

## Me<sub>6</sub>[14]N<sub>4</sub>dieneCu(ClO<sub>4</sub>)<sub>2</sub> and Me<sub>6</sub>[14]N<sub>4</sub>aneCu(ClO<sub>4</sub>)<sub>2</sub> Complexes as Catalysts for Hydroxylation of Phenol

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The hydroxylation of phenol to hydroquinone and catechol was catalyzed by complexes of copper(II) *i.e.*, Me<sub>6</sub>[14]N<sub>4</sub>dieneCu(ClO<sub>4</sub>)<sub>2</sub> and Me<sub>6</sub>[14]N<sub>4</sub>aneCu(ClO<sub>4</sub>)<sub>2</sub> using H<sub>2</sub>O<sub>2</sub> as oxidant and DMF as solvent. In the presence of the catalysts, the 37.7 % phenol conversion was obtained with 57.7 % selectivity to diphenol for Me<sub>6</sub>[14]N<sub>4</sub>dieneCu(ClO<sub>4</sub>)<sub>2</sub> and 35.2 % phenol conversion was obtained with 45.2 % selectivity to diphenol for Me<sub>6</sub>[14]N<sub>4</sub>aneCu(ClO<sub>4</sub>)<sub>2</sub> under the optimum reaction.

**Key Words:** Azamacrocycle, Copper(II) complexe, Catalyst, Phenol, Diphenol.

### INTRODUCTION

The dihydroxybenzenes, especially the hydroquinone (HQ) and catechol (CAT), are important organic chemical intermediates and widely used<sup>1-3</sup>. Direct hydroxylation of phenol with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as oxidant is one of the most important industrial synthesis methods for hydroquinone and catechol and is now the green catalytic synthesis technology research hotspot<sup>4,5</sup>. However, few examples were reported that the azamacrocyclic complexes as a catalyst for this reaction<sup>6,7</sup>.

In this paper, the catalytic activities of the two azamacrocyclic complexes of copper(II) *i.e.*, Me<sub>6</sub>[14]N<sub>4</sub>dieneCu(ClO<sub>4</sub>)<sub>2</sub> (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazamacrocyclic-4,11-dieneCu·2ClO<sub>4</sub>) and Me<sub>6</sub>[14]N<sub>4</sub>aneCu(ClO<sub>4</sub>)<sub>2</sub> (5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazamacrocyclotetradecaneCu·2ClO<sub>4</sub>) for the hydroxylation of phenol reaction were studied.

### EXPERIMENTAL

All reagents were of AR grade and used without further purification. The Me<sub>6</sub>[14]N<sub>4</sub>dieneCu(ClO<sub>4</sub>)<sub>2</sub> and Me<sub>6</sub>[14]N<sub>4</sub>aneCu(ClO<sub>4</sub>)<sub>2</sub> catalysts were synthesized according to the literature<sup>8,9</sup> and characterized by IR spectra and elemental analysis. The products of the catalytic phenol hydroxylation reaction were analyzed using an Agilent 1200 liquid chromatograph.

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**Catalytic activity studies:** The catalytic activity study towards the hydroxylation of phenol was carried out in a 50 mL flask fitted with a water-cooled condenser. In a typical reaction, phenol (1.0 g) and the catalyst (10 mg) were mixed in 20 mL of DMF and the reaction mixture was heated to 50 °C with stirring. An aqueous solution of 30 % H<sub>2</sub>O<sub>2</sub> (3 mL) was dripped to the reaction mixture slowly and reacted at 50 °C for 5 h. The products were analyzed using an Agilent 1200 liquid chromatograph. Yields of the main reaction product (HQ and CAT) reported in following section were defined as  $C_{\text{phen.}} (\text{mol } \%) = \{([\text{HQ}] + [\text{CAT}])/[\text{ph}]\} \times 100$ , where  $C_{\text{phen.}}$  is the conversion of phenol (%), [ph] is the mol number of phenol in the feed, and [HQ], [CAT] are the mol numbers of hydroquinone and catechol produced.

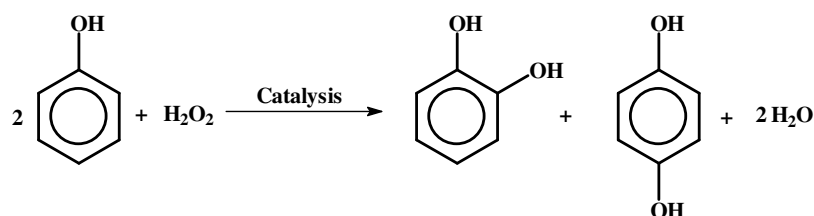


Fig. 1. Hydroxylation of phenol reaction using Me<sub>6</sub>[14]N<sub>4</sub>dieneCu(ClO<sub>4</sub>)<sub>2</sub> and Me<sub>6</sub>[14]N<sub>4</sub>aneCu(ClO<sub>4</sub>)<sub>2</sub> as catalysts and H<sub>2</sub>O<sub>2</sub> as oxidant

## RESULTS AND DISCUSSION

**Building of liquid chromatographic analysis method:** After repeated experiments, the phenol, hydroquinone and catechol could be well analyzed using an Agilent 1200 liquid chromatograph with a ZORBAX Eclipse XDB-C18 4.6 × 150 mm column (Fig. 2). The mobile phase was methanol and water ( $V_{\text{CH}_3\text{OH}}/V_{\text{H}_2\text{O}} = 2:3$ ), the flow velocity speed is 0.6 mL/min at 25 °C and UV-vis detection ( $\lambda = 277 \text{ nm}$ ). Resorcinol is internal standard and the minimum separation degree (R) is 1.4.

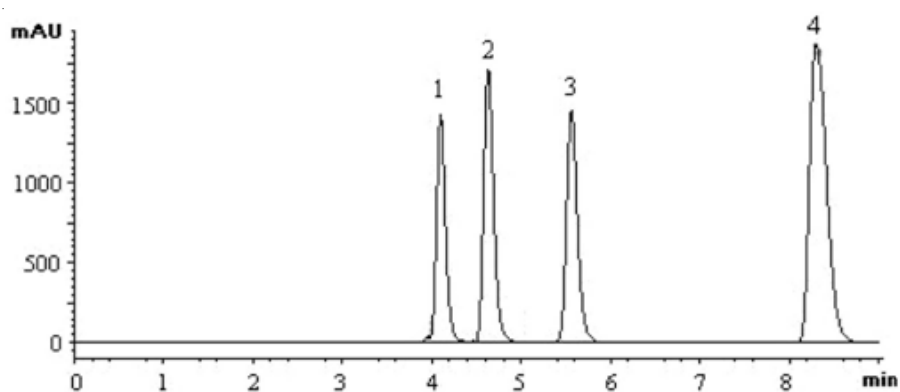


Fig. 2. Chromatogram of hydroquinone (1), resorcinol (2), catechol (3), phenol (4)

**Studies of the reaction conditions of the hydroxylation of phenol:** In order to achieve suitable reaction conditions for the maximum hydroxylation, the following experimental parameters such as reaction temperature, reaction time, pH value and H<sub>2</sub>O<sub>2</sub>/phenol molar ratio were studied in order to observe their effect on the reaction product pattern.

**Effect of reaction temperature:** The phenol conversion and product selectivity in reaction temperature range of 20-85 °C were studied. After many experiments, 50 °C was chosen as a suitable reaction temperature condition.

**Effect of reaction time:** The influence of reaction time on the catalytic activity of the two azamacrocyclic copper(II) complexes catalysts was studied at 50 °C. With the increase of reaction time, phenol conversion increased. After 5 h, the reaction achieves steady-state, so the suitable reaction time is about 5 h.

**Effect of pH value:** The acidity of reaction medium also has a remarkable influence on the phenol conversion. The experimental results showed that the suitable reaction pH is about 4.6.

**Effect of H<sub>2</sub>O<sub>2</sub>/phenol molar ratio:** The effect of the H<sub>2</sub>O<sub>2</sub>/phenol molar ratios on the phenol conversion and H<sub>2</sub>O<sub>2</sub> conversion was studied. A lower molar ratio of H<sub>2</sub>O<sub>2</sub>/phenol in the reaction leads to low phenol conversion and a higher H<sub>2</sub>O<sub>2</sub>/phenol molar ratio may lead to high by-product. The experimental results showed that the suitable H<sub>2</sub>O<sub>2</sub>/phenol molar ratio is about 3.

**Catalysts for hydroxylation of phenol:** The catalytic results of the hydroxylation of phenol reaction are listed in Table-1. It can be seen from Table-1 that Me<sub>6</sub>[14]N<sub>4</sub>dieneCu(ClO<sub>4</sub>)<sub>2</sub> and Me<sub>6</sub>[14]N<sub>4</sub>aneCu(ClO<sub>4</sub>)<sub>2</sub> catalysts have high phenol conversion and certain catalyzed selectivity for the hydroxylation of phenol.

TABLE-1  
CATALYTIC ACTIVITY IN THE HYDROXYLATION OF PHENOL WITH H<sub>2</sub>O<sub>2</sub>

Catalysts	Phenol (%)	Selectivity (%)		HQ/CAT
		HQ	CAT	
Me <sub>6</sub> [14]N <sub>4</sub> dieneCu(II)	37.7	36.3	21.4	1.70/1
Me <sub>6</sub> [14]N <sub>4</sub> aneCu(II)	35.2	25.4	19.8	1.28/1

Reaction conditions: reaction temperature 50 °C, reaction time 5 h.  
H<sub>2</sub>O<sub>2</sub>/phenol (molar ratio) about 3, solvent: DMF, pH = 4.6.

## Conclusion

The research results show that the Me<sub>6</sub>[14]N<sub>4</sub>aneCu(ClO<sub>4</sub>)<sub>2</sub> and Me<sub>6</sub>[14]N<sub>4</sub>dieneCu(ClO<sub>4</sub>)<sub>2</sub> catalysts exhibited good catalytic activity and certain catalytic selectivity in the reaction of hydroxylation of phenol with H<sub>2</sub>O<sub>2</sub> as oxidant, under mild reaction conditions.

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