

# Chemoselective Oxidation of Sulfides by Simple Metal-salen Catalyst

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**Abstract:** Two simple metal-salen catalysts Ni(III)-Salen (**1**) and Mn(III)-Salen (**2**) were developed and characterized by sharing the same ligand. The controlled oxidation of sulfide to sulfoxide and sulfone was studied under the optimized reaction condition. Complex **1** exhibit the catalytic activity for oxidizing sulfides to sulfoxides at room temperature regardless of heating or excess amount of oxidant. While, Complex **2** show high activity and selectivity of oxidizing sulfides to sulfones.

**Keywords:** metal-salen complex, oxidation, sulfides

## 1. Introduction

The synthesis of sulfoxide and sulfone compounds has been paid much attention in organic chemistry since they have a wide range of biological activity and broad application prospects in medicine and pesticide.<sup>1</sup> Although a lot of catalysts have been developed for the oxidizing of sulfide into sulfoxide or sulfone.<sup>(2,3,4)</sup> This transformation still suffered by either harmful or expensive reagents, complicated procedure and over-oxidation of sulfoxides to sulfones. Therefore, search for newer methods for the selective oxidation of sulfides to sulfoxides has continued. Herein, we report the selective oxidation of sulfide to sulfoxides and sulfones based on simple nickle and manganese catalysts using salen compound as ligand.(Figure 1)

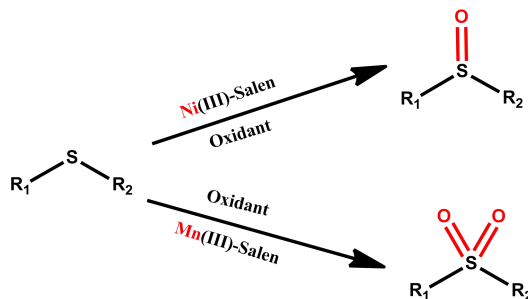


Figure 1. Oxidizing of sulfides catalyzed by metal-Salen complexes

## 2. Experimental

### 2.1. Synthesis of Salen ligand (**L**)

To a solution of ethylenediamine (0.45 g, 7.5 mmol) in EtOH (150 mL) was added 5-bromo-3-(tert-butyl)-2-hydroxybenzaldehyde (3.84 g, 15 mmol) in a 250 mL three-neck round-bottom flask. The reaction was heated to reflux for 12 h with stirred. After cooling to room temperature, the resulting solid was collected by filtration, and then washed with small amount of cold EtOH and dried in air to give yellow Salen ligand **L** (3.46 g, 6.45 mmol, 86 %). H NMR (CD<sub>3</sub>Cl, 400 MHz)  $\delta$  (ppm): 1.43 [s, 18 H, C(CH<sub>3</sub>)<sub>3</sub>], 3.93 (s, 4 H), 7.23 (s, 2 H), 7.39 (s, 2 H), 8.32 (d, J = 1.6 Hz, 2 H), 13.84 (s, 2 H, OH). IR:  $\nu$ (C=N): 1640.08 cm<sup>-1</sup>.

### 2.2. Synthesis of Mn (III)-Salen complex (**1**) and Ni (III)-(Salen) complex (**2**)

To a solution of **L** (0.54 g, 1.0 mmol) in 120 mL CHCl<sub>3</sub>/EtOH (v: v= 1: 1) was added Mn(OAc)<sub>2</sub>· 4H<sub>2</sub>O (0.29 g, 1.2 mmol) or Ni(OAc)<sub>2</sub>·6H<sub>2</sub>O (0.30 g, 1.2 mmol). The mixture was heated to reflux for 6 h with

stirred under N<sub>2</sub> atmosphere, and then O<sub>2</sub> was bubbled through the mixture, remaining refluxed another 24 h. After cooling to room temperature, the solvent was removed by evaporation. The residue was sonicated with water, collected by filtration and dried in the air to give brown solid **1** (0.56 g, 0.86 mmol, 86 %). HI-MS: Calculated: 590.9879, found: 590.9894. IR:  $\nu(\text{C}=\text{N})$ : 1615.52 cm<sup>-1</sup>. **2** (0.57 g, 0.88 mmol, 88 %). HI-MS: Calculated: 593.9848, found: 593.9836. IR:  $\nu(\text{C}=\text{N})$ : 1621.61 cm<sup>-1</sup>.

### 3. Results and discussion

Catalytic oxidation of sulfide using **1** or **2** as catalyst, PhI(OAc)<sub>2</sub> as the oxidant and methyl phenyl sulfide as substrate. Under the optimal conditions catalyst **1** give the sulfone products in excellent conversion of 100% and yield of 99%. While under the similar conditions, catalyst **2** show remarkable selectivity with the conversion of 100% and the yields of 99% on the transformation of methyl phenyl sulfide to sulfoxide. Meanwhile, regarding to catalyst **2** there is no sulfone product found regardless of heating or even adding overmuch of oxidant. Moreover, broad functional group compatibility and tolerance has been proved by using various substrates in this oxidation reaction, both catalyst **1** and **2** all give good to excellent conversion and yields.

### 4. Conclusions

Two simple metal-Salen catalysts Ni(III)-Salen (**1**) and Mn(III)-Salen (**2**) were developed and characterized. Catalyst property investigation of complex **1** show high activity of oxidizing methyl phenyl sulfide to sulfone with conversion of 100% and selectivity of 99%. While, complex **2** exhibit highly selective catalytic activity for oxidizing methyl phenyl sulfide to sulfoxide with conversion of 100% and selectivity of 99% at room temperature regardless of heating or excess amount of oxidant. Both of them show broad functional group compatibility and tolerance.

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### References

1. P. M. Gloria, J. Gut, L. M. Goncalves, P. J. Rosenthal, R. Moreira, M. M. Santos, *Bioorgan. Med. Chem.* 19 (2011) 7635.
2. S. Zhao, Y. Jia, Y. F. Song, *Appl. Catal. A-Gen.* 453 (2013) 188.
3. S. Ahammed, D. Kundu, M. N. Siddiqui, B. C. Ranu, *Tetrahedron. Lett.* 56 (2015) 335.
4. M. Mandal, D. Chakraborty, *RSC. Adv.* 5 (2015) 12111.