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# Dendrimers as an Efficient Catalyst for the Oxidation of Multi Substituted Alcohols

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**Abstract**

A new dendrimeric ligand (L) was synthesized by the Michael addition of ethylenediamine to methyl methacrylate. The prepared ligand was complexed Cu (II) ions, The ligand and its complex were characterized by elemental analysis and spectroscopic studies (FT-IR, UV-Vis, $^1$H NMR and ESI-MS). Square pyramidal geometry was proposed for copper complexes, on the basis of UV-Vis spectroscopic data and molar conductance measurements. The catalytic applications of ligand metal complex were recorded for the oxidation of cyclohexanol, benzyl alcohol, 1-phenyethanol, propanol, respectively and eco-friendly, non-toxic hydrogen peroxide.

**Keywords:** Dendrimeric ligand; Copper complexes; Catalytic oxidation; Hydrogen peroxide; Oxidant

## Introduction

Ideally, dendrimers are perfect mono disperse macromolecules with a regular and highly branched three-dimensional architecture. Dendrimers are produced in an iterative sequence of reaction steps, in which each additional interaction leads to a higher generation material. The first example of an iterative synthetic procedure toward well-defined branched structures has been reported by Vogtle, [1] who named this procedure a "cascade synthesis". A few years later, in the early 1980s, Denke walter 2-During the early years, the area blossomed and dendrimers based on a variety of repeat units appeared: these included amides, amines, carbo silanes, siloxanes, esters, ethers, phenyl acetylenes, various organometallics, amino acids and even nucleic acid based dendrimers [2-6]. In addition, secondary function was also incorporated into these systems. These included porphyrins, phthalocyanines, saccharides, mesogens, anionic and cationic groups and various chromophores. Over the next few years more and more applied systems began to be developed and this area of applied research is now one of the most vibrant areas of dendrimer chemistry. Examples of such applications are many and diverse: they include encapsulation and solubilisation, [7] medicinal and bio mimetic applications, [8] novel materials, [9,10]and catalysis (Figure 1).

## Experimental

### Materials and methods

All the chemicals were of AR Grades and used without further purification. Ethylenediamine and methylmethacrylate were purchased from S.D. Fine Chem. Ltd., Mumbai, India. Metal chlorides ($CuCl_2.2H_2O$ and $CoCl_2.6H_2O$) and methanol were procured from E. Merck, Mumbai, India. The percentages of C, H and N were determined by a Vario EL elemental analyzer. Electronic spectra were recorded on a Perkin Elmer Lambda- 40, double-beam UV-Visible spectrophotometer. FTIR spectra of the compounds were recorded on Perkin Elmer 1750 FTIR spectrophotometer (CT 06859 USA) using KBr pellets in the range of 4000-400 $cm^{-1}$. 1H NMR Spectra were achieved with a Bruker (DRX-400) spectrometer. Mass spectra were recorded using Model-Q-TOF Micro mass ESI source. Molar conductance measurements were carried out on Decibel conductivity meter at room temperature (DB-1038). Melting points were determined on Veego instrument (Model REC-2203882).

### Synthesis of ligand (L)

Ethylenediamine (0.1 mol) and methylmethacrylate (0.4 mol) in methanol were mixed together in a round bottom flask and stirred for 24 hrs at room temperature. Further, ethylenediamine (0.04 mol) was added and refluxed for further 24 hrs at 40-50°C. The golden yellow oily liquid obtained. Molecular weight 572.78 gm $mol^{-1}$, golden yellow oily liquid, anal. calc. for $C_{26}H_{56}N_{10}O_4$(%): found (calculated): C. 54.1% (54.52%); H, 9.2% (9.9%); N, 24.5% (24.45%); I.R. (KBr pellets, $cm^{-1}$).

### CuL:sss

Yield: 62.3%, mol. Wt.: 841.67 g $mol^{-1}$, m.p. >300°C, green colour, anal. Calc. for$[Cu_2(C_{26}H_{56}N_{10}O_4)]Cl_4$: found(calculated): C, 37.5% (37.1%); H, 6.31% (6.71%); N, 15.9%(16.64%); IR (KBr pellets, $cm^{-1}$): 3420 ($NH_2$)str., 1590 (C=O)str., 3090 (N-H)str., 1220 (CN)str., 450, 430, 475 (Cu-N) ; UV-Vis. ($H_2O$, nm): 219 (n→σ*), 262 (π→π*), 324 (n→π*), 709($2B_1g$→$2B_2g$); Molar conductance: 600.9 $\Omega^{-1}cm^2M^{-1}$; ESI-MS (m/z): 701.8 $[M\text{-}4Cl^+2H^+]$, 350.3$[(M\text{-}4Cl/2)^+1H^+]$, 288.2 $[\{(M\text{-}4Cl)/2\}\text{-}Cu^+2H^+]$, 257.3 $[\{(M\text{-}4Cl)/2\}\text{-}Cu\text{-}2O^+3H^+]$, 220.1$[\{(M\text{-}4Cl)/2\}\text{-}Cu\text{-}C_2H_6O_2\text{-}4H^+]$,161.2$[\{(M\text{-}4Cl)/2\}\text{-}Cu\text{-}C_4H_{13}N_2O_2\text{-}4H^+]$,104$[\{(M\text{-}4Cl)/2\}\text{-}Cu\text{-}C_6H_{20}N_4O_2\text{-}2H^+]$.

## Result and Discussion

### Catalytic oxidation reaction

Catalytic Activity for Oxidation, in order to carry out the catalytic oxidation of tested three different oxidants are used these are t-BuOOH, /$H_2O_2$, and PhIO.[11,12]. In this present research the most appropriate oxidant that I have used is hydrogen peroxide no dough whatever the yield is using peroxide but the importance of using this oxidant is its easily availability, non toxic nature and cheap. The oxidation reaction of 1-phenylethanol was conducted using a polymer-dendrimeric

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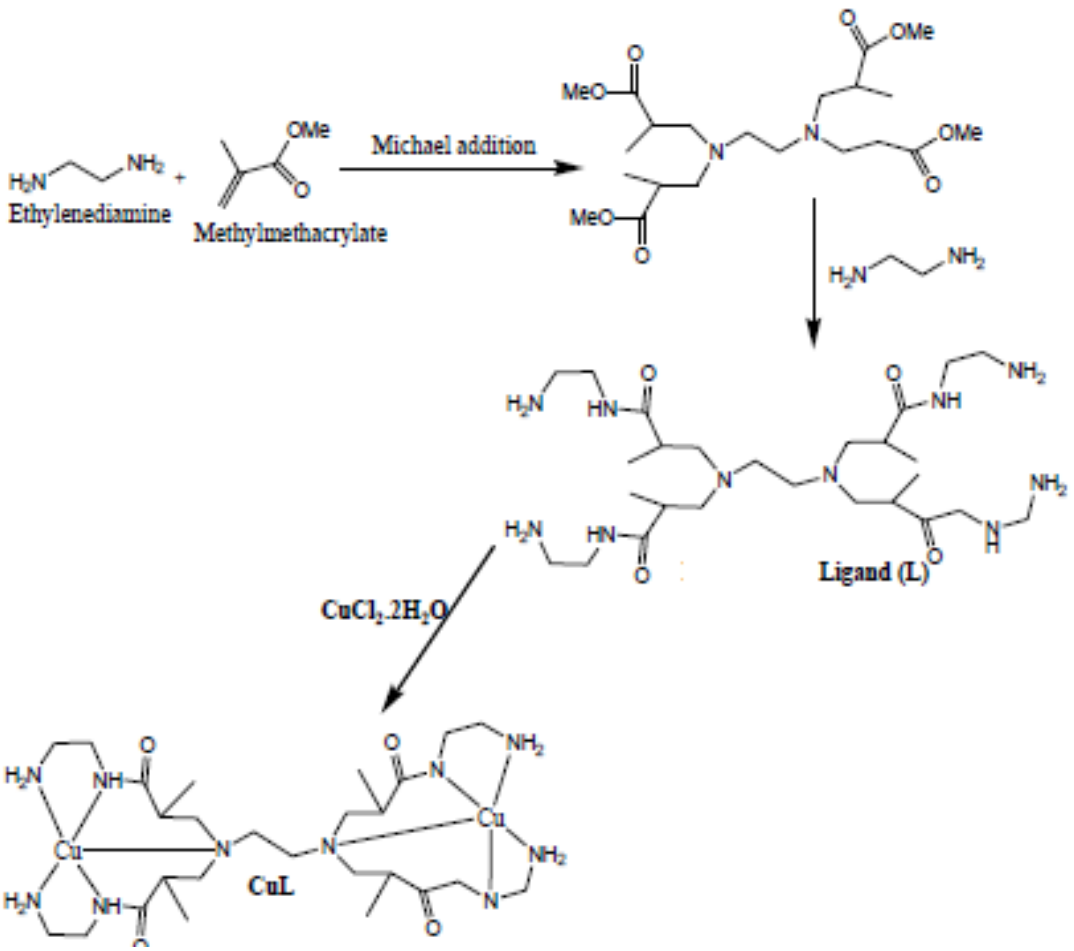


Figure 1: Scheme for the synthesis of dendrimer metal complex.

| Time(hr) | Substrate | Product | Yield | Selectivity |
|---|---|---|---|---|
| 3 | Cyclohexanol | Cyclohexanone | 65 | 52 |
| 3 | Benzylalcohol | Benzylaldehyde | 63 | 49 |
| 3 | 1-phenylethanol | 1-phenylethanol | 100 | 100 |
| 3 | Propanol | Propanone | 52 | 15 |

Reaction conditions: temperature 70°C, $H_2O_2$ (5mmol), Catalyst (0.05 mmol), acetonitrile(5 mmol).

Table1: Catalytic oxidation of alcohols.

copper metal complex. The catalytic activity is dependent on the type of oxidant. The oxidation with t-BuOOH gave a higher yield (expressed as a percentage) than $H_2O_2$, because t-BuOOH is a more-efficient oxidant, due to weaker O-O bonds, with respect to $H_2O_2$. This trend is similar to that which was reported previously. The suitable amount of oxidant used is 2.5 equiv and acetonitrile is a suitable solvent. To understand the effect of various reaction parameters on catalytic oxidation, a systematic study was performed on the oxidation of 1-phenylethanol as the substrate, using a dendrimeric copper metal complex and hydrogen peroxide as an oxidant [13,14]. The results are shown in Table 1. The results clearly shows that the temperature, amount of catalyst, and type of solvent affect the product yield (1-phenylethanol). The blank (control) experiment revealed that no reaction occurred in the absence of the oxidant [15]. When the oxidation of 1-phenylethanol was performed in different solvents, the results show that the catalytic activity is the highest in the absence of a solvent.

## Conclusion

The synthesis of dendrimeric ligand copper metal complex was successfully done. The complex was used as catalyst for the oxidation of various alcohols. The nature of O-O bond has influences the product yield. Hydrogen peroxide was used as oxidant it oxidized the alcohols into their respective oxides. Furthermore the effect of various reaction parameters was also recorded.

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