ligands.



The higher Lewis basicity of alkoxide bridges than terminal alkoxo groups caused that these fragments are more susceptible to the selective attack or substitution by protic  $\text{XOH}$  reagents [19,33]. The hydrolysis/condensation and substitution of alkoxide ligands by carboxylate groups leads to formation of the “open” dimeric system, e.g. **(3)** (eqn. 2 and 3).



The alkoxide bridges, which were found in the structure of intermediate complexes, influence on their higher reactivity towards hydrolysis, ester elimination and substitution of  $\text{O}^i\text{Bu}$  by  $\text{OOCR}'$  groups. This fact explains the tendency of intermediate complexes to the conversion towards the more structurally stable systems containing hexanuclear  $\{\text{Ti}_6(\mu_3\text{-O}_6)\}$  cores, e.g. **(2)**, **(5)**, and also **(4)**. In the last case, the esterification processes and steric effects caused the conversion of the “open” structure **(3)** (after 7 days) towards the “closed” complex  $[\text{Ti}_6\text{O}_6(\text{H}_2\text{O})_2(\text{O}^i\text{Bu})_6(\text{OOC}^i\text{Bu})_6]$  **(4)**, containing two water molecules. The stability of the intermediate complex **(3)** depends on the type of the solution. The use of toluene and parent



alcohol mixture (2:1 volume) stabilizes the “open” system. The conversion of (3) up to (4) was also observed but after 3-4 weeks.

The titanium alkoxides aggregation processes play an important role in the formation of complex (1). The detection of  $\{\text{Ti}_2\text{O}_6(\mu\text{-O}^i\text{Bu})_2(\text{HO}^i\text{Bu})_2\}$  species in the structure of this compound (Fig. 1) indicates that the Lewis acidity of titanium atoms and Lewis basicity of alcoholic species are suitable for the formation of alcohol adduct ( $[\text{Ti}_2(\text{O}^i\text{Bu})_6(\mu\text{-O}^i\text{Bu})_2(\text{HO}^i\text{Bu})_2]$ ) [3,36]. Considering results of our studies we assumed that “open” systems (similar to (3)) and above mentioned adducts are formed in the first stage of  $\text{Ti}(\text{O}^i\text{Bu})_4$  reaction with  $\text{HOCC}(\text{CH}_3)_2\text{Et}$ . The high reactivity of both systems enable the formation of the more stable intermediate complex (1). The presence of reactive alkoxides bridges in the structure of (1) favors their conversion towards the hexanuclear complex (2).

#### 4 Conclusions

New multinuclear  $\mu$ -oxo Ti(IV) complexes (1)-(5) have been synthesized in the 1:1 reactions of  $\text{Ti}(\text{O}^i\text{Bu})_4$  with three branched organic acids ( $\text{HOOCR}'$ ;  $\text{R}' = \text{C}(\text{CH}_3)_2\text{Et}$ ,  $^i\text{Bu}$ , and  $\text{CH}_2^i\text{Bu}$ ) at room temperature under the argon atmosphere. X-ray diffraction and spectroscopic studies proved the formation of metastable intermediate species ((1), (3)), which convert toward the more structurally stable Ti(IV) complexes containing hexanuclear  $\{\text{Ti}_6-(\mu_3\text{-O})_6\}$  cores during the next processes (e.g. hydrolysis, condensation, ester elimination, substitution OR ligands by  $\text{OOCR}'$  groups) ((2), (4), (5)). The following factors influence on the structure of multinuclear  $\mu$ -oxo Ti(IV) complexes and their possibility to the conversion; (a) the formation of the simple units containing more reactive alkoxide bridges, (b) steric effects of organic acids and alkoxide ligands, and (c) tendency of titanium(IV) alkoxides to aggregation processes, which proceed simultaneously with the formation of oxo Ti(IV) alkoxo carboxylate complexes.

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