



Geometric isomerism effect on catalytic activities of bis(oxalato)diaquochromates(III) for 2-chloroallyl alcohol oligomerization

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Abstract. The *cis*- and *trans*-potassium bis(oxalato)diaquochromates(III) have been studied towards their catalytic activity for the 2-chloroallyl alcohol oligomerization. The geometric isomerism effect on the oligomerization products under mild reaction conditions has been investigated. The molecular masses and tactic structures of obtained poly(2-chloroallyl alcohols) have been compared and analyzed. The mechanisms of oligomerization processes have been proposed. It has been proven that two studied complexes – *cis*-K[Cr(C₂O₄)₂(OH₂)₂] and *trans*-K[Cr(C₂O₄)₂(OH₂)₂].3H₂O are highly active catalysts for the oligomerization of the beta-olefin derivative.

Keywords. Chromium(III) complexes; catalytic activities; polymerization; oxalate ion.

1. Introduction

The products of olefin polymerization are used in industry for the production of various plastics, e.g. containers, household articles, orthopedic prostheses, laboratory and medical devices.^{1–3} The chromium(III) complexes are commonly used as catalysts to the olefin and its derivatives polymerization.^{4,5} The catalytic activity of the non-metallocene chromium(III) complexes for the olefin polymerization was discovered in the first half of the 1990s.⁴ This kind of chromium(III) complexes is the focus for the olefin polymerization researchers because these catalysts are very active and stable in the industrial production of oligomers.^{6,7}

Poly(vinyl alcohol) (PVA) and its derivatives have orthopedic applications.⁸ PVA is used as a synthetic cartilage.⁸ Moreover, PVA and its derivatives are used in the world production of adhesives, hydrogels and stabilizers for emulsions.^{9,10} Besides PVA, polypropylene (PP) is the material commonly used in the polymer industries,¹¹ such as, HVDC cable insulation.¹² The derivative of vinyl alcohol and propylene, i.e. 2-chloroallyl alcohol is a monomer used for the production of polymeric hydroxy compounds. The copolymers of 2-chloroallyl alcohol is used for the production of artificial glasses and elastomers.^{13–15} In the literature, there is little

information regarding the chromium(III) complexes used in the polymerization of 2-chloroallyl alcohol (2-chloro-2-propen-1-ol). Recently, the catalytic properties of the dipicolinate chromium(III) complexes with 2,2'-bipyridine and 4,4'-dimethoxy-2,2'-bipyridine for the preparation of poly(2-chloroallyl alcohol) at the atmospheric pressure and room temperature were described.⁷ These dicarboxylate chromium(III) complexes exhibit very high catalytic activities, i.e. 2609.86 and 2254.57 g·mmol⁻¹·h⁻¹ for [Cr(dipic)₂][Cr(bipy)(dipic)H₂O]·2H₂O and [Cr(dipic)₂]Hdmbipy·2.5H₂O, respectively.⁷

The aim of our studies described in this report is first of all to investigate the catalytic activities of dicarboxylate chromium(III) complexes *cis*-K[Cr(C₂O₄)₂(OH₂)₂] and *trans*-K[Cr(C₂O₄)₂(OH₂)₂].3H₂O for the 2-chloro-2-propen-1-ol oligomerization. Secondly, the geometric isomerism effect in the bis(oxalato)diaquochromates(III) has been analyzed for the values of the catalytic activity of the synthesized complexes and the identity of the oligomerization products.

2. Experimental

2.1 Materials

All the reagents used in this work, potassium dichromate (99% purity), oxalic acid (99% purity), 2-chloro-2-propen-1-ol

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(technical grade, 90% purity), modified methylaluminoxane (MMAO-12, 7 wt% aluminum in toluene), toluene (99% purity), were purchased from Sigma-Aldrich.

2.2 Synthesis of *cis*-K[Cr(C₂O₄)₂(OH₂)₂] and *trans*-K[Cr(C₂O₄)₂(OH₂)₂].3H₂O

The *cis*-K[Cr(C₂O₄)₂(OH₂)₂] and *trans*-K[Cr(C₂O₄)₂(OH₂)₂].3H₂O complexes were synthesized according to the method of Werner and his coworkers.^{16,17} The composition and purity of the synthesized bis(oxalato)diaquochromates (III) complexes were confirmed by elemental analysis of carbon and hydrogen using the CARLO ERBA type CHNS-O 1108 analyzer. Anal. Calcd. for *trans*-K[Cr(C₂O₄)₂(OH₂)₂].3H₂O: C, 13.66; H, 2.85%; and for *cis*-K[Cr(C₂O₄)₂(OH₂)₂].3H₂O: C, 15.91; H, 1.95%. Found for *trans*-K[Cr(C₂O₄)₂(OH₂)₂].3H₂O: C, 13.41; H, 2.82%, and for *cis*-K[Cr(C₂O₄)₂(OH₂)₂].3H₂O: C, 15.19.; H, 1.80%.

The crystallographic data for *cis*-K[Cr(C₂O₄)₂(OH₂)₂] and *trans*-K[Cr(C₂O₄)₂(OH₂)₂].3H₂O have been described in the literature.^{16,18} The physicochemical properties of *cis*-K[Cr(C₂O₄)₂(OH₂)₂] and *trans*-K[Cr(C₂O₄)₂(OH₂)₂].3H₂O have also been characterized earlier in the literature.¹⁹ The TG-MS analysis confirmed the thermodynamic stability of the synthesized isomers and it shows that the *trans*-K[Cr(C₂O₄)₂(OH₂)₂].3H₂O is more stable in the solid state than *cis*-K[Cr(C₂O₄)₂(OH₂)₂]. Moreover, both isomers undergo dehydration and decarboxylation.¹⁹

2.3 MS spectra

The positive-ion mode MALDI-TOF mass spectra of obtained poly(2-chloroallyl alcohols) with the 2,5-dihydroxybenzoic acid (DHB) matrix were recorded on the Bruker Biflex III spectrometer.

2.4 NMR spectra

The ¹H and ¹³C NMR spectra of the following mixtures were obtained using the Bruker Avance III 500 (500.13/

125.76 MHz) instrument (300 K): (1) poly(2-chloroallyl alcohols), *cis*-K[Cr(C₂O₄)₂(OH₂)₂] with MMAO-12; (2) poly(2-chloroallyl alcohols), *trans*-K[Cr(C₂O₄)₂(OH₂)₂].3H₂O with MMAO-12. 1,1,2,2-Tetrachloroethane-D₂ (C₂D₂Cl₄) was used as the solvent.

2.5 Synthesis of poly(2-chloroallyl alcohols)

The oligomerization processes were carried out under constant conditions: at the atmospheric pressure, at 21 °C, under the nitrogen atmosphere, continuous mixing using a magnetic stirrer. *Cis*-K[Cr(C₂O₄)₂(OH₂)₂] (3 μmol, 0.84 mg) was dissolved in toluene (2 mL). This chromium(III) complex was used as a catalyst. The obtained solution was placed in the glass cell with a sealed stopper. Subsequently, 3 mL of the MMAO-12 solution were dropped in to the complex solution in the glass cell. In the next step, 3 mL of 2-chloro-2-propen-1-ol were added to the MMAO-12 and *cis*-K[Cr(C₂O₄)₂(OH₂)₂] mixture in the glass cell. After 20 min, the oligomerization process was finished. The product of the oligomerization (2.17 g) has been studied by MALDI-TOF mass spectrometry and NMR spectroscopy.

The same oligomerization procedure was carried out using *trans*-K[Cr(C₂O₄)₂(OH₂)₂].3H₂O (3 μmol, 1.00 mg) instead of *cis*-K[Cr(C₂O₄)₂(OH₂)₂]. The product of the oligomerization weighed 3.49 g.

3. Results and Discussion

Two geometric isomers *cis*-K[Cr(C₂O₄)₂(OH₂)₂] and *trans*-K[Cr(C₂O₄)₂(OH₂)₂].3H₂O (Figure 1) after reaction with MMAO-12 were used as the catalyst systems for the preparation of poly(2-chloroallyl alcohols). Both the synthesized complexes contain two oxalate [O⁻, O⁻] ligands, however, with different positions in space. In our studies, two processes of 2-chloro-2-propen-1-ol oligomerization have been conducted: in the first sample, the *cis* isomer was used as a catalyst,

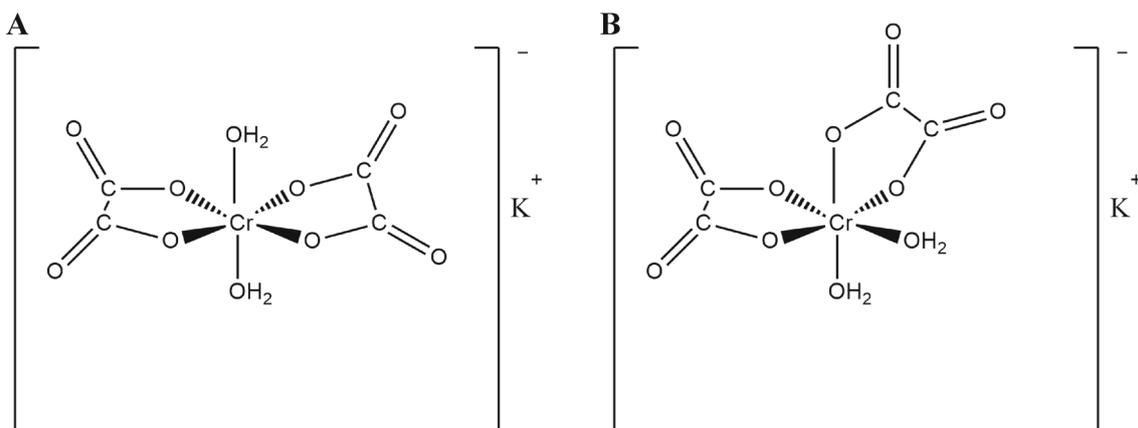


Figure 1. (A) *trans*-K[Cr(C₂O₄)₂(OH₂)₂].3H₂O; (B) *cis*-K[Cr(C₂O₄)₂(OH₂)₂].

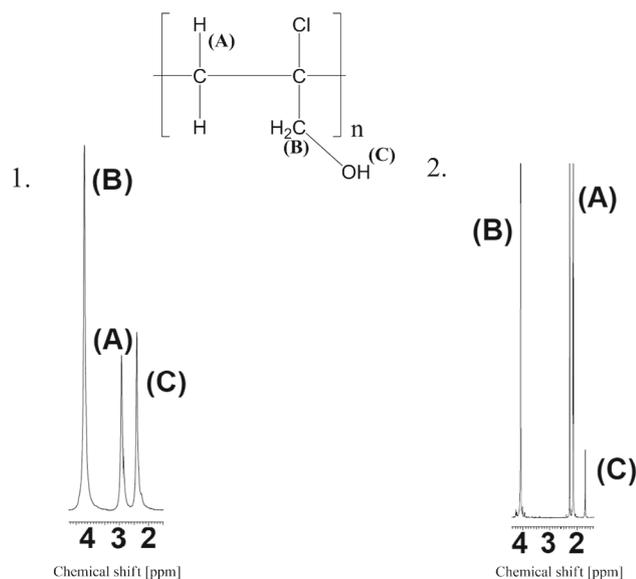


Figure 2. The ^1H NMR spectra for (1) the product of 2-chloro-2-propen-1-ol oligomerization catalyzed by *cis*- $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{OH}_2)_2]/\text{MMAO-12}$; (2) the product of 2-chloro-2-propen-1-ol oligomerization catalyzed by *trans*- $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{OH}_2)_2]\cdot 3\text{H}_2\text{O}/\text{MMAO-12}$.

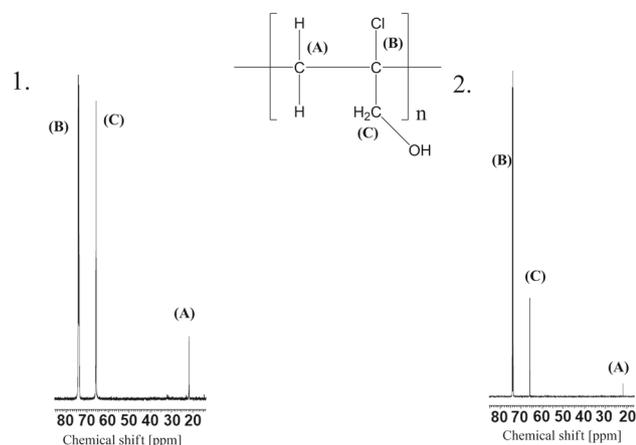


Figure 3. The ^{13}C NMR spectra for (1) the product of 2-chloro-2-propen-1-ol oligomerization catalyzed by *cis*- $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{OH}_2)_2]/\text{MMAO-12}$; (2) the product of 2-chloro-2-propen-1-ol oligomerization catalyzed by *trans*- $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{OH}_2)_2]\cdot 3\text{H}_2\text{O}/\text{MMAO-12}$.

and the *trans* isomer was used in the second one. The oligomerization products have been characterized by ^1H , ^{13}C NMR spectroscopy and MALDI-TOF mass spectrometry.

The ^1H and ^{13}C NMR spectra for the products of 2-chloro-2-propen-1-ol oligomerization catalyzed by *cis*- $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{OH}_2)_2]$ and *trans*- $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{OH}_2)_2]\cdot 3\text{H}_2\text{O}$ are presented in Figures 2 and 3, respectively. A low number of signals in the range of 20–80 ppm in the ^{13}C NMR spectra confirms the isotactic structure of the prepared oligomers.^{7,20} The specific carbon and

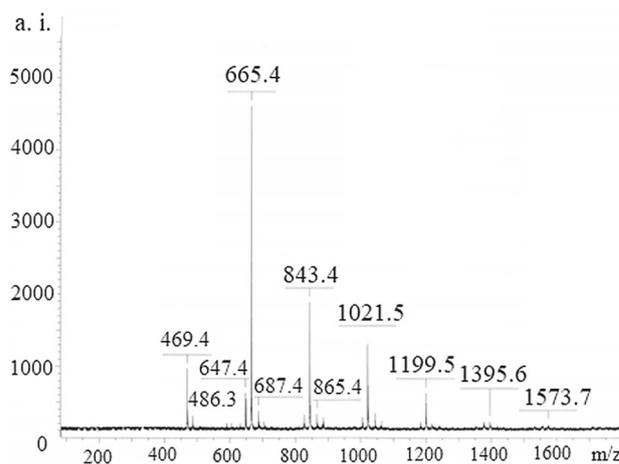


Figure 4. The MALDI-TOF mass spectrum for the product of 2-chloro-2-propen-1-ol oligomerization where *cis*- $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{OH}_2)_2]/\text{MMAO-12}$ was used as a catalyst system.

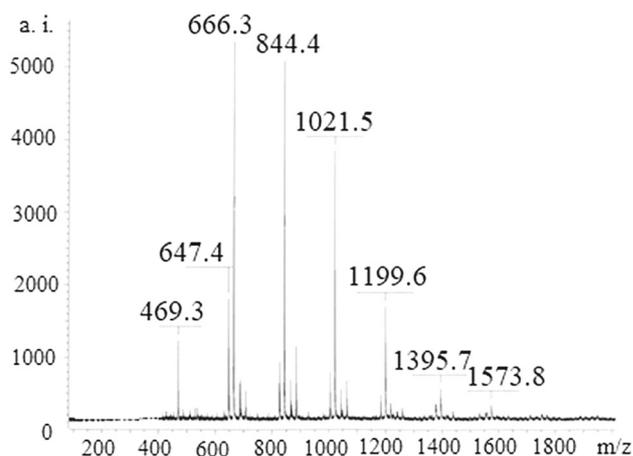


Figure 5. The MALDI-TOF mass spectrum for the product of 2-chloro-2-propen-1-ol oligomerization where *trans*- $\text{K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{OH}_2)_2]\cdot 3\text{H}_2\text{O}/\text{MMAO-12}$ was used as a catalyst system.

hydrogen atoms present in the obtained oligomers have been associated with the characteristic peaks in the ^{13}C NMR and ^1H and spectra (see Figures 2 and 3).²¹ In the ^1H NMR spectrum shown in Figure 2 at the panel (2), the satellite peaks are observed. These peaks confirm the protons interactions with carbon atoms in the oligomer.

The peaks corresponding to the signals from carbon atoms in the ^{13}C NMR spectra are shifted towards lower values of the chemical shift [ppm] as a result of the formation of the oligomer, in comparison with the signals of carbon atoms present in the 2-chloro-2-propen-1-ol molecule (monomer).^{22,23}

Moreover, the molecular masses of the obtained oligomers have been determined by MALDI-TOF mass spectrometry. The molecular peaks of the products

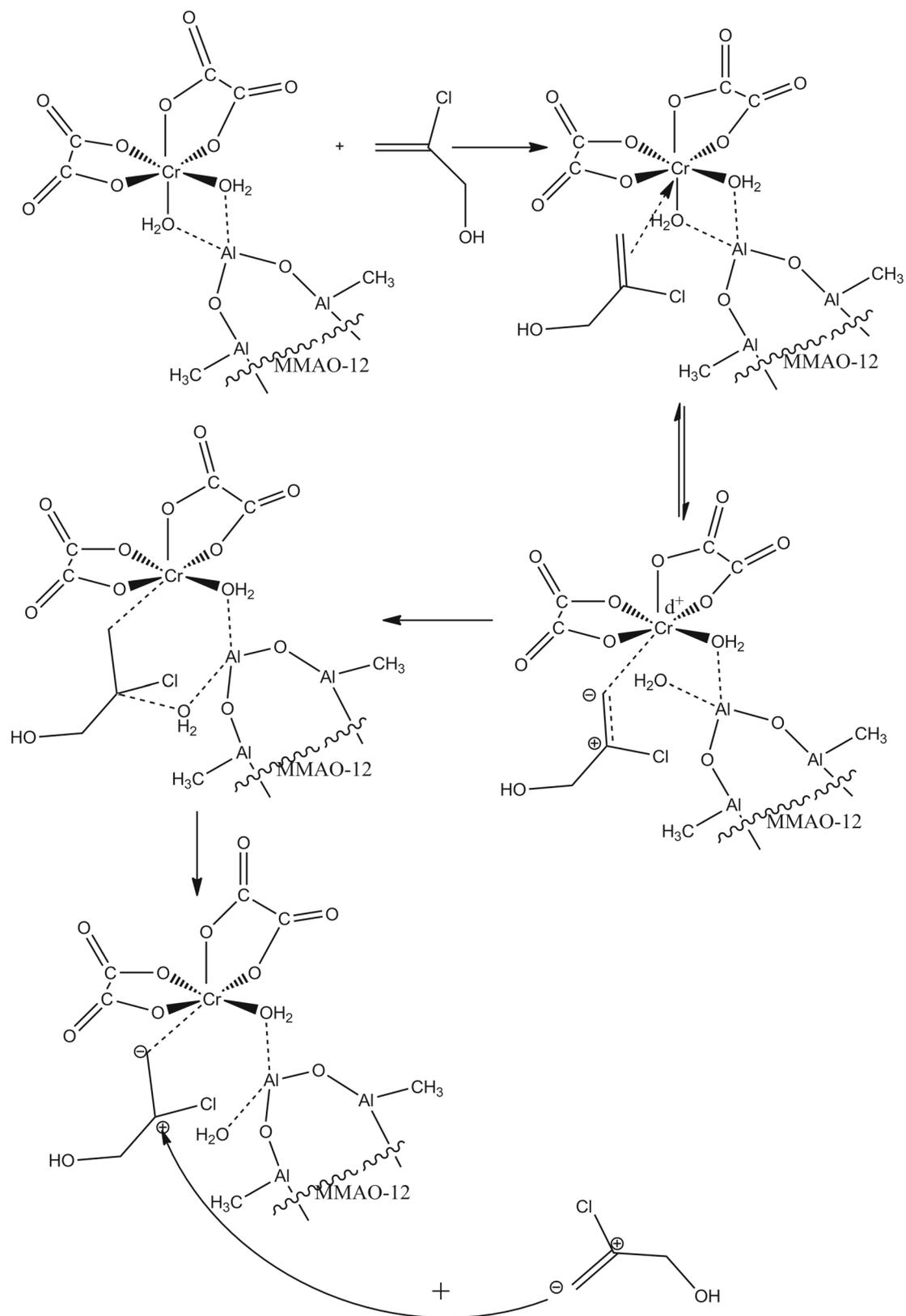


Figure 7. The proposed mechanism for the oligomerization reaction of 2-chloro-2-propen-1-ol using $trans\text{-K}[\text{Cr}(\text{C}_2\text{O}_4)_2(\text{OH}_2)_2] \cdot 3\text{H}_2\text{O}$ and MMAO-12.

of the 2-chloro-2-propen-1-ol oligomerization occur at 665.4 m/z and 666.3 m/z for the process catalyzed by *cis*-K[Cr(C₂O₄)₂(OH₂)₂]/MMAO-12 and *trans*-K[Cr(C₂O₄)₂(OH₂)₂]·3H₂O/MMAO-12, respectively (Figures 4 and 5). It can, therefore, be concluded that the obtained products consist of seven monomers of 2-chloro-2-propen-1-ol. The MS spectra analysis shows that the same 2-chloroallyl alcohol oligomerization products have been obtained using *cis*-K[Cr(C₂O₄)₂(OH₂)₂] and *trans*-K[Cr(C₂O₄)₂(OH₂)₂]·3H₂O as catalysts. In the MS spectra of both oligomers (Figures 4 and 5), besides the molecular peak, the peaks at 469.4 m/z and 469.3 m/z corresponding to the molecules of five monomers of 2-chloro-2-propen-1-ol are observed for *cis*-K[Cr(C₂O₄)₂(OH₂)₂]/MMAO-12 and *trans*-K[Cr(C₂O₄)₂(OH₂)₂]·3H₂O/MMAO-12, respectively. In the case of peaks occurring at the higher m/z values than the m/z values of the molecular peaks, it can be observed that they are the results of attaching two monomers to the obtained dominant oligomer. The difference in the values of the successive m/z peaks is within the range 178.0–196.1 m/z. This relationship responds to the molecular mass of two molecules of 2-chloro-2-propen-1-ol (185 g·mol⁻¹).

For both complex compounds, *cis*-K[Cr(C₂O₄)₂(OH₂)₂] and *trans*-K[Cr(C₂O₄)₂(OH₂)₂]·3H₂O, catalytic activities have been calculated. The values of the catalytic activities equal to 2163.25 and 3479.15 g·mmol⁻¹·h⁻¹ for *cis*-K[Cr(C₂O₄)₂(OH₂)₂] and *trans*-K[Cr(C₂O₄)₂(OH₂)₂]·3H₂O, respectively. The value of the catalytic activity of the compound was calculated as follows:

$$\text{Catalytic activity} = \frac{m_p}{n_{Cr} \cdot t}$$

where, m_p = the weight of obtained polymer [g], n_{Cr} = the quantity of Cr³⁺ moles (from the weight of the complex compound used in the experiment) [mmol], and t = the time of the polymerization [h]. The unit of catalytic activity was selected in this way so that the obtained value could be comparable with other values of the catalytic activity of the chromium(III) complex compounds described in the literature. The results of the calculations shows that *trans*-K[Cr(C₂O₄)₂(OH₂)₂]·3H₂O causes that a larger amount of the oligomer is formed than in the case of the oligomerization catalyzed by *cis*-K[Cr(C₂O₄)₂(OH₂)₂]. The catalyst system containing *trans*-K[Cr(C₂O₄)₂(OH₂)₂]·3H₂O exhibits about 1.5-fold higher catalytic activity for the oligomerization of poly(2-chloroallyl alcohol) in comparison with the catalytic activity of [Cr(dipic)₂][Cr(bipy)(dipic)H₂O]·2H₂O and [Cr(dipic)₂]Hdmbipy·2.5H₂O where dipic denotes dipicolinate, bipy means 2,2'-bipyridine and

Hdmbipy denotes the 4,4'-dimethoxy-2,2'-bipyridine organic cation.⁷

In addition, the mechanisms of the oligomerization have been proposed (Figures 6 and 7) on the basis of the knowledge of the behavior of Ziegler-Natta catalysts.^{24–26} The catalyst complex is formed between the chromium(III) complex compound and MMAO-12. The important stage is the connection of the monomer molecule to the oligomerization catalyst complex. Then the π bond is formed as a result of the interactions between the Cr(III) cation and the double bond in the monomer molecule. In the next step, the oligomer molecule is formed. The attachment of further monomer molecules is possible by creating partial positive and negative charges on the monomer molecule and the catalyzing complex. The proposed mechanisms may explain the different catalytic activity of the chromium(III) complexes described in this work. *Trans*-K[Cr(C₂O₄)₂(OH₂)₂]·3H₂O complex causes that a larger amount of oligomer is obtained than in the case of use of *cis*-K[Cr(C₂O₄)₂(OH₂)₂] complex. It may be explained by the fact that in the oligomerization mechanism, in the case of the catalytic complex containing *trans*-K[Cr(C₂O₄)₂(OH₂)₂]·3H₂O, the bonds between Al³⁺ from MMAO-12 and donor atoms from Cr(III) complex are formed with one kind of ligand (H₂O) in *trans*-K[Cr(C₂O₄)₂(OH₂)₂]·3H₂O, and oxalate anions do not play a direct role in the formation of the catalytic complex. In the mechanism of the oligomer formation using *trans*-K[Cr(C₂O₄)₂(OH₂)₂]·3H₂O, there is no steric hindrance such as oxalate anion.

4. Conclusions

In present study, the geometric isomerism effect on the oligomerization products of 2-chloro-2-propen-1-ol has been investigated using two complex compounds, *cis*-K[Cr(C₂O₄)₂(OH₂)₂] and *trans*-K[Cr(C₂O₄)₂(OH₂)₂]·3H₂O. The mechanisms of the oligomerization reaction have been proposed taking into account the geometric isomerism effect.

The investigated chromium(III) complexes exhibit very high catalytic activity. The advantage of the catalysts described in this report is the high-rate oligomerization in undemanding reaction conditions at the atmospheric pressure and at 21 °C, and that tactical oligomers are formed. *Trans*-K[Cr(C₂O₄)₂(OH₂)₂]·3H₂O has higher catalytic activity when compared to the chromium(III) complexes reported so far in the literature to obtain poly(2-chloroallyl alcohol). It has been found that the geometric isomerism of the chromium(III) complex compounds has no effect on the chain length of

the obtained oligomer. The *cis*-K[Cr(C₂O₄)₂(OH₂)₂] and *trans*-K[Cr(C₂O₄)₂(OH₂)₂]·3H₂O complexes under study, after the induction by MMAO-12, can be classified as the kind of Ziegler-Natta catalysts.

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