AMERICAN JOURNAL OF PHARMTECH RESEARCH

Journal home page: http://www.ajptr.com/

Synthesis, Characterization and Mechanism of Catalytic Oxidation of Dendrimer metal Complex

Mir Shabeer Ahmad[1]*, Ghulam Mohammad Jan[1]

1.Department of Chemistry, Govt. Degree College Boys Kulgam J&k (India)

ABSTRACT

The unique properties associated with these dendrimers such as uniform size, high degree of branching, water solubility, multivalency, well-defined molecular weight and available internal cavities make them attractive for biological and drug-delivery applications. Commercialization of dendrimers is now forthcoming. 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, 1H 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 dendrimer metal complex is active towards the oxidation of alcoholic substrates using molecular oxygen as substrate. The effect of various parameters on the rate of reaction is also explained.

Keywords: Dendrimers, Michael addition, Square pyramidal, Catalyst, Oxidation

*Corresponding Author Email: mirlaik2008@gmail.com

Received 01 October 2016, Accepted 09 October 2016

Please cite this article as: Ahmad MS *et al*., Synthesis, Characterization and Mechanism of Catalytic Oxidation of Dendrimer metal Complex. American Journal of PharmTech Research 2016.

INTRODUCTION

Dendrimers are nano-sized, radially symmetric molecules with well-defined, homogeneous, and monodisperse structure consisting of tree-like arms or branches [1]. These hyperbranched molecules were first discovered by Fritz Vogtle in 1978, by Donald Tomalia and co-workers in the early 1980s, and at the same time, but independently by George R. Newkome. The second group called synthesized macromolecules 'arborols' means, in Latin, 'trees'. Dendrimers might also be called 'cascade molecules', but this term is not as much established as 'dendrimers' [2-4]. Dendrimers are nearly monodisperse macromolecules that contain symmetric branching units built around a small molecule or a linear polymer core [5-7]. 'Dendrimer' is only an architectural motif and not a compound. Polyionic dendrimers do not have a persistent shape and may undergo changes in size, shape, and flexibility as a function of increasing generations [8-10]. Dendrimers are hyperbranched macromolecules with a carefully tailored architecture, the end-groups (i.e., the groups reaching the outer periphery), which can be functionalized, thus modifying their physicochemical or biological properties [11-16].

MATERIALS AND METHOD

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 (CuCl2.2H2O and CoCl2.6H2O) 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). Molecular modeling was performed with a semi empirical PM3 as implemented in hyper chem 8.0 software program package (Hypercube, Inc., USA).

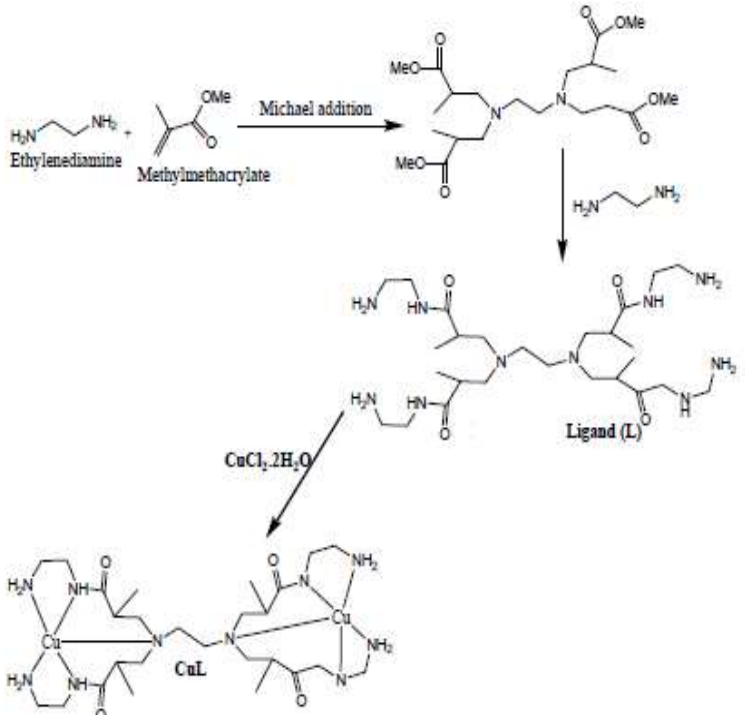
Synthesis of Ligand (L)

Ethylenediamine (0.1 mol) and methylmethacrylate (0.4 mol) in methanol were mixed together in a round bottom flask and stirred for 24 h at room temperature. Further, ethylenediamine (0.04 mol) was added and refluxed for further 24 h at 40-50 ºC. The golden yellow oily liquid obtained. Mol.

wt. 572.78 g 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:

Yield: 62.3%, mol. Wt.: 841.67 g mol-1, m.p. >300 ºC, green colour, anal. Calc. for[Cu2($C_{26}H_{56}N_{10}O_4$)]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 (NH2)str., 1590 (C=O)str., 3090 (N-H)str., 1220 (CN)str., 450, 430, 475 (Cu-N) ; UV-Vis. (H2O, nm): 219 (n→σ*), 262 (π→π*), 324 (n→π*), 709(2B1g→2B2g); Molar conductance: 600.9 Ω-1cm2M-1; ESI-MS (m/z): 701.8 [M-4Cl+2H+], 350.3[(M-4Cl/2)+1H+], 288.2 [{(M-4Cl)/2}-Cu+2H+], 257.3 [{(M-4Cl)/2}-Cu-2O+3H+], 220.1 [{(M-4Cl)/2}-Cu-C2H6O2-4H+],161.2[{(M-4Cl)/2}-Cu-C4H13N2O2-4H+],104[{(M-4Cl)/2}-Cu-C6H20N4O2-2H+].



RESULTS AND DISCUSSION

Catalytic Oxidation and the effect of various parameters on the rate of oxidation

Catalytic Evaluation The ability of the newly synthesized polymer bound Cu (II) -DMG complexes to catalyze organic reactions was explored by conducting a systematic study on oxidation of Alcohols. Various alcoholic substrates were subjected to catalytic oxidation using Cu molecular oxygen as oxidant. The oxidation reaction was carried out at room temperature (RT). And 70^0C for 6hr and 10hr. Blank experiments revealed that no reaction occurred in the absence of either the catalyst or the oxidant [17-19]. The results of oxidation carried out at two different temperatures are

compiled all compounds undergo oxidation in the presence of the Cu supported catalysts and, in some cases, very high selectivity are obtained depends upon the variation of physical parameters like Catalyst concentration, Temperature, Concentration and type of Solvent used. Benzyl alcohol shows highest catalytic activity towards oxidation than 2 propanol and 2-butanol. This variation in catalytic activity is due to the more stability of benzyl alcohol then 2-propanol and 2-butanol and also it may be the effect of ligand on the rate of substrate [20-22].

Effect of Solvent

Solvent plays an important role in the yield and product distribution of oxidation reactions. In order to study the effect of solvent, various solvents were employed. The oxidation reactions of alcohols (5mmol) with molecular oxygen as oxidant at 25^0C Keeping other parameters constant. The oxidation was carried out with some polar and non-polar solvents. The selected solvent should possess the property like stability and solubility in substrate and solvent. The quantitative yield is shown by polar solvents as compared to non-polar solvents .The efficiency of catalyst for oxidation of alcohols in different solvents decreases from more polar solvent to less polar solvent. The 9 higher yield of polar solvents is because of their high dielectric constant and better solubility of substrate.

Reusability of [dendrimer -Cu] complex

An important advantage of polymer supported metal catalysts is its reusability. The complex can be removed by simple filtration upon completion of the reaction and can be used several times without loss of its catalytic activity. The same catalyst was re-used for seven subsequent catalytic oxidation of various alcoholic substrates the conversion of different alcoholic substrates. The conversion of alcoholic substrates is not much affected until fourth catalytic run without affecting the selectivity of the corresponding products. But when we extend the reaction cycle (from the fifth to seventh) further, the activity of the complex decreases and reaches the lowest value for the seventh run .This significant change in the catalytic activity of the [Dentrimer-Cu] complex may be due to the poor chemical resistance and mechanical strength of polystyrene polymeric backbone which provides the heterogeneity to the complex. Therefore, we can use this studied complex for alcoholic substrate oxidation reaction till four cycles without major loss of its catalytic activity.

Reaction mechanisms

The reaction mechanism for oxidation of alcohols with molecular oxygen by metal Complexes in homogeneous medium was studied and the formation of peroxo and oxo Complexes was suggested to be responsible for the transfer of oxygen to substrate on the bases of experimental results as well as evidences from the literature, a probable mechanism can be suggested.

CONCLUSION

In this paper we synthesized the dendrimer copper metal complex by Michael addition. The catalytic application of dendrimer shows better activity towards the oxidation of alcoholic substrates using molecular oxygen as oxidant. 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

REFERENCES

1. Srinivasa-Gopalan S, Yarema KJ. Nanotechnologies for the Life Sciences: Dendrimers in Cancer Treatment and Diagnosis, Volume 7. New York: Wiley; 2007.
2. Klajnert B, Bryszewska M. Dendrimers: properties and applications. Acta Biochemical Polmer 2001;9:199–208.
3. Tomalia DA, Frechet JMJ. Discovery of dendrimers and dendritic polymers: a brief historical perspective. Journal of Polymer Science A 2002;9:2719–2728.
4. Tomalia DA. The dendritic state. Material Today. 2005;9:34–36.
5. Tomalia DA, Baker H, Dewald J, Hall M, Kallos M, Martin S, Roeck J, Ryder J, Smith P. A new class of polymers: starburst-dendritic macromolecules. Polymer journal (Tokyo) 1985;9:117.
6. Newkome GR, Yao Z-Q, Baker GR, Gupta VK. Cascade molecules: a new approach to micelles. Journal Organic Chemistry 1985;9:2003.
7. Hawker CJ, Frechet JMJ. Preparation of polymers with controlled molecular architecture: a new convergent approach to dendritic macromolecules. Journal of American Chemical Society 1990;9:7638–7647.
8. De Gennes PG, Hervet H. Statistics of starburst polymers. J de Physique Lett (Paris) 1983;9:9–351.
9. Mansfield ML, Klushin LI. Monte Carlo studies of dendrimer macromolecules. Macromolecules.1993;9:4262.
10. Bhalgat MK, Roberts JC. Molecular modeling of polyamidoamine (PAMAM) Starburst dendrimers. Europian Polymer journal. 2000;9:647–651.
11. Bosman AW, Meijer EW. About dendrimers: structure, physical properties, and applications. Chemistry Revisions 1999;9:1665–1688.
12. Gilles ER, Frechet JMJ. Dendrimers and dendritic polymers in drug delivery. Drug Discovery Today.2005;9:35–43.

13. Tomalia DA, Baker H, Dewald JR, Hall M, Kallos G, Martin S, Roeck J, Ryder J, Smith P. Dendrimers II: architecture, nanostructure and supramolecular chemistry. Macromolecules.1986;9:2466.
14. Kim Y, Zimmerman SC. Applications of dendrimers in bio-organic chemistry. Current Opinion in Chemistry Biol.1998;9:733–742.
15. Smith DK, Diederich F. Functional dendrimers: unique biological mimics. Chemistry European Journal.1998;9:1353–1361.
16. Stiriba S-E, Frey H, Haag R. Dendritic polymers in biomedical applications: from potential to clinical use in diagnostics and therapy. Angew Chemistry International Edition. 2002;9:1329–1334.
17. Imtiyaz R.parrey.; Syed Anatullah.; Athar. A.hashmi. Modern Research in Catalalysis. 3(2014)107116.
18. Imtiyaz R.parrey.; Athar A. hashmi.; Moroccan Journal of Chemistry . 3 N°1 (2015) 147-151.
19. Peyrovi, M. H.; Mahdavi, V.; Salehi, M. A.; Mahmoodian.; Catal. Commun. 6(2005)476.
20. Valodkar, V. B.; Tembe, G. L.; Ravindranathan, M.; Ram, R. N.; Rama, H. S.; Journal of Molecular Catalysis A: Chem. 208(2004)21.
21. Patel, S. A.; Sinha, S.; Mishra, A. N.; Kamath, B. V.; Ram, R. N. J. Mol. Catal., A: Ch192(2003)53.
22. W.Trakarnpruk.; W.kanjine.; Journal of Molecular Catalysis A: 161(2000) 17