Research Paper

Volume : 2 | Issue : 11 | November 2013 • ISSN No 2277 - 8179

Synthesis and Characterization of Polymer Anchored Cu (II) Complex Supported by N, N'-bis (2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1, 2-diamine Schiff Base

Chemistry

KEYWORDS : Schiff base; polymer support; catalysis; metal-organic catalyst/organometallic catalyst; copper

Alekha Kumar Sutar Catalysis Research Lab, Department of Chemistry, Ravenshaw University, Cuttack-3, Odisha, India

Ysobanta Das School of Applied Sciences (Chemistry), KIIT University, Bhubaneswar, Odisha, India

Prasanta Rath School of Applied Sciences (Chemistry), KIIT University, Bhubaneswar, Odisha, India

Tungabidya Maharana Department of Chemistry, National Institute of Technology, Raipur, India

Parna Gupta Department of Chemical Sciences, IISER Kolkata, West Bengal, India

ABSTRACT

The free and polymer anchored copper ion complexes [HMBdMBn-Cu and P-HMBdMBn-Cu], supported by -ONNO-tetradentate Schiff-base ligand are prepared by the reactions of copper chloride solution with one molar equivalent of unsupported HMBdMBn (N, N'-bis (2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine) or polymer supported (P-HMBdMBn) Schiff-base ligands in methanol. The efficiency of complexation of copper ion on the polymer anchored HMBdMBn Schiff base was more than unsupported one. The structural study reveal that copper(II) ion complex of HMBdMBn Schiff base is square planar geometry. Complexation of copper ion increased the thermal stability of HMBdMBn Schiff base.

1. INTRODUCTION

Schiff base complexes of transition-metal ions have shown significant catalytic activities in various reactions such as oxidation,[1] epoxidation of olefins,[2] polymerization of ethylenes,[3] etc. but supported metal-ion complexes have shown high catalytic activity [4-6] in comparison with unsupported catalysts. Cobalt(II) and manganese(II) ion complexes of salen on tailor-made polymer supports have shown considerable increases in activity due to a significant reduction in the mass transfer limitation for the reactants. Although metal ion complexes have been immobilized on various supports [7], their activity on polymer supports is quite high [8] because of the dynamic microenvironment [9] and liquid-phase conditions [10], in which an anchored catalyst is able to perform rotational and transnational motions. The homogeneity of catalysts on zeolite [11] and silica 12] supports is significantly different from that on polymer supports.

The activity of polymer-supported Schiff base complexes of iron(III), cobalt(II) and nickel(II) ions in the oxidation of phenol [13-14] also showed variation with temperature, time, etc, which might be due to the change in concentration of substrate or catalyst. Although a number of polymer supported catalysts have been reported, the polymer anchored metal-ion complexes of the HMBdMBn (N, N'-bis (2-hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine) Schiff base has not been reported in the literature; hence, attempts have been made to synthesize and characterize polymer-supported Cu(II) complex of the HMBdMBn Schiff base for different industrial use.

2. EXPERIMENTAL

2.1 Materials

Divinyl benzene cross-linked chloromethylated polystyrene beads were obtained from Ion Exchange India Ltd., Mumbai. The copper(II) chloride anhydrous was purchased from HiMedia Laboratories Pvt. Ltd, Mumbai. The 2-hydroxy-3-methylbenzaldehyde and 4-Methylbenzene-1,2-diamine were procured form E. Merck. Other chemicals and solvents were of analytical grade (>99.0 wt %) and used after purifications with standard methods [15].

2.2 Characterization of the HMBdMBn Schiff base and its copper(II) ion complex

IR spectra of HMBdMBn Schiff base and its copper complex were recorded on KBr pellet using Perkin-Elmer 1600 FTIR Spectrophotometer. The electronic spectra of HMBdMBn Schiff base and its copper complex were recorded with Shimadzu 1601 PC UV–Vis Spectrophotometer by using sample mull in a cuvette. Thermo gravimetric analysis (TGA) of HMBdMBn Schiff base and its copper(II) complex was carried out using Perkin-Elmer Pyris, Diamond Thermal Analyzer under nitrogen atmosphere at a heating rate of 10ºC min^{-1}. The loading of copper(II) ion on HMBdMBn Schiff base was determined by analyzing the loading solution with Perkin-Elmer 3100 Atomic Absorption Spectrometer at λ_{max} of corresponding copper(II) ion. The ^{1}H-NMR spectra of HMBdMBn Schiff base and its copper complex were recorded on an FT-NMR-Brucker 300 MHz Spectrometer using DMSO-d^{6} as a solvent and tetramethylsilane (TMS) as an internal reference. The magnetic moment (μ) of copper complex was measured using Vibrating Sample Magnetometer-155. The molecular weight of HMBdMBn Schiff base and its copper complex was determined using a Vapor Pressure Osmometer (Merck VAPRO 5600, Germany).

2.3 Synthesis of HMBdMBn and its copper complex

HMBdMBn Schiff base was synthesized by the modified procedure reported in the literature. [15] The reaction mixture containing 2-hydroxy-3-methylbenzaldehyde (20.00mmol, 2.72g) and 4-Methylbenzene-1,2-diamine (10.00mmol, 1.22g) in methanol was refluxed at 60ºC for about 1hr. The reaction mixture on cooling at low temperature produced light orange colored crystals, which were filtered and recrystallized with methanol. The copper complex of HMBdMBn Schiff base was prepared taking 100 ml methanolic solution of mixture of Schiff base (20.00mmol, 7.16g) and 20.00mmol of copper in a round bottom flask and refluxing at 60ºC. After 8 h, the solution was cooled and copper complex was separated from the mother liquor. All reactions were performed under nitrogen atmosphere. Finally, copper complex was recrystallized in methanol and dried in a vacuum desiccator.

2.4 Synthesis of P- HMBdMBn Schiff base and its copper complex

To prepare polymer-anchored copper complex of HMBdMBn Schiff base, the N, N'-bis (4-amino-2- hydroxy-3-methylbenzaldehyde) 4-Methylbenzene-1,2- diamine(A- HMBdMBn) Schiff base was prepared by carrying out nitrosation and reduction reactions on HMBdMBn Schiff base and then reacting resulted A-HMBdMBn Schiff base with cross-linked chloromethylated polystyrene beads. The nitrosation of HMBdMBn Schiff base was carried out using 20.00 mmol (7.16 g) of HMBdMBn Schiff base with sodium nitrite (20.00 mmol) in 1.0 N hydrochloric acid (100 ml) at -5ºC. The resultant N, N'-bis (4-nitroso-2-hydroxy- 3-methylbenzaldehyde) 4-Methylbenzene-1,2-diamine (NO-HMBdMBn) was filtered and washed with hot and cold water to remove reaction impurities. The reduction of NO-HMBdMBn was carried out using 20.00 mmol of nitrosated Schiff base in 1.0 N hydrochloric acid (50 ml) in the presence of metallic iron, which produced A-HMBdMBn Schiff base. To immobilize the prepared A- HMBdMBn Schiff base on cross-linked chloromethylated polystyrene, the methanol swollen polymer beads (5.0 g) were refluxed in 50 ml methanol containing 20.00 mmol (7.76 g) A-HMBdMBn Schiff base. After 8 h, the HMBdMBn Schiff base-anchored polymer beads were separated and dried in a vacuum desiccator. The amount of HMBdMBn Schiff base loaded on polymer beads was estimated with elemental analysis. Subsequently, the copper ion was loaded by keeping HMBdMBn loaded polymer beads (5.0 g) for 10 h in an aqueous solution (50 ml) of copper ion (20.00 mmol). Finally, the polymer beads were separated and dried at 70ºC in a vacuum oven after washing with hot and cold water. The loading of copper ion on polymer beads was determined by analyzing the loading solution with an Atomic Absorption Spectrometer. The loading of copper ion on free and polymer-supported HMBdMBn Schiff base was calculated as complexation of copper ion using the amount of HMBdMBn Schiff base taken initially and the amount of copper ion loaded on polymer beads.

$$\frac{\text{Amount of copper ion loaded}}{\text{Amount of Schiff base used for loading}} \text{ X } 100$$

3. RESULTS AND DISCUSSION

The polymer support plays a positive role in modifying the activity of metal-ion complexes, as reported in the literature [6]. The activity of a catalyst on a support is increased, provided that the nature of the catalyst is not destroyed and the support is able to provide a liquid-phase environment as found with polymer supports; hence, the properties of polymer supports influence the activity of anchored catalysts. Although the amount of loaded metal ions influences the activity of a supported catalyst, the activity of a supported catalyst is also influenced by leaching of the catalyst from the polymer support [13-14].

3.1 Characterization of HMBdMBn Schiff base

The HMBdMBn Schiff base was obtained by refluxing 2-hydroxy-3-methylbenzaldehyde and 4-Methylbenzene-1,2-diamine with a substantial yield (86.2 wt%) (Scheme 1). The IR spectrum of HMBdMBn Schiff base showed absorption bands at 1610 cm^{-1} (>C =N), 1268 cm^{-1} (>C–O) phenolic and a broad band between 3350 and 2910 cm^{-1} for phenolic OH. (Table 1) The elemental analysis of HMBdMBn Schiff base showed (wt%): C = 76.64, N = 8.06 and H = 5.79; Caltd (%): C = 77.07, N = 7.82 and H = 6.19, which corresponded to the empirical formula $C_{23}H_{22}N_2O_2$.

Table 1: FTIR and UV data for HMBdMBn Schiff base and its copper complexes

Compounds	Absorption frequencies / cm^{-1}					Frequencies λ_{max} / nm			
	$u_{C=N}$	u_{C-O}	$u_{OH\ (phenolic)}$	u_{M-O}	u_{M-N}	p®p*	n®p*	C®T	d®d
HMBdMBn P- HMBdMBn	1610 1602	1268 1260	2910-3350 2900-3300	- -	- -	284 281	346 341	- -	- -
HMBdMBn-Cu P- HMBdMBn-Cu	1597 1592	1316 1310	- -	572 563	459 452	277 271	307 301	354 349	561 557

The molecular weight of Schiff base was 357.37 g mol^{-1} (Caltd 358.43 g mol^{-1}). The electronic spectra of HMBdMBn Schiff base showed absorption bands at 284 nm and 346 nm, which were assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The 1H-NMR spectrum of the Schiff base showed signals at δ/ppm = 2.52(6H), 2.83(3H), 5.15(2H), 6.91(2H), 7.27(2H), 7.41(3H), 7.60(2H), and 8.66(2H) which corresponded to the structure of HMBdMBn Schiff base.

The TGA of P-HMBdMBn Schiff base showed a weight loss of 40.4 wt% at 500ºC, but its copper(II) ion complex showed a weight loss of 33.0 wt%, at same temperature. (Figure 1) In addition to thermal analysis, the free and polymer-supported copper complex of HMBdMBn Schiff base were also characterized by NMR, IR and UV techniques to provide a proof for the complexation of copper ion.

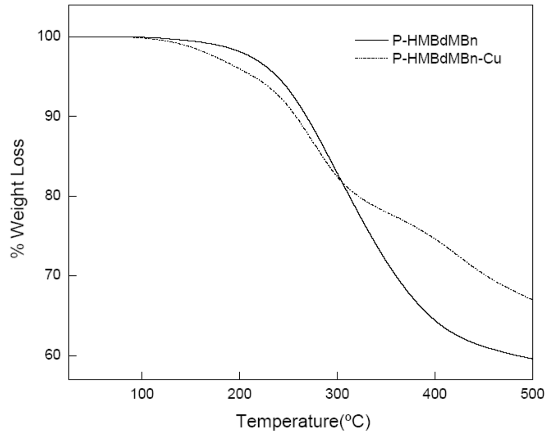
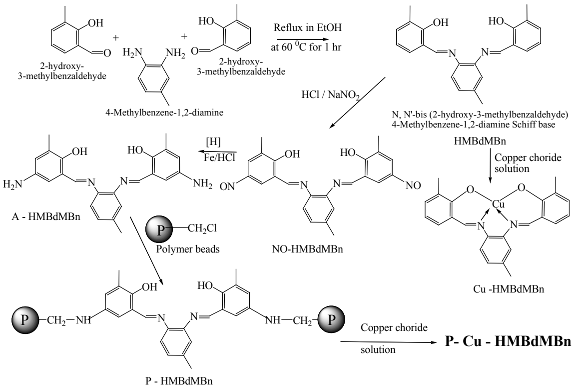


Figure 1. Thermal stability of the polymer-supported HMBdMBn Schiff base and its copper complex.



Scheme 1. Synthesis of unsupported and polymer supported copper complex supported by HMBdMBn Schiff base

3.2 Synthesis and characterization of Amino-HMBdMBn Schiff base and its anchoring on polymer beads

The nitrosation of HMBdMBn Schiff base was carried out in the presence of $NaNO_2$/HCl, which gave 86.5% yield of N,N'-bis(4-nitroso-2-hydroxy-3- methylbenzaldehyde) 4-Methylbenzene-1,2-diamine (NO-HMBdMBn) (Scheme 2). The elemental analysis showed (wt%): C = 67.00 , N = 12.63, and H = 5.00; Caltd (wt%): C = 66.34, N = 13.45, and H = 4.84, which corresponded to $C_{23}H_{20}N_4O_4$ formula of NO-HMBdMBn. The molecular weight

Volume : 2 | Issue : 11 | November 2013 • ISSN No 2277 - 8179

of NO-HMBdMBn was 415.03 g mol^{-1} (Caltd 416.43 g mol^{-1}). The IR spectrum of NO- HMBdMBn showed absorption bands at 1607 cm^{-1} (>C=N), 1266 cm^{-1} (>C–O)phenolic, and 1530 cm^{-1}and 1320 cm^{-1} for N–O group. The nitrosation of HMBdMBn Schiff base showed a shift in NMR signals in comparison to NMR signals observed with pure HMBdMBn Schiff base. The nitrosated HMBdMBn Schiff base showed proton signals at δ/ppm = 2.54(6H), 2.88(3H), 5.15(2H), 7.35(2H), 7.42(3H), 7.96(2H), and 8.69(2H), which corresponded to the structure of nitrosated HMBdMBn Schiff base. The protons ortho to nitroso group in HMBdMBn Schiff base were deshielded; hence, their signals appeared at 7.35 and 7.96 ppm in place of 7.27 and 7.60 ppm respectively, of pure HMBdMBn Schiff base. The proton signal at 6.91 ppm was missing due to the substitution of nitroso group in the benzene. The NO-HMBdMBn was reduced with iron(III) ions in the presence of hydrochloric acid, which gave 81.3 wt% yield of A- HMBdMBn Schiff base. The elemental analysis of A-HMBdMBn Schiff base showed (wt%): C = 70.54, N = 13.00, and H = 7.02, Caltd (wt%): C = 71.11, N = 14.42, and H = 6.23, which corresponded to $C_{23}H_{24}N_4O_2$ empirical formula. The molecular weight of A-HMBdMBn Schiff base was found to be 387.23 g mol^{-1} (Caltd 388.46 g mol^{-1}). The IR spectrum of A-HMBdMBn Schiff base showed absorption bands at 1605 cm^{-1} (>C= N), 1263 cm^{-1} (>C–O)phenolic, and a band between 1632 and 1618 cm^{-1} for >C–N group. The ^{1}H-NMR spectrum of A-HMBdMBn Schiff base showed proton signals at δ/ppm = 2.52(6H), 2.85(3H), 4.15 (4H), 5.15(2H), 6.36 (2H), 7.42(3H), 6.81(2H), and 8.69(2H), which corresponded to the structure of A- HMBdMBn.

The synthesized Schiff base was anchored on cross-linked chloromethylated polystyrene beads by refluxing A-HMBdMBn Schiff base with polymer beads in DMF for 8 h at 60^{0}C. The anchoring of A-HMBdMBn Schiff base on polymer beads was confirmed by comparing the IR spectrum of HMBdMBn Schiff base anchored polymer beads with IR spectrum of pure polymer beads. The IR spectrum of polymer-anchored Schiff base showed new absorption bands at 1602 cm^{-1} (>C=N), 1260 cm^{-1} (>C–O) phenolic, and a broadband between 1629 and 1610 cm^{-1} (>C=N), which were absent in the IR spectrum of pure polymer beads, but were present in free Schiff base. The IR spectrum of pure polymer beads showed absorption band at 1262 cm^{-1}, which is attributed to C–Cl bond of chloromethyl in cross-linked polymer beads. The decrease in the intensity of absorption band at 1262 cm^{-1} in polymer- anchored HMBdMBn Schiff base than pure polymer beads was an evidence for anchoring of HMBdMBn Schiff base on polymer beads. The amount of A-HMBdMBn Schiff base anchored on polymer beads was 87.0 wt% (Scheme 1).

3.3 Characterization of free and polymer-anchored copper complex of HMBdMBn Schiff base

The loading of copper ion on free and polymer-supported HMBdMBn Schiff base was carried out by refluxing free Schiff base and polymer-anchored Schiff base in copper chloride solution at 60°C for 6 h (Scheme 1). The copper complex of free Schiff base (HMBdMBn-Cu) and polymer-anchored Schiff base (P-HMBdMBn-Cu) after separation and purification were analyzed for their structures and loading of copper ion. The complexation of copper(II) ions on free HMBdMBn Schiff base and polymer-anchored Schiff base was 79.58 & 80.51 wt% respectively.

The complexation of copper ion with HMBdMBn Schiff base showed significant variations in IR bands for >C=N and >C–O groups and new absorption bands appeared due to the formation of M–O and M–N bonds in copper complexes. (Figure 2)

The disappearance of phenolic absorption band between 2910 and 3350 cm^{-1} in the IR spectrum of HMBdMBn Schiff base after the complexation of copper ion was an evidence for the complexation of copper ion with HMBdMBn Schiff base. The polymer-supported Schiff base showed absorption bands at low frequency in comparison to free Schiff base.

The complexation of copper(II) ion showed new absorption band at 572 cm^{-1} with free Schiff base and at 563 cm^{-1} with polymer-anchored Schiff base, which was due to the formation of Cu–N bond. And also another due to the formation of bond between copper ion and phenolic oxygen (–O–Cu). (Table 1)

The complexation of copper(II) ion with HMBdMBn Schiff base showed variation in $\pi \rightarrow \pi^*$ transition from 284 nm to 277 nm, and for the $n \rightarrow \pi^*$ transition was changed from 346 nm to 307 nm (Table 1). The complexation of copper(II) ion with HMBdMBn Schiff base showed CT transition and d → d transitions. These electronic transitions corresponded to $t_{2g}^6\ e_g^3$ configurations. The magnetic moment(μ) of Schiff base complexes of copper(II) ion was found to be 1.81BM, which indicated that copper(II) ion complex was paramagnetic in nature with one unpaired electron. The magnetic moment (μ) and electronic configurations have suggested a square planar structure with dsp^2 hybridization for copper(II) complex.

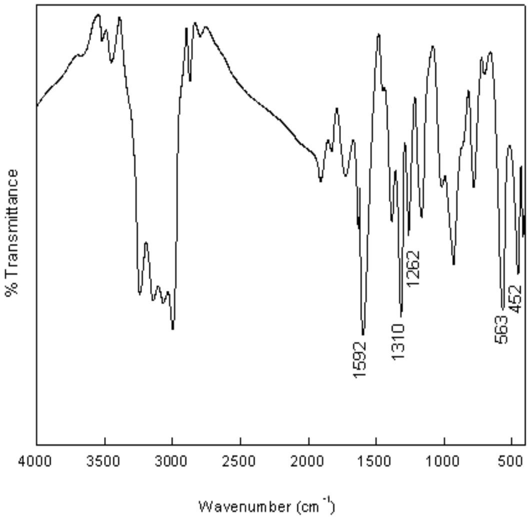


Figure 2. FTIR spectra of P-HMBdMBn-Cu complex

4. CONCLUSIONS

Polymer-supported copper-ion complex of the HMBdMBn Schiff base was synthesized and characterized for their structures. The experimental results showed that copper complex of HMBdMBn Schiff base is square planner geometry. And the polymer supported complex is more stable than unsupported analogue.

Acknowledgments
The authors are also grateful to Indian Academy of Sciences, India, CSIR, New Delhi for funding, IISER Kolkota, Ravenshaw University, KIIT University and National Institute of Technology, Raipur for providing research opportunity.

REFERENCE

1. K. C. Gupta, A. K. Sutar, Coord. Chem. Rev. 252 (2008)1420-1450. | 2. S.R.Thomas, K.D. Janda, J. Am. Chem. Soc. 122 (2000) 6929-6934. | 3. A. K. Sutar, T. Maharana, S. Dutta, Chi-Tien Chen, Chu-Chieh Lin, Chem. Soc. Rev. 39 (2010) 1724–1746. | 4. G. Grivani, A. Akherati. Inorg. Chem. Comm. 28 (2013) 90-93 | 5. K. C. Gupta, A. K. Sutar, J. Mol. Catal. A. Chem. 280 (2008) 173-185. | 6. K. C. Gupta, A. K. Sutar, C. C. Lin, Coord. Chem. Rev. 253 (2009) 1926–1946. | 7. K. Matkiewicz, A. Bukowska, W. Bukowski. J. Mol. Cat. A: Chem., 368–369 (2013) 43- 52 | 8. J. Escorihuela, L. González, B. Altava, M. I. Burguete, S. V. Luis. Appl. Catal. A: Gen. 462–463 (2013) 23-30. | 9. D.M.Vriezema, M.C. Aragones, J.A.A.W. Elemans, J.J.L.M. Cornelissen, A.E. Rowan, R.J.M.Nolte, Chem. Rev.105 (2005) 1445-1490. | 10. B. Saha, D. Gupta, M. M. Abu-Omar, A. Modak, A. Bhaumik. J. Catal. 299 (2013) 316-320 | 11. F.van de Velde, I.W.C.E. Arends, R.A. Sheldon, J. Inorg. Biochem. 80 (2000) 81-89. | 12. S.L.Scott, J.A.N. Ajjou, Chem. Eng. Sci. 56 (2001) 4155-4168. | 13. K. C. Gupta, A. K. Sutar, J. Mol. Catal. A: Chem. 272 (2007) 64-74. | 14. K. C. Gupta, A. K. Sutar, J. Macro mole. Sci. Part A: Pure and Appl. Chem. 44 (2007) 1171-118535. | 15. Vogel, A. I. Textbook of Practical Organic Chemistry; ELBS and Longman: London, 1978.