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Oligomerization of 2-chloroallyl alcohol by 2-pyridinecarboxylate complex of chromium(III) - new highly active and selective catalyst

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The new 2-pyridinecarboxylate (2-pic) complex of chromium(III) has been designed and synthesized as a new highly active and selective oligomerization catalyst. The crystal structure of the new compound has been determined by X-ray diffraction. The composition and purity of $[\text{Cr}(2\text{-pic})_2(\text{OH})_2]\text{NO}_3$ have been confirmed by several spectroscopic methods and the elemental analysis. Furthermore, the new complex has been investigated towards its catalytic activity for the oligomerization of 2-chloro-2-propen-1-ol under the atmospheric pressure and at room temperature. It has turned out that the novel catalyst exhibits a very high catalytic activity. Consequently, $[\text{Cr}(2\text{-pic})_2(\text{OH})_2]\text{NO}_3$ belongs to a new generation of non-metallocene catalysts.

The organometallic complexes of chromium(III) are known as catalysts for the olefin polymerization¹. The catalytic activity of the chromium(III) complexes is induced by the addition of methylaluminoxane (MAO) or its modified form (MMAO)². The metallocene chromium(III) complexes exhibit a very high catalytic activity but unfortunately they are unstable under an industrial polymerization of olefins and their derivatives conditions^{3,4}. Additionally, the decomposition of the metallocene complexes of chromium(III) is observed after their reaction with MAO.

Owing to the interesting catalytic activity of the non-metallocene complexes of chromium(III), these complexes are considered as a new generation of catalysts for olefins and their derivatives polymerization⁵. The example of the non-metallocene complex with a catalytic activity for ethylene polymerization is $\text{Cr}[\text{N}(\text{SiMe}_3)_2]_2\text{I}_2$ ($43 \text{ g}\cdot\text{mmol}^{-1}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$)⁶. This chromium(III) complex containing neutral ligands exhibits low catalytic properties. However, the non-metallocene catalysts include the chromium(III) complexes with monoanionic ligands with moderate or high catalytic activity e.g. the bis(phosphino)amide complex of chromium(III) with the activity equal $500 \text{ g}\cdot\text{mmol}^{-1}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ ^{7,8}, the chromium(III) complex with triptyceny and 2-pyridylmethyl exhibits the $6970 \text{ g}\cdot\text{mmol}^{-1}\cdot\text{h}^{-1}\cdot\text{bar}^{-1}$ catalytic activity¹. The chromium(III) complexes with pyrrole-imino-amine/ether pro-ligands $\{\text{ENN}^R\}\text{H}$ (E = NH, R = H, 1a; E = NH, R = tBu, 1b; E = O, R = H, 1c) have a very high catalytic activity for the ethylene polymerization⁹. Thus, the non-metallocene chromium(III) complexes with monoanionic ligands are promising catalysts for the industrial olefin polymerization^{10,11}.

Polyvinyl alcohol is used to produce hydrogels, to drugs production in the pharmaceutical industry and as a stabilizer in emulsions^{12,13}. 2-Chloro-2-propen-1-ol is the derivative of vinyl alcohol (hydroxyethene). Thus, the product of the polymerization of this monomer (2-chloro-2-propen-1-ol) may exhibit similar properties and applications as polyvinyl alcohol. Therefore, 2-methyl-2-propen-1-ol as the derivative of 2-chloro-2-propen-1-ol was investigated as the substrate in production of renewable hydrogels by oligomerization¹⁴. In the literature, there is lack of information about the polymerization of 2-chloro-2-propen-1-ol using complex compounds as the catalysts. Recently, the results of our studies on the new type of chromium(III) catalysts (dipicolinate complexes of Cr(III) with 2,2'-bipyridine and its derivative as ligands) containing both organic cations and anions designed for the polymerization of 2-chloro-2-propen-1-ol has been published¹⁵. These new catalysts exhibit a very high catalytic activity. It has to be mentioned that the poly(2-chloroallyl alcohol) is prepared at the atmospheric pressure and the room temperature (21 °C)¹⁵.

This report is a continuation of our previous studies. We describe the structure of the new $[\text{Cr}(2\text{-pic})_2(\text{OH})_2]\text{NO}_3$ complex compound where 2-pic denotes the 2-pyridinecarboxylate anion. Moreover, the catalytic activity

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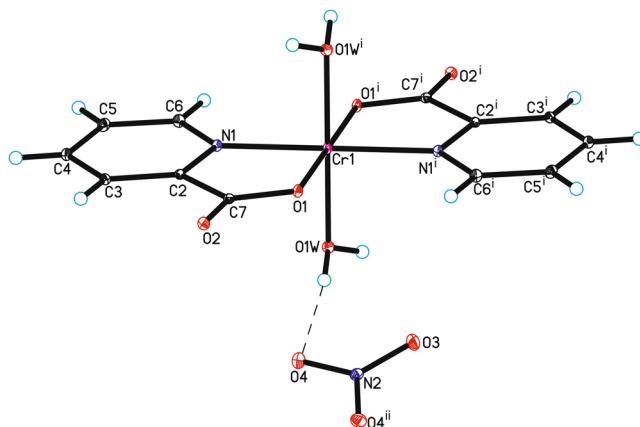


Figure 1. The molecular structure of $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$. Displacement ellipsoids are drawn at the 50% probability level (Symmetry codes: (i) $-x + 1, -y, -z + 1$ (ii) $-x + 1, y, -z + \frac{1}{2}$).

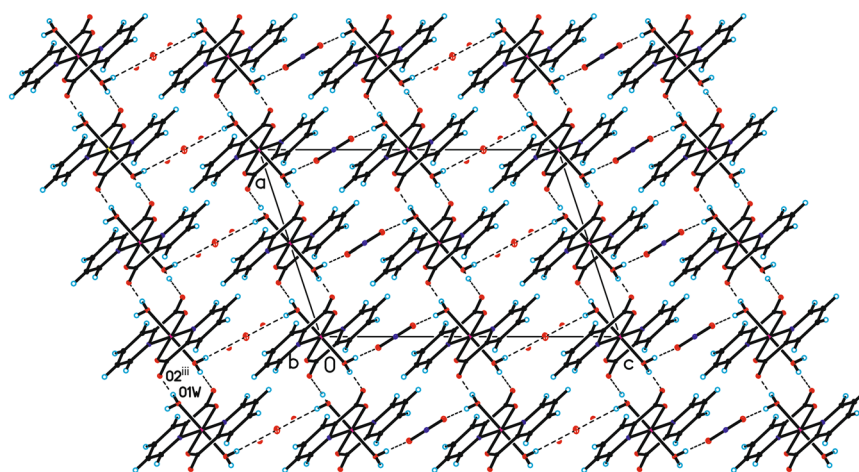


Figure 2. The crystal packing of the title compound viewed along the b -axis (hydrogen bonds and halogen bonds are represented by dashed lines; symmetry codes (iii) $\frac{1}{2} + x, -\frac{1}{2} + y, z$).

of the 2-pyridinecarboxylate complex of chromium(III) has been studied in the case of the 2-chloroallyl alcohol oligomerization. Furthermore, the catalytic activity of the novel catalyst has been compared with other known chromium(III)-based catalysts.

Results

The structure of the new complex. The crystal structure of the novel chromium(III) complex $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ has been studied by the X-ray diffraction method. The molecular structure of the new complex has been shown in Fig. 1. The crystallographic data for $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ have been collected in Supplementary Information. In the crystal structure of the $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]^+$ cation is arranged around a center of a symmetry, and in NO_3^- anion N2 and O3 atoms lying on the rotational 2-fold axis (Fig. 1).

The geometric parameters (bond lengths and angles) characterizing both $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]^+$ and in NO_3^- are typical for these units (see Supplementary Information). In the crystal packing of tile compounds $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]^+$ cations are linked via $\text{O1W}\cdots\text{H1WA}\cdots\text{O2}$ hydrogen bonds to form tapes along the $[110]$ direction. The neighboring tapes are linked by $\text{O}\cdots\text{H}\cdots\text{O}$ hydrogen bonds between water molecules and NO_3^- anion forming a three-dimensional framework structure (Fig. 2).

The purity and composition of $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ was confirmed by the elemental analysis. This test was conducted on the CARBO ERBA - O 1108 automated analyzer. Anal. Calcd for $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ (%): C, 36.54, H, 3.07, N, 10.67. Found: C, 36.53, H, 3.07, N, 10.55.

Additionally, the new complex has been studied using several spectroscopic methods, where the results are following:

UV-Vis: The regions of the maximum absorption occur at 409 nm and 548 nm (in DMSO).

MALDI-TOF-MS: m/z 394.0 (M)⁺, m/z 358.1 (M minus 2 H_2O)

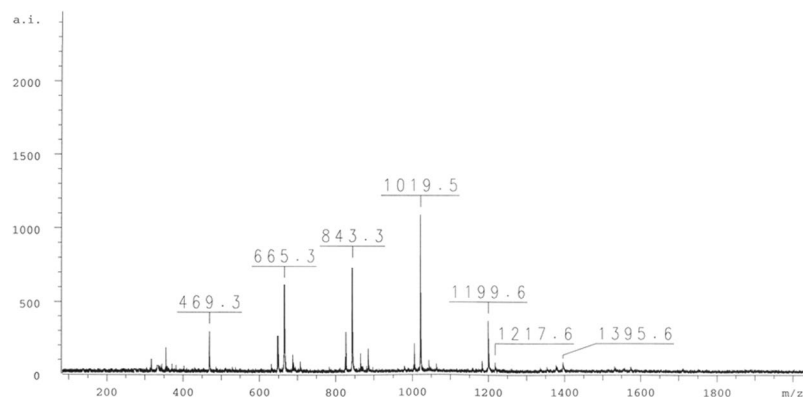


Figure 3. The MS spectrum for the oligomer consisting of 11 monomers (2-chloro-2-propen-1-ol).

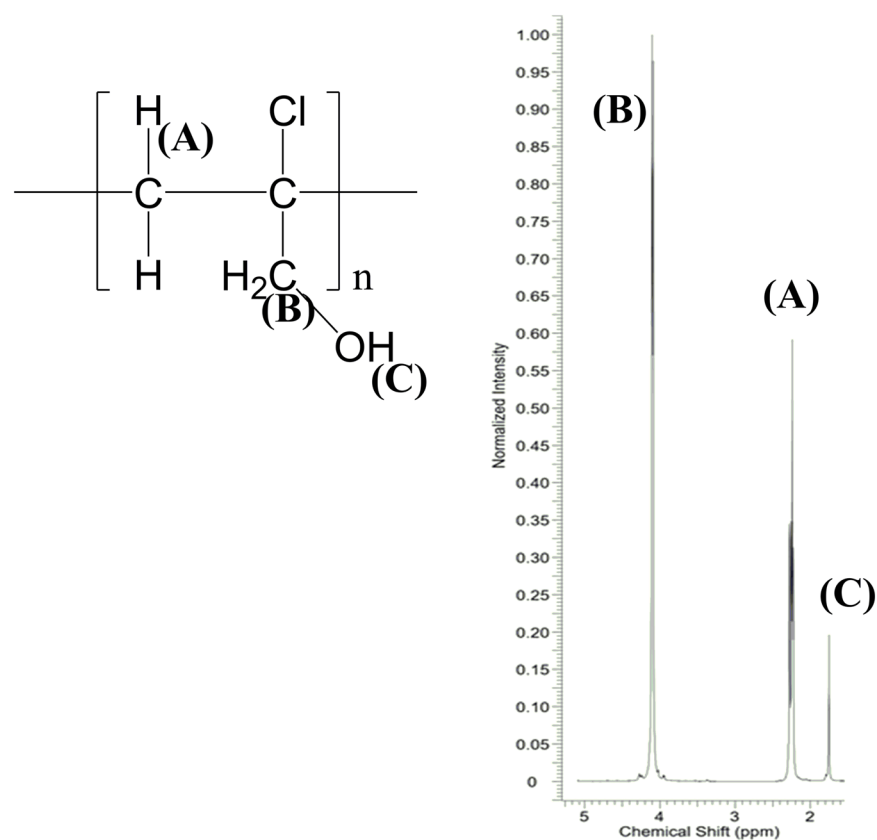


Figure 4. The ^1H NMR spectrum for the system: the oligomer of 2-chloro-2-propen-1-ol (11 monomers), $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ and MMAO-12.

IR: 3090.5 cm^{-1} hydrogen bonds, 1660.8 cm^{-1} C=O, 1476.6 cm^{-1} C-C (aromatic) stretching vibrations, 822.4 cm^{-1} C-N (aromatic), 1607.1 cm^{-1} O-C=O, 769.7 cm^{-1} Cr-O.

^1H NMR and ^{13}C NMR spectra were not recorded due to the low solubility of $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ in deuterated solvents.

The oligomerization of 2-chloro-2-propen-1-ol. The new complex compound has been investigated as catalyst in the case of the 2-chloro-2-propen-1-ol oligomerization. After mixing monomers and activated $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ (by MMAO-12) the oligomerization has been proceeded at the room temperature and at the atmospheric pressure. The poly-2-chloroallyl alcohol has been obtained as the product of the reaction. The oligomer of 2-chloro-2-propen-1-ol contains 11 monomers. The composition of the obtained oligomer has been confirmed by the spectroscopic methods including NMR and MS (Figs 3–5). Moreover, the catalytic activity of

Complex	Temperature [°C]	Catalytic activity (g·mmol ⁻¹ ·h ⁻¹ ·bar ⁻¹)	References
[Cr{2-[2-(diphenylphosphino)-1-(N-methylimidazol-2-yl) ethyl]-N-methyl imidazole}Cl ₃]	100	108	24
[Cr{tris(N-methylimidazol-2-yl)methoxymethane}Cl ₃]	100	208	24
[Cr(1,3,5-triazacyclohexane)]Cl ₃	40	717	25
[(2,6-Me ₂ Ph) ₂ (nacnac)Cr(OEt ₂)CH ₂ SiMe ₃]B(3,5-(CF ₃) ₂ C ₆ H ₃) ₄ (nacnac = 2,4-pentane-N,N'-bis(aryl)ketiminato)	75	228	26
CrMe[N(SiMe ₂ CH ₂ PPh ₂) ₂]	300	500	1
[2,6-bis(imino)pyridyl]CrCl ₃	70	1000	27

Table 1. The collection of catalytic activities of non-metallocene chromium(III) complexes for the ethylene polymerization.

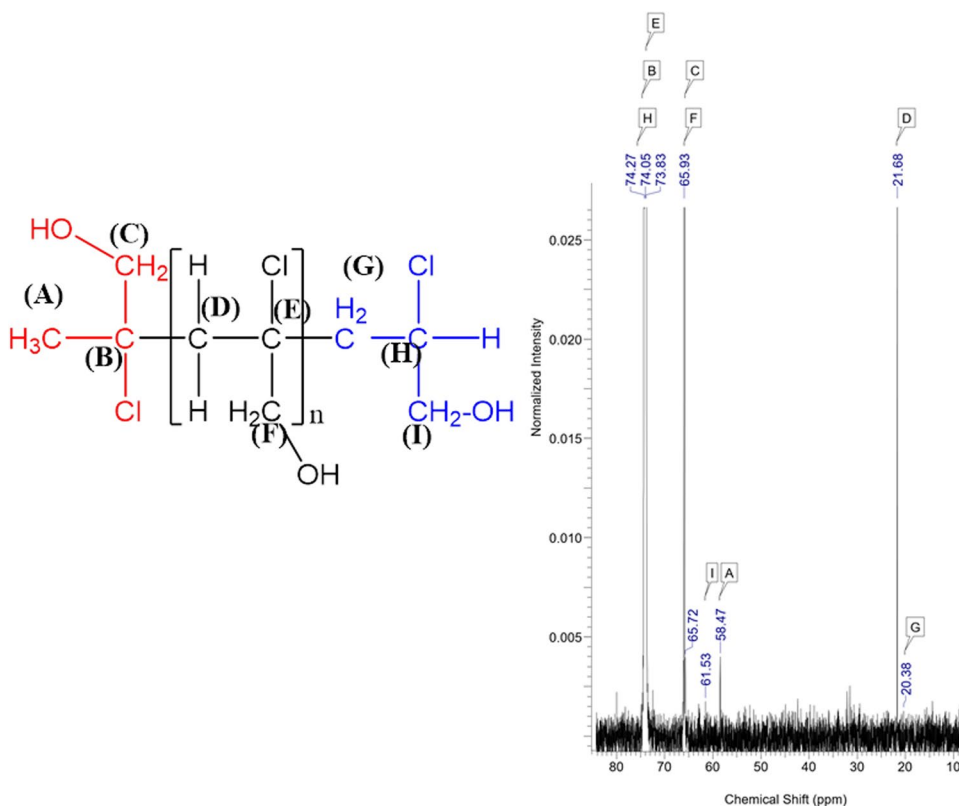


Figure 5. The ¹³C NMR spectrum for the system: the oligomer of 2-chloro-2-propen-1-ol (11 monomers), [Cr(2-pic)₂(OH₂)₂]₂NO₃ and MMAO-12.

[Cr(2-pic)₂(OH₂)₂]₂NO₃ has been calculated. It equals 1434.33 g·mmol⁻¹·h⁻¹ for the molar ratio complex[Cr(2-pic)₂(OH₂)₂]₂NO₃:MMAO = 1: 1000.

Discussion

The new complex - [Cr(2-pic)₂(OH₂)₂]₂NO₃ exhibits a very high catalytic activity for the oligomerization of 2-chloro-2-propen-1-ol. The catalysts with an activity higher than 1000 g·mmol⁻¹·h⁻¹ are assumed to be the very highly active catalysts³. Thus, it has been concluded that [Cr(2-pic)₂(OH₂)₂]₂NO₃ (1434.33 g·mmol⁻¹·h⁻¹) is a remarkably active catalyst. The analysis of the poly(2-chloroallyl alcohol) by mass spectrometry shows that the oligomer consisting of 11 monomers is formed. The molar mass of this oligomer is 1019.5 g·mol⁻¹ (Fig. 3). The MS spectrum of the oligomer shows that the peak of the highest intensity occurs at 1019.5 m/z. This value responds to 11 linked monomers of 2-chloro-2-propen-1-ol. Moreover, the distribution of mass peaks shows that the peaks differ about 185 m/z and this difference in the m/z value responds to the molecular weight of two monomers of 2-chloro-2-propen-1-ol. The MS spectrum confirms that the distribution of the obtained oligomer occurs every two molecules of 2-chloro-2-propen-1-ol. Figure 3 shows three oligomers: the first contains 5 monomers (469.3 m/z), the second contains 7 monomers (665.3 m/z) and the third oligomer about 9 monomers (843.3 m/z).

Furthermore, ¹H and ¹³C NMR methods reveal the isotactic molecular structure of the obtained oligomer. A small number of signals in range 20 ppm – 75 ppm in the ¹³C NMR spectrum of the system: the oligomer of

2-chloro-2-propen-1-ol (11 monomers), $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ and MMAO-12 confirms the isotactic structure of the obtained oligomer (Fig. 5)^{16,17}. ^{13}C NMR spectrum shows that there are three very high peaks at 74 ppm, 66 ppm and 22 ppm. Others peaks have a very low intensity. The configuration diversity visible on various carbon signals in ^{13}C NMR makes it possible to propose the tacticity of the obtained oligomer.

Recently, the first example of the poly(2-chloroallyl alcohol) preparation catalyzed by the complex compounds was reported in the literature¹⁵. Two chromium(III) complex compounds containing both organic cations and anions, namely $[\text{Cr}(\text{dipic})_2][\text{Cr}(\text{bipy})(\text{dipic})\text{H}_2\text{O}]\cdot 2\text{H}_2\text{O}$ and $[\text{Cr}(\text{dipic})_2]\text{Hdmbipy}\cdot 2.5\text{H}_2\text{O}$ were reported to exhibit a very high catalytic activity for the 2-chloro-2-propen-1-ol polymerization. These compounds have two times higher catalytic activity when compared to the catalyst described in this work - $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$. It may be explained by the fact that $[\text{Cr}(\text{dipic})_2][\text{Cr}(\text{bipy})(\text{dipic})\text{H}_2\text{O}]\cdot 2\text{H}_2\text{O}$ and $[\text{Cr}(\text{dipic})_2]\text{Hdmbipy}\cdot 2.5\text{H}_2\text{O}$ complexes contain organic anions which may play an important role in interactions with MMAO in the polymerization mechanism.

In addition to the report referred above¹⁵, so far in the literature there are no reports on the oligomerization or polymerization of 2-chloro-2-propen-1-ol catalyzed by any complex compound with MMAO. Thus, in order to compare the catalytic activity of the new catalyst - $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ with others catalysts known in the literature, we have collected the polymerization data for the selected chromium(III) complexes in Table 1. These complexes were selected for non-metallocene structure that they are as close as possible to the catalyst described in this work. As seen, $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ as catalyst exhibits minimum about 1.4 and maximum 13.3 times higher catalytic activity than the catalysts compiled in Table 1.

Conclusions

The composition and structure of the new complex catalyst- $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ has been confirmed by several methods: NMR, MS, IR, UV-Vis, elemental analysis and the X-ray diffraction. The designed and synthesized $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ exhibit the very high catalytic activity in the case of the 2-chloroallyl alcohol oligomerization. The oligomerization with the use of the new 2-pyridinecarboxylate complex of chromium(III) after the activation by MMAO-12 undergoes very easily at the room temperature and at atmospheric pressure. The product of the oligomerization reaction with the use of $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ as catalyst is the poly(2-chloro-allyl alcohol) consisting of 11 monomers. The obtained oligomer has an isotactic structure.

The reported oligomerization results are promising. This means that the results described in this report give perspectives of the use of the new catalyst to the oligomerization of other beta-olefin derivatives. This kind of oligomers is used in the industrial production of elastomers and coatings.

Methods

Materials. The reagents were purchased from Sigma-Aldrich: 2-pyridinecarboxylic acid (2-pic), 99% purity), chromium(III) nitrate hexahydrate (99% purity), lithium carbonate (99% purity), toluene (99% purity), modified methylaluminumoxane (MMAO-12, 7 wt% aluminum in toluene), 2-chloro-2-propen-1-ol (90%), and from Stanlab - nitric acid (65%).

Synthesis. 40 ml of the 0.7 M HNO_3 solution has been mixed with $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ (10 mmol, 4.0 g) and 2-pyridinecarboxylic acid (2-pic) (22 mmol, 2.7 g). The reaction mixture has been heated at reflux for 30 minutes. Then the solution obtained by dissolving (8 mmol, 0.59 g) of Li_2CO_3 in 8 mL H_2O was added to the reaction mixture. After the addition of Li_2CO_3 solution, the reaction mixture changed the color from green to purple. Then the solution has been heated for 5 hours at reflux. In the next step the reaction mixture has been cooled in a refrigerator. After cooling, the obtained product was filtered off and washed with water cooled to about 2 °C. To obtain the crystals of $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$, the powder was again dissolved in 0.1 M HNO_3 (preheated to 100 °C). Next, the hot solution was filtered and left to cool. Then the red crystals of $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ were obtained. The yield of the synthesis was 62%.

X-Ray measurements. Good-quality single-crystal samples of $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ were selected for the X-ray diffraction measurements (295(2) K) carried out on the Oxford Diffraction Gemini R ULTRA Ruby CCD diffractometer with the Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation. The structure of $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ was solved with the SHELX package and the SHELXL-97 program. CrysAlis CCD has been used to determine the lattice parameters^{18,19}. The standard geometrical calculations linked with the crystal structure of the new complex were made with the PLATON program²⁰. The following programs PLUTO-78, ORTEPII and Mercury were used to an analysis and a presentation of molecular structures²¹⁻²³.

Full crystallographic details of $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ have been deposited in the Cambridge Crystallographic Data Center (deposition No. CCDC 1811764) and they may be obtained from [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk), e-mail: deposit@ccdc.cam.ac.uk or The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK.

IR spectra. The IR spectrum (4000-650 cm^{-1} range) were obtained using the BRUKER IFS 66 spectrophotometer over the in a KBr pellet.

UV-Vis spectra. The UV-Vis spectrum were registered on the Perkin-Elmer Lambda 650. The instrument is linked with the temperature control system (with a scan accuracy of 1 nm and a 1 nm slit width at a scanning rate 120.00 nm min^{-1} (298 K) - Peltier System. The spectrum of $[\text{Cr}(2\text{-pic})_2(\text{OH}_2)_2]\text{NO}_3$ was recorded for the solution of this complex in DMSO ($C_{\text{complex}} = 5 \text{ mM}$).

MS spectra. The positive-ion mode MALDI-TOF mass spectrum were obtained using the Bruker Biflex III spectrometer. 2,5-Dihydroxybenzoic acid (DHB) was used as a matrix.

NMR spectra. The ^1H and ^{13}C NMR spectra of the system: the oligomer of 2-chloro-2-propen-1-ol (11 monomers), $[\text{Cr}(\text{2-pic})_2(\text{OH}_2)_2]\text{NO}_3$ and MMAO-12 were recorded on the Bruker Avance III 500 (500.13/125.76 MHz) instrument (300 K). The poly(2-chloroallyl alcohol) was dissolved in $\text{C}_2\text{D}_2\text{Cl}_4$.

The oligomerization process. The oligomerization experiments were carried out at atmospheric pressure and at 21 °C under the nitrogen atmosphere. The red solution of $[\text{Cr}(\text{2-pic})_2(\text{OH}_2)_2]\text{NO}_3$ (3 μmol , 1.2 mg) in toluene (2 mL) was placed using a glass syringe in the glass cell with a sealed stopper. The glass cell was placed on a magnetic stirrer throughout the duration of the experiments. In the next step, MMAO-12 solution (3 mL) was added to the toluenic solution of the new chromium(III) complex. After the addition of the MMAO-12 solution the reaction mixture changed color to brown. 2-chloro-2-propen-1-ol as monomer (3 mL) was added to the glass cell with MMAO-12 and the solution of chromium(III) complex. The oligomerization reaction was carried out for 45 minutes. After this time the sticky gel was obtained. The sample of the obtained oligomer, poly(2-chloroallyl alcohol), has been weighed. The product of the oligomerization has been characterized by the positive-ion mode MALDI-TOF mass spectrometry throughout selecting a matrix that facilitates its ionization (DHB). The MALDI-TOF was used to the direct molecular weight determination of the oligomeric poly(2-chloroallyl alcohol). Moreover, the oligomer has been examined by the NMR spectroscopy. The sample of the oligomer in a small vial was dissolved in 1,1,2,2-tetrachloro($^2\text{H}_2$)ethane. Next, it was transferred using a glass Pasteur pipette to the NMR tube. The analysis of the NMR spectra has been conducted on the ACD/NMR Processor Academic Edition computer program.

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Author Contributions

J.D. - designed the study, syntheses of the complex, oligomerization, data curation, formal analysis, writing of original draft; A.S. - X-Ray measurements, data analysis; L.C. - project administration, formal analysis; D.J. - supervising the work, project administration, formal analysis.

Additional Information

Supplementary information accompanies this paper at <https://doi.org/10.1038/s41598-018-26973-6>.

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