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RESEARCH ARTICLE

Microwave Assisted Synthesis, Characterization and Catalytic Activity of Tetra Dentate Macro cyclic ligand Complexes of Co (II), Ni (II), Fe (II) & Cu (II)

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ABSTRACT

Tetra dentate N_6-macrocyclic ligands of Co (II), Ni (II), Fe (II) and Cu (II) were synthesized in dry condition using microwave method from Trimethoprim and Diethyl phthalate as starting material in single step. Further it was purified by soxhlet apparatus. These complexes were characterized by elemental analysis with the help of IR Spectra, Electronic Spectra, ^1H- NMR Spectra, Molar conductance and Magnetic susceptibility. The catalytic activities of these complexes were performed on polluted water collected from various pulp industries, Dye industries and Sugar industries.

Key words: *Synthesis, Characterization, macrocyclic ligand complexes and polluted water.*

INTRODUCTION

"The word Macrocyclic may be defined as a cyclic molecule with three or more potential donor atoms in a hetero atom ring of at least nine atoms"**.** Owing to the presence of a central cavity, Macrocyclic ligands have long been employed as selective hosts for a wide range of guest molecules and ions. Now a days coordination chemistry of Macrocyclic complexes is a fascinating over which has attracted the attention of Inorganic chemists because of their close relationship to molecules of biological significance. The applications of Macrocyclic ligands and their metal complexes depend upon the nature of reactants and the corresponding metal ion. . This paper will exhibit the solvent free synthesis (Microwave assisted) and catalytic activity of tetra dentate Macrocyclic ligand complexes of Co, Ni, Fe and Cu and the starting material used in the preparation is the Trimethoprim (a pyrimidine derivative) which is a drug acting as antimicrobial and showing the biological importance as constituents of nucleic acids. The Macrocyclic systems are of significant interests not only for their pharmacological properties but also for their capacity for chemical recognition of anions and metal of biochemical, medical and environmental importance. It has been well established that many drugs have become resistant to microbes, recognizing the antimicrobial properties of Macrocyclic transition metal complexes.

Apart from the biological implications, aspects of the chemistry of Macrocyclic ligands are of a relevance to a diverse number of other areas. Indeed, there has been a remarkable expansion of research involving these other areas during recent times. Many of the developments impinge on topics such as metal-ion catalysis, organic synthesis, metal-ion discrimination and analytical methods, as well as number of potential, industrial, medical and other applications. Chemistry have recently created enzyme like catalysts called tetra amido Macrocyclic ligand activators (TAML) that can destroy stubborn pollutants by accelerating the cleansing reactions with hydrogen peroxide (H_2O_2) and other oxidants. TAMLs accomplish this task by mimicking the enzymes in our bodies that have evolved overtime to combat the toxic compounds. In laboratory and real world trials, TAMLs have proved they can destroy dangerous pesticides, dyes and other contaminants, greatly decrease the smell and colour from the waste water discharged by paper mills and kills bacterial spores similar to those of the deadly anthrax strains. If broadly adopted TAMLs could save millions of dollars in clean up costs.

The tetra dentate Macrocyclic ligand complexes of Co, Ni, Fe and Cu have been attracting many persons of current research in Inorganic chemistry and Bioinorganic chemistry all over the world due to its wider applications and unusual binding capacities.

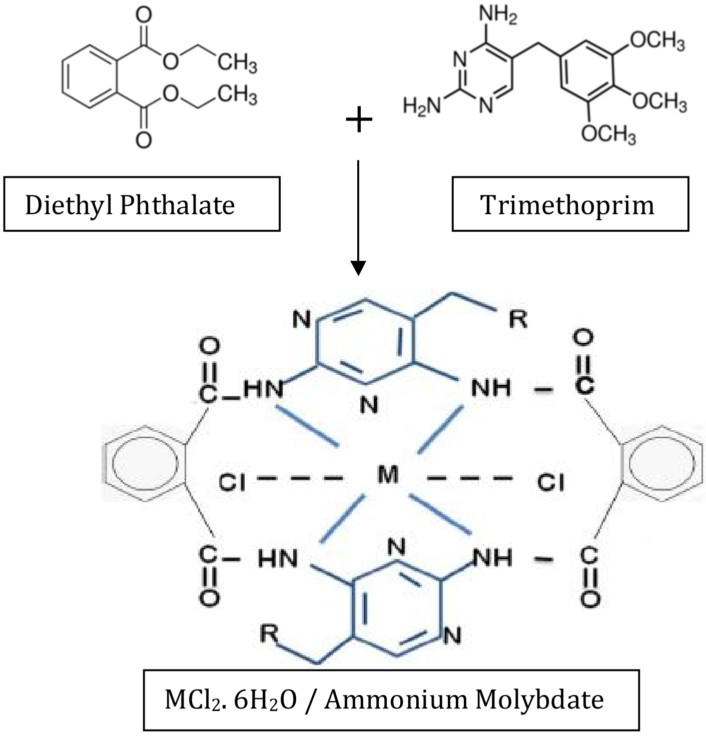
We therefore have chosen to work on the development of new Macrocyclic ligands and their metal complexes, which may provide additional options for the human needs. Several synthetic studies are now a day's available for the preparation of well organized macro molecular systems which exhibit peculiar physico-chemical properties or have well defined Pharmacological properties.

EXPERIMENT

All the starting materials and reagents used in the synthesis were of reagent grade (Sigma-Aldrich/ Himedia/ Qualigens). The solvents used for the purification of ligand metal complexes were distilled before use. All other chemicals were of AnalaR grade and used without purification. IR Spectra was recorded on a Shimadzu spectrometer; the Electronic spectra on UV VIS Spectrophotometer Systronics 2203, the magnetic moments were measured using gouy balance. The conductance was measured on a conductivity meter Systronics using dip type platinum electrode and purity of the compound checked by TLC.

MICROWAVE ASSISTED SOLVENT FREE METHOD OF SYNTHESIS

In a typical procedure for the synthesis of tetra dentate macrocyclic ligand of transition metal (Co, Ni, Fe & Cu) diethyl phthalate (mw: 222.24) 0.01 mole, trimethoprim (mw: 290.32) 0.01 mole, Metal chloride hexa hydrate 0.01 mole & ammonium molybdate 0.0005 gram (Catalyst) were placed in a beaker and irradiated in the microwave oven at high power for 2 min and low power for 4 min. The product was filtered and washed with 520ml of hot water and dried. The crude compound was subsequently reprecipitated from concentrated H_2SO_4. It was further by soxhlet extraction for 3hrs with acetone.



RESULT AND DISCUSSION

All the complexes were soluble in water, Ethanol and 1-propanol. They were thermodynamically stable upto 210-220^0 C.

Physical Measurements:

Molar conductivities & Magnetic momentum:

The molar conductances of these macrocyclic complexes in acetonotrile were measured and then calculated molar conductance values of metal complexes are reported as follows.

The conductivities of the complexes were in the range of 10 to 28 Ohm^{-1}. Cm^2. mol^{-1} which is characteristics of 1:0 electrolytes suggests that all of them are non electrolytes. The presence of chloride ions is evident only after decomposition of the complexes, probably due to their presence in the coordination spear. Based on the conductance metal chloride complexes are assigned the structure [M (ML) Cl_2] ML-macrocyclic ligand. M- Metal ion/atom.

S. No.	Complex	Molar conductance Ohm^{-1}. Cm^2. mol^{-1}	Magnetic momentum in B.M
1	[Fe(ML)Cl2]	24.21	4.89
2	[Co(ML)Cl2]	36.03	4.03
3	[Ni(ML)Cl2]	20.57	2.67
4	[Cu(ML)Cl2]	09.56	1.44

Electronic Spectra:

The electronic spectral data of Fe (II) complex exhibit two to three very weak bands at 16000 Cm^{-1}, 21000 Cm^{-1} and 26650 Cm^{-1}. Which are assigned to $^6A_{1g} \rightarrow {}^4T_{1g}$ (G), $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4T_{2g}$ (D) transition respectively. These observations reveal that the stereochemistry of this complex is consisting with the six coordinated octahedral geometries. The electronic spectra of Co (II) complexes consist in general of three spin allowed transition, although it will not always be possible observed all the three bands. In the electronic spectra of High spin octahedral complexes of Cobalt (II). One should expect three bands corresponding to the transitions. $^4T_{1g} \rightarrow {}^4T_{2g}$, $^4T_{1g} \rightarrow {}^4T_{2g}{}^*$ and $^4T_{1g} \rightarrow {}^4T_{1g}$ (p). Once the Cobalt (II) complex display a very broad band at 22380 Cm^{-1} which is assigned to $^4T_{1g} \rightarrow {}^4T_{1g}$ (p) transitions of distorted octahedral geometry. Nickel (II0 complex one should expect three bands corresponding to $^3A_{2g} \rightarrow {}^3T_{2g}$, $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) transition suggesting octahedral geometry. In most of the Copper (II) complexes bands in region 12000 to 16000 Cm^{-1}. The synthesized macrocyclic complex of Copper (II) displays a band at 13100 Cm^{-1} due to $^2E_g \rightarrow {}^2T_{2g}$ transition characteristics of octahedral geometry.

IR Spectra:

The Infra Red spectra of the macrocyclic complexes are very useful to give some important information regarding to the skeleton of the complexes. The shifts in the peaks indicate the mode of linkage in the complexes. Comparision of the IR spectra of the macrocyclic ligand and the complexes confirmed the formation of the complexes. Very strong bands appearing in the region 3325-3410 Cm^{-1} may be assigned to secondary amine group. N-H stretching frequency of macrocyclic ligand at 3325 Cm^{-1} shifted to 3335 Cm^{-1} in iron complex, 3381 Cm^{-1} in Cobalt complex, 3398 Cm^{-1} in Nickel complex and 3405 Cm^{-1} in Copper complex. N-H def of macrocyclic ligand at 3167 Cm^{-1} which is shifted to 3170 Cm^{-1} in Iron complex, 3171 Cm^{-1} for Cobalt complex 3154 Cm^{-1} for Nickel complex and 3180 Cm^{-1} for Copper complex. C-H stretching frequency of macrocyclic ligand at 2729 Cm^{-1} shifted to 2890 Cm^{-1} for Iron complex, 2839 Cm^{-1} for Cobalt complex, 2755 Cm^{-1} for Nickel complex and 2745 cm^{-1} for Copper Complex. C-H def frequency of macrocyclic ligand at

1226 Cm^{-1} which is shifted to 1245 Cm^{-1} for Iron complex, 1230 Cm^{-1} for Cobalt complex, 1238 Cm^{-1} for Nickel complex and 1230 Cm^{-1} for Copper complex. C-N stretching of macrocyclic ligand at 1662 Cm^{-1} which is shifted to 1589 Cm^{-1} for Iron complex, 1676 Cm^{-1} for Cobalt complex, 1428 Cm^{-1} for Nickel complex and 1667 Cm^{-1} for Copper complex. C-C stretching of macrocyclic ligand at 765.74 Cm^{-1} which is shifted to 780 Cm^{-1} for Iron complex, 785 Cm^{-1} for Cobalt complex, 801 Cm^{-1} for Nickel complex and 745 Cm^{-1} for Copper complex. It indicates that all four secondary amino groups are coordinate to metal ion. The slight upward shift of carbonyl frequency of amide group from 1662 to 1676 Cm^{-1} support the coordination through only secondary amino groups not through carbonyl group. There are fairly strong IR spectral band in the region 3165 to 2635 Cm^{-1}due to the C-H and C-C stretching of pyrimidine ring, benzyl aromatic ring and methoxy groups also appear in the spectra of the complexes. In the same region indicates that they do not take part in coordination. Pyridine Nitrogen is not involved in coordination because the lone pair of electrons is engaged for resonance. The rings of flipping enhance the steric hindrance which prevents the carbonyl from coordination. At the same time amidic Nitrogen with the lone pair is more readily available for coordination. Thus only four secondary amino groups are involved in coordination. The appearance of a new moderately intense band in the region 495 Cm^{-1} assignable to stretching of (M-N) bond. Further confirms the involvement of Nitrogen in coordination. Spectral data reveals bands at 481 to 429 Cm^{-1} which may be assigned Fe-Cl, Co-Cl, Ni-Cl and Cu-Cl coordination.

^{1}H NMR spectra:

The proton magnetic resonance spectrum of the macrocyclic ligand and its metal complexes were taken in DMSO solvent. The spectrum shows six different types of protons. Since signals are observed at four different regions from the TMS (Internal standard). The intensities of the peaks are in the ratio 9:2:2:6.^{1}H-NMR spectrum of the macrocyclic ligand display peaks at δ2.43-2.53(4H,S,-CH_2): δ3.7 (18H, M, O-CH3): δ5.7-6.1(4H, S, Pyridine-H): δ6.2-6.48(4H, S, Ar ring of trimethoprim-H): δ6.64 (2H, S, ring NH): δ7.2-7.53(12H, M, Ar-H): Thus, the ^{1}H-NMR spectrum confirms the presence of Trimethoprim and Diethyl phthalate moieties in the macrocyclic complex.

S. No.	Chemical shift	Assignment	Stereochemistry of the complex
1	δ2.43-2.53	4H,S,-CH_2	Octahedral
2	δ3.7	18H, M, O-CH3	Octahedral
3	δ5.7-6.1	4H, S, Pyridine-H	Octahedral
4	δ6.2-6.48	4H, S, Ar ring of trimethoprim-H	Octahedral
5	δ6.64	2H, S, ring NH	Octahedral
6	δ7.2-7.53	12H, M, Ar-H	Octahedral

ADVANTAGES OF MICROWAVE ASSISTED SYNTHESIS OVER CONVENTIONAL METHOD

The effect of microwave irradiation in Inorganic & Organic Synthesis is a combination of thermal effects, arising from the heating rate, super heating or hotspot and the selective absorption of radiation by polar substances. Such phenomenon is usually assessable by classical heating and existence of non thermal effects of highly polarizing radiation. Microwave assisted Inorganic & Organic synthesis is characterized by the spectacular acceleration produced in many reactions as a consequence of the heating rate, which cannot be reproduced by classical heating. Even reactions that do not occur by conventional heating can be performed using microwaves. This technology include highly accelerated rate of the reaction, reduction in reaction time with an improvement in the yield and quality of the product. Conventional method of Inorganic synthesis usually need longer heating time tedious apparatus setup, which result in higher cost of process and excessive use of solvents or reagents lead to environmental pollution. Microwave heating has been shown to dramatically reduced reaction times, increase product yield, high efficiency of heating, reproducibility, environmental heat loss can be avoided, enhance product purities by reducing unwanted side reactions and substantial elimination of reaction solvents, facilitation of purification compared to conventional synthetic method. This method is appropriate for Green chemistry and energy saving process.

Microwave irradiation in commercial domestic ovens has been recently used to accelerate organic reactions. Remarkable rate enhancement dramatic reduction of reaction time and increased specificity are the great impact caused by microwave. Although these procedures are seriously limited in solution chemistry because the use of solvent in microwave oven gives elevated temperatures and consequently high pressure, leading to dangerous situation in some cases.

Although compounds synthesized by both methods were in close agreement in the terms of their outputs. But microwave assisted synthesis has demonstrated enormous advantages over the conventional method and can be opted as first choice by synthetic chemists.

CATALYTIC ACTIVITY

Many pollutants released into water ways, such as dyes and pesticides, have become so omnipresent that they pose a serious threat to human health. The synthesized enzyme like catalyst called tetra dentate macrocyclic ligand complexes of Fe, Co, Ni & Cu -TAMLs that can destroy stubborn pollutants by accelerating cleansing reactions with Hydrogen peroxide. The polluted water containing the effluents of dyes and pesticides from textile mills, pulp industries and sugar industries in bleaching the colour found in effluent from Chlorine dioxide pulp bleaching plants for inhibiting dye transfer in laundry application for organo chlorine pollutants such as chlorinated phenols and for the bleaching of wood pulp. TAML catalyst activate hydrogen peroxide to give polluting chlorine based technology and a new oxidation process.

They are water soluble, easy to use and work over a broad P^H range. They lead to highly selective chemistry in commercial process such as pulp bleaching selectivity is vital. These are effective in minute concentration and are capable of more than 10000 turnovers per hour in process that used in virtually all peroxides for target task. Peroxide process based on TAML activators can work below the temperature. Hydrogen peroxide is halfway between water and organic molecule. This compound is also strong oxidizing agent. In water hydrogen peroxide produce a kind of liquid of fire that demolishes the organic molecule. So catalyst would probably need to have an iron atom placed inside a molecular matrix of organic group. So we hard to develop a big outer ring called as Macrocycle. It is more useful catalyst TAML decompose on time scale ranged from minutes from hour. The new tandem TAML-GO system introduced to minimize hazard because it removes the need for the transport and storage of concentrated oxidized storage. The demonstrated ability to crude sugars from readily available waste sources is an intriguing development in the sustainable chemistry of TAML Catalyst. Hydrogen peroxide itself oxidizes dyes like Amaranthus, Bromothymol Blue, Celestine Blue and Rhodamine- B very slowly. Fe (III) –TAML activators increase the rate immensely.

The Fe-TAML/H_2O_2 process for removal of concentrated dyes offer advantages over traditional decolourisation method in bleaching of water polluted due to the effluents released from the textile industries, Pulp Industries and sugar industries. We have collected water samples from various sugar industries, textile industries and pulp industries. The samples collected were treated with oxidizing agents like H_2O_2 and time taken for the bleaching of above said effluents took many hours to few days and any Chemistry involving oxygen can be destructive because the bonds it makes with other elements are so strong. Because each molecule of H_2O_2 is half way between water and molecular oxygen, the compound is also strongly oxidizing. In water H_2O_2 often produces a kind of liquid fire that demolishes the organic molecules around it. When compared to the catalytic activity of remaining tetra dentate macrocyclic ligand complexes of Co, Ni & Cu the tetra dentate macrocyclic ligand complexes of Iron are more effectively worked to break down the harmful effluents of water from various industries like pulp industries, sugar industries and textile industries.

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