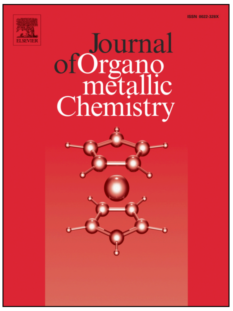

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PII: S0022-328X(17)30721-0

DOI: 10.1016/j.jorganchem.2017.12.027

Reference: JOM 20222

To appear in: *Journal of Organometallic Chemistry*

Received Date: 27 October 2017

Revised Date: 22 December 2017

Accepted Date: 23 December 2017

Please cite this article as: V.A. Tuskaev, S.C. Gagieva, D.A. Kurmaev, S.V. Zubkevich, N.A. Kolosov, E.K. Golubev, G.G. Nikiforova, V.N. Khrustalev, B.M. Bulychev, Novel titanium(IV) complexes stabilized by 2-hydroxybenzyl alcohol derivatives as catalysts for UHMWPE production, *Journal of Organometallic Chemistry* (2018), doi: 10.1016/j.jorganchem.2017.12.027.

To: *Journal of Organometallic Chemistry*, Special Issue "Organometallic Chemistry in Russia" is dedicated to Prof. I.P. Beletskaya.
Research Paper

Novel titanium(IV) complexes stabilized by 2-hydroxybenzyl alcohol derivatives as catalysts for UHMWPE production

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Keywords: Ziegler-Natta Polymerization, titanium, ethylene, Ultra-High Molecular Weight Polyethylene

ABSTRACT *A series of titanium (IV) complexes (**2, 5-7**) stabilized by a substituted 2-hydroxybenzyl alcohols (**1, 4**) – were synthesized. Structures of complexes **6-7** were determined by X-ray diffraction. Titanium atom in the tetrameric complex **6** has an octahedral environment created by chlorine atom and five oxygen atoms. The main structural feature of **7** is a centrosymmetric Ti_4O_6 cage which is built of two seco-norcubanes Ti_4O_3 sharing a common Ti_2O_2-face. A coordination polyhedron around the titanium atoms is the distorted octahedron, with the long Ti─μ-O and short Ti─O bonds. All resulting complexes are moderately or highly active in ethylene polymerization in the presence of {$3Et_2AlCl$ + Bu_2Mg} binary co-catalyst. Resulting polymers are linear ultrahigh molecular weight polyethylenes (up to 7.9 10^6 g/mole). Polymers are suitable for the modern processing methods – the solvent-free solid state formation of super high-strength (tensile strength over 2.0 – 2.4 GPa) and high-modulus (elastic modulus up to 130 GPa) oriented film tapes.*

1. **Introduction**

Ultrahigh molecular weight polyethylene (UHMWPE) is a unique polymer with outstanding physical and mechanical properties (i.e., high strength and stiffness, good wear characteristics, chemical resistance, low coefficient of friction), and the ability to maintain these properties over a wide temperature range. Therefore, it is one of the most promising construction materials and can be used in a wide range of applications such as bearings, pulleys, and joint replacement prostheses in the human body [1].

UHMWPE cannot be processed by conventional methods due to the extremely high viscosity of the polymer melt, resulting from the large number of entanglements between chains [2]. Lately some novel synthetic methods for synthesis of a UHMWPE with a reduced number of entanglements have been developed by using traditional Ziegler-Natta catalysts [3-4] and homogeneous single-site catalysts [5-7]. The basic principle of these methods is to create conditions for fast crystallization of polymeric chains and to reduce the entanglement density. Thus, by careful selection of a catalyst, an activator and the conditions of the polymerization process, in some cases, it is possible to obtain a nascent reactor powder with a morphology close to that of PE single-crystal mats, which, in turn, can allow to use the solventless methods for its processing. We have previously shown that a disentangled UHMWPE can also be obtained on titanium complexes with OO-type ligands [8-9]. Examples of such structures are shown in Figure 1.

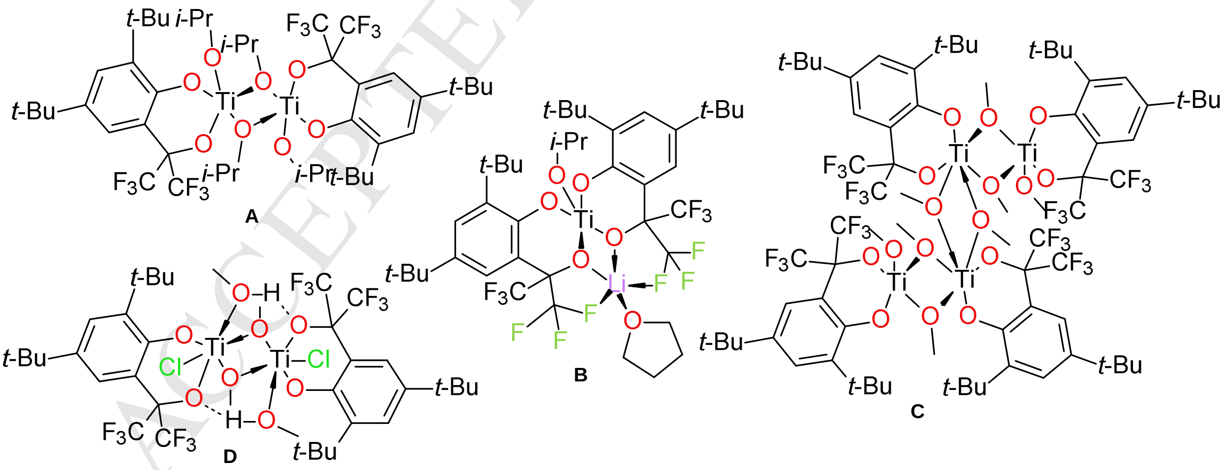


Fig. 1. Examples of titanium(IV) complexes with 2-hydroxybenzyl alcohol derivatives, catalyzing the synthesis of UHMWPE.

In contrast to bis(phenoxyimine) titanium complexes, which require large amounts of methylalumoxane activator, complexes with OO-type ligands “work” in the presence of “conventional” organoaluminum compounds. Unlike the MAO, these substances are stoichiometric compounds and are substantially cheaper. Taking into account the fact that high quality reactor powder is obtained during the first 15-30 minutes of the polymerization process, the possibility of activator cost reduction seems very attractive at the stage of large-scale production of UHMWPE

It was shown in [8-13] that the ability to produce UHMWPE using titanium (IV) complexes with OO-type ligands is determined not only by the structure of the pre-catalyst, but also by the nature of the activator. Thus, the activation of such pre-catalysts with “pure” organoaluminium compounds (MAO, $AlAlk_3$ or Et_2AlCl) at best leads to the production of low molecular weight ($< 5\cdot10^5$ D) polyethylene. The formation of polyethylene with MW $> 1\cdot10^6$ D was observed only when a binary activator containing magnesium and aluminum alkyl halides was used or when mixtures of Ti complex and magnesium chloride, obtained *in situ*, were activated with “conventional” organoaluminum compounds [10-13]. The best and reproducible results were obtained by activating the complexes with a mixture of $\{3Et_2AlCl + Bu_2Mg\}$, proposed in [14]. The use of this activator leads to a sharp increase in the rate of the polymerization reaction and to significant changes in the morphology of the resulting polyethylene. This effect was explained by the formation of heterometallic titanium-magnesium complexes forming the active centers of these catalytic systems [10, 15-16].

The aim of this work is to synthesize of titanium (IV) complexes with modified OO^{2-}-type saligenin ligands, whose structures were expected to be more convenient for the formation of heterometallic titanium-magnesium complexes and to study their catalytic properties in the ethylene polymerization reaction.

Experimental

All manipulations with air-sensitive materials were performed with rigorous exclusion of oxygen and moisture in oven-dried Schlenk glassware on a dual manifold Schlenk line, interfaced to a high-vacuum line. Argon and ethylene of special-purity grade (Linde gas) were dried by purging through a Super Clean™ Gas Filters.

Toluene was distilled over Na/benzophenone ketyl and the water content was periodically controlled by Karl-Fischer coulometry by using a Methrom 756 KF apparatus. Ligand **2**, 2-Hydroxy-3-methoxy-5-bromo-benzaldehyde was obtained in accordance to [17], its reduction with sodium borohydride in methanol yielded a ligand **2** [18]. Ligand **1**, 2,4-di-*tert*-bytyl-6-hydroxymethylphenol, was synthesized as described [19]. Coordination compound **2** was synthesized according to [20]. The ^1H and ^{13}C NMR spectra of these compounds were found to match the published data. Dichloro-bis(isopropoxy)titanium was prepared following literature procedures [21]. Diethylaluminum chloride and di-n-butylmagnesium (Aldrich) were used as 1.0 M solution in heptane.

NMR spectra were recorded on Bruker AMX-400 instrument. Deuterated solvents ($CDCl_3$, THF-d8) were degassed by freeze-pump-thaw vacuum cycles and stored over 3 Å molecular sieves. Chemical shifts are reported in ppm vs. $SiMe_4$ and were determined by reference to the residual solvent peaks. All coupling constants are given in Hertz.

4-Bromo-2-(hydroxymethyl)-6-methoxyphenol (4)

The yield was 0.50 g (70%). Found (%): C, 41.17; H, 3.85; Br, 34.26. $C_8H_9BrO_3$. Calculated (%): C, 41.23; H, 3.89; Br, 34.28. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 3.88 (s, 3H); 4.12 (s, 1H); 4.70 (s, 2H); 6.03 (s. 1 H); 6.93 (s. 1 H); 7.03 (s. 1 H).

(2-methanolato-3-methoxy-5-bromo-phenolato)dichlorodi(propan-2-ol)titanium (IV), LTiCl$_2$(iPrOH)$_2$ (5). Compound **4** (0.23 g, 1 mmol) and toluene (5 mL) were placed into a Schlenk tube equipped with a magnetic stirrer under argon, followed by the addition of $TiCl_2(O^iPr)_2$ (0.24 g, 1 mmol) in toluene (5 mL) (0^{o}C). The resulting red precipitate was filtered off and recrystallized from toluene. The yield was 0.32 g (68%). Found (%): C, 35.66; H, 4.89; Cl, 14.95; Ti, 10.07. $C_{14}H_{23}BrCl_2O_5Ti$. Calculated (%): C, 35.78; H, 4.93; Cl, 15.09; Br, 17.00; Ti, 10.18. ^{1}H NMR (400 MHz, THF-d8), δ: 1.08 (d, 12H); 3.82 (s, 3H); 3.88 (m, 2H); 4.59 (s, 2 H); 5.52 (s, 2H); 6.93 (s, 1H, Ar-H); 7.14 (s, 1 H, Ar-H).

Tetrakis-{(2-methoxy-4-bromo-6-cloromethylphenolato)-(isopropoxy)-chloro-di(μ-oxy)} tetra-titanium (IV), L$_4$Ti$_4$Cl$_4$(iPrO)$_4$ (μ-O)$_4$ (6)

Compound **4** (0.23 g, 1 mmol) and toluene (5 mL) were placed into a Schlenk tube equipped with a magnetic stirrer under argon, followed by the addition of $TiCl_2(O^iPr)_2$ (0.24 g, 1 mmol) in toluene (5 mL). The reaction mixture was stirred at 50 ^{o}C. The resulting dark red precipitate was filtered off and recrystallized from toluene. The yield was 0.35 g (86%). Found (%): C, 32.26; H, 3.39; Cl, 17.31; Ti, 11.67. $C_{44}H_{56}Br_4Cl_8O_{16}Ti_4$. Calculated (%): C, 32.31; H, 3.45; Cl, 17.34; Br, 19.54; Ti, 11.71. ^{1}H NMR (400 MHz, thf-d8), δ: 1.06 (s, 12H); 1.09 (s. 12H); 3.45 (s, 4 H); 3.90 (s, 12H); 4.07 (s, 4H); 4.68 (s, 8 H); 7.27- 7.41 (m, 8 H).

Hexakis-{(2-methanolato-3-methoxy-5-bromo-phenolato)(tetra-isopropoxy} tetra-titanium (IV), L$_6$Ti$_4$(iPrO)$_4$ (μ-O)$_4$ (7)

Compound **4** (0.23 g, 1 mmol) and toluene (5 mL) were placed into a Schlenk tube equipped with a magnetic stirrer under argon, followed by the addition of $Ti(OPr^i)_4$ (0.28 g, 1 mmol) in toluene (5 mL). The resulting yellow precipitate was filtered off and recrystallized from toluene. The yield was 0.24 g (80%). Found (%): C, 39.58; H, 3.87; Ti, 10.42. $C_{60}H_{71}Br_6O_{22}Ti_4$. Calculated (%): C, 39.70; H, 3.94; Br, 26.41; Ti, 10.55. ^{1}H NMR (400 MHz, thf-d8), δ: 1.07 (s, 12H), 1.09 (s, 12H), 3.80 (s, 4 H); 3.93 (s, 18H); 4.77 (s, 2H); 4.89 (s, 12 H); 7.13-7.35 (m, 12 H).

The single-crystal X-ray diffraction data for **6** and **7** were collected on a three-circle Bruker APEX-II CCD diffractometer (λ(MoK_α)-radiation, graphite monochromator, φ and ω scan mode) and corrected for absorption using the SADABS program [22]. The data were indexed and integrated using the SAINT program [23]. For details, see Table S1. The structures were determined by direct methods and refined by full-matrix least square technique on F^2 in anisotropic approximation for non-hydrogen atoms. The independent parts of the unit cells contained one (in the case of **6**) and half (in the case of **7**) toluene solvate molecules. The hydrogen atom of the OH-group in **1** was objectively localized in the difference-Fourier map and refined isotropically with fixed displacement parameters [U_{iso}(H) = 1.5U_{eq}(O)]. The other hydrogen atoms in **6** and **7** were placed in calculated positions and refined within the riding model with fixed isotropic displacement parameters [U_{iso}(H) = 1.5U_{eq}(C) for the methyl groups and 1.2U_{eq}(C) for the other groups]. All calculations were carried out using the SHELXTL program suite [24]. Crystallographic data for **6** · 4$CH_3C_6H_5$ and **7** · $CH_3C_6H_5$ have been deposited with the Cambridge Crystallographic Data Center, CCDC 1570592 and CCDC 1570593, respectively. The supplementary crystallographic data can be obtained free of charge from the Cambridge Crystallographic Data Centre via **www.ccdc.cam.ac.uk/data_request/cif**.

Polymerization of ethylene

The ethylene polymerization was performed in a 100-ml reactor (Parr Instrument Co.) equipped with a magnetic stirrer and inlets for loading components of catalytic systems and ethylene at a total pressure of ethylene and toluene vapours of 0.7 atm. Toluene (100 ml) and the necessary amount of a co-catalyst - $3Et_2AlCl/Bu_2Mg$ or $3Et_3Al_2Cl_3/Bu_2Mg$ were loaded in the reactor. The reactor was heated to a specified temperature, and the reaction mixture was saturated with ethylene. Polymerization was started by the addition of pre-catalyst to the reaction mixture. The pressure of ethylene was maintained constant during polymerization. Polymerization was stopped through the addition of 10% HCl solution in ethanol to the reactor. The polymer was filtered off, washed several times with water-ethanol mixture, and dried under vacuum at 50-60 ºC until a constant weight was achieved.

Polymer evaluation methods

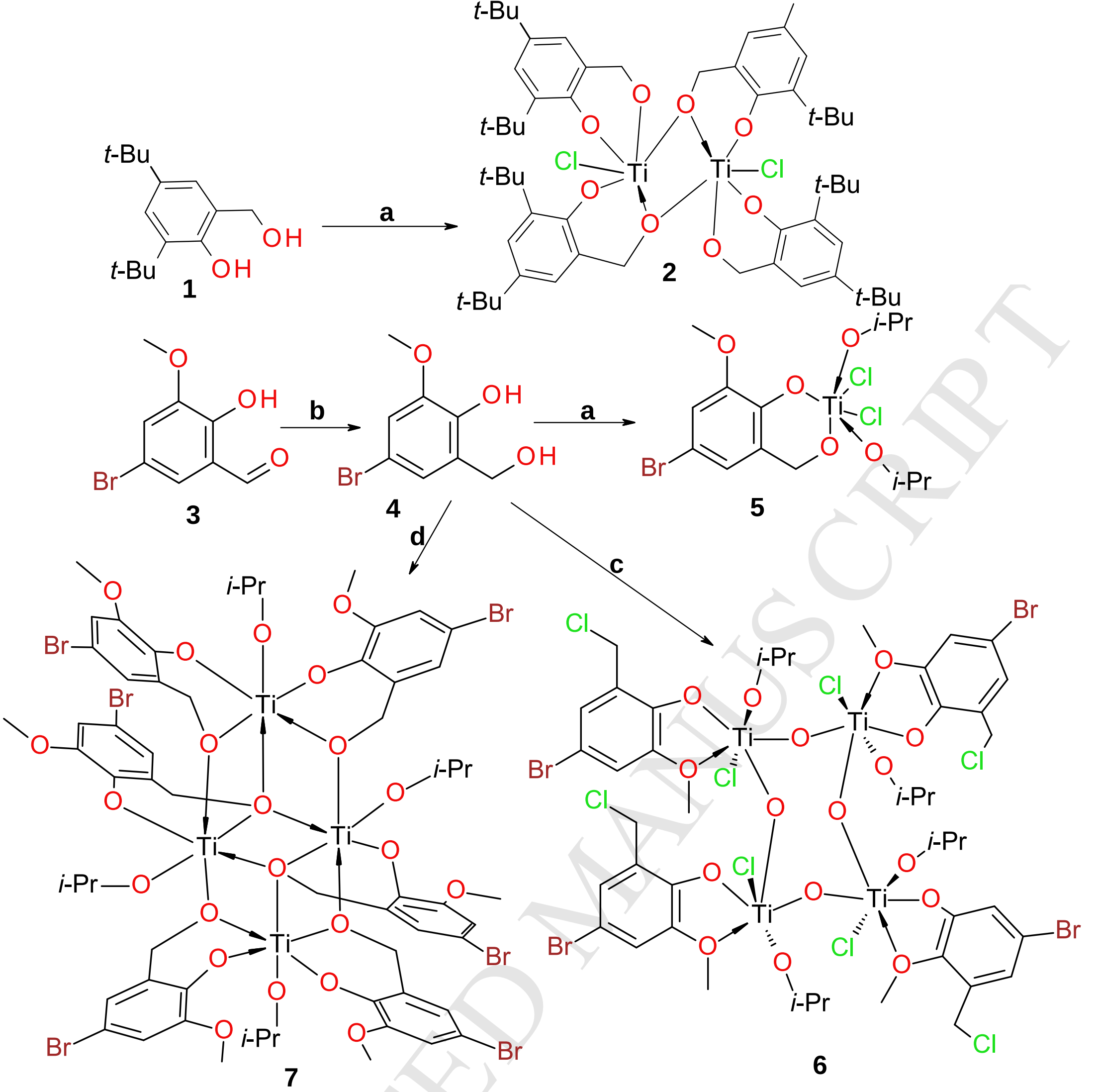
DSC was performed by the differential scanning calorimeter DSC-822e (Mettler-Toledo, Switzerland) at the heating rate 10 ºC/min in air. Viscosity-average molecular weight of synthesized UHMWPE samples was calculated with the Mark-Houwink equation:

$MW = 5.37 \cdot 10^4 [\eta]^{1.37}$ [25], where: MW = viscosity-average molecular weight (g/mol); [η] = intrinsic viscosity in decalin at 135°C (dl/g); $[\eta] = (2\eta_{sp} - 2 ln\eta_r)^{1/2}/0.056$ (η_{sp} - specific viscosity decalin at 135°C; η_r - relative viscosity in decalin at 135°C; $\eta_r = \eta_{sp} + 1$.

The mechanical characteristics of the oriented materials prepared with the synthesized polymers were evaluated on the oriented tapes obtained by a solid state processing of UHMWPE nascent reactor powders according to the procedure outlined in [7]. Monolithic tapes uniform over the entire length (100 mm in thickness and 10 mm in width) were formed at a pressure and shear deformation below the polymer melting point (124-126 ºC). The tapes were subjected to uniaxial drawing while using a Spinline Daca equipment. The drawing temperature was set 4 ºC below the polymer melting point. The mechanical characteristics of the tapes were measured with a Hounsfield H1KS machine at the gauge length of the tested samples 120 mm with 2 mm/min initial deformation rate. The reported values were the average of at least 8 samples.

2. Results and discussion

In the present work, the OO^{2-} type ligands - derivatives of 2-(hydroxymethyl)-phenols were used for the synthesis of titanium (IV) complexes. This type of ligand contains two hydroxyl groups, which differ significantly in acidity and, in addition, can be easily modified by introducing electron-donating or electron-withdrawing substituents that substantially change the electronic properties of chelating ligands. Thus, by the interaction of ligand **1**, containing two bulky *tert*-butyl groups, with dichloro-bis(isopropoxy)titanium (IV) (Scheme 1), complex **2** was obtained, (its structure was established by X-ray diffraction [20]). Complex **2** in the presence of Et_2AlCl oligomerizes higher α-olefins [20], but when a binary activator is used, as shown in present paper, it catalyzes the formation of UHMWPE.



a $TiCl_2(OiPr)_2$, toluene, r.t.; **b** $NaBH_4$, MeOH; **c** $TiCl_2(OiPr)_2$, toluene, Δ; **d** $Ti(OiPr)_2$

Scheme 1. Synthesis of Ti(IV) complexes **2, 5-7**.

It was assumed that the introduction of electron-withdrawing substitution, eg bromine in 5th position of ligand **4**, would lead to a decrease in the electron density at the titanium atom, and introduction of the methoxy group into the *ortho*-position to the phenolic hydroxyl would promote the formation of heterometallic titanium-magnesium complexes, considered in the works [10-13, 15-16]) To verify this assumption, ligand **4** was obtained by the reduction of 3-methoxy-5-bromosalicylic aldehyde **3** with sodium borohydride, and further interaction with $TiCl_2(O^iPr)_2$ in toluene at room temperature led to the formation of a complex **5**. The fact of the formation of this compound was confirmed only by elemental analysis, NMR spectroscopy and mass spectrometry.

The interaction of ligand **4** with $TiCl_2(OiPr)_2$ at an elevated temperature (50 °C) is accompanied by the replacement of oxygen from hydroxymethyl group with chlorine atom, resulting in the formation of a tetrameric guaiacol complex **6**. The Ti-O-Ti bridging oxygen atoms in **6** result most likely from hydrolysis by adventitious water in the solvent. At the same time, the interaction of ligand **4** with titanium (IV) isopropoxide leads to the formation of a tetranuclear complex **7**.

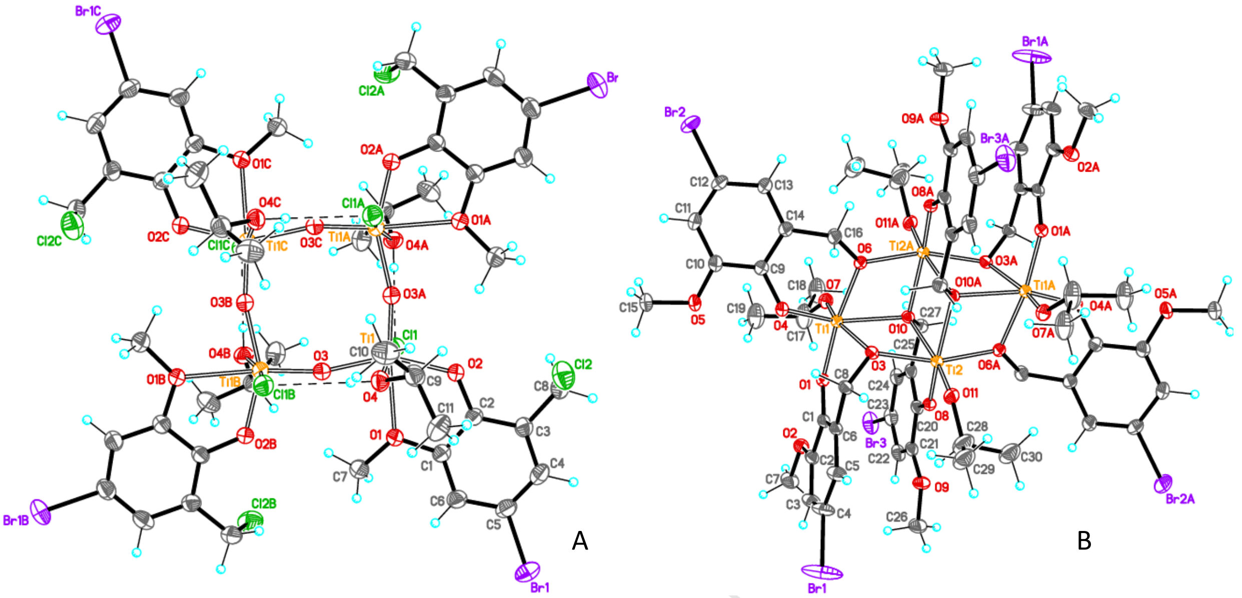


Fig. 2. A. Molecular structure of complex **6** (50% ellipsoids). Hydrogen atoms are omitted for clarity. **B**. Molecular structure of complex **7** (50% ellipsoids). The alternative position of the disordered propoxy substituent is depicted by dashed lines. The disordered toluene solvate molecule is not shown.

The structures of the products **6** and **7** were unambiguously established by X-ray diffraction study and are shown in Figures 2A and 2B respectively, along with the atomic numbering schemes. The pertinent bond lengths and angles are given in Table S2-S3.

The titanium complex **6** crystallizes in the tetragonal space group $I4_1/a$ and represents a tetramer [(HOPr^i)(L)(Cl)Ti─O─]$_4$ (L = organic ligand) comprising the central eight-membered Ti$_4$O$_4$-ring. The observed tetra-nuclear complex has the intrinsic S_4 ($\bar{4}$) symmetry and, in the crystal, occupies a special position on the 4-fold rotoinversion axis. The Ti$_4$O$_4$-ring is roughly planar (rms deviation is 0.159 Å). Each titanium atom has the distorted octahedral environment by the two bridged-O atoms, two O atoms of organic ligand, O atom of coordinated isopropanol, and Cl atom of terminal chloride ligand. The organic ligands are bidentate and form the chelate five-membered rings to titanium atoms, with the oxygen atoms arranged coplanar to the bridged-O atoms (rms deviation is 0.064 Å). Consequently, the isopropanolic and chloride ligands are disposed above and below the main plane of complex **6** alternating along the perimeter of the Ti$_4$O$_4$-ring. This structure is stabilized by the four intramolecular O─H···Cl hydrogen bonds [O4─H4O···Cl1 (¾+*y*, 1¼–*x*, ¼–*z*), O···Cl 3.140(3), H···Cl 2.33(6) Å, ∠O─H···Cl 175(5)°] (Figure 3A). The bridged oxygen atoms are not equidistant relative to the two titanium atoms, apparently, due to the *trans*-effect. The *endo*-cyclic O─Ti─O bond angles in the Ti$_4$O$_4$-ring are larger than 90°, and the intra-chelate O─Ti─O bond angles in the organic ligands are smaller than 90°.

The main structural feature of **7** is centrosymmetric Ti_4O_6 cage which is built of two seco-norcubanes Ti_4O_3 sharing a common Ti_2O_2-face. The two ─CH_2O-groups of the central four-membered Ti_2O_2-ring are μ^3, and the other ─CH_2O-groups are μ^2-bridges. All six organic ligands are bidentate and form the six-membered chelate rings to titanium atoms making each of them penta-coordinated. The terminal isopropoxy groups occupy sixth coordination positions at the titanium atoms. Hence, a coordination polyhedron around the titanium atoms is the distorted octahedron, with the long Ti─μ-O and short Ti─O bonds (Table S3). As expected, the Ti─μ^3-O bonds are longer than the Ti─μ^2-O bonds, and the Ti─$O_{terminal}$ bonds are shorter than the Ti─$O_{chelate}$ bonds. Moreover, the *endo*-cyclic O─Ti─O bond angles (<90°) are significantly smaller than the *exo*-cyclic (>90°) ones. It should be noted that the methoxy substituents of the organic ligands lie practically within their aromatic planes (planes of benzene ring and adjacent atoms).

It should be noted that the titanium complexes with unsubstituted guaiacol $[Ti_2(\mu\text{-}O)Cl_2(\eta^2\text{-guaiacolato})_4]$ and $[Ti_4(\eta^2\text{-guaiacolato})_8]$ are described in the work [20].

According to X-ray data, each complex contains alkoxo-groups and/or chlorine atoms, that easily exchange on alkyl-groups during treatment with magnesium- or organoaluminum compounds, that is a necessary condition for the formation of catalytic systems of the Ziegler type.

Catalytic properties of compounds **2, 5–7** in ethylene polymerization are summarized in Table 1

Table 1. Ethylene Polymerization by **2, 5 -7** /(Et_2AlCl:Bu_2Mg) catalytic systems.)[a]

Run	Complex	[Al]/[Ti]	Weight of PE, g	Bulk density, g/cm^3	A [b]	Deg. of crystal.,[d] %	T_m [c]	M_w [d], 10^6
1.	**2**	300	2.5	0.092	1430	65	142	1.87
2.	**2**	500	4.1	0.072	2340	68	143	2.04
3.	**5**	300	3.8	0.05	2190	73	144	3.20
4.	**5**[f]	300	2.1	0.075	1200	76	145	6.00
5.	**6**	300	4.8	0.047	2740	81	145	3.14
6.	**7**	300	4.5	0.044	2570	71	145	2.90
7.	**7** [f]	300	1.5	0.089	860	63	142	7.90

[a] Polymerizations carried out in 100 mL of toluene with 5 10^{-6} mol of catalyst at a constant 0.7 atm ethylene pressure for 30 min, temperature 30 °C, [Et_2AlCl]/[Bu_2Mg] = 3:1.

[b] kg of PE (mol of Ti atm)$^{-1}$ h^{-1}.

[c] Melting temperatures determined by DSC at second heating of PE samples.
[d] Degree of crystallinity were determined by DSC by use of value $\Delta H_m 100\% = 288$ J/g [26].
[e] M_w was measured by viscosimetry;
[f] $Et_3Al_2Cl_3$ instead of Et_2AlCl

The maximum catalytic activity in this series - 2740 kg PE / mole Ti h atm was demonstrated by complex **6**, activated by the binary cocatalyst {$3Et_2AlCl$ + $MgBu_2$}. Probably this fact can be related to the presence of the μ2-oxygen bridge in the complex **6**. It is known that the chiral Lewis acid possessing the key Ti-O-Ti unit showed higher reactivity and selectivity in asymmetric synthesis [27]. Similar dimeric structures with oxygen bridges are much less commonly used as catalysts for ethylene polymerization. For example, catalytic systems based on heterometallic titanium-aluminum complexes $LAlCH_3(\mu\text{-}O)M(CH_3)_2Cp$, when M=Ti, Zr; Cp = C_5H_5 or C_5Me_5 and L = $CH(N(2,6\text{-}i\text{-}Pr_2C_6H_3)(CMe))_2$, are significantly superior in terms of thermal stability and activity to monometallic half-sandwich titanium trialkyl compounds [28]. The tetrameric complex $Ti_2(\mu\text{-}O)(\eta_2\text{-guaiacolato})_4$ exceeds the activity (per gram of metal) of the monomeric complex $TiCl_2(\eta^2\text{-guaiacolato})_2$ by more than 25 times. It should also be noted that in this case the activation was carried out by the mixture of $AlEt_3$/$AlEt_2Cl$ and the high productivity of the systems was achieved with the use of complexes immobilized on $MgCl_2$ [29].

The catalytic activities of complexes **5** and **7** also are rather high – 2200 - 2570 kg PE / mole Ti atm h. Replacement Et_2AlCl on $Et_3Al_2Cl_3$ in a binary activator leads to a significant decrease in the activity of both complex **5** and **7.** At the same time, this replacement is accompanied by a significant increase in the molecular weight of the polymer - from 3.2 to 6 10^6 D for complex **5** and from 2.9 to 7.9 10^6 D for pre-catalyst **7.**

The activity of complex **2**, which does not contain a methoxy-group capable to bind a metal atom in the *ortho* position to the phenolic hydroxyl, is significantly inferior to complexes stabilized with ligand **4**. The degree of crystallinity and molecular weight of PE obtained on complex **2**, as well as the mechanical properties of oriented film tapes, also have the worst performance in this series. This fact indirectly confirms the advisability of introducing additional donor atoms into this series of ligands.

All obtained polymers lack branching at the main chain which is evident from the absence of IR absorption band at 1378 cm^{-1} characteristic of the symmetric deformational vibrations of CH_3 groups. The bulk density of UHMPE nascent reactor powders has anomalously low values - from 0.04 to 0.09 g/cm^3 (Table 1), which indirectly indicates an irregular highly porous surface of the particles. The melting point and degree of crystallinity are typical for UHMWPE [25, 30] and are in the range of 142-145 ºC and 65-81% respectively (Table 1). At the same time, explicit differences in the values of the bulk density, melting points, and degree of crystallinity of reactor powders were not found.

The processing of UHMWPE reactor powders obtained on pre-catalysts **2, 5-7** into high-modulus oriented film tapes was carried out by preparing monolithic samples under pressure and shear deformation at an elevated temperature below polymer melting point with subsequent uniaxial stretching by the method described in [7]. Criteria for the quality of the resulting oriented film tapes were: homogeneity of the resulting filament along the width and homogeneity of the samples masses within one multiplicity at one length.

Table 2 shows the mechanical characteristics of film tapes prepared from reactor powders obtained in runs 2-3 and 5-6 (table 1) with MW = 2.0 - 3.2·10^6 D.

Table2. Mechanical properties of monolithic UHMWPE film tapes

Run [a]	Complex	Drawing ratio	Breaking strength, GPa	Elongation, %	Elastic modulus, GPa
2	**2**	20	1.90	1.88	90
2	**2**	24	1.95	2.18	100
3	**5**	24	2.14	2.50	130
3	**5**	28	1.94	2.74	113
5	**6**	24	2.21	2.07	133
5	**6**	28	2.35	2.39	112
6	**7**	20	2.14	2.98	90
6	**7**	24	1.94	2.83	110

[a] Numbering corresponds to Table 1.

Stress-strain curves of UHMWPE orientated film tapes are shown in Figure 3. In a number of cases (curve b in Fig. 3), a single-stage character of film rupture is observed, indicating uniformity of the samples, and close values of elongations and elastic modulus for a series of samples with the same drawing ratio confirm the high quality of UHMWPE reactor powder.

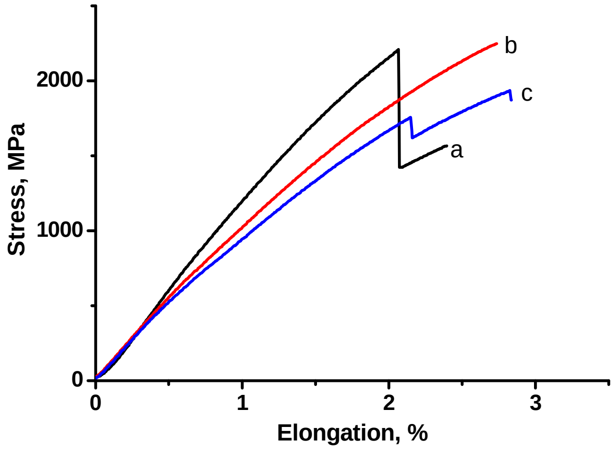


Fig. 3. Stress-elongation curves for UHMWPE orientated tapes from UHMWPE powder obtained in runs 5 (a); 3(b) and 6(c).

The maximum value of tensile strength (2.4 GPa), with an average tensile modulus (112-133 GPa), was observed for UHMWPE powder, obtained on pre-catalyst **6**. This may be due to high degree of crystallinity, since other known properties of the obtained UHMWPE samples differ little from each other.

Conclusion

In summary, three novel mono- and tetranuclear titanium(IV) complexes (**5-7**) bearing $[OO]^{2-}$ ligand were synthesized in high yields. Structures of complexes **6-7** were established by X-ray diffraction. Titanium atom in the tetrameric complex **6** has an octahedral environment created by chlorine atoms and five oxygen atoms. A coordination polyhedron around the titanium atoms in complex **7** is the distorted octahedron. The main structural feature of **7** is a centrosymmetric Ti_4O_6 cage which is built of two seco-norcubanes Ti_4O_3 sharing a common Ti_2O_2-face. these complexes contains alkoxo-groups and chlorine atoms, which are easily removed by treatment with organometallic compounds. All complexes discussed in present work were activated only in the presence of a binary co-catalyst $\{3Et_2AlCl + Bu_2Mg\}$ and exhibited moderate to high activities towards ethylene polymerization (860-2700 kg of PE (mol of Ti atm)$^{-1}$ h^{-1}), giving UHMWPE with high T_m. It was shown that the replacement of Et_2AlCl for $Et_3Al_2Cl_3$ is accompanied by a decrease in activity; with a simultaneous significant increase in the molecular weight of the polymer. Proposed catalysts in suitable reaction conditions (room temperature, low monomer pressure, low catalyst concentration) produce nascent UHMWPE powders with a low bulk density (0.05-0.09 g/cm^3), which can be processed to super high-strength (tensile strength up to 2.4 GPa) and high-modulus (elastic modulus up to 130 GPa) oriented film tapes by solvent-free solid state method.

Acknowledgments

This work was financially supported by the Russian Science Foundation (Project No 16-13-10502).

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Highlights

Novel titanium complexes bearing $[OO]^{2-}$ ligands were synthesized and fully characterized.

Complexes in the presence of $\{Et_2AlCl+Bu_2Mg\}$ produced high molecular weight polyethylene (up to $7.9\ 10^6$ g/mole).

Polymers are suitable for the solvent-free formation of high-strength (up 2.4 GPa) and high-modulus (up to 130 GPa) oriented film tapes.