

**SYNTHESIS OF Co(II) COMPLEX WITH LIGAND OF Salen TYPE BEARING
"FREE" CARBOXY-GROUPS AND ITS CATALYTIC ACTIVITY
IN ASYMMETRIC OXIDATION OF METHYLPHENYLSULFIDE**

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Recently, the metal complexes with ligands of Salen type have been actively studied as catalysts for various organic reactions. Selective sulfoxidation of sulfides to chiral sulfoxides is one of the important ways to obtain useful compounds that have been widely used in organic synthesis and medical chemistry. Some metal-salen complexes of Mn(III) and Ti(IV) showed catalytic activity in selective sulfoxidation of sulfides, but this processes were carried out in environmentally non-friendly solvents, such as chlorinated ones. There were multiple attempts to replace organic solvents by water.

In our work, we attempted to adjust the Co(II)-salen catalyzed sulfoxidation of sulfides to 'green chemistry' principles. The idea of the study was to develop water-soluble Co-Salen unit. For this purpose, Co-Salen moiety was modified by carboxy-groups.

The Co(II)-salen was obtained as a result of interaction of Co(II) acetate and Salen ligand (L), prepared using chiral (1R,2R)-(-)-1,2-diaminocyclohexane (Fig. 1). The composition of the obtained complex was confirmed by CHN analysis and correspond to formula $\text{Co}\{\text{Co}(\text{L})\}(\text{AcOH})(\text{DMF})$. The Co(II)-salen synthesized in the work showed high catalytic activity in the oxidation of methylphenylsulfide (thioanisole) by hydrogen peroxide as an oxidant in water at room temperature for 16 hours. The reaction mixture was analyzed by NMR spectroscopy and GCMS method. Two blank experiments with Co(II) acetate as catalyst and without any catalyst were performed at the same reaction conditions and only corresponding sulfone was obtained with 95 % and 97 % yield, respectively, evidencing that the reaction was indeed catalyzed by the Co-Salen complex. Methylphenylsulfoxide was obtained as a major product (95 % yield) and only 5 % of the sulfone were detected.

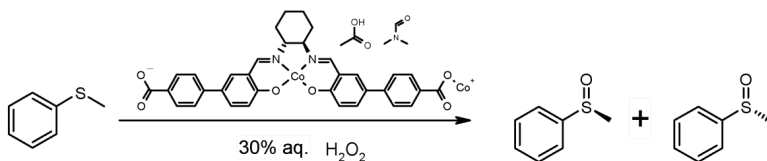


Fig. 1. Sulfoxidation of thioanisole catalyzed by $\text{Co}\{\text{Co}(\text{L})\}(\text{AcOH})(\text{DMF})$

The methylphenylsulfoxide was isolated by column chromatography on SiO_2 using Hex:EtOAc mixture 2:1 as eluent. R- and S- isomers of methylphenylsulfoxide were isolated by chiral chromatography; their content was 51 % and 49 %, respectively.

The prepared compound has potential of application as water-soluble catalyst for transformation of sulfides to sulfoxides with low quantity of sulfone by-product, and has potential for further development of the asymmetric oxidation catalysts.