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# Synthesis, crystal structures and spectroscopic characterization of $[Ti_8O_8(OOCR)_{16}]$ (where $R = Bu^t$ , $CH_2Bu^t$ , $C(CH_3)_2Et$ )

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#### Abstract

Multinuclear titanium(IV) oxo carboxylates of the general formula  $[Ti_8O_8(OOCR)_{16}]$  (where R = Bu'(1),  $CH_2Bu'(2)$ ,  $C(CH_3)_2Et$ (3)) have been synthesized in a reaction of titanium isopropoxide with the appropriate organic acids in a molar ratio of 1:2. The composition and structure of these compounds were identified by elemental analysis, IR, NMR and X-ray single-crystal diffraction. The crystal structure of **1** was solved in the orthorhombic space group *Pbca*. Titanium atoms form oligomeric  $[Ti_8(\mu_2-O)_8]$  rings, where each Ti cation is surrounded by six oxygen atoms (two  $\mu_2$ -oxo and four  $\mu$ -carboxylato bridges). Within the ring the Ti–Ti distances between neighboring titanium ions range from 3.333(1) to 3.366(1) Å and the mean value of the Ti–Ti–Ti angle is 134.2(1.3)°. Results of IR, NMR and MS studies proved that in the structures of **2** and **3**, multinuclear  $[Ti_8(\mu_2-O)_8]$  clusters stabilized by carboxylate bridges are also formed. TGA/DTG, MS and variable temperature IR + (VT-IR) studies have been carried out in order to determine the thermal stability and thermal decomposition mechanism of the Ti(IV) carboxylates mentioned above. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Titanium(IV); Multinuclear carboxylates; X-ray structure; IR; NMR; TGA; MS

# 1. Introduction

The study of the synthesis of titanium(IV) oxo carboxylates, structural characteristics and pyrolysis pathway are motivated by their potential applications as sol-gel or chemical vapor deposition (CVD) precursors. According to the literature reports, two methods are used in preparation of Ti(IV) oxo carboxylate derivatives. Complexes of the general formula O[Ti(OOCR)<sub>3</sub>]<sub>2</sub> were the main products of a multistage reaction of titanium tetrachlorine with organic acids [1,2]. During the process mentioned above, [TiCl<sub>4 - x</sub>(OOCR)<sub>x</sub>] (x = 1-4) derivatives have also been isolated [3–5]. Barrow et al. [6,7] showed that titanium(IV) oxo chloro-carboxylates O[TiCl<sub>2</sub>(OOCBu<sup>'</sup>)(Bu<sup>'</sup>COOH)]<sub>2</sub> and O[TiCl  $(OOCBu')_{2}_{2}$  were the main products of the reaction between TiCl<sub>4</sub> and trimethylacetic acid in a 1:2.5 molar ratio. The crystal structure of [{TiCl<sub>2</sub>(OOCBu')(Bu'-COOH)}<sub>2</sub>O] is formed of dimers, composed of Ti atoms octahedrally surrounded by oxygen atoms of one oxygen bridge ( $\mu_2$ -O) and two bifurcated carboxylates ( $\mu$ -O) of the *syn-syn* type. The Ti–O distances were 1.77 Å for Ti-( $\mu_2$ -O) and 1.99–2.09 Å for Ti-( $\mu$ -O) [7].

The stoichiometric reaction of titanium alkoxides  $(Ti(OR')_4; R' = Et, Pr^i)$  with carboxylic acids is the next method of synthesizing titanium oxo carboxylates [8,9]. Titanium oxo carboxylato alkoxides were crystallized from 1:1–4 molar ratio mixtures of  $Ti(OR')_4/HOOCR$ . X-ray diffraction studies exhibited that the following four types of complexes may be formed: (a)  $[Ti_6O_4(OR)_{12}(O_2CR')_4]$ , (b)  $[Ti_6O_4(OR)_8(O_2CR')_8]$ , (c)  $[Ti_4O_4(OR)_4(O_2CR')_4]$  and (d)  $[Ti_6O_6(OR)_6(O_2CR')_6]$  (R = Et, Pr<sup>*i*</sup>, R' = Me, Np (neopentyl), Bu<sup>*i*</sup>, Ph) [10–16].

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The main factor influencing the formation of these types of multinuclear Ti(IV) clusters is the nature of the alkoxide and carboxylate ligands [13]. Ammala et al. [17] report that  $[Ti_6O_6(OCH_2Bu')_6(O_2CPh)_6]$  and  $[Ti_6O_4(OPr'')_8(O_2CPh)_8]$  were also synthesized in the reaction of  $[Fe_4(\mu_3-O)_2(O_2CPh)_8(py)_2]$  with Ti(OPr'')\_4 in toluene. The application of the large excess of organic acid leads to the formation of Ti(IV) oxo carboxylato derivatives (e.g., polymeric chains of  $[TiO(OAc)_2]_n$  were obtained for the ratio 1:10) [8,9].

In the reported work we have focused on structural studies and spectral characteristics of multinuclear Ti(IV) carboxylato derivatives, synthesized from titanium isopropoxide and HOOCR,  $R = Bu^t$ ,  $CH_2Bu^t$ ,  $C(CH_3)_2Et$ . Analysis of the thermogravimetric (TGA), MS-EI, and variable temperature IR spectroscopy have been used in order to study the thermal stability of the synthesized compounds and their thermal decomposition pathway.

## 2. Experimental

The studied compounds were synthesized under argon atmosphere, using standard Schlenk line and glovebox techniques.  $Ti(OPr^i)_4$  (prepared from  $TiCl_4$ (Aldrich) and 2-propanol (Aldrich) in the presence of trimethylamine) was freshly vacuum distilled prior to use, whereas  $Bu^tCOOH$ ,  $Bu^tCH_2COOH$  and  $Et(Me)_2$ -CCOOH, (Aldrich) were used as received.

Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum 2000 spectrometer within the range 160–4000  $\text{cm}^{-1}$  with a medium slit width and a peak resolution of 2.0 cm<sup>-1</sup>. The crystals were studied as a powder dispersed in a KBr pellet (400–4000  $\text{cm}^{-1}$ ) and as a Nujol suspension between CsI plates  $(160-700 \text{ cm}^{-1})$ . The low temperature IR spectra (liquid nitrogen temperature (LNT)) have been recorded using a SPECAC variable temperature cell. Solution <sup>1</sup>H and <sup>13</sup>C NMR spectra ([D<sub>8</sub>]toluene) were recorded using a 5-mm solution probe on a Varian Gemini 200. Solid state <sup>13</sup>C NMR spectra were registered on a Bruker AMX 300. Thermogravimetric analysis (TGA) was carried out using the SDT 2960 TA Instrument, in nitrogen atmosphere from 25 to 500 °C at a ramp rate of  $3^{\circ}$  min<sup>-1</sup>. Mass spectra were recorded with a MS AMD-604 spectrometer, using the EI method, at 70 eV, in the range 150-350 °C.

# 2.1. Preparation of $[Ti_8O_8(OOCR)_{16}]$

Ti(OPr<sup>*i*</sup>)<sub>4</sub> (1.00 g, 3.52 mmol) was added dropwise to a solution of organic acid (7.04 mmol, 0.72 g of Bu<sup>*i*</sup>COOH, 6.90 mmol, 0.80 g of Bu<sup>*i*</sup>CH<sub>2</sub>COOH or 0.80 g of Et(CH<sub>3</sub>)<sub>2</sub>CCOOH) in toluene (3.00 cm<sup>3</sup>), and stirred for 12 h. Crystals were grown by slow evaporation of the reaction mixture under argon atmosphere (glovebox). The colorless crystals were obtained after 2-3 days.

# 2.1.1. $Ti_8O_8(OOCBu^t)_{16}$ (1)

Yield: 0.56 g (55.0%). The % Ti was gravimetrically determined as TiO<sub>2</sub>, according to the Meth-Cohn et al. method [13]. *Anal*. Calc. for  $C_{80}H_{144}O_{40}Ti_8 \times C_7H_8$ : C, 47.03; H, 6.85; Ti, 17.30. Found: C, 47.33; H, 7.03; Ti, 17.46%. IR (KBr, cm<sup>-1</sup>) 1545 (s, COO), 1512 (m, COO), 1429 (s, COO), 1417 (m, COO), 1229 (m, C-Me<sub>3</sub>), 750 (m, Ti–O), 611 (m, Ti–O), 504 (m, Ti–O). <sup>13</sup>C NMR (solid,  $\delta$ , ppm) 26.5 (CH<sub>3</sub>), 38.7 (C–(CH<sub>3</sub>)<sub>3</sub>), 188.2, 186.7 (COO).

## 2.1.2. $Ti_8O_8(OOCCH_2Bu^t)_{16}$ (2)

Yield: 0.25 g (24.2%). Anal. Calc. for  $C_{81}H_{146}O_{40}$ -Ti<sub>8</sub>: C, 48.99; H, 7.47; Ti, 16.30. Found: C, 47.66; H, 7.45; Ti, 16.80%. IR (KBr, cm<sup>-1</sup>) 1540 (s, COO), 1507 (m, COO), 1421 (s, COO), 1410 (s, COO), 1209 (m, C-Me<sub>3</sub>), 754 (m, Ti–O), 601 (m, Ti–O), 507 (m, Ti–O).<sup>13</sup>C NMR (solid,  $\delta$ , ppm) 49.5 (CH<sub>3</sub>), 29.8 (C–(CH<sub>3</sub>)<sub>3</sub>), 181.5 (COO).

Table 1

Crystal data and structure refinement for [Ti<sub>8</sub>O<sub>8</sub>(OOCBu<sup>t</sup>)<sub>16</sub>]

	[8 = 8( = = = )10]
Empirical formula (chemical unit)	$C_{80}H_{144}O_{40}Ti_8$
Formula weight	2129.18
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	orthorhombic
Space group	<i>Pbca</i> (no. 61)
Unit cell dimensions	
a (Å)	30.464(4)
b (Å)	27.361(4)
<i>c</i> (Å)	32.549(4)
Volume (Å <sup>3</sup> )	27130.42(629)
Z	8
$D_{\text{calc}}$ (Mg/m <sup>3</sup> )	1.222
Absorption coefficient (mm <sup>-1</sup> )	0.52
<i>F</i> (0 0 0)	10 552
Crystal size (mm)	$0.30 \times 0.25 \times 0.20$
Theta range for data collection (deg)	3.30-28.56
Index ranges	
h	-40 to 29
k	-36 to 34
l	-42 to 43
Reflections collected	181 753
Independent reflections $[R_{int}]$	32 502 [0.0857]
Refinement method	full-matrix least-squares on $F^2$
Data/parameters/restraints	32 502/1627/90
Goodness-of-fit on $F^2$	1.086
Final R indices $[I > 2 \text{sigma}(I)]$	$R_1 = 0.0999; wR_2 = 0.2523$
R indices (all data)	$R_1 = 0.1587; wR_2 = 0.3132$
Largest difference between	3.341; -0.754
peak and hole	

 $R_1 = \sum (||F_0| - |F_c||) / \sum |F_0|.$ 

 $wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum (w|F_o|^2)^2\right]^{1/2}.$ 



Fig. 1. Crystal structure of 1 with the atom numbering scheme, Bu<sup>t</sup> groups have been omitted for clarity.

## 2.1.3. $Ti_8O_8(OOCC(CH_3)_2Et)_{16}$ (3)

Yield: 0.30 g (29.0%). *Anal.* Calc. for  $C_{81}H_{146}O_{40}T_{i8}$ : C, 48.99; H, 7.47; Ti, 16.30. Found: C, 48.77; H, 7.70; Ti, 16.06%. IR (KBr, cm<sup>-1</sup>) 1552 (s, COO), 1411 (s, COO), 1417 (m, COO), 1203 (m, C–Me<sub>3</sub>), 756 (m, Ti– O), 641 (m, Ti–O), 552 (m, Ti–O). <sup>13</sup>C NMR (solid,  $\delta$ , ppm) 9.1, 33.9 (Et), 24.5 (CH<sub>3</sub>), 43.3, 43.1 (C–(CH<sub>3</sub>)<sub>2</sub>Et), 188.0, 186.5 (COO).

Table 2

Atomic coordinates of the  $[Ti_8(\mu_2\text{-}O)_8(O_2C)_{16}]$  cluster  $(\times 10^4)$  and equivalent isotropic displacement parameters  $(\mathring{A}^2\times 10^3)$  for glow

	x	У	Ζ	$U_{\rm eq}$
Ti1	1596(1)	5768(1)	5804(1)	31(1)
Ti2	2119(1)	6119(1)	4945(1)	30(1)
Ti3	3142(1)	6493(1)	4716(1)	28(1)
Ti4	4033(1)	6734(1)	5285(1)	31(1)
Ti5	4329(1)	6473(1)	6246(1)	29(1)
Ti6	3768(1)	6206(1)	7098(1)	29(1)
Ti7	2757(1)	5809(1)	7321(1)	28(1)
Ti8	1807(1)	5865(1)	6810(1)	29(1)
01	1981(1)	6137(1)	5463(1)	30(1)
O2	2742(1)	6159(1)	4977(1)	29(1)
O3	3475(1)	6708(1)	5171(1)	29(1)
O4	4047(1)	6387(1)	5789(1)	28(1)
O5	3844(1)	6451(1)	6612(1)	30(1)
O6	3228(1)	5863(1)	7024(1)	29(1)
<b>O</b> 7	2339(1)	6042(1)	6937(1)	28(1)
O8	1910(1)	5716(1)	6244(1)	30(1)
O11	1128(1)	5828(1)	5314(1)	38(1)
O12	1483(1)	6091(1)	4758(1)	38(1)
O21	1793(1)	5158(1)	5519(1)	35(1)
O22	2116(1)	5383(1)	4928(1)	32(1)
O31	2222(1)	6057(1)	4298(1)	40(1)
O32	2904(1)	6318(1)	4160(1)	36(1)
O41	2094(1)	6840(1)	4844(1)	38(1)

Table 2 (continued)							
	X	У	Ζ	$U_{ m eq}$			
O42	2767(1)	7105(1)	4687(1)	31(1)			
O51	3586(1)	6948(1)	4369(1)	35(1)			
O52	4158(1)	7116(1)	4775(1)	41(1)			
O61	3561(1)	5930(1)	4638(1)	36(1)			
O62	4174(1)	6108(1)	4984(1)	38(1)			
O71	4725(1)	6792(1)	5340(1)	38(1)			
O72	4920(1)	6518(1)	5960(1)	38(1)			
O81	4005(1)	7373(1)	5595(1)	37(1)			
O82	4284(1)	7204(1)	6214(1)	38(1)			
O91	4721(1)	6653(1)	6765(1)	38(1)			
O92	4313(1)	6512(1)	7326(1)	40(1)			
O101	4464(1)	5773(1)	6378(1)	36(1)			
O102	4123(1)	5602(1)	6970(1)	35(1)			
0111	3750(1)	5931(1)	7704(1)	41(1)			
O112	3095(1)	5584(1)	7821(1)	36(1)			
0121	3441(1)	6783(1)	7327(1)	36(1)			
O122	2796(1)	6493(1)	7549(1)	36(1)			
0131	2216(1)	5761(1)	7735(1)	33(1)			
O132	1595(1)	5954(1)	7393(1)	35(1)			
O141	2609(1)	5112(1)	7181(1)	34(1)			
O142	1917(1)	5161(1)	6944(1)	34(1)			
O151	1153(1)	5592(1)	6717(1)	35(1)			
0152	1088(1)	5393(1)	6052(1)	40(1)			
O161	1549(1)	6512(1)	6644(1)	33(1)			
O162	1313(1)	6391(1)	5998(1)	36(1)			
C11	1143(2)	5979(2)	4959(2)	36(1)			
C21	1951(2)	5067(2)	5163(2)	34(1)			
C31	2531(2)	6133(2)	4061(2)	37(1)			
C41	2354(2)	7162(2)	4716(2)	32(1)			
C51	3914(2)	7192(2)	4464(2)	34(1)			
C61	3930(2)	5820(2)	4782(2)	37(1)			
C71	5005(2)	6670(2)	5607(2)	34(1)			
C81	4129(2)	7496(2)	5950(2)	36(1)			
C91	4658(2)	6687(2)	7146(2)	37(1)			
C101	4386(2)	5497(2)	6677(2)	33(1)			
C111	3491(2)	5688(2)	7919(1)	33(1)			
C121	3084(2)	6827(2)	7517(2)	35(1)			
C131	1819(2)	5890(2)	7727(2)	31(1)			
C141	2258(2)	4919(2)	7050(1)	31(1)			
C151	963(1)	5381(2)	6426(1)	31(1)			
C161	1344(2)	6644(2)	6322(2)	35(1)			

 $U_{\rm eq}$  is defined as one third of the trace of the orthogonalized Uij tensor.

#### 2.2. X-ray crystallography

The diffraction data were collected at 100(2) K for a  $0.30 \times 0.25 \times 0.20$  mm single crystal using Kuma CCD diffractometer, Mo K $\alpha$  radiation  $\lambda = 0.71073$  Å. The 181753 reflections were measured with the  $\omega - 2\theta$  method. A shape-based absorption correction was applied for 1 (RED167 package of programs, Oxford Diffraction, 2000) with the maximum and minimum transmissions of 0.9037 and 0.8603. The structure was solved by direct methods and refined with a full-matrix least-squares procedure on  $F^2$  using the shelx-97 program package [18]. Details of the data collection and structure refinement are presented in Table 1.

Table 3 Selected bond distances  $[\mathring{A}]$  and angles  $[^\circ]$  for 1

Distances [Å]	
<i>Ti-</i> (μ- <i>O</i> )	
Til-O1	1.904(3)
Ti1–O8	1.727(3)
Ti2–O1	1.738(3)
Ti2–O2	1.904(3)
Ti3–O2	1.746(3)
Ti3-O3	1.892(3)
Ti4-O3	1.741(3)
114-04	1.896(3)
115-04	1.733(3)
TID-05	1.900(3)
Ti6-05	1./31(3) 1.010(2)
Ti7_06	1.910(3) 1.734(3)
Ti7_00	1.734(3) 1.804(3)
Ti8_O8	1.094(3) 1.015(3)
Ti8_07	1.739(3)
	1.757(5)
Ti-(OOCBu <sup>t</sup> )	
Til-Oll	2.146(3)
Til-O21	2.001(3)
Ti1-0152	2.025(3)
Ti1–O162	2.013(3)
Ti2-022	2.015(3)
Ti2-012	2.030(3)
Ti2-041	2.002(3)
Ti2-051	2.138(4) 2.156(2)
Ti3-031	2.130(3) 2.021(2)
Ti3_042	2.031(3) 2.006(3)
Ti3-O61	2.000(3) 2.014(3)
Ti4-062	2.014(3) 2.020(3)
Ti4-O52	1.996(3)
Ti4-071	2.120(3)
Ti4-O81	2.021(4)
Ti5–O72	2.031(3)
Ti5–O82	2.006(3)
Ti5-O101	2.007(3)
Ti5-O91	2.128(3)
Ti6-O111	2.112(3)
Ti6-O121	2.010(3)
Ti6-O102	2.019(3)
Ti6–O92	2.003(3)
Ti7–O122	2.016(3)
Ti7–O112	2.024(3)
Ti7-O141	2.013(3)
117–0131	2.134(3)
T18-0142	2.003(3)
T18-0132	2.018(3)
Ti8-0151	2.152(3)
116-0101	2.010(5)
Ti–Ti	
Ti1–Ti2	3.358(12)
Ti2–Ti3	3.366(12)
Ti3–Ti4	3.352(12)
Ti4-Ti5	3.333(12)
Ti5–Ti6	3.338(12)
116–117	3.344(12)
11/-118	3.341(12)
$\frac{118-111}{11}$	3.348(13)
<i>Ti</i> -( <i>µ</i> - <i>O</i> )- <i>Ti</i>	124 24(10)
111-01-112 Tia 02 Tia	134.34(18)
112-02-113	134.45(17)

Table 3 (continued)

Angles [°]	
Ti3–O3–Ti4	134.67(18)
Ti4-O4-Ti5	133.32(17)
Ti5–O5–Ti6	133.59(18)
Ti6–O6–Ti7	133.14(18)
Ti7–O7–Ti8	133.63(18)
Ti8–O8–Ti1	133.60(18)

#### 3. Results and discussion

# 3.1. Synthesis

 $Ti(OPr^{i})_{4}$  was added to a stirred solution of HOOCR ( $R = Bu^t$ ,  $CH_2Bu^t$ ,  $C(CH_3)_2Et$ ) in toluene, (molar ratio alkoxide/acid = 1:2, Ar atmosphere, room temperature (RT)). At the beginning, the reaction mixture became turbid but after 2 h, a clear solution was formed. Colorless crystals were grown by slow evaporation (glovebox) of the solvent over 2-3 days. Based on the results of elemental analysis, the general formula of the synthesized complexes was determined as  $[Ti_8O_8(OOCR)_{16}]$ , where  $R = Bu^t$  (1),  $CH_2Bu^t$  (2),  $C(CH_3)_2Et$  (3). However microanalysis data suggest the presence of solvent molecules (toluene) in the crystal lattice of 1. Single crystals, suitable for crystallographic studies were obtained only for compound 1, but their stability was very low, and they were destroyed in air (RT), with the formation of a white crystalline powder. During the crystallization of 2 and 3 only crystalline powder was formed. Compounds 1-3 were insoluble in aliphatic and sparingly soluble in aromatic solvents.

#### 3.2. Crystal structure

Due to the low stability of 1 in the air at RT, the X-ray measurements were carried out at low temperature (~100 K). The poor quality of crystals obtained for 2 and 3 made their crystallographic studies impossible. The chemical unit of 1, with the atom-numbering scheme, is shown in Fig. 1. Crystal data and atomic coordinates are listed in Tables 1 and 2. The selected bond distances and angles are presented in Table 3.

The ring molecule of the reported complex is composed of eight distorted [TiO<sub>6</sub>] octahedra linked by two  $\mu_2$ -O (*cis*) and four  $\mu$ -O (carboxylate) bridges (Fig. 1, Table 3). The [Ti<sub>8</sub>( $\mu_2$ -O)<sub>8</sub>] ring is not planar. The Ti<sub>8</sub> ring conformation with alternating positive and negative values of Ti–Ti–Ti–Ti torsion angles resembles the cyclohexane chair conformation, but their absolute values vary from 5.11(7)° for Ti1–Ti2–Ti3–Ti4 to 37.14(7)° for Ti6–Ti7–Ti8–Ti1. The *rms* deviation of Ti ions from the Ti<sub>8</sub> best plane is 0.2073 Å.

Eight of the bridging carboxylates are positioned approximately in the ring plane (Fig. 1), the dihedral angles between the Ti<sub>2</sub>COO planes and the best plane of the Ti<sub>8</sub> ring range from  $8.88(5)^{\circ}$  to  $21.85(3)^{\circ}$ , with the mean value being  $16.5(4)^{\circ}$ . The remaining eight carboxylates form the bridges between the Ti ions alternating between the two sides of the ring plane and are approximately perpendicular to that plane. The dihedral angles between the Ti<sub>8</sub> best plane and the Ti<sub>2</sub>COO planes vary from  $72.81(7)^{\circ}$  to  $81.29(6)^{\circ}$ , with a mean value of  $77.8(3)^{\circ}$ .

The bridging oxygen atoms in the  $[Ti_8(\mu_2-O)_8]$  rings form alternating longer and shorter Ti-O bonds, the average Ti-O distances and esd in the series being 1.904(8) and 1.735(7) Å for the longer and shorter bonds, respectively. The angles in that ring vary from 133.15(1)°-134.67(1)° to 132.42(1)°-136.28(1)° for Ti-O-Ti and Ti-Ti-Ti, respectively (Table 3). Also the oxo bridges form alternating shorter 1.997(3)-2.031(3) Å and longer 2.114(3)-2.156(3) Å Ti-O bonds. In the octahedral environment of each Ti ion, they occupy the trans positions relative to the shorter and longer carboxylate Ti-O bonds mentioned above. The other two trans trimethyl acetate bridges are positioned outside the  $[Ti_8(\mu_2-O)_8]$  rings, and the corresponding Ti-O(carboxylate) distances vary in the range 2.002(3)-2.013(3) and 2.013(3)-2.031(3) A.

Kickelbick and Scubert [16] reported an oligomeric ring structure of the general formula  $[Ti_9O_8-(OPr^i)_4(OOCC(Me)=CH_2)_{16}]$  (monoclinic, space group *Ia*). That complex consisted of a ring of nine  $[TiO_6]$  octahedra linked by six  $\mu_2$ -O, two  $\mu_3$ -O and 16  $\mu_2$ -O(OOC) bridges. Also in that case, the non-equivalent Ti–O bonds of  $\mu_2$ -oxo bridges (1.90–1.93 and 1.72–1.74 Å) were compensated by asymmetric Ti–O distances of *trans* carboxylate groups (1.97–2.11 and 2.09–2.16 Å). Analysis of the literature reports exhibited that in another type of  $[\text{Ti}_x(\mu_n\text{-}O)_y]$  (n = 2, 3) cluster the Ti–O distances were shorter, e.g., in the structure of ( $[\text{Ti}_6\text{O}_6(\text{OPr}^i)_6(\text{O}_2\text{CBu}^i)_6]$ , Ti-( $\mu_3$ -O) = 1.878(4), 1.890(2) and 2.142(3) Å [14], and in  $[\text{Ti}_6\text{O}_4(\text{Opr}^n)_8(\text{O}_2\text{CR})_8]$ (R = CH<sub>3</sub>, Ph), Ti-( $_2$ -O) = 1.724(6)–1.768(2) and 1.900(6)–1.942(2) Å, and Ti-( $\mu_3$ -O) = 1.911(2), 1.941(2) and 2.082(2) Å [9,16].

The low temperature experiment for the reported complex 1 allowed building a satisfactory model for the majority of the OOCBu<sup>t</sup> moieties. Only for two Bu<sup>t</sup> groups the rotational disorder was accounted for in the final model. Both these groups do not participate in intermolecular interactions between the adjacent rings. The complex molecules of 1 form some hydrophobic interactions with the adjacent molecules via their Bu<sup>t</sup> groups on the side surfaces and around the ring. However, the important component of the packing interactions is due to the toluene molecules found in the structure. Two of them are positioned near the ring center, between the OOCBu<sup>t</sup> moieties perpendicular to the molecule ring plane. Another two toluene molecules participate in the packing interactions involving the carboxylate ligands positioned in the ring plane.

#### 3.3. Analysis of NMR data

The <sup>13</sup>C NMR spectroscopy in the solid state have been used to study the structural similarities between 1, 2 and 3. Also, <sup>1</sup>H and <sup>13</sup>C NMR spectra of  $[D_8]$ toluene solutions of these compounds were registered in

Table 4

The solid-state and solution NMR studies of  $[Ti_8O_8(OOCR)_{16}]$  (R = Bu<sup>t</sup> (1), CH<sub>2</sub>Bu<sup>t</sup> (2), C(CH<sub>3</sub>)<sub>2</sub>Et (3))

Compound	Method	∂ [ppm]							
		CH <sub>3</sub> (Et)	CH <sub>2</sub> (Et)	$CH_2$	CH <sub>3</sub> (CMe <sub>2</sub> )	$CH_3$ (Bu <sup>t</sup> )	C (CMe <sub>2</sub> )	C (Bu <sup>t</sup> )	C (COO)
(1)	$^{13}C - s. st.$					26.5		38.7	186.7
	$^{13}C - C_7D_8$					27.2		39.3	188.2 187.4
	$^{1}H-C_{7}D_{8} \\$					27.4 1.2 (s) 1.1 (s)		39.5	188.6
(2)	<sup>13</sup> C – s. st.			49.5		29.8			181.5
	$^{13}C-C_{7}D_{8} \\$			48.9 50.1		30.1		30.9 31.1	183.6 182.7
	$^{1}H-C_{7}D_{8} \\$			2.3 (s)		1.2 (s)		51.1	102.7
(3)	$^{13}C - s. st.$	9.1	33.9		24.5		43.3		186.5
	$^{13}C - C_7 \ D_8$	9.7	34.3		25.0		43.1 43.6		188.0 187.4
		10.3	34.6		25.6		43.7		189.0
	$^{1}H-C_{7}D_{8} \\$	1.1 (t) $J_{\rm H-H} = 4.0~{\rm Hz}$	1.7 (q) J <sub>H-H</sub> = 4.0 Hz		1.3 (s)				

The solid-state <sup>13</sup>C NMR spectra were registered on a Bruker AMX 300, solution <sup>1</sup>H, <sup>13</sup>C NMR spectra ([D<sub>8</sub>] toluene) were recorded using a 5-mm solution probe on a Varian Gemini 200 spectrometer.

order to determine the structural changes of the investigated compounds after their solubilization. The observed chemical shifts are listed in Table 4.

The signals due to the carbon atoms of coordinated carboxylate groups are located between 180.3 and 188.2 ppm in the solid-state <sup>13</sup>C NMR spectra of 1-3. In spectra of 1 and 3, the carbon atoms show two lines of equal intensity at 186.6 and 188.1 ppm, whereas a wide single signal at 180.5 ppm is found in the spectrum of 2 (Table 4). However, a detailed analysis of the C(COO) peak in the spectrum of this compound revealed that it also consists of two components, with  $\delta$  = 180.3 and 180.7 ppm. Considering crystallographic data, the above phenomenon can be explained by the presence of two different types of carboxylate groups in the structures of 1-3. Crystallographic data showed that the COO groups formed the bridges in the plane of the  $[Ti_8(\mu_2 - O)_8]$  ring, exhibiting asymmetry of the C-O bond lengths, 1.237(6)-1.250(5) (shorter) and 1.263(6)–1.299(6) A (longer). Differences in the length of bonds formed by the carboxylate group bridges outside of the ring plane were smaller (1.258(6)-1.276(5))and 1.261(5)-1.275(6) Å). The <sup>13</sup>C NMR studies suggest that 1 and 3 form a similar type of carboxylate group interaction in [Ti<sub>8</sub>O<sub>8</sub>(OOCR)<sub>16</sub>] molecules. Undetected splitting of the C(COO) signal, observed in the <sup>13</sup>C NMR spectrum of 2, can be interpreted as a result of the smaller differences between the length of the C–O bonds formed by COO groups outside compared to within the  $[Ti_8(\mu_2-O)_8]$  ring plane.

Analysis of <sup>13</sup>C NMR spectra of 1-3 [D<sub>8</sub>]toluene solutions shows clear similarities in the chemical shift and splitting of the resonance signals with their analogs in the solid state spectra (Table 4). The NMR data reveal the presence of two types of carboxylate groups in the structure of the studied compounds, which is consistent with the X-ray structure of 1. In <sup>1</sup>H NMR spectra of 1-3 [D<sub>8</sub>]toluene solutions, only the signals attributed to appropriate hydrocarbon groups were detected.

#### 3.4. Infrared spectra studies

IR spectra of the studied carboxylates were registered at liquid nitrogen temperature (LNT), in conditions analogous to the single crystal X-ray measurements. In order to study similarities between the structures of 1-3, a detailed analysis of IR spectra in the following ranges (a)  $1350-1600 \text{ cm}^{-1}$  and (b)  $400-900 \text{ cm}^{-1}$  have been carried out. The wavenumbers of absorption bands registered in the above regions are listed in Table 5.

#### 3.4.1. Stretching frequencies of carboxylate ligands

The split bands attributed to  $v_{as}(COO)$  and  $v_s(COO)$  vibrations were found in the ranges 1500–1575 and 1400–1440 cm<sup>-1</sup> (Table 5). Values of the  $\Delta[v_{as}-(COO) - v_s(COO)]$  parameter, calculated for the suitable

#### Table 5

Wavenumbers  $[cm^{-1}]$  for the vibrations of acetate ions and oxo bridges (M–O–M) in LNT spectra of  $[Ti_8O_8(OOCR)_{16}]$  (where R = Bu' (1),  $CH_2Bu'$  (2),  $C(CH_3)_2Et$  (3))

Modes	$1  [cm^{-1}]$	<b>2</b> [cm <sup>-1</sup> ]	$3  [cm^{-1}]$
			1574 (m)
$v_{\rm as}(\rm COO)$	1546 (s)	1552 (s)	1552 (s)
		1540 (s)	
	1512 (m)	1507 (m)	1519 (m)
$\delta_{as}(CH_3), \delta_{as}(CH_2)$	1486 (m)	1478 (m)	1477 (m)
	1458 (w)	1463 (m)	1455 (m)
$v_{\rm s}({\rm COO}),  \delta_{\rm as}({\rm CH}_3)$	1429 (s)	1421 (s)	1436 (m)
	1419 (m)	1405 (m)	1413 (m)
$\delta(CH_3)$	1378 (m)	1376 (m)	1388 (m)
$\delta(CH_3)$			1371 (m)
$\delta(CH_3)$	1361 (m)	1357 (m)	1367 (m)
vas(Ti–O–Ti)(µ3-O)	750 (s)	754 (m)	758 (m)
		714 (m)	722 (m)
$\delta(OCO)$	611 (s)		641 (m)
$\delta(OCO)$	583 (m)	601 (s)	552 (w)
$\rho$ (OCO); out of plane	504 (m)	507 (w)	502 (m)
$\rho(OCO)$ ; out of plane	481 (m)	480 (w)	478 (m)
v(CCC)		460 (w)	450 (w)
$\rho$ (OCO); in plane	443 (m)	435 (w)	435 (vw)
$\rho(OCO)$ ; in plane	431 (w)	429 (w)	420 (w)

band components were 116 and  $94 \text{ cm}^{-1}$ , 116 and 107 cm<sup>-1</sup> for **1** and **3**, as well as 131 and 103 cm<sup>-1</sup> for **2**. Comparison of the above results with the literature data [19–22] indicate that the detected  $v_{as}$ (COO) frequencies and  $\Delta$  parameter values correspond to bidendate carboxylate groups, participating in *syn–syn* bridges. The different interactions of COO ligands in the structure of the studied compounds are the main factor that causes splitting of the structural and NMR data presented in this paper.

# 3.4.2. Absorption bands between 400 and 900 cm<sup>-1</sup>

The bands due to vibrations of carboxylate ligands and M–O–M titanium-oxide bridges of  $[Ti_8(\mu_2-O)_8]$ rings have been found in the range 400–900 cm<sup>-1</sup> (Table 5). According to the literature data [19,22], their frequencies can be assigned to COO bending ( $\delta_s$ (O-CO) = 551–641 cm<sup>-1</sup>) and rocking ( $\rho$ (COO) = 419– 507 cm<sup>-1</sup>) modes.

The band for Ti–O–Ti stretching modes ( $v_a$ (Ti–O–Ti)) was found in the range 714–758 cm<sup>-1</sup> (Table 5). According to Nakamoto's report on vibrational spectra of complexes containing M-( $\mu_2$ -O) bridges in their structure [19], the bands assigned to M–O–M asymmetric vibrations appear in the IR spectrum, while symmetric ones appear in the Raman spectrum. The frequency for the bands mentioned above depends on the type of oxygen bridge and the number of concomitant carboxylate bridges. For the linear M-( $\mu_2$ -O) monobridges  $v_a$ (M–O–M)  $\cong$  843–885 cm<sup>-1</sup>, and for non-linear one,

 $v_a(M-O-M) \cong 827 \text{ cm}^{-1}$ . Presence of the oxygen bridge in the vicinity of carboxylate bridges causes the frequency shift of the  $v_a(M-O-M)$  vibrations towards 749–772 cm<sup>-1</sup> [19]. In IR spectra of 2 and 3, the appearance of  $v_a(\text{TiOTi})$  bands at 714, 754 cm<sup>-1</sup> (2), and at 722, 758 cm<sup>-1</sup> (3) was observed. That confirms the formation of non-linear Ti–O–Ti bridges near the Ti-carboxylate ones in the structure of these compounds, similar to those found in the structure of 1.

The possible low temperature phase transition and thermal stability of Ti–O bonds in  $[Ti_8(\mu_2-O)_8]$  clusters have been investigated by means of variable temperature IR spectroscopy (VT-IR). Analysis of the dependence between the frequency of Ti–O–Ti motions (v<sub>a</sub>(TiOTi)) and the temperature exhibited only insignificant shifts  $(6-7 \text{ cm}^{-1})$  of this band towards higher wavenumbers in the spectra of 2 and 3. These results suggest that the stability of  $[Ti_8(\mu_2-O)_8]$  rings is very high and a temperature phase transition does not occur. The temperature evolution of the  $v_a$ (TiOTi) frequency, observed in VT-IR spectra of 1, was significantly higher (15- $16 \text{ cm}^{-1}$ ). Moreover only for this compound, clear changes in the diagram slopes between 0 and 60 °C were observed (Fig. 2). Considering crystallographic and TGA data, the latter effect can be explained by the loss of solvent molecules from the crystal lattice of 1.

#### 3.5. Thermal characterization

The thermal decomposition mechanism of Ti(IV) ring carboxylates was studied using thermogravimetric and differential thermal analysis (TG/DTA) methods over



Fig. 2. Temperature evolution of the  $v_a$ (TiOTi) band in the VT-IR spectra of [Ti<sub>8</sub>O<sub>8</sub>(O<sub>2</sub>CBu')<sub>16</sub>] (SPECTRUM 2000, KBr, -175 to 250 °C).

the temperature range 25–550 °C with a heating rate of 3 °C min<sup>-1</sup> under a nitrogen atmosphere. The TGA/DTA data of 1 show that the decomposition proceeded in four endothermic stages, with maxima at 63, 260, 370 and 421 °C, with a weight loss of 73.4%. A multistep thermal decomposition was also observed for **2** and **3**; the maxima of endothermic stages were found at 108, 311, 381, 417 °C (weight loss: 70.1%) for **2**, and 300, 340, 393, 410 °C (weight loss: 71.2%) for **3**. Thermogravimetric analysis exhibited that the pyrolysis of **1–3** proceed with their complete conversion to TiO<sub>2</sub>. Moreover, one endothermic peak near 63 °C is observed for **1**, which can be explained by the loss of solvent molecules from the crystal lattice of this compound.

Table 6

The mass spectra of  $[Ti_8O_8(OOCR)_{16}]$ , where R = Bu'(1),  $CH_2Bu'(2)$ ,  $C(Me)_2Et(3)$ , registered between 150 and 350 °C (MS-EI 70 eV)

	Fragmentation Ion	m/z	<i>T</i> [°C]							
			150	200	240	260	280	300	320	350
(1)	$[Ti_4O_4(O_2CBu')(O_2CH)_2]^+$	448	53.3	85.7						
	$[Ti_3O(O_2CBu')_2(O_2CCH_3)_2]^+$	480	100	100						
	$[Ti_8O_8(O_2CBu')_7(O_2CC_2H_2)]^+$	1286	15.3	30.4						
	$[Ti_8O_{10}(O_2CBu')_{10}]^+$	1554				5.7	43.9	38.1	32.2	28.9
	$[Ti_8O_{10}(O_2CBu')_{11}]^+$	1655						49.7	100	100
	$[Ti_8O_8(O_2CBu')_{14}]^+$	1926				11.0	10.6			
	$[Ti_8O_8(O_2CBu')_{15}]^+$	2027	5.5	29.4	100	100	63.2	14.6		
(2)	$[Ti_2O_2(O_2CCH_2Bu')_2]^+$	356	68.8	62.8				6.6		
	$[Ti_8O_8(O_2CCH_2Bu^t)(O_2CCH_3)_3(O_2CH)]^+$	849			41.1	41.8	35.0	35.2	22.1	1.7
	$[Ti_8O_8(O_2CCH_2Bu^t)_3(O_2CC_4H_8)]^+$	956		3.9	36.5	43.5	6.2	14.2	8.2	
	$[Ti_8O_8(O_2CCH_2Bu^t)_4(O_2CCH_3)_4(O_2CC_3H_6)]^+$	1064			19.5	14.5	4.3	5.8	6.7	
	$[Ti_8O_8(O_2CCH_2Bu^t)_9(O_2CCH_3)(O_2CCH)_2]^+$	1696		5.6	21.0	20.3	17.6	16.7	18.8	1.1
	$[Ti_8O_8(O_2CCH_2Bu^t)_{10}(O_2CH)_2(O_2CCH_3)]^+$	1811		29.6	100	100	100	70.7	90.4	4.6
	$[Ti_8O_8(O_2CCH_2Bu')_{14}(O_2CCH_3)_2]^+$	2241		6.6	75.6	58.4	28.2	20.3	11.4	
(3)	$[Ti_2O(O_2CCMe_2Et)(O_2CCH)(O_2CC_2H_4)]^+$	356	100	100						
	$[Ti_8O_8(O_2CCMe_2Et)(O_2CCH_3)_3(O_2CH)]^+$	849			37.9	15.4	10.2	3.1	6.2	7.1
	$[Ti_8O_8(O_2CCMe_2Et)_2(O_2CCH_3)_4(O_2CC_3H_6)]^+$	1064			56.3	54.4	45.0	13.2	13.7	1.5
	$[Ti_8O_8(O_2CCMe_2Et)_8(O_2CBu')]^+$	1534			22.4	13.3	10.5	6.4	7.7	8.2
	$[Ti_8O_8(O_2CCMe_2Et)_9(O_2CCH_3)(O_2CH)_2]^+$	1696			15.8	10.6	6.8	3.6	9.8	13.6
	$[Ti_8O_8(O_2CCMe_2Et)_9(O_2CCH_3)_3(O_2CH)_2]^+$	1814		2.8	41.7	20.4	11.4	7.4	33.0	41.1
	$[Ti_8O_8(O_2CCMe_2Et)_{14}(O_2CCH_3)_2]^+$	2240		4.7	100	100	100	100	100	100

Analysis of MS-EI spectra, registered in the temperature range 150-350 °C confirms the formation of the  $[Ti-(\mu_2-O)]_8$  rings stabilized by carboxylate bridges in the structures of all the studied compounds. Results of MS-EI experiments are presented in Table 6. Multinuclear titanium species were detected below 200 °C, which indicates partial decomposition of these compounds at lower temperatures. The characteristic peaks at m/z = 2027 ([Ti<sub>8</sub>O<sub>8</sub>(OOCBu<sup>t</sup>)<sub>15</sub>]<sup>+</sup>), m/z = 1811 $([Ti_8O_8(OOCCH_2Bu^t)_{10}(OOCCH_3)(OOCH)_2]^+)$ and m/z = 2240 $([Ti_8O_8(OOCC(Me)_2Et)_{14}(OOCCH_3)_2]^+)$ with 100% intensity appear above 240 °C. Also TG/ DTA data show the beginning of the mass detachment of samples 1–3 at this temperature. Simultaneously, the presence of multinuclear fragmentation ions above 240 °C indicates their thermal stability, which may be useful for their transport in the gas phase. That factor may be important for application of these compounds as precursors in the chemical vapor deposition methods. Comparison of 1–3 MS data showed that the thermal stability of multinuclear Ti(IV) fragmentation ions increases in the row  $Bu^{t} < CH_{2}Bu^{t} < C(Me)_{2}Et$ .

#### 4. Conclusions

New titanium multinuclear Ti(IV) oxo carboxylates, with the general formula  $[Ti_8O_8(OOCR)_{16}]$ , where  $R = Bu^{t}$  (1),  $CH_{2}Bu^{t}$  (2),  $C(CH_{3})_{2}Et$  (3), have been synthesized in a reaction of titanium isopropoxide  $(Ti(OPr')_4)$  with suitable organic acids, in the molar ratio 1:2. X-ray studies of 1 revealed that the structure of this compound is formed by rings, composed of eight distorted [TiO<sub>6</sub>] octahedra connected by two  $\mu_2$ -O and four  $\mu_2$ -O (carboxylate) bridges. Structural data exhibited the presence of solvent molecules (toluene) in the crystal lattice of 1. The thermogravimetric and IR studies proved that solvent molecules are removed from the structure of this compound between 0 and 60 °C. The obtained results prove that the low stability of the crystals of 1 is caused by the presence of solvent molecules in the crystal lattice and their loss at room temperature. Spectral analysis of 1-3 powders showed that these compounds form a ring structure of the general formula  $[Ti_8O_8(OOCR)_{16}]$ . Variable temperature IR studies indicate the high thermal stability of the studied multinuclear Ti(IV) oxo carboxylates. Analysis of MS-EI data suggests that during the thermal decomposition of 1-3, volatile multinuclear Tioxide species are formed above 240 °C. The stability of these species changes in the row  $Bu^t < CH_2Bu^t <$ C(Me)<sub>2</sub>Et.

#### 5. Supplementary data

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 256553. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam. ac.uk or www: http://www.ccdc.cam.ac.uk).

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