



Cationic $[\text{TiCl}_6]^{+2}$ and anionic $[\text{TiCl}_{6-x}\text{L}_x]^{-(2-x)}$ titanium complexes with crown ether as pre-catalyst for ethylene polymerization

Svetlana Ch. Gagieva^a, Dmitrii A. Kurmaev^a, Kasim F. Magomedov^a, Vladislav A. Tuskaev^{a,b}, Gleb L. Denisov^b, Ekaterina A. Khakina^b, Elena N. Zakharchenko^b, Evgenii K. Golubev^c, Maria D. Evseeva^a, Pavel B. Dzevakov^a, Boris M. Bulychev^{a,*}

^a Department of Chemistry, M. V. Lomonosov Moscow State University, 1 Leninskie Gory, 119992 Moscow, Russian Federation

^b A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilova St. 28, 119991 Moscow, Russian Federation

^c Enikolopov Institute of Synthetic Polymer Materials, Russian Academy of Sciences, Profsoyuznaya Str., 70, 117393 Moscow, Russian Federation

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ABSTRACT

A series of ionic complexes of composition $[\text{M}(\text{Crown})]^+[\text{TiCl}_5]^-$, where M - Li, Na, K; Crown - dibenzo-18-Crown-6, benzo-15-crown-5, dibenzo-24-crown-8 has been synthesized by the interaction of alkali metal chlorides, titanium tetrachloride and crown ethers in anhydrous toluene. Carrying out these syntheses in acetonitrile results in crystallization of complexes solvated with acetonitrile. The structure of three complexes was determined by X-ray diffraction. In the presence of an activator - $\{\text{Et}_2\text{AlCl} + \text{Bu}_2\text{Mg}\}$, the complexes catalyze the polymerization of ethylene with a productivity of up to 4500 kg PE/mol Ti h atm. The resulting ultra-high molecular weight polyethylene (M_v in the range $1.4 - 2.8 \cdot 10^6$ Da) can be processed by a solventless method into high-strength (up to 2.1 GPa) and high-modulus (up to 118 GPa) oriented films.

1. Introduction

Despite more than 70 years of history, the mechanism of the Ziegler-Natta polymerization of olefins remains largely mysterious and debatable. If in 1960–1970 s the most popular point of view was the molecular nature of the catalytically active centers with an octahedral environment of the transition metal atom [1–2], and the version of its cationic nature proposed in the works of A.E. Shilov et al [3–4], was somewhat marginal, then at the end of the 20th century, due to the work of T. J. Marks et al. [5], this viewpoint became commonly accepted. The postulate about the cationic nature of the active center was quickly accepted by the majority of the scientific community for all types of Ziegler catalysts - heterogeneous classical and supported, homogeneous metallocene and post-metallocene - and for all transition metals in various degrees of oxidation. However, in recent years, a number of theoretical works in which molecular complexes of the post-metallocene type are considered as active centers was published [6–9]. This configuration is quite close to the early ideas about octahedral structure of active centers. Moreover, very few coordination compounds containing a transition metal in the anion are capable of serving as ethylene polymerization catalysts. Perhaps the most striking example is the anionic

complex of nickel(II) with triadamantylphosphine (Compound A, Chart 1), which in the presence of alkylalumoxane (PMAO-IP) catalyzes the synthesis of UHMWPE with initial activities reaching 3.7 million turnovers per h^{-1} at 10 °C, as well as the copolymerization of ethylene with 1-hexene, 1-octadecene, and *tert*-butyldimethyl(dec-9-en-1-yloxy)silane [9]. Anionic titanium tetrachloride complexes with 1,3-bis(3,5-dialkylpyrazol-1-yl)propan-2-ol derivatives (compounds B-C, Chart 1) catalyze ethylene polymerization in the presence of MAO. The productivity of these systems does not exceed 124 kg PE/mol Ti h bar, however, they are characterized by increased thermal stability (up to 100 °C) producing a polymer with a molecular weight ca. 100,000 and a narrow molecular weight distribution [10].

In continuation of our studies of the catalytic activity of complexes with crown ethers in the polymerization of olefins [11], here we describe the synthesis of anionic heterometallic titanium chloride complexes with alkali metal, formed in the systems $\{\text{MCl-TiCl}_4\text{-CE-toluene}\}$ or $\{\text{MCl-TiCl}_4\text{-CE-MeCN}\}$, where M is Li, Na, K; CE - crown ether: B15C5, DB18C6, DB24C8, as well as the structures of some of these compounds and their catalytic properties in the ethylene polymerization reaction.

One of the goals of this work is to evaluate the possibilities of using

* Corresponding author.

E-mail addresses: tuskaev@yandex.ru, bmbulychev@gmail.com (B.M. Bulychev).

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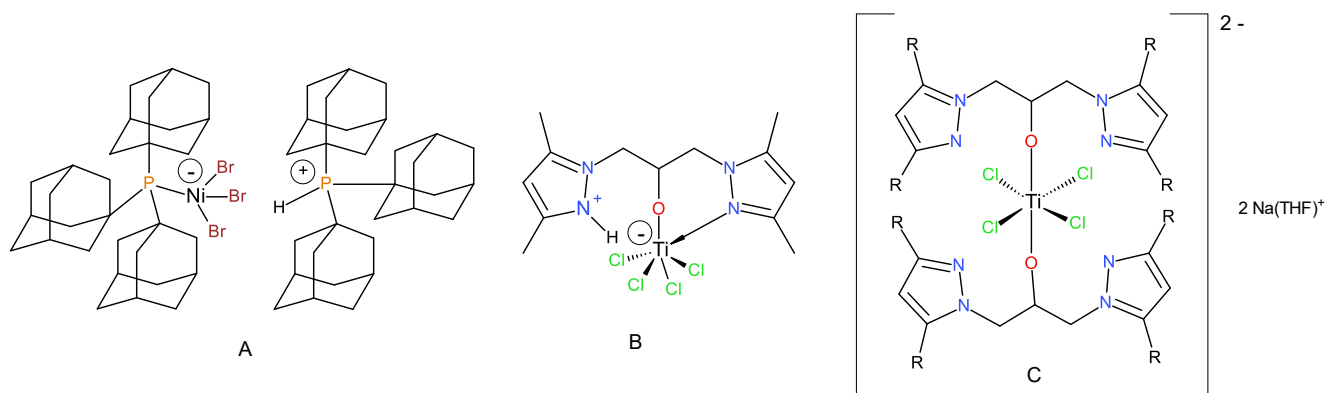
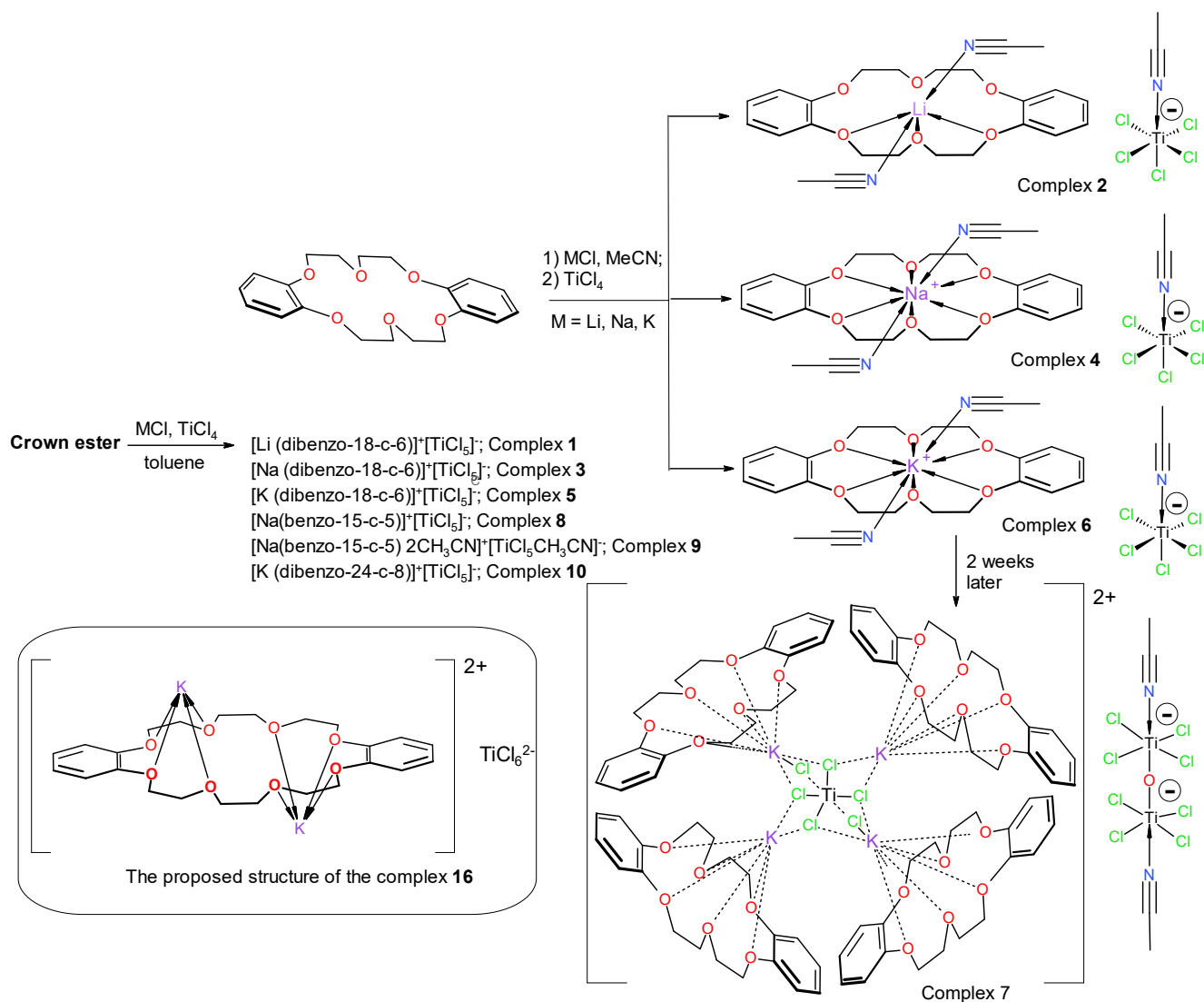


Chart 1. Examples of anionic complexes, active in ethylene polymerization.



Scheme 1. Synthesis of complexes having the general composition [M crown CH₃CN]⁺[TiCl₅ CH₃CN]⁻ (M = Li, Na, K). The ORTEP diagrams of complexes 1–2 and 4 are depicted in Figs. 1–3.

new catalyst systems for the synthesis of ultra-high molecular weight polyethylene (UHMWPE) with reduced entanglement density. The current state of research aimed at developing catalysts for the synthesis of UHMWPE is reflected in reviews [12–14]. UHMWPE is a very promising structural material, however, its inherent high melt viscosity and lack of

fluidity greatly hinders its processing by standard polymer processing methods. A decrease in the degree of interlacing of macromolecules would make it possible to expand the range of methods for processing such a polymer, in particular, through the use of solution-free spinning of oriented high-modulus filaments and films. The basics of this method,

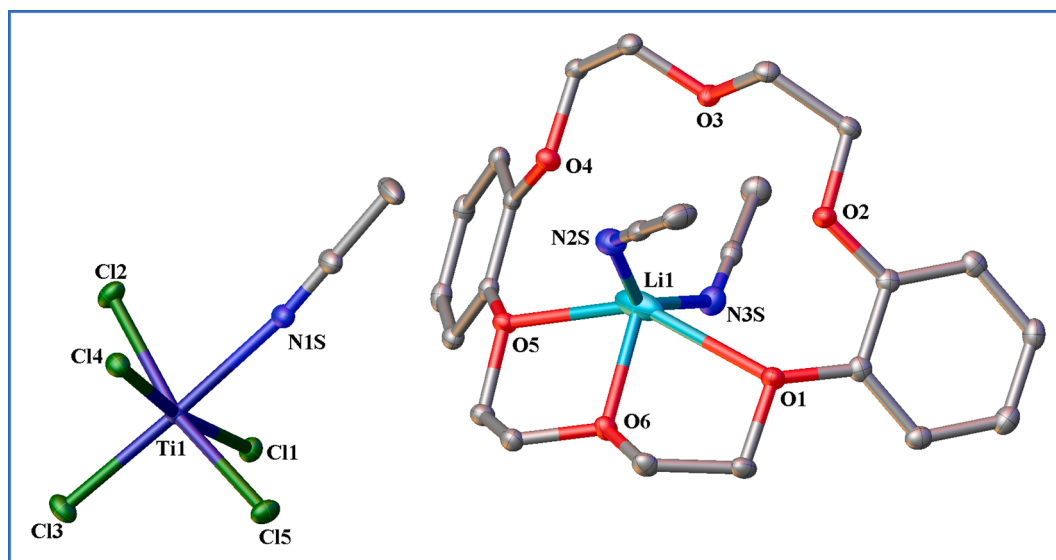


Fig. 1. The structure of the ionic complex $[\text{DB18C6} \supset \text{Li} \cdot 2\text{MeCN}]^+ [\text{TiCl}_5 \cdot \text{MeCN}]^-$ (complex 2).

Table 1

Main geometric parameters and symmetry measures as obtained from X-ray diffraction for $[\text{DB18C6} \supset \text{Li} \cdot 2\text{MeCN}]^+ [\text{TiCl}_5 \cdot \text{MeCN}]^-$ (complex 2).

Parameter ^a	Li	Ti
M–O _{crown} , Å	2.008(7)–2.645(7)	–
M–Cl, Å	–	2.2555(7)–2.3182(7)
M–N _{CH₃CN} , Å	2.025(6)–2.081(7)	2.229(2)
S(OC-6)	–	0.317
S(TPR-6)	–	15.740

^a O_{crown}, Cl, N_{CH₃CN} – oxygen atoms in crown-ester; chloride-anions and nitrogen atoms in solvate acetonitrile molecules, respectively. S(OC-6) and S(TPR-6) are octahedral and trigonal prism symmetry measures.

developed by Smith et al., [15–16] have been significantly developed by Rastogi et al. [17–18].

2. Experimental section

All manipulations with air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in oven-dried Schlenk

glassware on a dual manifold Schlenk line equipped with a high-vacuum line. Some operations were carried out in a Braun M glove box under argon atmosphere. Argon and ethylene of special-purity grade (Linde gas) were dried by purging through a Super Clean™ Gas Filters. Toluene was purified by boiling and following distillation over sodium benzophenone ketyl. Hexane was boiled and distilled over Na/K alloy. Acetonitrile was purified according to [19]. Crown ethers: B15C5,

Table 2

Main geometric parameters and symmetry measures as obtained from X-ray diffraction for $[\text{DB18C6} \supset \text{Na} \cdot 2\text{MeCN}]^+ [\text{TiCl}_5 \cdot \text{MeCN}]^-$ (complex 4).

Parameter ^a	Na	Ti
M–O _{crown} , Å	2.522(3)–2.792(3)	–
M–Cl, Å	–	2.2434(16)–2.3277(14)
M–N _{CH₃CN} , Å	2.377(5)–2.418(5)	2.228(4)
S(OC-6)	–	0.349
S(TPR-6)	–	15.854

^a O_{crown}, Cl, N_{CH₃CN} – oxygen atoms in crown-ester; chloride-anions and nitrogen atoms in solvate acetonitrile molecules, respectively. S(OC-6) and S(TPR-6) are octahedral and trigonal prism symmetry measures.

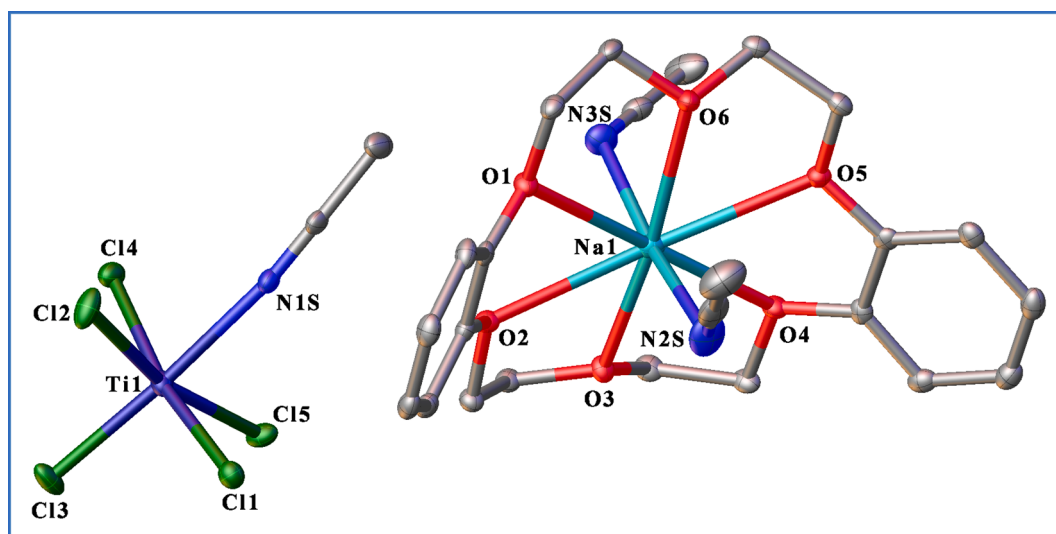


Fig. 2. The structure of the ionic complex $[\text{DB18C6} \supset \text{Na} \cdot 2\text{MeCN}]^+ [\text{TiCl}_5 \cdot \text{MeCN}]^-$ (complex 4).

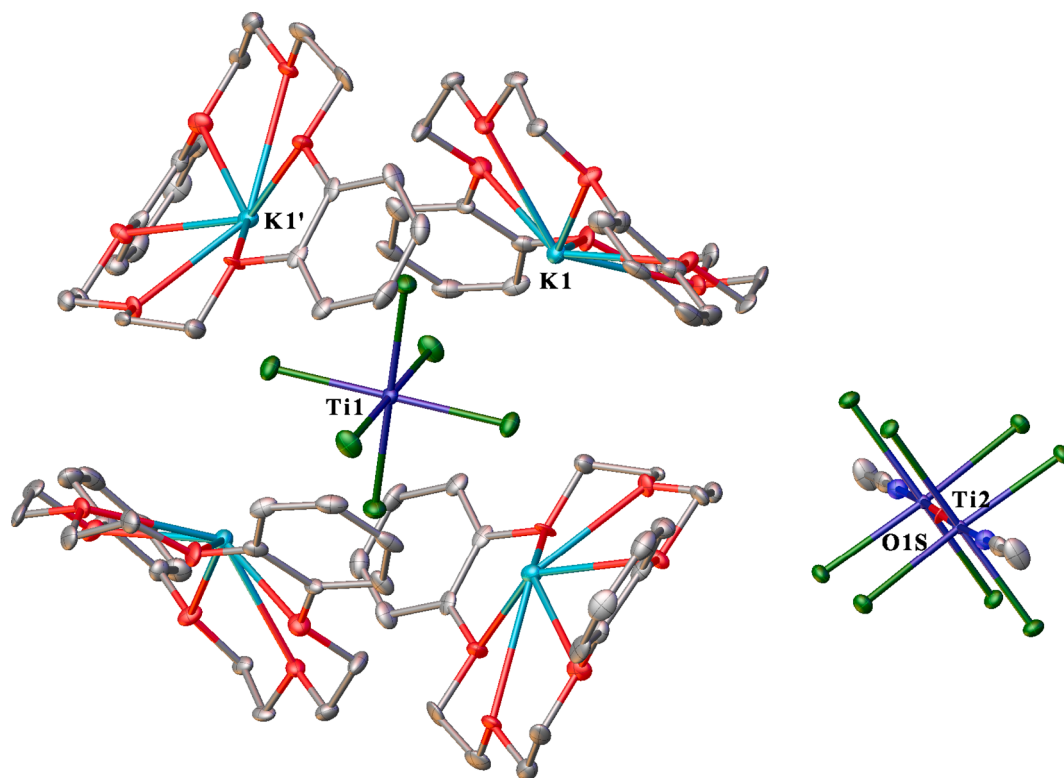


Fig. 3. The fragment of crystal packing of the $[4\{\text{KCl} \cdot \text{DB18C6}\} \cdot \text{TiCl}_4]^{+2} [\text{Ti}_2\text{Cl}_8\text{O} \cdot 2\text{MeCN}]^{-2}$ (complex 7) illustrating the formation of the egg-like structure by four crown-ether molecules with K^+ cations around the TiCl_4 anion.

Table 3

Main geometric parameters and symmetry measures as obtained from X-ray diffraction for complex $[4\{\text{KCl} \cdot \text{DB18C6}\} \cdot \text{TiCl}_4]^{+2} [\text{Ti}_2\text{Cl}_8\text{O} \cdot 2\text{MeCN}]^{-2}$ (complex 7).

Parametr*	K1	K1'	Ti1	Ti2
M–O _{crown} , Å	2.789(5) – 2.961(4)	2.824(3)– 2.933(5)	–	–
M–Cl, Å	–	–	2.318(2)– 2.3506(12)	2.3279(19)– 2.3455(12)
M–N _{CH₃CN} , Å	–	–	–	2.251(5)
M–O _{anion} , Å	–	–	–	1.7797(11)
S(OC-6)	–	–	0.018	0.600
S(TPR-6)	–	–	16.524	16.529

* O_{crown}, Cl, N_{CH₃CN} – oxygen atoms in crown ether; chloride atoms and nitrogen atoms in solvate acetonitrile molecules, respectively. S(OC-6) and S(TPR-6) are octahedral and trigonal prism symmetry measures.

DB18C6, DB24C8 (Sigma-Aldrich) were dried over 4 Å molecular sieves or degassed in vacuum and stored under argon.

NMR spectra were recorded on Bruker DPX 300 and Bruker AMX-400 instruments. Elemental analysis (C, H, Cl) was performed by the microanalytical laboratory at A. N. Nesmeyanov Institute of Organoelement Compounds on Carlo Erba-1106 and Carlo Erba-1108 instruments. The content of Ti was measured by X-ray fluorescence analysis on the VRA-30 device (Karl Zeiss, Germany).

MALDI mass spectra were recorded on the Axima Confidence time-of-flight spectrometer (Shimadzu Biotech) in the reflectron high resolution mode with nitrogen laser ($\lambda = 337$ nm). Positive ions were recorded. The mass range between 200 and 1000 was scanned. 2,4,6-Trihydroxyacetophenone (THAP) was used as a matrix for all experiments. The target was prepared as follows. Crown-containing complexes were dissolved in acetonitrile to give a concentration 0.1 mg/ml. 20 μl of the obtained solutions were mixed with 20 μl of the 10 mg/ml matrix

solution in acetonitrile. Resulting mixtures were deposited on a stainless-steel target and dried in air.

2.1. Complexes without donor solvents

[DB18C6 $\supset$ Li⁺] ⁺ [TiCl₅][−] (Complex 1).

In a 50 mL flame-dried Schlenk flask, titanium tetrachloride (0.105 g, 0.061 mmol) was dissolved in anhydrous toluene (20 mL). Anhydrous lithium chloride (23 mg, 0.56 mmol) was added to the solution and resulting suspension was stirred at room temperature for 24 h under argon. Then DB18C6 (200 mg, 0.56 mmol) was added and the suspension was stirred for 5 days. The precipitate was filtered off, washed with anhydrous toluene, and dried under vacuum. Calculated (%) for $\text{C}_{20}\text{H}_{24}\text{LiO}_6\text{Cl}_5\text{Ti}$ (589.96): C, 40.5; H, 4.1; Cl, 29.9; Li, 1.2; O, 16.2; Ti, 8.1. Found (%): C, 40.42; H, 4.21; Cl, 29.83; Ti, 8.05. MS-maldi: found m/z 367.15 [Li dibenzo-18-Crown-6]⁺, 383.19 [Na dibenzo-18-Crown-6]⁺; calculated for $[\text{C}_{20}\text{H}_{24}\text{LiO}_6]^+$ and $[\text{C}_{20}\text{H}_{24}\text{NaO}_6]^+$ 367.17 and 383.15, respectively.

[DB18C6 $\supset$ Na⁺] [TiCl₅][−] (Complex 3) prepared according to the method for complex 1. Calculated (%) for $\text{C}_{20}\text{H}_{24}\text{Cl}_5\text{NaO}_6\text{Ti}$ (608.52): C, 39.47; H, 3.98; O, 15.78; Cl, 29.13; Na, 3.78; Ti, 7.87. Found (%): C, 39.43; H, 3.93; Cl, 29.10; Ti, 7.84. MS-maldi: found m/z 383.12 [DB18C6 $\supset$ Na⁺]; calculated for $[\text{C}_{20}\text{H}_{24}\text{NaO}_6]^+$ 383.15.

[DB18C6 $\supset$ K⁺] [TiCl₅][−] (Complex 5) prepared according to the method for complex 1. Calculated (%) for $\text{C}_{20}\text{H}_{24}\text{KO}_6\text{Cl}_5\text{Ti}$ (621.91): C, 38.5; H, 3.9; Cl, 28.4; K, 6.3; Ti, 7.65. Found (%): C, 38.31; H, 3.94; Cl, 28.30; Ti, 7.61. MS-maldi: found m/z 400.02 [DB18C6 $\supset$ K⁺]; calculated for $[\text{C}_{20}\text{H}_{24}\text{KO}_6]^+$ 399.12.

[B15C5 $\supset$ Na⁺] [TiCl₅][−] (Complex 8) prepared according to the method for complex 1.

Calculated (%) for $\text{C}_{14}\text{H}_{20}\text{Cl}_5\text{NaO}_5\text{Ti}$ (516.43): C, 32.56; H, 3.90; O, 15.49; Cl, 34.33; Na, 4.45; Ti, 9.27. Found (%): C, 32.56; H, 3.90; O, 15.49; Cl, 34.33; Na, 4.45; Ti, 9.27.

[DB24C8 $\supset$ K⁺] [TiCl₅][−] (Complex 10) prepared according to the

Table 4Ethylene Polymerization by complexes **1-10^a**.

Entry	Pre-Catalyst	A ^b	Bulk density	m.p. °C	Crystal-linity ^c %	M _v *10 ^{-6 d}
1	[DB18C6 ⊃ Li] ⁺ [TiCl ₅] ⁻	4110	0.082	136	70	2.01
2	[DB18C6 ⊃ Li•2MeCN] [TiCl ₅ MeCN] ⁻	4280	0.096	132	54	1.82
3	[DB18C6 ⊃ Na] ⁺ [TiCl ₅] ⁻	3540	0.060	139	69	1.79
4	[DB18C6 ⊃ Na•2MeCN] ⁺ [TiCl ₅ MeCN] ⁻	3890	0.080	137	55	1.36
5	[DB18C6 ⊃ K] ⁺ [TiCl ₅] ⁻	4060	0.075	138	76	1.43
6	[DB18C6 ⊃ K•2MeCN] ⁺ [TiCl ₅ MeCN] ⁻	3620	0.069	133	60	1.77
7	[4KCl•4DB18C6•TiCl ₂] ⁺² [Ti ₂ Cl ₈ O•2MeCN] ⁻²	3680	0.053	140	79	1.99
8	[B15C5 ⊃ Na] ⁺ [TiCl ₅] ⁻	3850	0.086	135	69	1.81
9	[B15C5 ⊃ Na•2CH ₃ CN] ⁺ [TiCl ₅ CH ₃ CN] ⁻	4230	0.075	137	76	1.90
10	[DB24C8 ⊃ K] ⁺ [TiCl ₅] ⁻	4460	0.080	133	62	2.82
11	[DB18C6 ⊃ Li] ⁺² [TiCl ₆] ⁻²	4439	0.068	137	65	
12	[DB18C6 ⊃ 3Li] ⁺³ [TiCl ₆] ⁻³	4210	0.082	134	48	
13	[B15C5 ⊃ Li] ⁺ [TiCl ₅] ⁻	4343	0.071	n.d		
14	[B15C5 ⊃ 2Na] ⁺² [TiCl ₆] ⁻²	4230	0.068	n.d		
15	[DB24C8 ⊃ 2 K] ⁺² [TiCl ₆] ⁻²	4457	0.070	n.d		
16	[DB18C6 ⊃ 2 K] ⁺² [TiCl ₆] ⁻²	4114	0.077	n.d		

^a Polymerizations were carried out in 100 mL of toluene with 5 · 10⁻⁶ mol of precatalyst at a constant 1 atm excessive ethylene pressure for 15 min., activator - Et₂AlCl/Bu₂Mg = 300/100.

^b Productivity, in kg_{PE}/mol Ti · h·atm.

^c Crystallinity was determined by DSC at the first and second heating runs, $\chi = (\Delta H_m / \Delta H_m^0) \times 100$ %, where $\Delta H_m^0 = 293.0$ J/g.

^d Molecular weight was determined by the viscosimetric method.

Table 5

Mechanical properties of UHMWPE oriented film tapes.

Entry ^a	Pre-catalyst	E ^b GPa	σ ^c GPa
1	[DB18C6 ⊃ Li] ⁺ [TiCl ₅] ⁻	125.9	1.95
2	[DB18C6 ⊃ Li•2MeCN] ⁺ [TiCl ₅ MeCN] ⁻	110.7	1.85
3	[DB18C6 ⊃ Na] ⁺ [TiCl ₅] ⁻	124.5	1.86
4	[DB18C6 ⊃ Na•2MeCN] ⁺ [TiCl ₅ MeCN] ⁻	104.1	1.49
8	[B15C5 ⊃ Na] ⁺ [TiCl ₅] ⁻	120.9	1.63
9	[B15C5 ⊃ Na•2CH ₃ CN] ⁺ [TiCl ₅ CH ₃ CN] ⁻	103.6	1.54

^a Numbering corresponds to Table 1.

^b E – average tensile modulus, GPa;

^c σ – tensile strength, GPa.

method for complex **1**. Calculated (%) for C₂₄H₃₂Cl₅KO₈Ti (712.73): C, 40.39; H, 4.66; O, 17.93; Cl, 24.84; K, 5.48; Ti, 6.71. Found (%): C, 40.34; H, 4.61; Cl, 24.80; Ti, 6.68. MS-maldi: found *m/z* 486.94 [DB24C8 ⊃ K]⁺; calculated for [C₂₄H₃₂KO₈]⁺ 487.17.

[DB18C6 ⊃ Li]⁺² [TiCl₆]⁻² (Complex **11**) prepared according to the method for complex **1**. Calculated (%) for C₂₀H₃₂Cl₆Li₂O₆Ti (640.01): C, 37.36; H, 5.02; O, 14.93; Cl, 33.09; Li, 2.16; Ti, 7.45. Found (%): C, 37.31; H, 4.95; Cl, 33.03; Ti, 7.43.

[DB18C6 ⊃ Li]⁺³ [TiCl₆]⁻³ (Complex **12**).

In a 50 mL flame-dried Schlenk flask, titanium tetrachloride TiCl₄ 3TGF (0.207 g, 0.56 mmol) was dissolved in anhydrous toluene (20 mL). Anhydrous lithium chloride (75 mg, 1.68 mmol) was added to the solution and resulting suspension was stirred at room temperature for 24 h under argon. Then dibenzo-18-Crown-6 (200 mg, 0.56 mmol) was added and the suspension was stirred for 5 days. The precipitate was filtered off, washed with anhydrous toluene, and dried under vacuum. Calculated (%) for C₂₀H₂₄Cl₇Li₃O₆Ti (673.94): C, 35.47; H, 3.57; O, 14.17; Cl, 36.64; Li, 3.07; Ti, 7.07. Found (%): C, 35.43; H, 3.54; Cl, 36.60; Ti, 7.02.

[B15C5 ⊃ Li]⁺ [TiCl₅]⁻ (Complex **13**) prepared according to the method for complex **1**. Calculated (%) for C₁₄H₂₀O₅Cl₅TiLi (498.95): C,

33.54; H, 4.22; O, 15.96; Cl, 35.35; Li, 1.38; Ti 9.55. Found (%): C, 33.50; H, 4.18; Cl, 35.31; Ti 9.52.

[B15C5 ⊃ Na]⁺² [TiCl₆]⁻² (Complex **14**) prepared according to the method for complex **1**. Calculated (%) for C₁₄H₂₀O₅NaCl₆Ti (571.87): C, 29.25; H, 3.51; O, 13.92; Cl, 37.00; Na, 8.00; Ti, 8.33. Found (%): C, 29.20; H, 3.47; Cl, 36.95; Na, 7.94; Ti, 8.39.

[DB24C8 ⊃ K]⁺² [TiCl₆]⁻² (Complex **15**) prepared according to the method for complex **1**. Calculated (%) for C₂₄H₃₂O₈K₂Cl₆Ti (783.90): C, 36.61; H, 4.10; O, 16.26; Cl, 27.02; K, 9.93; Ti, 6.08. Found (%): C, 36.58; H, 4.08; Cl, 26.98; K, 9.90; Ti, 6.03.

[DB18C6 ⊃ K]⁺² [TiCl₆]⁻² (Complex **16**) prepared according to the method for complex **1**. Calculated (%) for C₂₀H₂₄O₆K₂Cl₆Ti (695.85): C, 34.36; H, 3.46; O, 13.73; Cl, 30.42; K, 11.18; Ti, 6.85. Found (%): C, 34.31; H, 3.42; Cl, 30.37; K, 11.15; Ti, 6.81.

2.2. Complexes containing coordinated acetonitrile

[DB18C6 ⊃ Li•2MeCN]⁺ [TiCl₅•MeCN]⁻ (complex **2**).

In a 50 mL flame-dried Schlenk flask, anhydrous lithium chloride (23 mg, 0.56 mmol) and DB18C6 (200 mg, 0.56 mmol) were combined under argon. Acetonitrile (20 mL) was added and the mixture was stirred for 2 h. Titanium tetrachloride (0.105 g, 0.061 mL, 0.56 mmol) was added and the reaction mixture was stirred for another 10 h. The supernatant liquid was removed via cannula and the remaining solid was dried under vacuum. The resulting pale-yellow solid was dissolved in acetonitrile and cooled down to -30 °C. X-ray quality crystals were selected in a separate ampoule. The main amount of the complex was filtered, washed with cold acetonitrile and dried under vacuum to give **1** (281 mg, 0.24 mmol, 48 %) as a pale-yellow solid. Calculated (%) for C₂₆H₃₄Cl₅LiN₃O₆Ti (714.05): C, 43.58; H, 4.78; O, 13.40; N, 5.86; Cl, 24.74; Li, 0.97; Ti 6.68. Found (%): C, 43.52; H, 4.71; N, 5.84; Cl, 24.69; Ti, 6.63. MS-maldi: found *m/z* 367.17 [DB18C6 ⊃ Li]⁺, 383.15 [DB18C6 ⊃ Na]⁺; calculated for [C₂₀H₂₄LiO₆]⁺ and [C₂₀H₂₄NaO₆]⁺ 367.17 and 383.15, respectively.

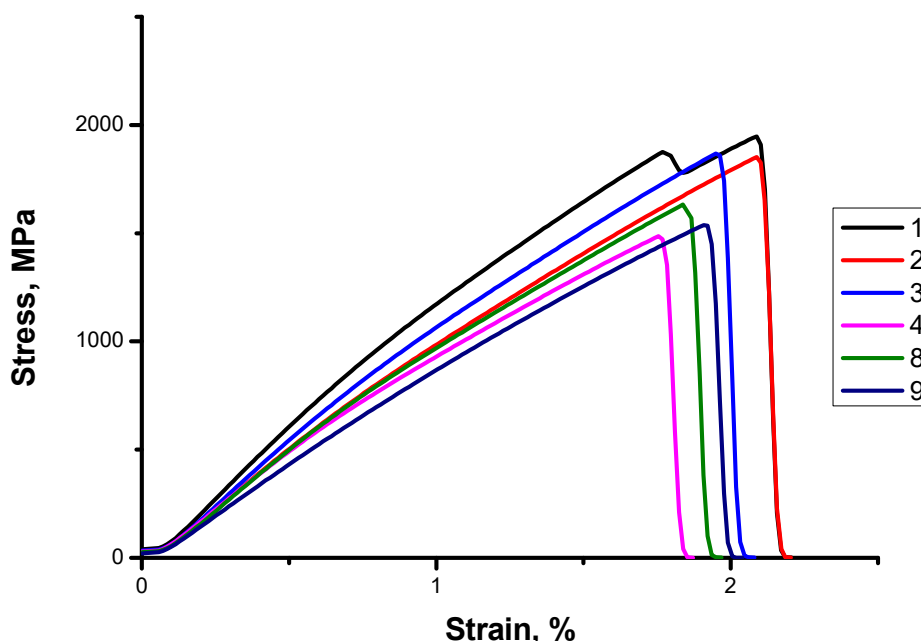


Fig. 4. Stress-elongation curves for UHMWPE orientated tapes.

$[\text{DB18C6} \supset \text{Na} \cdot 2\text{MeCN}]^+ [\text{TiCl}_5 \cdot \text{MeCN}]^-$ (complex 4) was obtained by a similar procedure from sodium chloride (33 mg, 0.56 mmol) and DB18C6 (200 mg, 0.56 mmol) and titanium tetrachloride (0.105 g, 0.061 mL, 0.56 mmol). Calculated (%) for $\text{C}_{26}\text{H}_{34}\text{Cl}_5\text{N}_3\text{NaO}_6\text{Ti}$ (729.02): C, 42.62; H, 4.68; O, 13.10; N, 5.74; Cl, 24.19; Na, 3.14; Ti, 6.53. Found (%): 42.58; H, 4.63; N, 5.70; Cl, 24.15; Ti, 6.59. MS-maldi: found m/z 383.08 $[\text{Na dibenzo-18-Crown-6}]^+$; calculated for $[\text{C}_{20}\text{H}_{24}\text{NaO}_6]^+$ 383.15.

$[\text{DB18C6} \supset \text{K} \cdot 2\text{MeCN}]^+ [\text{TiCl}_5 \cdot \text{MeCN}]^-$ (complex 6) was obtained by a similar procedure from potassium chloride (42 mg, 0.56 mmol) and dibenzo-18-Crown-6 (200 mg, 0.56 mmol) and titanium tetrachloride (0.105 g, 0.061 mL, 0.56 mmol). Calculated (%) for $\text{C}_{26}\text{H}_{34}\text{Cl}_5\text{N}_3\text{KO}_6\text{Ti}$ (748.80): C, 41.70; H, 4.58; O, 12.82; N, 5.61; Cl, 23.67; K, 5.22; Ti, 6.39. Found (%): 41.67; H, 4.54; N, 5.58; Cl, 23.62; Ti, 6.34. MS-maldi: found m/z 399.03 $[\text{DB18C6} \supset \text{K}]^+$; calculated for $[\text{C}_{20}\text{H}_{24}\text{KO}_6]^+$ 399.12.

$[\text{4 (DB18C6} \supset \text{K)} \cdot \text{TiCl}_6]^{+2} [\text{Ti}_2\text{Cl}_8\text{O} \cdot 2\text{MeCN}]^{-2}$ (complex 7).

The reaction mixture prepared according to the method for complex 3 was stored in a Schlenk tube filled with argon for 2 weeks. The precipitated orange crystals were filtered off and recrystallized from acetonitrile. Single crystals suitable for XRD were selected in an ampoule. Calculated (%) for $\text{C}_{84}\text{H}_{104}\text{Cl}_{14}\text{K}_4\text{O}_{25}\text{Ti}_3$ (2329.95): C, 43.15; H, 4.48; O, 15.75; N, 1.20; Cl, 21.23; K, 6.69; Ti, 6.14. Found (%): C, 43.15; H, 4.48; N, 1.20; Cl, 21.23; K, 6.69; Ti, 6.14.

$[\text{DB18C6} \supset \text{Na} \cdot 2\text{CH}_3\text{CN}]^+ [\text{TiCl}_5 \cdot \text{CH}_3\text{CN}]^-$ (Complex 9) was obtained by a similar procedure from sodium chloride (33 mg, 0.56 mmol) and DB18C6 (150 mg, 0.56 mmol) and titanium tetrachloride (0.105 g, 0.061 mL, 0.56 mmol). Calculated (%) for $\text{C}_{20}\text{H}_{29}\text{Cl}_5\text{N}_3\text{NaO}_5\text{Ti}$ (639.58): C, 37.6; H, 4.6; Cl, 27.7; N, 6.6; Na, 3.6; O, 12.5; Ti, 7.5. Found (%): C, 37.51; H, 4.53; N, 6.52; Cl, 27.67; Ti, 7.45.

2.3. X-ray crystal structure determination

Single crystals of the compounds 2, 4 and 7 were obtained by slow crystallization from acetonitrile solution. The X-ray diffraction data were collected at 100 K with a Bruker D8 Quest CMOS Diffractometer using the graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$, ω -scans). Using Olex2 [20], the structures were solved with the ShelXT [21] structure solution program using Intrinsic Phasing and refined with the XL refinement package [22] using the Least-Squares minimization.

Positions of hydrogen atoms were calculated and refined in the isotropic approximation within the riding model. Crystal data and structure refinement parameters for these complexes are given in Table S1.

CCDC 2184032–2184034 contain the supplementary crystallographic data for complexes 2, 4 and 7 respectively.

2.4. Ethylene polymerization

The polymerization was carried out in a 150 mL steel reactor (Parr Company). Before starting the experiment, the reactor was evacuated at a temperature of about 90°C for 40 min, then it was filled with purified argon. A solvent (toluene) and a pre-catalyst with a titanium content of $5 \cdot 10^{-6}$ mol were introduced. The total volume of the solvent did not exceed 100 mL. The slurry was stirred and ethylene was fed to the reactor under pressure of 0.7 atm (10 psi) for 30 min with vigorous stirring (600 rpm) at temperature of 30°C , which was maintained with a thermostat. At the end of the experiment, the reaction mixture was cooled, and 20 mL of ethyl alcohol and 20 mL of 1 M HCl solution were added to the reactor to deactivate unreacted organoaluminum compounds. The resulting polymer was filtered and treated with mixture of 200 mL of alcohol and 20 mL of 1 M HCl solution for 30–40 min at 60°C under stirring. After that, the suspension was settled at room temperature for 2 days, the precipitate was filtered off, washed with distilled water, alcohol and dried in vacuum for 3–4 h at 70°C .

2.5. Polymer characterization methods

DSC was performed by a differential scanning calorimeter DSC-822e (Mettler-Toledo, Switzerland) at a heating rate $10^\circ\text{C min}^{-1}$ in argon.

Viscosity-average MW of synthesized UHMWPE samples was calculated with the Mark-Houwink equation: $M_v = 5.37 \cdot 10^4 [\eta]^{1.37}$, [23] where M_v = viscosity-average MW (g mol^{-1}); $[\eta]$ = intrinsic viscosity in decalin at 135°C (dl g^{-1}); and $[\eta] = (2\eta_{sp} - 2\ln\eta_r)^{1/2} / 0.056$ (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 from the synthesized polymers were evaluated using the oriented tapes obtained by a solid-state processing of UHMWPE nascent reactor powders [24]. The monolithic tapes uniform over the entire length (100 μm in thickness and 10 mm in width) were formed at a pressure and shear

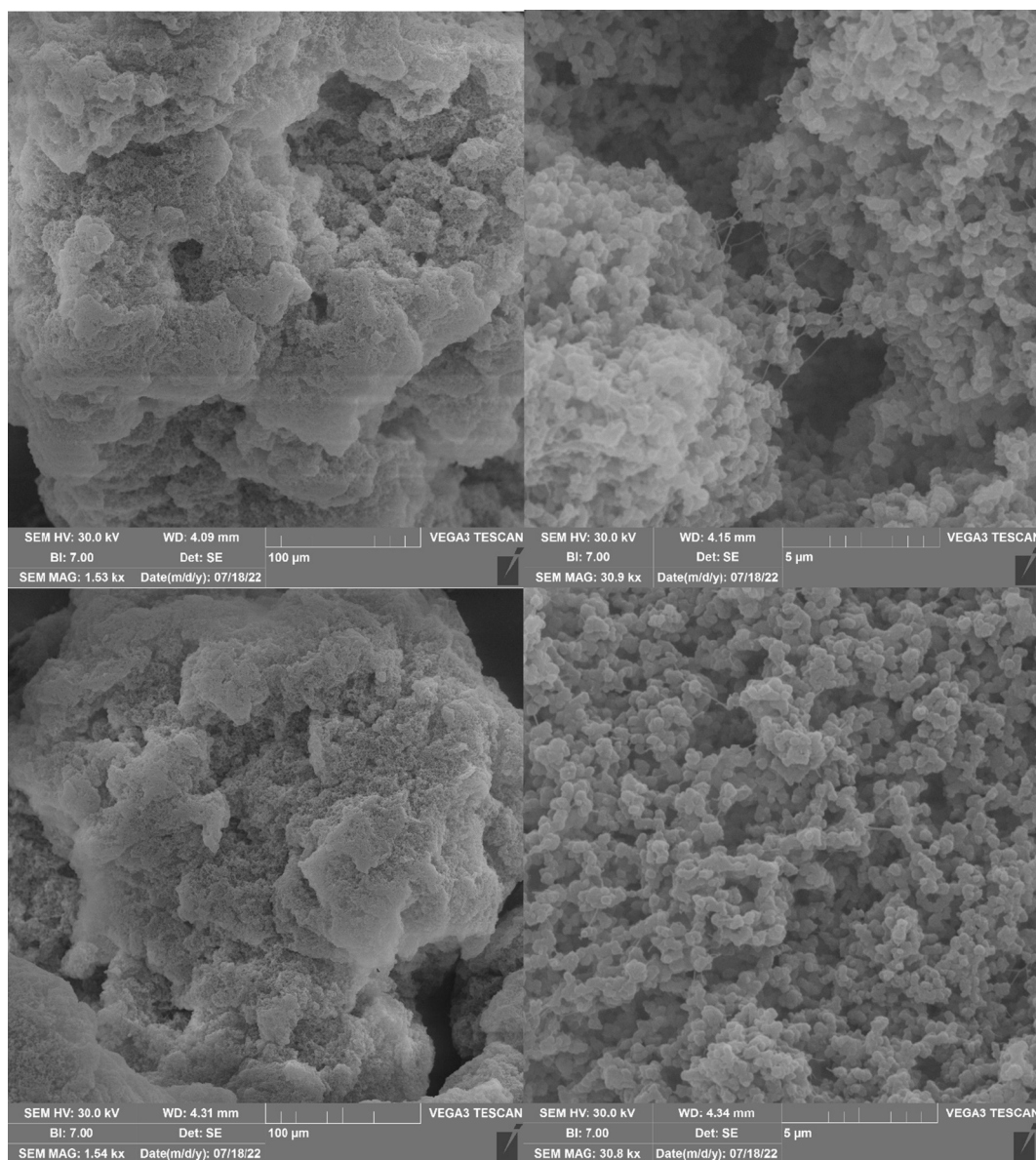


Fig. 5. SEM images of the surface morphology of UHMWPE powders obtained with catalytic system $[\text{DB18C6} \supset \text{Na}]^+ [\text{TiCl}_5]^- / \text{Et}_2\text{AlCl} + \text{Bu}_2\text{Mg}$ (top, entry 3, Tables 1-2) and $[\text{B15C5} \supset \text{Na}]^+ [\text{TiCl}_5]^- / \text{Et}_2\text{AlCl} + \text{Bu}_2\text{Mg}$ (bottom, entry 8, Tables 1-2).

deformation below the polymer melting point (124–126 °C). The tapes were subjected to uniaxial drawing while using a Spline Dac equipment. The drawing temperature was set 4 °C 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 100 mm/min initial deformation rate. The reported values were the average of at least 8 samples.

Scanning electron microscopy investigations of morphologies of nascent reactor powders were carried out with a high resolution Tescan VEGA3 SEM operated at 5 kV. As-polymerized particles were carefully deposited on SEM stubs, and the samples were coated with gold by a sputtering technique.

3. Results and discussion

The studied complexes were prepared by the interaction of an alkali metal chlorides, a crown ether, and titanium (IV) tetrachloride in anhydrous toluene or acetonitrile under an inert atmosphere using standard Schlenk techniques. When performing the synthesis in toluene,

the products were obtained in the form of highly dispersed and X-ray amorphous powders, the exact composition and structure of which remain largely speculative. In acetonitrile, products containing the coordinated solvent were formed. For some of complexes quality crystals were obtained and their structure determined by X-ray crystallography. Scheme 1 shows the synthesis conditions and structures of studied complexes.

All complexes were obtained in moderate yields, and no attempts to increase them were made. The resultant complexes were identified on the basis of ^1H , ^{13}C NMR spectra and elemental analyses. The ^1H NMR spectra of the complexes show the entire set of signals characteristic of the initial ligands (Supporting Information, Figures S7-S20). Ethylidene proton signals undergo a slight upfield shift which confirms the formation of the host-guest complex.

Positive ion MALDI MS spectra of studied complexes contain a single signal, corresponding to the complex of an alkali metal cation with a crown ether (Figures S2-S6). Regardless of the size of the crown ether cavity, $[\text{M}(\text{crown})]^+$ cations are formed.

According to X-ray diffraction analysis of the prismatic red colored

crystals, the asymmetric fragment of **2** contains the lithium cation surrounded by the dibenzo-18-crown-6 and the counter-ion $[\text{TiCl}_5\text{CH}_3\text{CN}]^-$ (Fig. 1). The lithium cation forms coordination bonds with three oxygen atoms of crown ether (Li-O 2.008(7)–2.645(7) Å (Table 1), and two solvate molecules of acetonitrile as well (Li-N 2.025(6)–2.081(7) Å), that lead to the horizontal offset of lithium cation relative to the center of plane formed by six oxygen atoms of crown-ester by 0.658(7) Å.

The coordination polyhedron of titanium(IV) ion is formed by one solvent molecule of acetonitrile (Ti-N 2.229(2) Å) and five coordinated chloride anions with reduced bond lengths compared to the average values of both calculated covalent and ionic radii (Ti-Cl 2.2555(7)–2.3182(7) Å vs 2.62 Å [25]) and 3.20 Å [26], respectively) (Fig. 1).

For a quantitative description of polyhedrons, we used the symmetry measures [27], which characterize the deviation of their shape from the ideal octahedron $S(\text{OC-6})$ and trigonal prism $S(\text{TPR-6})$. The lower of the dimensionless value of the symmetry measure $S(\text{OC-6})$ (Table 1) corresponds to a smaller deviation from the ideal octahedron and confirms the observed high symmetry of the coordination polyhedron of cation titanium (IV) in this complex. The crystalline packing is formed by multiple weak Cl... HC and O... HC interactions.

In complex $[\text{DB18C6} \supset \text{Na } 2\text{MeCN}]^+ [\text{TiCl}_5 \text{MeCN}]^-$ (Fig. 2, complex 4) the sodium cation is slightly shifted from the center of the plane formed by six oxygen atoms of crown ether by 0.0612(19) Å, that, unlike in was seen in complex **2**, lead to formation of coordination bonds with all of them (Na-O 2.522(3)–2.792(3) Å) (Table 2).

In the coordination environment of the sodium cation are also two coordinated solvate molecules of acetonitrile (Na-N 2.377(5)–2.418(5) Å), located on different sides of the plane of the crown-ester (Fig. 2). The coordination polyhedron of the titanium(IV) cation is close to octahedral (symmetry measure $S(\text{OC-6})$ is 0.349) and also formed by five coordinated chloride anions with short Ti-Cl bonds (2.2434(16)–2.3277(14) Å) and one solvate molecule of acetonitrile (Ti-N 2.228(4) Å), which is involved in the intermolecular interactions Cl... HC и O... HC as well.

According to the X-ray diffraction data (Figure S1), the general structure motif of the potassium complex **6** is structurally similar to the Li and Na analogs though insufficient single crystal quality didn't allow the structure refinement.

During storage of complex **3** in a glove box, we noticed that the shape and color of the crystals changed from yellow to orange. According to the results of X-ray diffraction analysis (Fig. 3), the complex **7** has a composition $[\text{4(KCl} \cdot \text{DB18C6)} \cdot \text{TiCl}_2]^{+2} [\text{Ti}_2\text{Cl}_8\text{O} \cdot 2\text{MeCN}]^{2-}$. The mechanism of formation of this compound is not clear, but the appearance of oxygen in the anion can be explained by the high oxophilicity of titanium and the presence of trace amounts of moisture in the solvent, despite their thorough purification and the use of the Schlenk technique. Therefore, the loss of two chlorine atoms in the form of hydrogen chloride is a result of a partial hydrolysis reaction.

In complex **7** the cation TiCl_2^{2+} is supplemented to the octahedral polyhedron of composition $[\text{TiCl}_6]^{+2}$ (Ti-Cl 2.318(2)–2.3506(12) Å) with the symmetry measure of 0.018 due the formation of donor–acceptor K-Cl $\rightarrow$ Ti1 bond with four KCl molecules with increased K-Cl bond length (K-Cl 3.2175(18)–3.521(2) Å vs 3.147(2) Å in crystalline potassium chloride) (Fig. 3) similar to previously reported structure in [28]. Each potassium atoms in KCl molecule form coordination bonds with six oxygen of crown-ester molecule (K1-O 2.789(5) – 2.961(4) Å and K1'-O 2.824(3)–2.933(5) Å) and is significantly moved from the oxygen atoms plane towards to the central cation Ti1 (1.020(3) Å and 0.9024(18) Å for cations K1 and K1', respectively). The anion of complex **7** of the composition $[\text{Ti}_2\text{Cl}_8\text{O} \cdot 2\text{MeCN}]^{2-}$ consist of two moieties' $\text{Ti}_2(\text{IV})$ also in the octahedral coordination polyhedron with symmetry measure $S(\text{OC-6})$ of 0.600 (Table 3), each connected with the oxygen atom placed on the inversion center (Ti2-O 1.780(1) Å), four chloride atoms (Ti2-Cl 2.328(2)–2.347(1) Å) and coordinated molecule of acetonitrile (Ti2-N 2.251(5) Å) (Fig. 3). An anion of a similar composition and structure was previously described in [29].

Unfortunately, all complexes obtained in the absence of acetonitrile are insoluble in toluene or THF and immediately precipitate reaction mixture as semi-X-ray amorphous solids upon the addition of crown ethers. Therefore, the compositions of these compounds were derived only from elemental analysis data and MS-maldi data, according to which they all contain alkali metal cations located in crown ether cavities.

All compounds obtained in the work were tested in the reaction of ethylene polymerization. All experiments were carried out under standard conditions - in 100 mL of toluene with $5 \cdot 10^{-6}$ mol of precatalyst at a constant 1 atm excessive ethylene pressure for 15 min. To activate the pre-catalysts, a mixture $\text{Et}_2\text{AlCl}/\text{Bu}_2\text{Mg}$ in the molar ratio Ti:Al:Mg = 1:300:100 was used, which has proven itself for the activation of cationic complexes of titanium with crown ethers [11]. The results are presented in the Table 4.

All tested complexes showed high catalytic activity in the range of 3540–4460 kg PE/mol Ti h atm.

The presence of coordinated acetonitrile in most cases leads to a slight increase in activity (with the exception of experiments 5 and 6) with a simultaneous decrease in the molecular weight of the polymer. In most cases, complexes with two alkali metal atoms and an anion of the proposed composition $[\text{TiCl}_6]^{2-}$, even in cases where they cannot be accommodated in the macrocycle cavity, show higher activity compared to compounds with one metal atom. The melting points and degrees of crystallinity of all samples are typical for UHMWPE [23] and are in the range of 136–140 °C and 65–75 %, respectively (Table 1).

Comparing the catalytic behavior of anionic titanium complexes with previously published results on cationic titanium complexes with crown ethers [11] and neutral titanium complexes with OO-type ligands [30–32] in the polymerization of ethylene in the presence of Al/Mg activators, it can be noted that both the productivity of these catalytic systems and the properties of the resulting polymers are quite similar. It seems that for the formation of catalytically active sites in the above-mentioned catalytic systems, the nature of the pre-catalyst - cationic, anionic, cationic-anionic (complex **7**) or molecular does not play an important role. In other words, in the presence of an Al/Mg activator and a monomer, all these types of pre-catalysts form similar type of active center. Unfortunately, existing data does not allow to elucidate its composition and structure. Slight difference in activity and molecular weight of resulting polymer for complexes with the same anion and different alkali metal-crown ether cations may indicate an ionic nature of the active center. Evidently, according to the generally accepted mechanism, in any case the formation of the active center from anionic titanium(IV) precursors should include metal alkylation followed by the formation of a coordinatively unsaturated ionic complex, but it is unclear if the catalytically active ions are negatively or positively charged.

The processing of obtained UHMWPE reactor powders into high-modulus oriented films was carried out by preparing monolithic samples under pressure and shear deformation at an elevated temperature below polymer melting point with subsequent uniaxial drawing [24]. Samples 5–7 and 10 were found to be unsuitable for such processing, despite the rather high molecular weights ($1.4 \cdot 10^6$ and $2.8 \cdot 10^6$, respectively). Table 5 shows the mechanical characteristics of film tapes prepared from obtained reactor powders. Stress–strain curves of UHMWPE-orientated film tapes are shown in Fig. 4. To determine the mechanical characteristics, we used film tapes obtained at a pre-break drawing ratio, that is, practically devoid of the possibility of further orientation, therefore, the breaking elongation does not exceed 2 %.

It can be noted that pre-catalysts containing coordinated acetonitrile produce UHMWPE with worse mechanical characteristics (entries 1 vs 2, 3 vs 4 and 8 vs 9).

To examine the morphologies of these powders, SEM technique was used (Fig. 5, S35–S40). At low magnification, the polymer particles have the irregular shape and porous structure, which determines the low bulk density (0.05–0.09 g/cm³) of the obtained samples. At high magnification, the surface of UHMWPE powders predominantly has the broccoli-

like morphology.

4. Conclusions

A series of ionic complexes of titanium(IV) chloride, an alkali metal chloride and various crown ethers has been synthesized. According X-ray analysis and MS data, structures of these complexes are built from alkali metal cations in the cavity of a crown ether and octahedral solvated $\text{TiCl}_5(\text{MeCN})^-$ or unsolvated TiCl_5 anions.

In the presence of Al/Mg activators ($\text{Et}_2\text{AlCl}/\text{Bu}_2\text{Mg}$), all tested complexes catalyze the polymerization of ethylene with high productivity (up to 4500 kg $\text{PE}/\text{mol Ti h atm}$). The obtained polymers are characterized by molecular weight in the range 1.4–2.8 $\times 10^6$ Da.

The UHMWPE nascent reactor powders were processed by a solvent-free method into high-strength (up to 1.9 GPa) and high-modulus (up to 125 GPa) oriented film tapes. The mechanical characteristics of oriented materials obtained on cationic titanium complexes with crown ethers [11] are only slightly inferior to those obtained in this work.

We can suggest two possible options for the formation of active sites during activation of the studied anionic complexes by organoaluminum and organomagnesium compounds. One option assumes preservation of the octahedral structure of the active center [1,2] with a titanium atom in + 3 oxidation state. Another is the complete destruction of ionic compounds with the formation of simple Ti(IV) or Ti(III) alkyl chlorides and a complex of a macrocyclic ligand with an alkali metal chloride. In this pathway, the crown ether should play no role in the formation of the active center. However, the fact that the activity of the $\text{TiCl}_4\text{-Al/Mg}$ and $\text{TiCl}_3\text{-Al/Mg}$ systems, studied by us in [32] is noticeably smaller than that found in this study (1840 and 1420 kg $\text{PE}/\text{mol Ti h atm}$ for Ti(IV) and Ti(III), respectively and noticeable effect of the cation on catalytic activity make this option, in our opinion, less likely. The second option involves returning to the consideration of the octahedral structure of the active center [1,2] with a titanium atom in + 3 oxidation state. The results of the experimental verification of both versions will be published in future publications.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Svetlana Ch. Gagieva reports financial support was provided by Russian Science Foundation; Vladislav A. Tuskaev reports financial support was provided by Lomonosov Moscow State University Department of Chemistry. Vladislav A Tuskaev reports a relationship with Lomonosov Moscow State University Department of Chemistry that includes: funding grants.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.eurpolymj.2022.111611>.

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