RESEARCH ARTICLE Am. J. PharmTech Res. 2016; 6(4) ISSN: 2249-3387

AMERICAN JOURNAL OF PHARMTECH RESEARCH

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

Synthesis, Characterization and Catalytic Applications of Water Soluble Ni (II) and Mn (II) Metal Complexes

Haroon Rashid Boked[1], G.M.Mir[2], Ghulam Mohammad Jan[1], Fayaz Ahmad Bhat[1], ImtiyazRasool Parrey[2*]

1 Department of Chemistry, Govt. Degree College Boys Anantnag Jammu & Kashmir (India)

2.Department of Chemistry, Govt. Degree College for WomensAnantnag Jammu & Kashmir (India)

ABSTRACT

Ni (II) and Mn (II) metal complexes of Schiff base derived from ethylenediamine, succinic acid and formaldehyde. The newly synthesized Schiff base complexes were characterized by elemental analysis, Melting point, conductivity, IR and UV-VIS spectral methods. The complexes have been tested using for the catalytic oxidation of benzylacohol using ecofriendly molecular oxygen as catalyst. The results show that Nickel complex shows highest yield oxidation product as compared to Manganese at 35°C temperature, 90mg catalyst amount and 25 min. time.

Keywords: Schiff base complex synthesis, characterization, Catalytic activity.

*Corresponding Author Email:imtiyazchemistry@gmail.com

Received 14 June 2016, Accepted 06 July 2016

Please cite this article as: Parrey IR *et al.*,Synthesis, Characterization and Catalytic Applications of Water Soluble Ni (II) and Mn (II) Metal Complexes. American Journal of PharmTech Research 2016.

INTRODUCTION

Catalysis is the process of acceleration of a chemical reaction by means of a substance, called 'catalyst', that itself not consumed in the overall reaction. A catalyst provides an alternative route of chemical reaction where the activation energy is lower than the original one. It works by providing an alternative pathway for the reaction to occur, thus reducing the activation energy. More generally, one may at times call anything that accelerates a reaction without being consumed or changed, as a 'catalyst'. Today really 95% of all the chemical processes are based on catalysis. To mention some are catalytic hydrogenation, synthesis of ammonia, catalytic cracking, and polymerization.

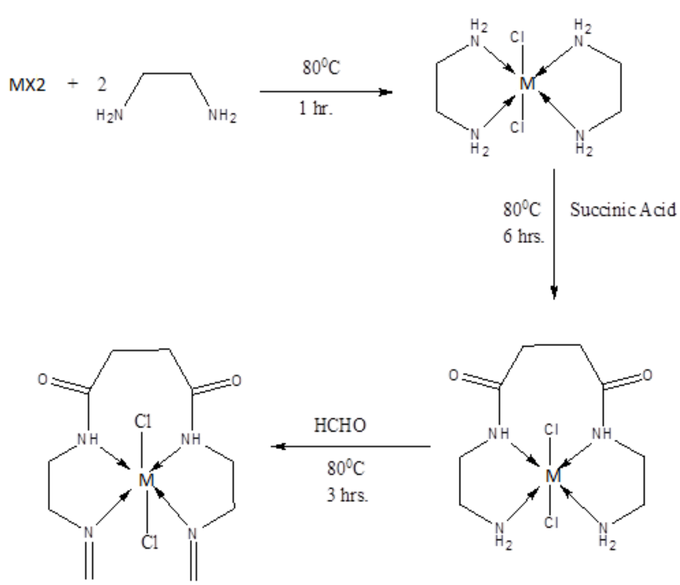
Transition metal catalysts play an important role in modern organic chemistry promoting a number of fundamental reactions such as carbon-carbon, carbon-nitrogen, carbon-hydrogen, and carbon-oxygen bond formation. The immobilization of the catalytically active transition metal complexes onto suitably stable solid support is of great interest from the economic as well as the ecological point of view, since it allows efficient catalyst recovery and reuse, thereby minimizingboth catalyst cost and contamination of the reaction products[1-2]. The oxidation of primary and secondary alcohols into the corresponding carbonyl compounds plays a central role in organic synthesis. Selective oxidation of aliphatic alcohols to aldehydes with molecular oxygen is presumably the most demanding transformation. A great number of new catalysts have been suggested in recent years for the "clean" oxidation of alcohols with molecular oxygen. Many of them are based on ruthenium and to a smaller extent, on palladium species in various forms. The large number of patents reflects a considerable industrial interest in the application of supported Pt-group metal catalysts, dominantly in aqueous media [3-5].There are some reports of oxidation using molecular oxygen at ambient conditions. In a series of communications Taqui khan et al reported the catalytic oxidations of olefins, saturated hydrocarbons and amines using Ru (III) EDTA complex and molecular oxygen [6-10].Mahesh Dalal et al observed that the rate of oxidation of benzyl alcohol increased linearly with increase in substrate concentration using polymer anchored Ru (III) Schiff base complex and polymer anchored Ru (III) salen complexes. [11-12]. Sivadasan et al reported that functionalized polymers are found to be highly efficient for immobilizing transition metal ions. Cross-linked polystyrene supported Schiff's base complexes of metal ions such as Fe (III), Co (II) and Cu (II) are active for epoxidation of cyclohexene and styrene [13]. Haresh G. Manyar et al reported green catalytic oxidation of alcohols in water using highly efficient manganosilicate molecular sieves. Primary alcohols are selectively oxidized to aldehydes and secondary alcohols are selectively oxidized to ketones [14]. Charon Zondervan et al observed that binuclear manganese (IV) catalyst is capable of oxidizing benzylic alcohols to benzaldehyde with very high turnover numbers and high selectivity [15]. Brinksma et al prepared some manganese complexes supported on polymer and found that these catalysts were highly active and selective in oxidation of alcohols to aldehydes or ketones [16].

Manurul Islam et al reported a new polymer anchored copper (II) azo complex capable of oxidation of cyclohexane, styrene, bezylalcohol and ethylbenzene in presence of tert – butylhydroperoxide (TBHP) as a oxidant [17]. Hao-Yu-Shen et al achieved the selective oxidation of alcohols with molecular oxygen using polymer – bound ruthenium complex with high conversion and selectivity under mild reaction conditions [18].

MATERIALS AND METHOD

All chemicals used were of analytical grade (AR) reagents and of the highest purity available. They included ferric chloride anhydrous (fisher scientific), cobalt(II) chloride hexahydrate (RANKEM), cupric(II) chloride dihydrate (fisher scientific), ethylenediamine(MERCK), succinic acid (sd.finechem ltd.) and formaldehyde (MERCK).

Elemental analyses were performed using an elemental analyser. The conductance of the complexes was measured on a conductometer at 25^{0}C. The IR spectra were recorded in a spectrometer (4000-400 cm^{-1}). The UV –VIS electronic spectra (200-800 nm) were recorded using double beam spectrophotometer. The geometries of the metal complexes were evaluated using the molecular calculation.



Where M= Ni, Mn

Template synthesis of Schiff base metal complexes

An ethanolic solution of MXn (0.00105 moles) M=Ni(II),Mn(II) is added slowly to an ethanolic solution of ethylenediamine (0.0021 moles) with constant stirring. The mixture is refluxed for one hour at 80^0C. Then an ethanolic solution of succinic acid (0.00105 moles) is added dropwise and the mixture is refluxed for about 6 hours at 80^0C. Finally an ethanolic solution of formaldehyde (0.0021 moles) is added dropwise and the reaction mixture is refluxed for about 3 hours at 80^0C.The mixture is then filtered, washed with ethanol and dried the residue Figure 1.

RESULTS AND DISCUSSION

Elemental analysis and molar conductance

The metal complexes NiSAF and MnSAF are soluble in water. The analytical data and physical properties of the complexes are presented in the Table 1. The data are consistent with the calculated results from the empirical formula of each compound.

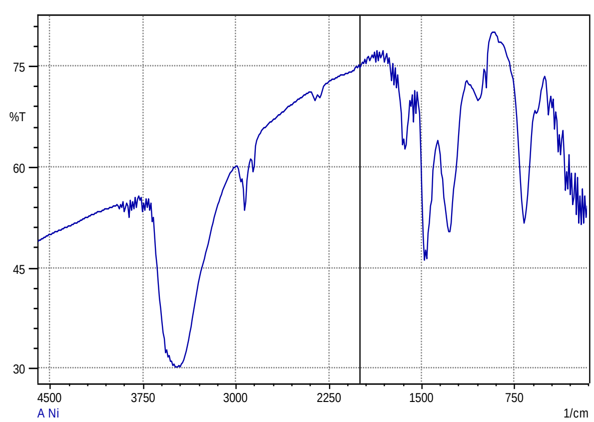
Specific conductance of Ni-complex=0.32mS/cm at 25^0C

Specific conductance of Mn-complex=0.22mS/cm at 25^0C

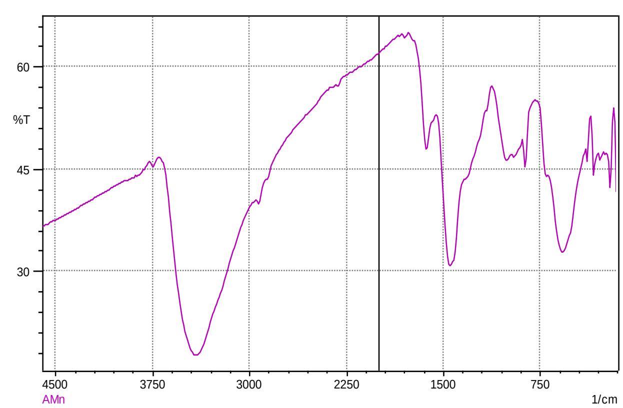
The above conductance values indicate that the complexes are electrolytes Table 2.

IR Spectra

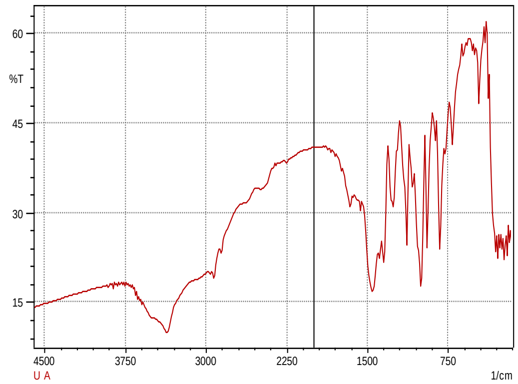
The significant IR bands for the complexes are compiled and presented in Table-2. The IR spectrum of the complexes, a sharp band observed at 1616 cm^{-1} is assigned to the (C=N) mode of the azomethine group. This shifts to lower wave number 1606- 1609 cm^{-1} in all the complexes suggesting the co-ordination of the azomethine nitrogen to the metal centers. A strong band observed at 1640-1690 cm-1 is assigned to (C=Amide) of the ligand.



(a) L



(b) L-Ni



(c) L-Mn

Figures showing the FT-IR spectra of (a) L (b) L-Ni (c) L-Mn

UV-Vis Electronic spectra

The UV-VIS spectral data of the complexes are presented. The electronic absorption spectra of the complexes of Cobalt and Copper were recorded in double distilled water while that of Fe-complex was recorded in DMSO in the range 200-700 nm. For the complex of Cobalt absorption peak was found at 478 nm and 413 nm and for the complex of iron absorption peak was found at 644.5 nm, 463.0 nm, 446.5 nm, 363.5 nm and209.0 nm. For the complex of Copper absorption peak was found at 236.4 nm and 213.0 nm.

Table1: Elemental analysis, specific conductivity and melting points of the complexes.

Compounds	**Empirical formula**	**mol.wt., g/mol**	**Elemental analysis found(calculated)%**			**Specific conductance mS/cm**	**Melting point ^{0}C**
			C	H	N		
Ni-complex	$C_{10}H_{18}O_2N_4NiCl_2$	356	31.38 (33.21)	4.91 (5.06)	12.94 (14.73)	0.32	296
Mn-complex	$C_{10}H_{18}O_2N_4MnCl_2$	353	33.42 (33.99)	4.91 (5.4)	24.21 (25.96)	0.22	289

Table 2: FT-IR spectral data for the metal complexes

Componds	**V(C=O), cm^{-1}**	**V(C=N), cm^{-1}**	**V(M-N), cm^{-1}**	**V(C-N), cm^{-1}**	**V(N-H), cm^{-1}**
Ni-complex	1640-1690	1600-1620	457-490	1080-1380	3100-3500
Mn- complex	1640-1690	1600-1620	457-475	1080-1360	3100-3500

Catalytic Oxidation:

The catalytic activity of two complexes were investigated by using alcohols (Benzyl alcohol) as solvent in presence of molecular oxygen as oxidant under optimum conditions of (35°C temperature 90mg catalyst and 25 min. time) it was found that the oxidation of benzylalcohol occurs highest at this condition. The results are similar as the results were found during the oxidation of chitosan copper metal complex [19-22]. The results show that Ni catalyst shows highest oxidation yield than Mn.

CONCLUSIONS

Two catalysts (Ni and Mn) were prepared. Both the catalysts were characterized by some physiochemical techniques. Both were found to be active for the oxidation of some alcoholic substrates under mild conditions of temperature and pressure using molecular oxygen as the oxidant. The influence of concentration of the catalyst and the substrate on the rate of reaction has been carried out. In the case of benzyl alcohol as the substrate, the formation of benzaldehyde as the oxidation product was confirmed by GC – MS technique. The catalyst Ni was found to be more active than the catalyst Mn.

REFERENCES:

1. D.C Sherrington and A.P. Kybett. Supported Catalysts and Their Applications, Royal Society of Chemistry, (2001).
2. G. Centi and R.A Van Santen, Catalysis for Renewables, Wiley VCH VerlagGmb H & co KGaA, (2007).
3. S. J. Shuttleworth, S.M. Allin, R.D.Wilson, D. Nasturica, Synthesis (2000), 1035.
4. S.V. Ley, J. Norman, W.P. Griffith, S.P. Marsden, Synthesis (1994) 639.
5. M. Huddlicky, Oxidations in Organic Chemistry, ACS, Washington, DC, 1990.
6. M. M. Taqui Khan, H. C. Bajaj and D. Chatterjee, Synthesis of the complex $Ru^{V}O(edta)^{-}$ and its application in the oxidation of saturated substrates by oxygen atom transfer reaction J. Mol. Catal. (1992), 71, 177.
7. M. M. Taqui Khan and A. PrakashRao, A ruthenium(III) analogue of the Udenfriend system: Ru(III)-EDTA-ascorbate-molecular oxygen in the effective oxygen atom transfer reaction of saturated and unsaturated organic compounds J. Mol. Catal, (1987), 39, 331.
8. M. M. Taqui Khan and H. C. Bajaj, R. S. Shukla and S. A. Mirsa, Kinetics and Mechanism of EDTA-Catalyzed Oxidation of (S)-Phenylmercaptoacetic Acid by Chromium(VI) J. Mol. Catal. (1989), 45, 51.
9. M. M. Taqui Khan, R. S. Shukla and A. PrakashRao, A ruthenium(III) analogue of the Udenfriend system: Ru(III)-EDTA-ascorbate-molecular oxygen in the effective oxygen atom transfer reaction of saturated and unsaturated organic compoundsInorg. Chem. (1989), 28, 452.
10. M. M. Taqui Khan, S. A. Mirsa and H. C. Bajaj, The Oxidation of Organic Substrates By Molecular Oxygen; Catalysis By Ru(III) And Ru(III)-EdtaJ. Mol. Catal, (1986), 37, 253.
11. M. M. Taqui Khan, S. A. Mirsa and H. C. Bajaj, The Oxidation of Organic Substrates By Molecular Oxygen; Catalysis By Ru(III) And Ru(III)-EdtaJ. Mol. Catal., (1987), 39, 323.

12. K. Mahesh Dalal and R. N. Ram, Catalytic Activity of Polymer Bound Ru (III)-EDTA Complex. Mol. Catal A: Chem., (2000), 159,285.
13. K. Mahesh Dalal, M.J. Upadhyay, R.N. Ram, Catalytic Activity of Polymer Bound Ru (III)-EDTA Complex.J. Mol. Catal A: Chem., (1999), 142, 325.
14. K. ShivadasanChettiar and K. Sreekumar, Supported Polyperoxometallates, Highly Selective Catalyst in Oxidation of Alcohols to Aldehydes.Polym. Int, (1999), 48, 455.
15. Haresh, G. Manyar, G. S. Chaurean and A. Kumar, The green catalytic oxidation of alcohols in water by using highly efficient mangano silicate molecular sieves.Green Chem, (2006), 8, 344.
16. C. Zondervan, R. Hage and B. l. Feringa, Chem..Commun., (1997), 419.
17. J. Brinksma, M. T. Rispens, R. Hage and B. L. Feringa, Manganese complexes for alcohol oxidation Inorg. Chim. Acta., (2002), 337, 75.
18. M. Islam, P. Mondal, S. Mondal, S. Mukherjee, A. S. Roy, M. Mubarak and M. Paul A reusable polymer anchored copper(II) complex catalyst for the efficient oxidation of olefins and aromatic alcohol J. Inorg. Organomet. Polymer. Mater., (2009),
19. Hao-Yu Shen, Sai-Chun Zhou, Min-hui-wei and Han-xinZong, Peroxidation of Benzaldehyde by Polymer Immobilized Cobalt-EDTA Complex.React. Funct. Polym., (2006), 66, 827-831.
20. ImtiyazRasoolParrey, AtharAdilHashmi, BabuLal Swami, Shaeel Ahmad Al-Thabaitib Synthesis, Characterization and Catalytic activity of Schiff base Cu(II) Metal Complexes“ .Iranian journal of catalysis 5(2015) 204-212
21. ImtiyazRasoolParrey, AtharAdilHashmi “Effect of Various Parameters on the Catalytic Oxidation of Cyclohexane Using Schiff Base Cu (II) Metal Complex Catalyst”. Journal of Green Science and Technology, 1(2014) 1-5
22. ImtiyazRasoolParrey, AtharAdilHashmi“Chitosan Biopolymer an Effective Catalyst towards Oxidation of Benzyl Alcohol”. Journal of Chitin and Chitosan. 3(2015)1-