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# Synthesis, structural study, and application of novel copper (II) oligocatecholate

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ABSTRACT

The simple and effective synthesis of novel oligomer based on catechol-ligated copper was described in this study. The physicochemical and morphological characterizations of the resulting oligomer were characterized using PXRD, XRF, FT-IR, MALDI-TOF, DSC, SEM-EDS, GLC. The XRD study argued that the copper oligocatecholate possesses a helical structure, in which three catechol fragments were fitted into one turn of the helix. Additionally, the catalytic activity of novel oligomer was also preliminarily investigated in the aqueous oxidation of methanethiol in alkaline solution.

## 1. Introduction

Oligomer has recently progressed from a novel research field of macromolecular chemistry to a critical one, making significant and valuable contributions to biochemistry, organic synthesis, catalysis, specific separation, and analysis. Oligomer is a lower molecular weight polymer analog, comprising a relatively small number of repeat units [1]. Oligomers can be used as macromolecules to synthesize complex macromolecular structures and block copolymers[2]. These polymeric reagents can also find direct application in materials science since their processability and general properties may be more desirable than those of their polymer homologs[3]. Additionally, oligomers are essential intermediates in polymerization[4]. Therefore, research and synthesis of effective oligomers play a significant role in macromolecular chemistry.

Oligohydroxyarylenes containing hydroxyl groups that form strong coordination complexes with transition metal ions are well-known as effective macromolecular ligands. Catechol (Cat) occupies a unique position both in the synthesis of oligohydroxyarylenes and in the area of coordination chemistry[5].

Since the catecholate ligands ($Cat^{2-}$) are capable of coordinating with the transition metal at its various oxidation states, coordination complexes incorporating these ligands are often characterized by attractive electronic or magnetic properties, which in turn leads to their diverse potential applications[6]. Therefore, the design and synthesis of redox-active oligomers based on $Cat^{2-}$ have proliferated in recent years, not only because of their intriguing structural features but also due to their crucial role as advanced materials in diverse fields, such as catalysis, sorption, and storage, magnetism, optics, sensing, ion exchange, ionic/electronic conductivity, molecular recognition, and drug delivery [6–8].

In this work, we report a approach for synthesizing a new oligomer based on catechol-ligated copper (oligoCat-Cu). This simple synthesis does not consume much energy, especially using non-toxic and environmentally friendly chemicals. Specifically, firstly oligocatechol is synthesized by oxidative polymerization of catechol in the simultaneous presences of NaOH solution and 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone. The by-product of oligocatechol synthesis being 3,3′,5,5′-tetra-t-butyl-4,4′-biphenyl-diol is used as an effective antioxidant[9] as well as allergy medicine[10]. After oligomerizing catechol, a further step toward oligoCat-Cu synthesis is the binding of transition metal ions to units of oligocatechol, which consists of the synthesis of sodium oligocatecholate (oligoCat-$Na_2$) and the cation exchange between the

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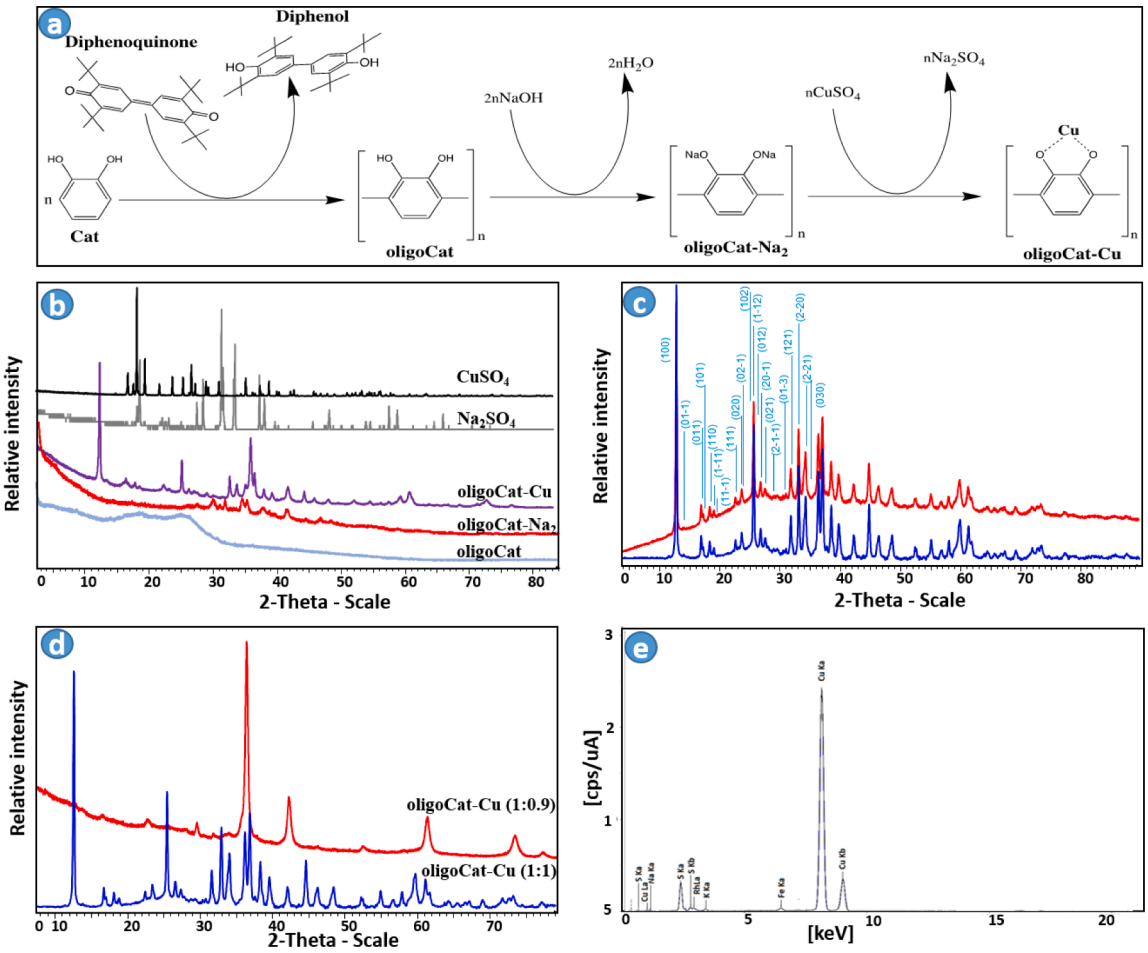


**Fig. 1.** Overall scheme for the oligoCat-Cu synthesis(a), PXRD patterns of oligomeric compounds and inorganic salts in this synthesis(b), XRD of oligoCat-Cu before (red curve) and after purification (blue curve)(c), PXRD patterns of the oligoCat-Cu samples synthesized from non-equimolar and equimolar ratios of initial raw materials(d), XRP spectrum of oligoCat-Cu(e). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

obtained oligoCat-$Na_2$ and $CuSO_4$ to give oligoCat-Cu. The overall scheme for oligoCat-Cu synthesis was described in Fig. 1a. The as-synthesized oligomer was characterized by powder X-ray diffraction (PXRD), X-Ray fluorescence (XRF) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, Matrix-assisted laser desorption/ionization-time of flight mass spectrometry (MALDI-TOF), Differential scanning calorimetry (DSC). Additionally, oligoCat-Cu dispersed in high-density polyethylene was first assessed for its catalytic activity toward oxidative degradation of methyl mercaptide.

## 2. Experimental

The detailed information on oligoCat-Cu synthesis, its physico-chemical characterization, and catalytic oxidative degradation of the mercaptide was presented in the Supplementary Material.

## 3. Results and discussion

Fig. 1b shows PXRD patterns of oligomers and inorganic salts mentioned in the oligoCat-Cu synthesis. As expected, the diffractogram of oligoCat-Cu differs significantly from those of other oligomers. While the oligoCat-Cu diffractogram exhibits a crystalline phase with a minimal amorphous component, the intense crystalline phase peaks appear weakly in the PXRD patterns of oligoCat and oligoCat-$Na_2$. Additionally, contrasting the diffractogram of oligoCat-Cu with those of two inorganic salts reveals their absence in the oligomeric sample. Specifically, the inorganic salts are individual crystalline phases, the diffraction patterns of which correspond to those present in the PDF-2 powder diffraction database for similar metal salts. Together these results provide a judgment that analysis of the obtained diffraction patterns can be considered indirect evidence that the as-synthesized substance possesses a homogeneous structure consisting of oligocatechol fragments and cupric ions.

However, the possibility of the coexistence of several crystalline phases in the studied sample should also be taken into account. This greatly complicates the indexing of powder diffraction patterns as well as establishing the crystallographic parameters of oligoCat-Cu. As a result, a series of attempts were made to purify the investigated sample to improve its crystallinity. After repeated synthesis and additional purification of the oligoCat-Cu sample, PXRD of which were also collected. The data obtained showed that the diffractograms of oligoCat-Cu samples before and after being purified were all the same (Fig. 1c).

As mentioned above, the diffraction pattern of oligoCat-$Na_2$ was notable for the presence of weak interference peaks characterizing crystalline substances. An even more surprising finding was that the partial substitution of hydrogen ions of hydroxyl groups with sodium ions did not alter the diffraction pattern of oligoCat-$Na_2$ (Fig.S1). Therefore, one question was whether the same phenomenon could occur with oligoCat-Cu. To answer that question, an oligoCat-Cu sample was further synthesized from a non-equimolar ratio of initial raw materials (oligoCat-$Na_2$:$CuSO_4$ = 1:0.9). Its diffraction pattern was also compared with that of the initial oligoCat-Cu. The obtained outcome showed that the XRD of oligoCat-Cu obtained from the non-equimolar mixture of

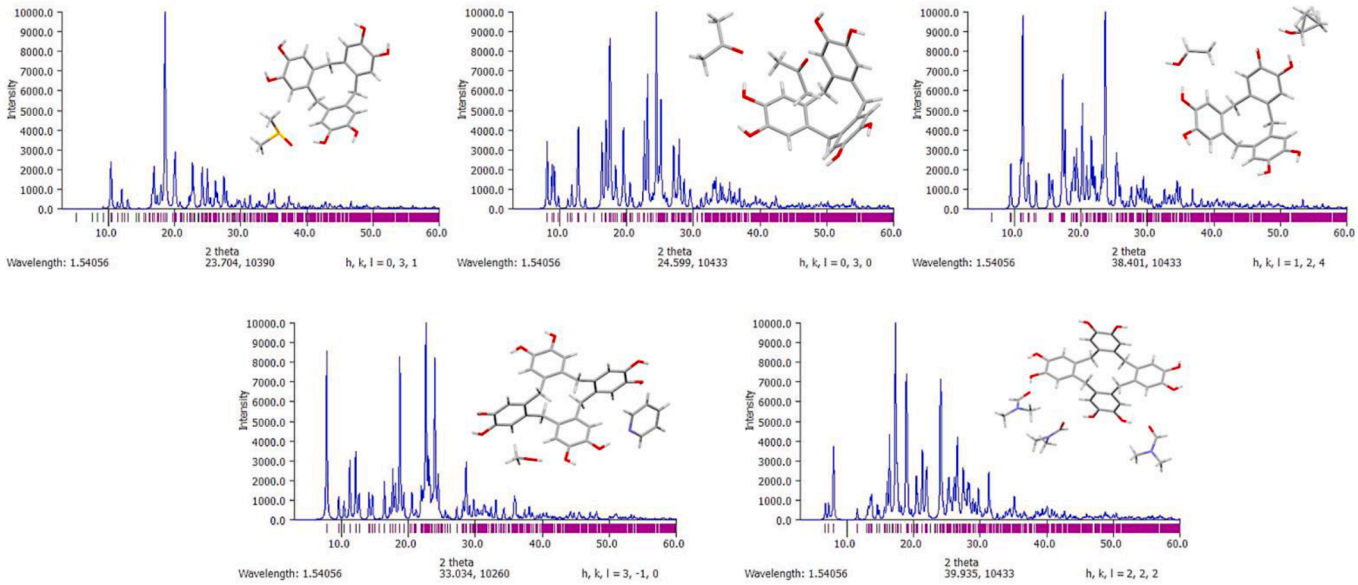


**Fig. 2.** Geometric crystal structures of several cyclic catechols and their corresponding theoretical XRD were collected from CSD.

reagents (1:09) was distinctly different from the diffraction curve of the initial oligomer (Fig. 1d). The simultaneous presence of copper and sodium atoms in the oligomer molecular could lead to the formation of mixed compounds. Furthermore, XRF analysis of the initial oligoCat-Cu sample showed a predominant substitution of copper for sodium atoms (Fig. 1e), specifically the copper content in the oligomer accounted for almost 80%. These findings unambiguously indicated that the resulting oligoCat-Cu was a product of the oligomerization of catechol with the transition metal.

Taking into account that the freshly prepared and purified sample of oligoCat-Cu is completely crystallized and can presumably represent an individual crystalline phase, an attempt was made to index the obtained diffractogram using the TOPAS software package (Fig.S2). During whole powder pattern decomposition (LeBail methods) and full profile Rietveld refinement, the crystallite sizes were constrained to the same value of mean isotropic crystal-lite size parameter, corresponding to the Lorentz-type peak broadening. One of the most suitable from the viewpoint of consistency between the observed and calculated diffraction data was a triclinic crystal with the following unit cell parameters: a = 6.9427(2)Å, b = 7.7114(2)Å, c = 8.8327(4) Å, α = 101.116(3)°, β = 95.323(4)°, γ = 94.9093(23)°, cell volume 459.41(3)Å3, space group P1, $R_{Bragg}$ = 0.22 and average crystallite size was 46.3 (2)nm. However, it should be borne in mind that this triclinic cell was not optimal in terms of symmetry, since the molecular weight of the repeating structural unit of oligoCat-Cu was 151. In this case, there are only two repeating oligomer units per cell. The available crystallographic data for copper oligocatecholates is insufficient. For a more thorough analysis of the crystal structure, information from the literature was used to generalize the structure of the synthesized compound.

If the oligomeric catechol ligated transition metal is obtained, one may not exclude the possibility of forming cyclic structures based on catechol. In this regard, a search for such structures in the Cambridge Structural Database (CSD) and an analysis of their structures were undertaken. As it turned out, compounds with two or more catechol fragments are represented by only 29 structures, most of which have crystal structures of trimers and tetramers. The powder diffraction patterns of these compounds are characterized by the presence of reflections corresponding to the base planes in the scattering angle range 2θ 8–12°, which corresponds to the minimum unit cell parameter in the range of 11–7 Å (Fig. 2). Fortunately, these values are close to the unit cell parameters of oligoCat-Cu. Using the coordinates of the atoms of the catechol fragment, the chain structures of oligoCat and oligoCat-Cu were modeled, and the geometry of the obtained molecular structures was also optimized (Fig. 3).

As can be seen from Fig. 3, the structure of studied oligomers includes repeated catechol fragments, the repeatability period of the resulting helical structure from a linear oligocatechol molecule is about 8.7 Å, and three catechol fragments are fitted into one turn of the helix.

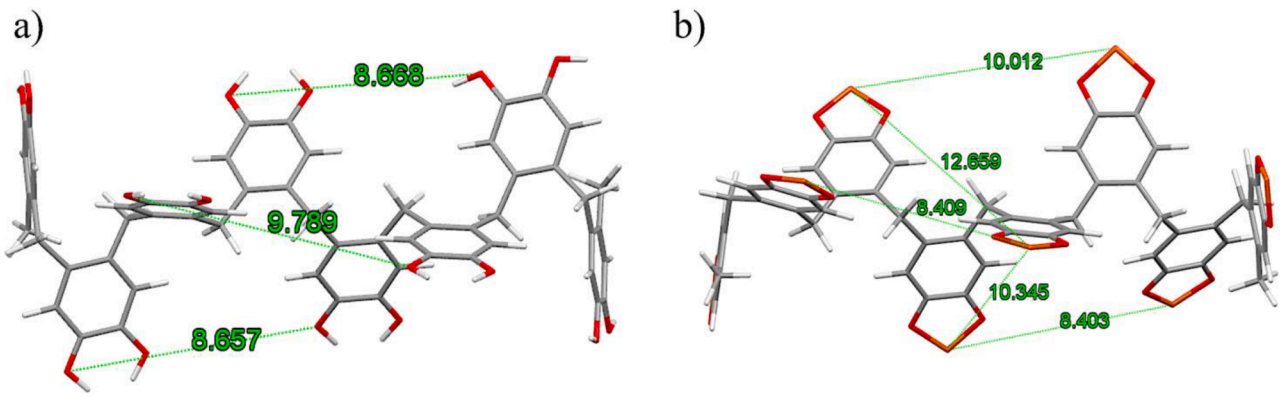


**Fig. 3.** (a)Model-optimized structures of oligocatechol and (b)copper oligocatecholate.

Thus, on the whole, the crystallographic parameters obtained by us for oligocatecholates are quite reasonable and significant.

After being synthesized, oligoCat-Cu was used to catalyze the aqueous oxidation of methanethiol in NaOH solution. Although oligoCat-Cu is entirely insoluble in water, using its powder form may raise the risk of releasing a large amount of catalytic compound into the environment. To avoid this situation, oligoCat-Cu was dispersed in high-density polyethylene. The SEM-EDX analysis of this composite was illustrated in Fig.S3. Under the catalysis of this composite, the rate constant of methyl mercaptan oxidation by oxygen was raised from 0.003 $min^{-1}$ to 0.016 $min^{-1}$, corresponding to an increase of more than 5 times (Fig.S4). This finding demonstrated the high catalytic activity of the synthesized oligomer.

## 4. Conclusion

A simple and efficient approach has been developed to synthesize novel copper oligocatecholate via oligomerization reaction of catechol and the ion-exchange reaction of sodium and cupric ion in the oligomeric system. The physicochemical analysis showed that the unit number of the as-synthesized oligomer ranges from 5 to 15, and the molecular weight of the repeating structural unit is 151. Additionally, PXRD study indicated that copper oligocatecholate possesses a helical structure, in which the repeatability period is about 8.7 Å, and three catechol fragments are fitted into one turn of the helix. The resulting oligomer dispersed in high-density polyethylene can be used as a promising catalyst for mercaptan removal. Accordingly, the rate of methyl mercaptan oxidation by oxygen increased more than five times in the presence of a catalyst based on copper oligocatecholate.

*CRediT authorship contribution statement*

**R.M. Akhmadullin:** Project administration, Conceptualization. **H.Y Hoang:** Supervision, Methodology, Conceptualization, Data curation, Software, Formal analysis, Writing - original draft, Writing - review & editing. **A.T. Gubaidullin:** Conceptualization, Methodology, Data curation. **T.F. Nigmatullin:** Methodology. **S.R. Kurbankurov:** Methodology. **A.G. Akhmadullina:** Methodology. **V.T. Le:** . **Y. Vasseghian:** . **M.U. Dao:** Methodology, Software, Visualization, Formal analysis.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2022.131847.

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