

Abstract

The work aimed to develop a new group of biomimetic iron(III) and copper(II) complexes and study the activity as analogues of enzymes – catechol dioxygenases and catechol oxidases. Literature reports indicate that the structure of ligands in complex compounds plays a key role in the context of biomimetic activity and the mechanism of catechol conversion, which was the basis for designing new N, O-donor ligands being Schiff bases.

Three series of ligands (27 compounds) were obtained by chemical synthesis, derivatives of 3-(Dimethylamino)-1-propylamine, 2-(Dimethylamino)ethylamine and 2-(Diethylamino)ethylamine. The structure of Schiff bases was confirmed by ^1H and ^{13}C NMR magnetic resonance spectroscopy, infrared spectroscopy, and elemental analysis. For 7 compounds (S17L, S18L, S19L, S23L, S24L, S27L, and S28L) single crystals were obtained, for which structural studies were performed to confirm their structure. The obtained ligands were used in the syntheses of biomimetics. For this purpose, a series of syntheses of iron(III) and copper(II) complexes were performed. In the crystalline form, 3 Fe(III) complexes (S17-Fe, S19-Fe and S29-Fe), 13 Cu(II) complexes (S6-Cu, S7-Cu, S8-Cu, S9-Cu, S22-Cu, S26-Cu, S27-Cu, S28-Cu, S29-Cu, S31-Cu, S32-Cu, S33-Cu and S34-Cu) and 8 complexes containing the substrate – catechol (S7-Fe-CAT, S9-Fe-CAT, S17-Fe-CAT, S18-Fe-CAT, S19-Fe-CAT, S27-Fe-CAT-H₂O, S27-Fe-CAT-MeOH and S28-Fe-CAT) were obtained. No ternary complex with copper(II) ion could be obtained. Structural studies were carried out for the crystals of complex compounds, which allowed for determining the exact structure of the obtained systems.

For 16 obtained copper(II) and iron(III) complexes, activity towards 3,5-di-tert-butylcatechol (3,5-DTBC) was confirmed by monitoring the course of the reaction in the UV-VIS spectrum. The appearance of a band with a maximum of approx. 400 nm confirmed that the main product of 3,5-DTBC conversion by the obtained compounds is 3,5-di-tert-butylquinone (3,5-DTBQ). In the studied systems, no spectral changes characteristic of catechol dioxygenase biomimetics were observed. Moreover, the presence of 3,5-DTBQ in the post-reaction mixture was confirmed by structural studies of single crystals obtained after the conducted conversion reaction. The best activity among all tested complexes was obtained for S6-Cu, in which the ligand

contained a hydroxyl group in position 4 of the aromatic ring. The least active complex was S28-Cu, containing bromide substituents in positions 3 and 5 of the aromatic ring. Among the iron(III) complexes, the best activity was shown by S19-Fe, in which the ligand contained tert-butyl groups substituted in positions 3 and 5 of the aromatic ring.

Analysis of the obtained results indicates correlations between the catalytic activity of the obtained compounds and their structure. All obtained iron(III) and copper(II) complexes with designed ligands act following the mechanism of action of catechol oxidases. The obtained results indicate that the presence of an unbound protonated amine group significantly increases the activity of the obtained complexes, while the electron-accepting properties of chloride and bromide substituents in the aromatic ring reduce the activity. Studies have shown that the presence of a propyldiamine bridge in the ligand structure increases the efficiency of the catalyst compared to compounds containing an ethylenediamine bridge.

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