

## Synthesis, structure characterization and thermal properties of $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{OOCCH}_2^t\text{Bu})_9(\mu_2\text{-OH})_3]_2$

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### ABSTRACT

Oxo/hydroxo zirconium(IV) complex of the general formula  $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{OOCCH}_2^t\text{Bu})_9(\mu_2\text{-OH})_3]_2$  has been isolated, when  $\text{Zr}(\text{O}^i\text{Pr})_4$  reacted with a 2-fold excess of 3,3-dimethylbutyric acid. Single crystal X-ray diffraction data, collected at 103 and 153 K, showed that the studied compound crystallizes in hexagonal system ( $P6_3/m$  (no. 176)). Structure consists of dimers composed of  $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{OOCCH}_2^t\text{Bu})_9]$  sub-units, linked by six  $\mu_2\text{-OH}$  bridges. Infrared spectroscopic studies proved the presence of hydroxo groups in the structure of studied clusters and formation of different types of oxo/hydroxo bridges. The application of variable temperature infrared spectroscopy and differential scanning calorimetry revealed that the structure of this complex undergoes the phase transitions at 143–183 and 203–293 K. Comparison of spectral and crystallographic data suggests that these phase transitions might be related to changes in the strength of Zr–O bonds of  $\mu_2\text{-OH}$  bridges linking complex sub-units, and change in symmetry of the crystal lattice (from hexagonal to trigonal). Analysis of thermogravimetric data showed that decomposition of  $[\text{Zr}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4(\text{OOCCH}_2^t\text{Bu})_9(\mu_2\text{-OH})_3]_2$  proceeds with complete conversion to  $\text{ZrO}_2$  (monoclinic form) between 603 and 803 K.

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### 1. Introduction

Synthesis, structure, and properties of zirconium oxo clusters have been studied extensively in a search of the novel types of hybrid materials having interesting optical, magnetic, and catalytic properties [1–5]. Recently Kicelbick, Schubert et al. have described syntheses and crystal structures of the group of multinuclear Ti(IV) and Zr(IV) oxo acrylate or methacrylate derivatives, which were efficiently used as sol–gel precursors in the fabrication of organic–inorganic materials [6–8]. According to these reports, the reaction of Zr(IV) isopropoxides with corresponding organic acids, using a molar ratio 1:4 and 1:16, respectively, leads to the formation of carboxylate derivatives of general formulas  $[\text{Zr}_6(\text{OH})_4\text{O}_4(\text{OMc})_{12}]$  or  $[\text{Zr}_4\text{O}_2(\text{OMc})_{12}]$  [6–8]. In the structure of  $[\text{Zr}_6(\text{OH})_4\text{O}_4(\text{OMc})_{12}]$ , zirconium atoms (coordination number 8) form hexanuclear cores with  $\mu_3\text{-oxo}$  and  $\mu_3\text{-hydroxo}$  bridges, which are stabilized by 12 methacrylate ligands. Three carboxylate ligands form the chelate interactions with Zr(IV) atoms, while other nine participate in *syn–syn* bridges. The reaction of  $\text{Zr}(\text{O}^i\text{Pr})_4$  with a 6.5-fold excess of acrylic acid, under the same conditions, proceeds with a formation of approximately 1:3 mixture of an amorphous powder and crystals [8]. The X-ray structural studies revealed the formation of dimers, composed of two  $[\text{Zr}_6$

$(\text{OH})_4\text{O}_4(\text{OAc})_{12}]$  units linked by four carboxylate bridges. Zr(IV) compounds, also formed by two multinuclear Zr(IV) sub-units linked by alkoxide bridges, were synthesized in the reaction of  $\text{Zr}(\text{O}^n\text{Bu})_4$  with 1.6 equiv. of methacrylic acid [9]. The use of ~16-fold excess of the methacrylic acid led to the formation of  $[\text{Zr}_4\text{O}_2(\text{OMc})_{12}]$  [6]. Literature reports concerning oxo zirconate acrylate or methacrylate derivatives, suggest that the type of the formed cluster depends on (a) the  $\text{M}(\text{OR})_4/\text{HOOCR}'$  ratio and (b) the kind of OR groups [9]. The application of sterically diverse carboxylic acids ( $\text{HOOCR}'$ ;  $\text{R}' = \text{H}, \text{CH}_3, ^i\text{Pr}, ^t\text{Bu}, \text{CH}_2^t\text{Bu}$ ) in the reaction with zirconium(IV) isopropoxide ( $[\text{Zr}(\text{O}^i\text{Pr})_4 \cdot \text{HO}^i\text{Pr}]_2$ , molar ratio 1:1) leads to the formation of the following products:  $[\text{Zr}_4\text{O}_2(\text{O}_2\text{CH})_2(\text{O}^i\text{Pr})_{10}]$ ,  $[\text{Zr}_3\text{O}(\text{O}_2\text{CCH}_3)_5(\text{O}^i\text{Pr})_5]$ ,  $[\text{Zr}_2(\text{O}^i\text{Pr})_6(\text{O}_2\text{C}^i\text{Pr})_2]$ ,  $[\text{Zr}_2\text{O}(\text{O}_2\text{C}^t\text{Bu})(\text{O}^i\text{Pr})_7](\text{HO}^i\text{Pr})_2$ ,  $[\text{Zr}_2\text{O}(\text{O}_2\text{CH}_2^t\text{Bu})_2(\text{O}^i\text{Pr})_6](\text{HO}^i\text{Pr})$  [10]. The use of the 2-fold excess of organic branched acids ( $\text{HOOCR}'$ ;  $\text{R}' = ^t\text{Bu}, \text{C}(\text{CH}_3)_2\text{Et}$ ) in the above reaction results in a formation of  $[\text{Zr}_6(\text{OH})_4\text{O}_4(\text{OOCR}')_{12}]$  ( $\text{R}' = ^t\text{Bu}, \text{C}(\text{CH}_3)_2\text{Et}$ ) clusters [11]. Also in this case, the hexanuclear zirconium core was linked by four  $\mu_3\text{-oxo}$  and four  $\mu_3\text{-hydroxo}$  bridges and stabilized by 12 carboxylate *syn–syn* bridges. Simultaneously, spectroscopic studies revealed that the more complicated type of multinuclear Zr(IV) oxo clusters was formed during the 1:2 reaction of  $\text{Zr}(\text{O}^i\text{Pr})_4$  with  $\text{HOOCCH}_2^t\text{Bu}$  [11]. Although the stability of single crystals at room temperature was sufficient, their crystal structure has not been solved. Therefore, the aim of the presented paper is the structural and spectral characterization of the multinuclear Zr(IV) oxo

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carboxylate derivatives, obtained in a reaction of  $Zr(O^iPr)_4$  with 2-fold excess of 3,3-dimethylbutyric acid under the inert atmosphere.

## 2. Results and discussion

### 2.1. Synthesis and spectral characterization

The studied complex was obtained in the 1:2 reaction of the zirconium isopropoxide ( $Zr(O^iPr)_4$ ) with 3,3-dimethylbutyric acid under Ar atmosphere at room temperature. The colorless crystals were isolated by slow evaporation (glovebox) of the solvent after 1 day. The general formula defined on the basis of the elemental analysis is  $Zr_6O_{29}C_{54}H_{103}$ , suggesting the possible formation of a similar type of cluster as described for  $[Zr_6(\mu_3-O)_4(\mu_3-OH)_4(OOCR')_{12}]$  ( $R' = ^iBu$ ,  $C(CH_3)_2Et$ ). However, the clear differences between IR spectra of synthesized compound and those reported in [11] indicate the formation of different type of structure (Fig. 1).

The synthesized complex has been characterized by multinuclear NMR spectroscopy in the solid phase and solution ( $[D_6]$  benzene) and chemical shifts of the resonance signals are listed in Table 1. The coordination effects were studied mainly as a result of the chemical shift of resonance signals descended from carbon atoms of carboxylate ligands. Three resonance signals attributed to carbon atoms of COO group were found at  $\delta = 174.7$ , 178.1, and 179.4 ppm (Table 1). Coordination of carboxylate groups caused the shift of resonance signals towards lower fields in comparison to the spectrum of 3,3-dimethylbutyric acid ( $\delta$  (COO) = 179.9 ppm). Simultaneously, analysis of chemical shifts of carboxylate carbon in spectra of dimeric complex and  $[Zr_6(\mu_3-O)_4(\mu_3-OH)_4(OOCR')_{12}]$  ( $R' = ^iBu$ ,  $\delta = 184.5$ , 183.9 ppm,  $C(CH_3)_2Et$ ),  $\delta = 184.3$ , 183.9 ppm [11]) reveals that the shift of the resonance signals of COO group is significantly influenced by the type of the carboxylate ligand. Moreover, splitting of the resonance signals of carboxylate atoms suggests that carboxylate ligands form non-equivalent interactions with zirconium ions of  $[Zr_6-(\mu_3-O)_4(\mu_3-OH)_4]$  cores.

Analysis of  $^{13}C$  NMR data, registered in  $[D_6]$  benzene solution (Table 1) revealed no significant difference in chemical shifts of resonance signals attributed to the methyl, methylene, and butyl

**Table 1**

Results of NMR studies of compound synthesized in the reaction  $Zr(O^iPr)_4$  with  $HOOCCH_2^iBu$ , reported in this paper.

Method	$\delta$ (ppm)			
	CH <sub>2</sub>	CH <sub>3</sub> ( <sup>i</sup> Bu)	C ( <sup>i</sup> Bu)	C (COO)
<sup>13</sup> C-s.st	50.6	30.3	43.5	179.4
				178.1
				174.7
<sup>13</sup> C-C <sub>6</sub> D <sub>6</sub>	50.7	30.2		179.0
<sup>1</sup> H-C <sub>6</sub> D <sub>6</sub>	2.3	1.5		

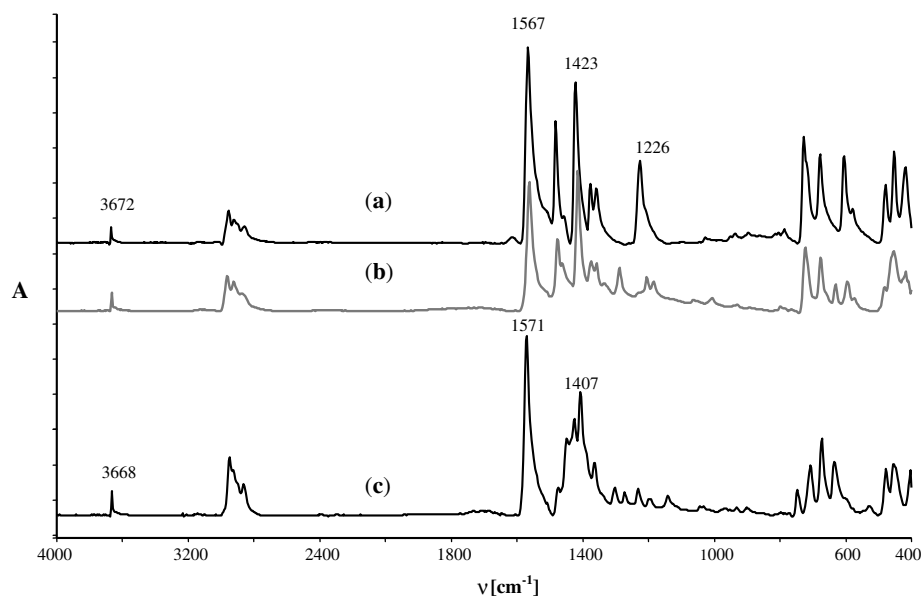
moiety of the  $-CH_2C(CH_3)_3$  group. Simultaneously, only a single peak assigned as the COO group ( $\delta = 179.0$  ppm) has been found. This indicates that the stable and highly symmetrical molecules of the synthesized complex exist also in solution.

The XRD patterns, collected one week and one month after crystallization, proved the high stability of crystalline powders stored at room temperature on the air. The obtained compound was insoluble in aliphatic and sparingly soluble in aromatic solvents.

### 2.2. Description of the structures

Multiple attempts to determine the X-ray crystal structure at room temperature showed that the studied compound crystallized in the trigonal space group  $P3$  (no. 143). Although X-ray diffraction measurements at room temperature have been carried out for numerous crystals, their structure has not been solved due to the poor data quality. Therefore, the low temperature measurements at 103 K and 153 K have been carried out. The details of the X-ray analysis are listed in Table 2, selected bond lengths and angles are listed in Table 3.

Low temperature X-ray crystal structure determination revealed that the studied compound crystallizes in the hexagonal system ( $P6_3/m$ ). Its structure consists of dimers composed of  $[Zr_6(\mu_3-O)_4(\mu_3-OH)_4(OOCR')_9]$  sub-units, linked by six oxygen bridges (Fig. 2). Average distances between Zr–Zr atoms, within the sub-unit are 3.56 Å and between neighboring units are 3.58 Å at 103 K and 3.57 Å at 153 K. Simultaneously, these distances are slightly larger than analogous average distances within



**Fig. 1.** IR spectra of (a)  $[Zr_6O_4(OH)_4(OOC^iBu)_{12}]$ , (b)  $[Zr_6O_4(OH)_4(OOCC(CH_3)_2Et)_{12}]$ , and (c) compound synthesized in the reaction  $Zr(O^iPr)_4$  with  $HOOCCH_2^iBu$ , reported in this paper.

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