Journal Of Harmonized Research (JOHR)

Journal Of Harmonized Research in Applied Sciences
7(2), 2019, 34-38

ISSN 2321 – 7456

Original Research Article

MANGANESE (II) AND COBALT (II) COMPLEXES OF SCHIFF BASE: SYNTHESIS AND CHARACTERIZATION

Kalpataru Halder and Dr. Utpal Saha

Department of Biochemistry, Sri Satya Sai University of Technology & Medical Sciences, Sehore-466001

Abstract: Synthesis of two Schiff base metal complexes of Mn(II) and Co(II). The complexes were analyzed by different Spectrochemical techniques like Vib. FT-IR spectrum - UV-vis spectrum, EPR spectrum. Both the complexes show better activity towards the oxidation of substrates (cyclohexane and benzyl alcohol). In both the substrates the complex Co (II) shows better activity than Mn(II).

Keywords: Schiff base, Metal Complex, UV-Spectrophotometer, Chelate.

Introduction*:* In coordination chemistry; ligands comprising more than single donor sites are broadly used for the research of metal centers with numerous pharmacological activities. Amongst these ligands, Schiff bases comprising hetero atoms as donor atoms are of significant importance due to their possible application in catalysis, medicine and material science [1-5].

The Transition metal centers of these ligands display variable conformations, structural obligation and sensitivity to molecular surroundings. The central metal ions in these developments act as vigorous places for catalyzing chemical reactions.

For Correspondence:
om11agra85@gmail.com.
Received on: March 2018
Accepted after revision: April 2019
DOI: 10.30876/JOHR.7.2.2019.34-38

Based on the useful applications on these transition metal complexes in catalytic oxidation reaction number of reports where initiate some reports were oxidation is carried out using molecular oxygen at ambient circumstances.

In a series of research done by, Taqui khan *et al.* reported the catalytic oxidations of olefins, saturated hydrocarbons and amines using Ru (III) EDTA complex and molecular oxygen [6, 7, 8]. Mahesh Dalal *et al.* experiential that the rate of oxidation of benzyl alcohol improved linearly with growing in substrate concentration by polymer anchored Ru (III) Schiff base compounds and polymer anchored Ru (III) salen complexes [9, 10]. Anthony The odore David stated the catalytic oxidation of Schiff base improved chitosan in the oxidation of cyclohexane [11, 12]. Haresh G. Manyar *et al.* stated green catalytic oxidation of alcohols in water by very effective mangano silicate molecular sieves. Primary alcohols are selectively oxidized to aldehydes and secondary alcohols are selectively oxidized to ketones [13, 14]. I.R Parrey *et al.* study the Catalytic oxidation of alcohols using polystyrene EDTA Cu(II) metal compound and Catalytic oxidation of phenols using Schiff base Cu(II) metal complex using L-histadine [15].

Materials and Methods: Manganese (II) acetate tetrahydrate purchased from Merck; Copper (II) cobalt dihydrate also purchased from Merck, The amines, were procured from Sigma Aldrich Chemicals Private Limited, Bangalore Orthophenylenediamine (Lobachemie), D-glucose (SD Fine Chem Limited), sodium sulphate (Merck), sodium metaperiodate (Merck), glacial acetic acid, hydrazine hydrate (Qualigens), soidum bicarbonate (Sisco Research Laboratories Limited), bromine (Merck) and sodium pyruvate (Sisco Research Laboratories Limited) were used in the current study. Hydrogen peroxide (Merck), cyclohexane (Qualigens), was used for the catalytic action using metal complexes. All other reagents were of analytical reagent grade and the solvents working were either of 99% purity or refined by known process. The EPR spectra of the centers in DMF were recorded on Varian E-112 X/Q band spectrophotometer at liquid nitrogen temperature and the standard used was tetracyanoethylene (TCNE) with a g value of 2.0027. The electronic spectra were recorded in the region 200-1100 nm on a Thermo electron Nicolet evolution 300 UV-Vis spectrophotometer.

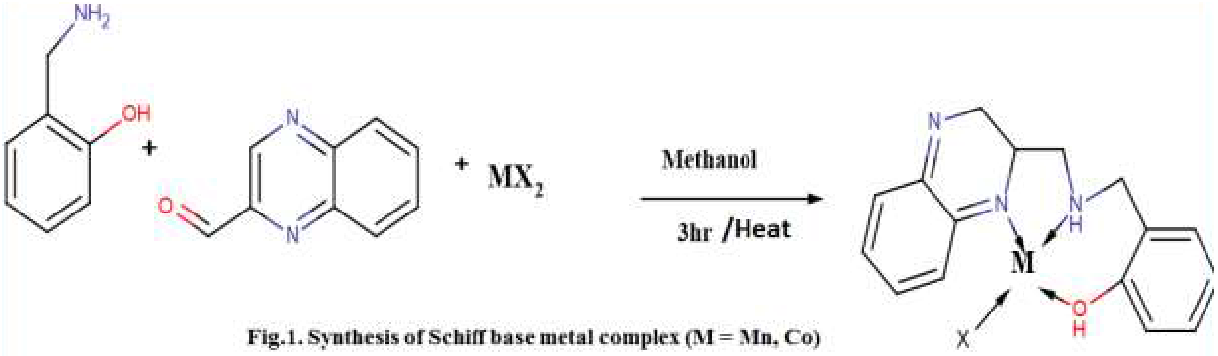

Fig.1. Synthesis of Schiff base metal complex (M = Mn, Co)

Synthesized of quinoxaline- 2-carboxaldehyde: Refluxing D-glucose (36 g, 0.2 mol) with orthophenylenediamine (21.6 g, 0.2 mol) in the presence of hydrazine hydrate (5 mL, 0.1 mol) and glacial acetic acid (6 mL) on a boiling water bath below carbon dioxide air (providing by the adding of a pinch of sodium bicarbonate) for 5 hours gave the compound, 2(D-arabinotetrahydroxybutyl) quinoxaline. The resultant products were purified by recrystallization using hot water. The re-crystallized 2(D-arabino tetrahydroxy butyl) quinoxaline (5 g, 0.02 mol) was dissolved in water (300 mL) containing glacial acetic acid (10 mL) and sodium metaperiodate (13 g, 0.06 mol) and was kept at room temperature with control stirring for 16 hours. It was then filtered and the filtrate was neutralized with sodium bicarbonate. The neutral solution was then extracted with ether. The ether extract was dried with anhydrous sodium sulphate. It was then filtered and evaporated to dryness. The resulting residue was recrystallized from petroleum ether to give pure quinoxaline- 2-carboxaldehyde (Yield): 70%, M.P 104 °C.

Preparation of Schiff base complexes of manganese and cobalt

Quinoxaldehyde (1.580 g, 0.01mol) were mix in methanol (50 mL) was added to 2-amino 5-methylphenol (1.550 g, 0.01 mol) in water (30 mL). The solution was then refluxed on a water bath for half an hour. The colour of the solution turns from pale yellow to dark brown. To this hot solution, cobalt chloride (1.700 g, 0.01 mol) or manganese acetate tetra hydrate (2.190 g, 0.01 mol) in methanol (20 mL) was added. Immediate formation of a precipitous was experiential, and the refluxing was sustained for three hours to confirm comprehensive precipitation. The rapid was cleaned and washed with methanol covering water and then with acetone.

L: Yield 90%, m. p. 160-165°C, yellow colour, anal cald. for $C_{16}H_{15}N_3O$(%): calcd C(72.46), H(4.21), N(15.64); Found C (72.99), H(4.98), N(15.96); I.R(KBr Pallets, cm^{-1}): 3330 ν(0-H), 1626 ν(CN), 1261 ν(CO).

MnL: Yield 65%, m. p. 165-170°C, Red colour, anal caldfo $MnC_{20}H_{23}N_3O_8$(%): calcd C(54.78), H(3.98), N(10.69) Mn (13.96); Found C (54.83), H(4.35), N(10.66), Mn(13.96);; I.R(KBr Pallets, cm-1): 3300 ν(0- H), 1606 ν(CN), 1234 ν(CO), 465 ν(M-O), 413 ν(M-N).

CoL: Yield 85%, m. p. 165-170 °C, violet colour, anal cald for $CoC_{32}H_{30}N_6O_2$(%): calcd C(63.73), H(4.23), N(14.24), Co(9.75); Found C(63.70), H(4.36), N(13.97), Co(9.80);; I.R(KBr Pallets, cm-1): 3390 ν(0-H), 1664ν(CN), 1252 ν(CO), 567 ν(M-O), 468 ν(M-N).

Result and Discussion

Vibrational Spectrum: The IR spectrum of ligand and complexes shown bands at 3386 cm^{-1} is due to the OH stretching vibrations of Schiff base ligand. The ligand exhibits azomethine C=N stretching at 1600 cm^{-1} and C=N of quinoxaline ring at 1770 cm^{-1} [16]. There is a sharp intense band at 1665 cm^{-1} which shows the presence of keto group. The majority of the bands due to the free ligand are present in the spectra of complexes. A new broad band at around 3300 cm^{-1} is seen for all the complexes which may be due to the presence of hydrated or coordinated water molecule. The strong band observed at 1633 cm^{-1} for the cobalt (II) complex suggests that the Schiff base acts as a monobasic tridentate ligand. Appearance of new bands in the spectra of all complexes in the regions 500-450 and 420-400 cm^{-1}.

UV-vis spectrum of Schiff base metal complex

Electronic spectra of the Schiff base and its complexes were occupied in methanol (~$5x10^{-4}$ molar) in the range 50000-10000 cm^{-1}. The absorption maxima of spectra are given in Fig. 1. The UV-Vis spectrum of the Schiff base shows two strong bands at 42500 and 26000 cm^{-1} due to benzene π-π*, imino π-π* and quinoxiline transitions of Schiff base ligand transitions . The intense bands in the complexes are observed above 30000 cm-1 are due to charge transfer and intra ligand transitions. The electronic spectrum of the manganese (II) complex in methanol contains two intense broad bands at 29800 and 21500 cm-1 [17]. In the electronic spectrum of Co (II) complex the d–d transitions are almost masked by the high-intensity charge transfer bands. However, a shoulder is observed around 17000 cm^{-1}. Which may be assigned to the 4T1g (F) to 4T1g (P) transition and transitions in this region have been reported for octahedral Co (II) complexes Fig.2.

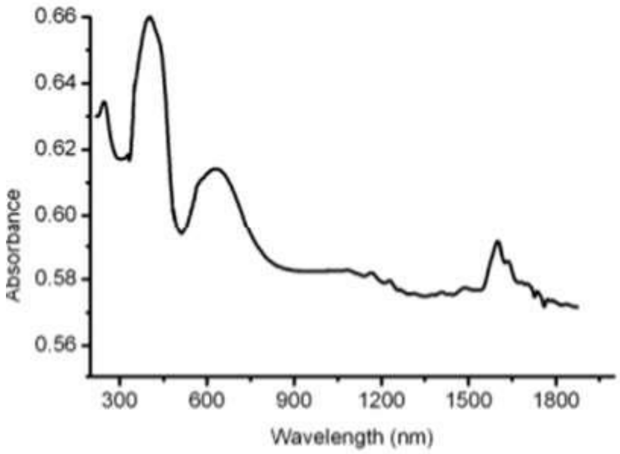

Fig. 1: Shows the UV-Vis Spectra of Cobalt Complex

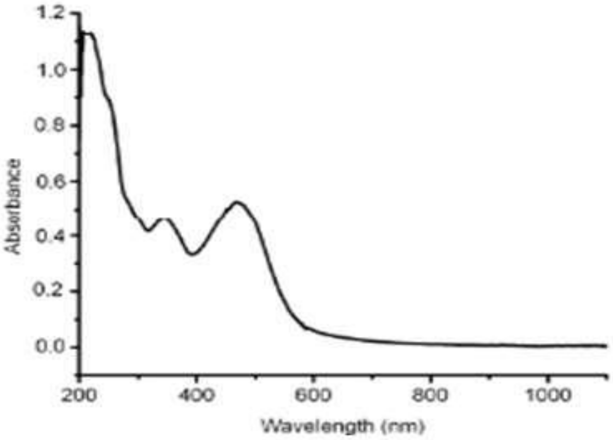

Fig. 2: Shows the UV-Vis Spectra of Manganese Complex

EPR spectrum of Schiff base Mn(II) metal complex

The spectrum at 77 K in DMSO exhibits six hyperfine lines. The lines are poorly resolved, which may be due to the poor glass formation. The spectrum gives a g value of 1.99 with an A value of 0.00929 cm^{-1}.

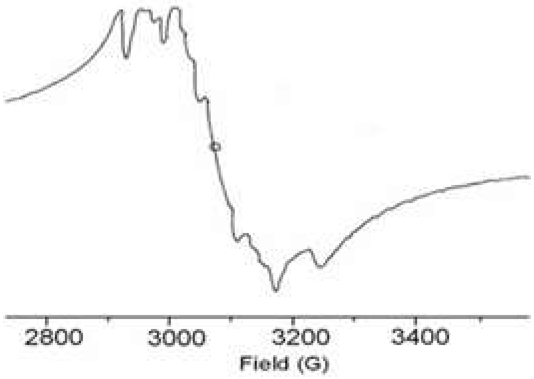

Fig. 3. EPR Spectrum of Mn (II) Complex

Conclusion: Two Schiff base complexes were synthesized successfully. Both complexes were analyzed by spectro chemical methods. UV-vis spectrum suggested the octahedral geometry of Co (II) complexes and tetrahedral geometry of Mn(II) complex.

References

1. Gupta, K. C.;Sutar, A.K. Lin, C.C. Polymer-supported Schiff base complexes in oxidation reactions. *Coord. Chem. Rev*. **2009**, *253*, 1926-1946.
2. Trakarnpruk,W. Preparation, Characterization, and Oxidation Catalysis of Polymer-Supported Ruthenium and Cobalt Complexes. *Ind. Eng. Chem. Res*.**2008,** *47*,964–968.
3. Donald, J. Darensbourg.; Eric, B. Frantz. Manganese (III) Schiff Base Complexes: Chemistry Relevant to the Copolymerization of Epoxides and Carbon Dioxide. *Inorg. Chem*. **2007**, *46*, 5967–5978.
4. Cozzi, P.G. Metal-Salen Schiff base complexes in catalysis: practical aspects *Chem. Soc. Rev*. **2004**, *33*, 410-421.
5. Gupta, K.C.; Sutar, A.K. Catalytic activities of Schiff base transition metal complexes. *Coord. Chem. Rev*. **2008**, *252*, 1420-1450.
6. Omid, P.; Chamayou, A.C.C.; Monfared, H.H. Hydrazone Schiff base-manganese (II) complexes: Synthesis, crystal structure and catalytic reactivity. *Inorginica chemical acta*. **2007,** *360*, 1599-1608.
7. Taqui Khan, M. M.; Chatterjee, D. Merchant.; Paul, R. R.; Abdi, P.; S. H. R.; Srinivas, D.; Siddiqui, M. R. H; Moiz, M. A.; Bhadbhade, M. M.; Venkata, S. K. Synthesis of the mono oxo ruthenium(V) complexes containing the amino poly carboxylic acid ligands EDTA and PDTA and their reactivities in the oxidation of organic substrates.(b) X-ray crystal structures of K[RuIII(EDTA-H)Cl].cntdot.2H2O and K[RuIII(PDTA-H)Cl].cntdot.0.5H2O. *Inorg. Chem*. **1992,** *31*,2711–2718, DOI: 10.1021/ic00039a010
8. Taqui Khan, M.M.; Hussain, A.; Ramachandraiah, G.; Moiz, M. A. Equilibrium and Electrochemical Studies on the Complexes Formed by the Interaction of K[Ru(EDTA-H)Cl].2H2O with Oxygen and Hydrogen Peroxide. *Inorg. Chem*. **1986,** *25*, 3023-3030.
9. Taqui Khan, M. M.; Srinivas, D. R.; Kuresh, I.; Khan, N. H. Synthesis, characterization, and EPR studies of stable ruthenium(III) Schiff base chloro and carbonyl complexes, *Inorg. Chem.***1990,** 29, 2320–2326. **DOI:** 10.1021/ic00337a026
10. Dalal, M.K.; Ram, R.N. Surface characterization and catalytic activity of polymer-anchored Ru III – Schiff base complex, Journal of Molecular Catalysis A: Chemical. **2000,***159*, 285–292.
11. Dalal, M.K.; Upadhyay, M.J.; Ram, R. N. Oxidation of benzyl alcohol using polymer anchored Ru (III)/complex as catalyst, Journal of Molecular Catalysis A: Chemical. **1999**1, *42*,325–332.
12. Antony,R.;Theodore,S.David.;Saravanan,K.; Karuppasamy, K.Synthesis, Spectrochemical characterization and catalytic activity of transition metal complexes derived from Schiff base modified chitosan Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy.**2013,** *103*,423-430.

13. Haresh, G. Manyar.; G. S. Chaurean.; Kumar, A.The green catalytic oxidation of alcohols in water by using highly efficient mangano silicate molecular sieves. *Green Chem*, **2006,** *8***,** 344-348.
14. Parrey, I.R.; Anayutullah, S.; Hashmi, A.A. Preparation Physicochemical Characterization and Catalytic Applications of Polystyrene Ethylenediamine Tetra Acetic Acid Cu (II) Metal Complex. .mrc. **2014,** *3*, 107-116.
15. Parrey, I.R.; Hashmi, A. A. Catalytic hydrolyxation of phenols using Schiff base complexes of Copper metal complexes derived from L-histidine. *Mor. J. Chem.* **2015,** *3 N°1* 147-15.
16. Samal, P.K.; Patra, A.K.; Nethaji, M.; Chakravarthy, A.R. Oxovanadium (IV)-based near-IR PDT agents: design to biological evaluation *Inorg. Chem*. **2007**, *46*, 111.