NATIONAL SEMINAR on RECENT TRENDS IN COMPUTATIONAL CHEMISTRY AND DRUG DESIGN

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Keynote Lectures

Oral Presentations

EPR Aspects of Metal Complexes of Aroylhydrazones

M.R.Prathapachandra Kurup
Professor, Department of Chemistry
Central University of Kerala, Kasaragod, Kerala, India
E-mail: mrp@cukerala.ac.in

EPR spectroscopy plays an important role in determining the stereochemistry of copper complexes. For coordination geometries corresponding to an elongated octahedron, a square pyramid or square planar, the ground state is $d_{x^2-y^2}$. When the coordination around Cu(II) ion is a compressed octahedron or a trigonal bipyramid, the ground state is d_{z^2}. EPR spectroscopy can distinguish the ground states $d_{x^2-y^2}$ and d_{z^2} on the basis ofthe principal values of the g tensor in the anisotropic spectra. For copper(II) in most environments, the ground state magnetism is essentially spin only and orbital motion is said to be quenched. The g factors are shifted from the free electron value of 2.0023 by spin-orbit coupling of the ground state to excited states. The EPR spectra of some metal complexes of aroyl hydrazones in polycrystalline state at 298 K and in frozen DMF at 77 K recorded in the X band using 100 kHz field modulation and 9.4 GHz microwave frequency are discussed.

HF and Post-HF Methods

Jayasree E. G.
Assistant Professor, Department of Chemistry
University of Kerala, Thiruvananthapuram
E-mail: jelambal@keralauniversity.ac.in

The time independent Schrodinger equation is exactly solvable only for hydrogen atom, not for any other elements in the periodic table due to many electron interactions. This many body problem is circumvented by incorporating various approximation methods in many electron systems. Simplest and fundamental yet powerful theory that is used for solving Schrodinger equation for molecules is Hartree-Fock molecular orbital theory. Starting from Born-Oppenheimer approximation, various steps involved in Hartree-Fock self-consistent method will be detailed. Hartree-Fock energy equation including coulomb integral and exchange integral terms will be derived. Certain post-HF methods incorporating correlation energy also will be discussed.

Computational Modelling in Drug Discovery

Pattiyil Parameswaran
Associate Professor, Department of Chemistry,
National Institute of Technology Calicut
Kozhikode, Kerala, India - 673 601
Tel: 0091-495-228-5304, Fax: 0091-495-228-7250
E-mail: param@nitc.ac.in

The process for drug discovery and development is challenging, time consuming and expensive. Additionally, increasing knowledge of biological structures, as well as increasing computer power have made it possible to use computational methods effectively in various phases of the drug discovery. Computer-aided drug discovery (CADD) tools can act as a virtual shortcut, assisting in the expedition of this long process and potentially reducing the cost of research and development. Today CADD has become an effective and indispensable tool in therapeutic development. Computational methods are nowadays routinely used to accelerate the long and costly drug discovery process. These methods are broadly classified as either structure-based or ligand-based methods. Structure-based methods are in principle analogous to high-throughput screening in that both target and ligand structure information is imperative. Structure-based approaches include ligand docking, pharmacophore and ligand design methods. The method has the advantage of requiring minimal compound design or prior knowledge, and technologies required to screen large libraries have become more efficient. In the past decade, CADD has reemerged as a way to significantly decrease the number of compounds necessary to screen while retaining the same level of lead compound discovery. Many compounds predicted to be inactive can be skipped and those predicted to be active can be prioritized. This reduces the cost and workload of a full HTS screen without compromising lead discovery. Because CADD requires significantly less preparation time, experimenters can perform CADD studies while the traditional HTS assay is being prepared. CADD had a significant impact on the discovery of various therapeutics that are currently helping to treat patients.

Molecular Docking of DNA and Proteins with Metal Complexes

Dr. Sreejith S.
National Post-Doctoral Fellow, IISER, Kolkata
E-mail: sreejithomkaram@gmail.com

Molecular docking is an *insiico* method to predict the drug biomolecular interactions for the rational drug design and discovery, as well as in the mechanistic study by placing a molecule (ligand/metal complex) into the preferred binding site of the target specific region of the DNA/protein (receptor). The interactions involved are of non-covalent type and form a stable complex of potential efficacy and more specificity. Further the docking studies provide the binding energy, free energy and stability of complexes. Through molecular docking one could have an insight on the ligand-receptor complex with optimized conformation which helps in the prediction of one with less binding free energy. At present, docking technique is utilized to predict the tentative binding parameters of ligand-receptor complex beforehand. The aforementioned factors make molecular docking an increasingly important tool for drug discovery.

Since the molecular docking approach can be used to model the interaction between a small molecule and a protein at the atomic level, the behavior of small molecules in the binding site of target proteins can be used to elucidate fundamental biochemical processes. There are two basic steps involved in the docking process: prediction of the ligand conformation as well as its position and orientation within these sites (usually referred to as pose) and assessment of the binding affinity. The target or DNA is generally taken from the protein data bank. While performing docking, different interacting conformers of the ligands are generated and compared with each other. In the condition of rejection, new conformers are obtained and again search procedure continues to its endpoint after acceptance of one conformation.

Further molecular docking can demonstrate the feasibility of any biochemical reaction as it is carried out before experimental part of any investigation. The judicious choice of target proteins can augment the impact of the study. For instance, selecting a target protein like enzyme can be used to predict the activation or inhibition of enzyme by monitoring the interaction of the small molecules (ligand) with that of the target protein which is enzyme. This information can be used as raw material which can eventually be employed for the rational drug designing.

Drug-DNA interaction

Molecular docking plays a prominent role in the initial prediction of drug's binding properties to nucleic acid. This information establishes the correlation between drug's molecular structure and its cytotoxicity. Keeping this in view, medicinal chemists are constantly putting their efforts to elucidate the underlying anticancer mechanism of drugs at molecular level by investigating the interaction mode between nucleic acid and drugs. Medicinal chemists are doing in silico observations where their main finding is to predict whether the compound/drug is interacting with the protein/DNA. If the docking programme is predicting the said interaction, then the experimental procedures are made available to find out the real binding mode of the complex. This leads to the development of new anticancer drug. Furthermore, this knowledge would be instrumental in the detection of those structural modifications in a drug that could result in sequence/structure specific binding to their target.

Here a study of binding characteristics of the Pd(II) salen type Schiff base complex is carried out against B-DNAdodecamer and Human Serum Albumin (HSA). AutodockVina was used to carry out docking of the prepared compounds with DNA/protein. Out of the different conformers obtained from the docking studies, an energetically favourable docked position is obtained for the complexes with the tested DNA and protein. The **Table 1** contains the results of the docking studies of the complex with B-DNA and human serum albumin (HSA). To test the binding characteristics of the complex with DNA, B-DNA dodecamer was selected (PDB ID 1BNA). On evaluating the interactions, one can see that the docked complexes bind to the DNA effectively with DNA functional groups without disturbing the double helical structure of DNA (**Fig. 1**). It is seen that best binding mode is seen to bind at the major groove of the DNA.

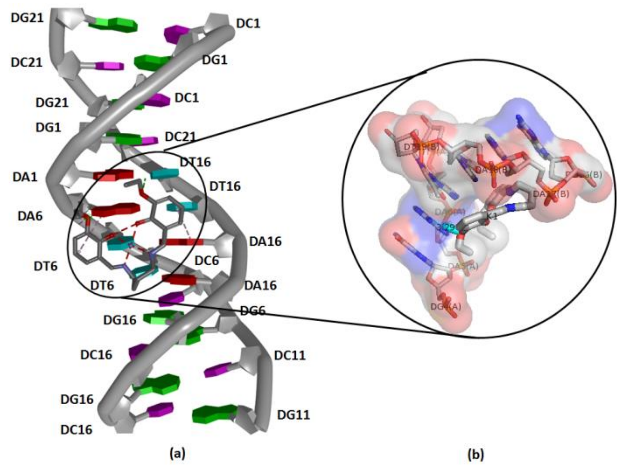


Fig.1. (a) Molecular docked model of the complex with B-DNA dodecamer (b) Specific interactions with residues.

Table 1 Different binding modes of the complex with DNA and HSA

Mode	B-DNA			HSA		
	Affinity (kcal/mol)	distance from best mode (Å)		Affinity (kcal/mol)	distance from best mode (Å)	
		RMSD l.b.	RMSD u.b.		RMSD l.b.	RMSD u.b.
1	-7.1	0.000	0.000	-7.6	0.000	0.000
2	-6.7	2.850	8.351	-7.6	2.429	5.224
3	-6.5	3.440	6.852	-7.6	2.474	5.722
4	-6.4	12.164	15.101	-7.4	17.938	21.719
5	-6.2	12.632	15.482	-7.3	2.378	6.430
6	-6.2	2.126	6.743	-7.3	31.236	34.406
7	-6.2	13.090	14.793	-7.1	2.129	5.930
8	-6.2	13.337	15.449	-7.1	1.930	6.523
9	-6.1	13.508	15.817	-6.9	2.574	6.738

The complex was also subjected to molecular docking with human serum albumin, HSA (PDB ID 1AO6) (**Fig. 2**). The docking studies revealed that the interactions of the best binding conformer of the complex occur between subdomains I and III of HSA with majority of the interactions occurring in III. In general the electron rich nature of the DNA/protein and electron deficient character of the metal ions may be pointed out as the reason for strong interactions and this can be decisive in designing a potential pharmacological drug.

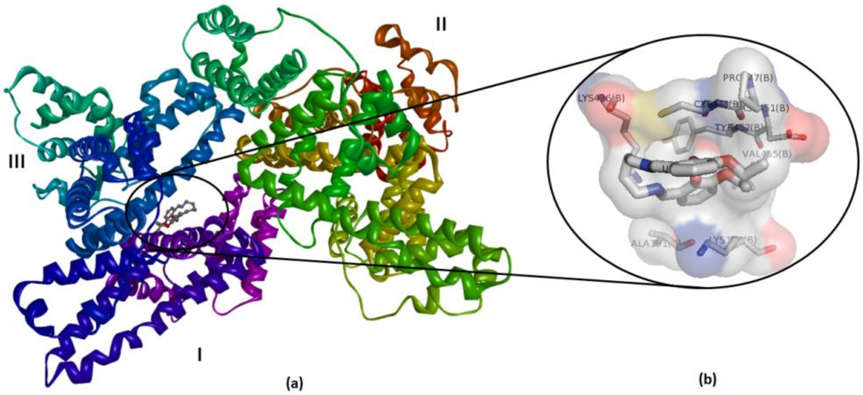


Fig. 2.(a) Molecular docked model of the complex with HSA (b) Specific interactions with labelled residues.

Stability of Secondary Structures of Proteins - A Molecular Mechanics Approach

Padmesh A.
Assistant Professor, Department of Chemistry
IIT, Palakkad, Kerala
E-mail: padmesh@iitpkd.ac.in

One of the most regularly found secondary structure in polypeptides is α-helices. These are conventionally described as being stabilized by hydrogen bonds between the adjacent atoms in the peptide groups along the main chain. Another relevant secondary motif is the β-sheet. Contrary to α helices making intramolecular hydrogen bonds locally for stabilization, the β-sheets form hydrogen bonds with adjacent polymer strands. The major difference between the α helix and β sheet is the interactions takes place amongst residues which are in close proximity in the primary structure where as in the latter case the interactions take place between the residues of the different parts of the protein that can be far apart in the primary structure. Disulfide bridges are no longer considered to merely stabilize protein structure, but are increasingly recognized to play a functional role in many regulatory biomolecular processes. Disulfide bonds play a crucial role in the smooth functioning of protein machinery. Among the proteins, the disulfides are classified into two distinct sets - structural and functional disulfides. The structural disulfides are believed to be added in different protein systems during the evolution to enhance the stability of proteins owing to its strong covalent nature. On the other hand, the comparatively newly defined class of disulfides known as the functional ones is those which are capable of regulating the chemico-biological activity of the protein by themselves undergoing frequent reduction and oxidation. These disulfide bonds are enriched by the very chemistry of sulfur bonds, which can easily undergo redox reactions at mild, physiological conditions. Theoretical studies can be utilized to look at the molecular details at the finest level.

Molecular Modeling of Biomolecules: A QM/MM approach

Susmita De
Assistant Professor, Department of Applied Chemistry
Cochin University of Science and Technology
E-mail: susmitade1980@gmail.com

“Much of what is understood in the field (biology) is based on the structure of molecules and the properties of molecules in relation to their structure.” - Linus Pauling

In the beginning, different computational methods used for modeling structure and reactivity of complex biological systems will be introduced with a special emphasis on QM/MM approach. The relation between the structure and function of a protein will be discussed by taking example of K^+ ion transport protein and binding of beryllium with immunoprotein for the development of chronic beryllium disease.

Chemical Bonding And Reactivity Of Carbyne Type Bimetallic Carbido Complex, Tp'(Co)$_2$mo≡C-Fe(Co)$_2$cp (Tp'= Tris(3,5 -Dimethylpyrazolyl)Borate)

[a]**Treesa Chakko A.**, [b]**Pattiyil Parameswaran**
[a] St. Mary's College, Thrissur
[b]National Institute of Technology Calicut
Kozhikode, Kerala, India - 673 601
E-mail: param@nitc.ac.in

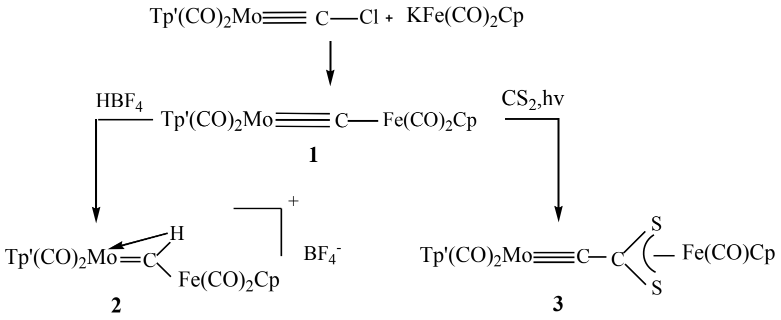
Bimetallic carbido complexes, in which naked carbon atom acts as bridging ligand, are one of the emerging areas of research in chemistry. They are considered as key intermediate in several processes, such as Fischer-Tropsch, olefin metathesis etc. Here we have predicted the bonding study of the chemical bond between Mo and carbido Carbon in the complex Tp'(CO)$_2$Mo≡C-Fe(CO)$_2$Cp (Tp'= tris(3,5 -dimethylpyrazolyl)borate), using computational quantum mechanical calculations. The molecular orbital (MO) and natural bond orbital (NBO) of Mo-C-Fe bond have been carried out at the M06/def2-TZVPP//BP86/def2-SVP level of theory. The MO and NBO analysis suggested a triple bond character between Mo and C and single bond character between Fe and C. For further understanding of bonding, the reactivity of complex **1** towards proton and hydride were carried out. The result predicts an electron sharing interaction in Mo-C bond and C- Fe bond and two donor acceptor interactions between Mo and carbido C. ie, the predicted representation is $\mathrm{Mo}\overset{\longleftarrow}{\underset{\longrightarrow}{\text{---}}}\mathrm{C}\text{---}\mathrm{Fe}$.

Introduction

Carbon, one of the most versatile element, exhibits traditional as well as unusual bonding modes.[1] Carbones, carbido complexes, hyper coordinated Carbon compounds, planar tetra coordinated Carbon, etc. are some of the typical examples where Carbon shows non classical bonding pattern.[1-3] Recently, significant progress has been made on the bimetallic carbido complexes, where the naked Carbon atom acts as a bridging ligand. [4-16] This fascinating area of carbido complexes was emerged by the invention of first homo-metallic carbido complex [(TPP)Fe=C=Fe(TPP)] by Munsay.[12]

Here in this work we are mainly concentrating on the bonding study of class **c** complexes taking Tp'(CO)$_2$Mo≡C-Fe(CO)$_2$Cp (Tp'= tris(3,5 -dimethylpyrazolyl)borate) **1** as an example.

In 1990 it was J. L. Templeton and his coworkers who synthesized Tp'(CO)$_2$Mo≡C-Fe(CO)$_2$Cp (Tp'= tris(3,5 -dimethylpyrazolyl)borate) **1**, by the reaction of Lalor's chlorocarbyne Tp'(CO)$_2$Mo≡CCl with Fp anion [Fp= Cp Fe(CO)$_2$] in THF.[16] The complex **1** on reaction with CS$_2$ results in the insertion of CS$_2$ into C-Fe bond resulting complex **3** **(scheme1**). The product of simple prtotonation resembled the high oxidation state agostic alkylidene complexes of groups V[17] and VI[18] where the hydrogen on the α-carbon is also bound simultaneously to the metal. The net result of the insertion of CS$_2$ into carbido-iron bond was the formation of a dithio acid derivative which was chelated to iron in the Tp'(CO)$_2$Mo≡CCS$_2$Fe(CO) Cp product.[16]



Scheme 1. Schematic representation of the synthesis of **1** and its reaction with HBF$_4$ and CS$_2$.

The reactivity of the complex **1** towards proton and CS$_2$ suggests weak Fe-C bond and donor-acceptor interaction between carbido Carbon and Fe. Here we have carried out detailed computational quantum mechanical calculations to explore the nature of Mo-C and Fe-C bonds. Since the studies on unusual bonding character of carbon compounds, such as transition metal complexes with the bare carbon atom as a terminal ligand and 'carbones', in which the central carbon atom forms two donor-acceptor L→ C←L bonds, are a developing field of science, this study has a significant aspect. We have employed molecular orbital (MO) and natural bond orbital (NBO) at the M06/def2-TZVPP//BP86/def2-SVP level of theory.

Results and Discussion

Molecular Orbital (MO) And Natural Bond Orbital (NBO) Analysis

The molecular orbital analysis shows that HOMO-1 and HOMO-2 are the π-MOs formed by the Mo and carbido carbon. HOMO-6, HOMO-8, HOMO-9, HOMO-10, HOMO-12, and HOMO-14 are MOs having contribution towards Fe-C bonds. HOMO-18 is the σ-MO. HOMO-11 is the π-MO formed between Mo, carbido carbon and Fe. All other MOs are ligand based. LUMO+2 is the antibonding π^* orbital formed between Mo and carbido carbon. LUMO+1 is the antibonding σ^* orbital formed between Fe and carbido carbon.

The natural bond orbital (NBO) also predicts three bonds between Mo and carbido C with bond occupancies 1.79, 1.80, and 1.78. The corresponding bond order is 2.166, which is greater than the bond order of the Mo1-C3 (1.192) and Mo1-C4 (1.190). This indicates the presence of a multiple bond between Mo and carbido C. On analyzing the group charge, it is found that the group charge of Tp-Mo (CO)$_2$ is -0.3677 and that of C-Fe(CO)$_2$Cp is +0.3677. The group charge indicates that the charge flows from molybdenum group to carbido group.

Conclusions

The chemical bonding and reactivity of Mo-C-Fe bond in the Tp'(CO)$_2$ Mo≡C-Fe(CO)$_2$ Cp, **1** have been carried out at the M06/def2-TZVPP//BP86/def2-SVP level of theory by employing molecular orbital (MO) and natural bond orbital (NBO) analysis. The results from MO and NBO suggest a Mo-C triple bond and Fe-C single bond in the complex **1**. For further understanding and prediction of Mo-C-Fe bond we have analyzed the reactivity of **1** towards proton and hydride. The high values of proton affinity and hydride affinity show that there may be a vacant and fully filled P orbital in the carbide carbon. The bonding representation that satisfies this condition is the fourth bonding representation in the interaction diagram, i.e., $\mathrm{Mo} \leftrightarrows \mathrm{C} - \mathrm{Fe}$ where there is an electron sharing σ bond between Mo-C-Fe and there are two donor acceptor interaction ($\pi_1$and π_2) between Mo and carbido C.

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Oxide Thermoelectrics and Photocatalysts: Synthesis, Characterization and Property Evaluation

Nivedita Sudheer, Daneshwaran B, R Vijayaraghavan*
*Vellore Institute of Technology, Vellore, India – 632014
E-mail: rvijayaraghavan@vit.ac.in

$MgCo_2O_4$ is extensively studied as anode materials in Li-ion batteries and electrode material for asymmetric supercapacitor applications. In the present work, synthesis of $Mg_{1-x}Zn_xCo_2O_4$ ($x = 0.0$ to 1.0) and $MgCo_{2-x}Fe_xO_4$ ($x = 0.0$ to 0.4) nanoparticles are carried out by solution combustion technique using urea as a fuel. The synthesized nanoparticles are characterized by different instruments such as powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR) and diffuse reflectance spectroscopy (DRS). From the XRD analysis, the synthesized compounds were found to be occupying cubic crystal system. A decrease in band gap was observed with the substitution of Zn and Fe in $MgCo_2O_4$ from the UV-DRS technique. The prepared nanoparticles were investigated for the thermoelectric and photo-catalytic applications. The thermoelectric properties were measured by electrical conductivity, seebeck coefficient and thermal conductivity. The photo-degradation of Rhodamine B using synthesized nanoparticles under sunlight and UV-light irradiation were also studied. The degradation of Rhodamine B was observed within 100 mins for the parent compound and the rate constant was calculated to be $k = 4.3 \times 10^{-2}\ min^{-1}$.

Dihydrogen Binding Affinity of Anions of Different Sizes and Shapes: A DFT Approach

Della Therese Davis and Cherumuttathu H. Suresh*
Chemical Sciences and Technology Division,
Academy of Scientific & Innovative Research,
CSIR-National Institute for Interdisciplinary Science and Technology,
Thiruvananthapuram 695 019, India
E-mail: dellatherese@gmail.com

Dihydrogen binding affinity of several anionic systems such as monoatomic and polyatomic anions, anionic polyynes, bowl-shaped sumanene anion and anion encapsulated endohedral C_{60} has been studied using *ab initio* CCSD(T)//CCSD and density functional theory and *ab initio* methods. For monoatomic and polyatomic anions, the H_2 coordination number of these anions varies from 12 – 20 which corresponds to good interaction energy (E_{int}) and interaction energy per H_2 ($E_{int/H2}$). The highest coordinated dihydrogen complexes of these anions show substantially good values of interaction energy per H_2 $E_{int/H2}$ in the range 4.2 – 1.6 kcal/mol. A high weight percent of H_2 (25 – 56 wt%) is noted for these anion-H_2 complexes. Similarly, anionic and dianionic polyynes display massive dihydrogen uptake capability of 45 to 63 wt%. Anionic sumanene and anion encapsulated endohedral C_{60} exhibited the uptake of 40 – 50 H_2 molecules with $E_{int/H2}$ in the range 1 – 2 kcal/mol. A 'bowl effect' is observed in neutral, anion and dianion forms of sumanene which enhanced their H_2 binding affinity compared to planar aromatic molecules. The ion-pair complexes of anionic, dianionic and trianionic sumanenes with K^+ also show a noteworthy H_2 binding ability. Anion encapsulation in C_{60} leads to substantial increase in electron density over the outer surface of the carbon cage which promotes the interaction of the system with a large number of H_2 molecules. The stability of various dihydrogen complexes of anions can be attributed to the formation of large number of non-covalent bonds as revealed by the identification of bond critical points in the quantum theory of atoms in molecules (QTAIM) analysis. Further, electronic parameters derived from molecular electrostatic potential (MESP) are used to correlate the stability of these complexes and their charge delocalization. These studies establish that anions have a

remarkable ability to bind with a large number of dihydrogen molecules and this property can be utilized for the development of novel salt systems for hydrogen storage.

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Fluorescence sensor for the Selective Determination of Norepinephrine

E.V. Anuja*, **K. Girish Kumar**

Department of Chemistry, Sacred Heart College, Chalakudy680307, India

Department of Applied Chemistry, Cochin University of Science and Technology, Cochin 682022, India

E-mail: evanuja@gmail.com, giri@cusat.ac.in

Abstract

Bovine serum albumin stabilized gold nanoclusters (AuNCs) were used as the luminescent probe for the selective determination of norepinephrine (NE). The aqueous solution of the protein stabilized AuNCs was deep brown in color under visible light and exhibited bright-red fluorescence under UV irradiation. Upon addition of NE, the fluorescence emission intensity of AuNCs increased remarkably, which can be attributed to the restricted intramolecular rotation resulting from the aggregation of AuNCs. Under optimum conditions, the relative fluorescence intensity, I/I_0 showed a linear relationship with the concentration of NE in the range 4.76×10^{-7} M to 4.98×10^{-8} M, and the limit of detection was found to be 8.55×10^{-9} M. The developed method was applied for the quantification of NE in urine sample.

Keywords:* *Gold nanoclusters, norepinephrine, fluorescent probe, bovine serum albumin, intramolecular rotation

Introduction

Norepinephrine (NE) otherwise known as noradrinaline, is one of the most important catecholamine neurotransmitter in the mammalian central nervous system. Many automatic functions of the body, such as heart rate and blood pressure are controlled by the sympathetic nervous system.[1]The low level of NE is related with mental depression, DNA breakagein cardiac myoblast cells, heart failure, and diabetes. Recent studies revealed that abnormal level ofNE enhances adhesion of human immune deficiency virus-1 (HIV-1)-infected leukocytes to cardiac microvascular endothelial cells and also accelerates HIV replication viaproteinkinase.[2]Hence the development of a sensitive and convenient method for quantitative determination of NE in biological fluids is of great significance in clinical medicine.

Fluorescence has proved to be a powerful optical technique for the quantification of low level of analytes, owing to its simplicity and excellent selectivity. Recent advances in nanotechnology have given rise to a new class of fluorescent materials namelygold nanoclusters (AuNCs), which consist of several to hundred atoms and exhibit molecule like properties.[3]They exhibit remarkable properties including the discrete electronic states and size-dependent fluorescence.[4]

AuNCs based fluorescence sensor has been designed for monitoring of NE in body fluids, since it can be used as a powerful indicator for an early warning sign of certain diseases. Fluorescent AuNCs were synthesized using bovine serum albumin (BSA) as reducing and capping agent [5] and employed as a novel platform for simple and sensitive determination of NE. The fluorescence intensity of AuNCs increased with increasing concentration of NE and thelimit of detection was found to be 8.55×10^{-9} M. Application study of the developed sensor has been carried out in urine sample.

Experimental

Synthesis of BSA stabilized AuNCs

BSA protected AuNCs (AuNCs@BSA)were synthesized by the method described by Chen *et al.*[5]with minor modification.

Analytical procedure

AuNCs@BSA solution was mixed with phosphate buffer solution of pH 7 in the volume ratio 1:4. Appropriate amount of NE solution was added to 2 mL of the above solution, and the fluorescence emission spectrum was recorded. The luminescence intensity of AuNCs@BSA before and after the addition of NE was assigned as I_0 and I respectively.

Results and discussion

The synthesized BSA protected AuNCs were characterized by UV-Vis spectroscopy, fluorescence spectroscopy, FTIR spectroscopy and TEM. Upon excitation at 400 nm, the photoluminescence spectrum of AuNCs@BSAshowed an emission maximum at 653 nm.

The fluorescence intensity of AuNCs were strongly enhanced upon the addition of NE (Figure 1), and the enhancement of fluorescence intensity at 653 nm was proportional to the concentration of NE. Effect of buffer solutions, pH and time on the fluorescence intensity of AuNCs by NE was also studied. A good linear relationship between I/I_0 and concentration of NE was obtained over the range of 4.76×10^{-7}M to 4.98×10^{-8} M, with a detectionlimit of 8.55×10^{-9}M.

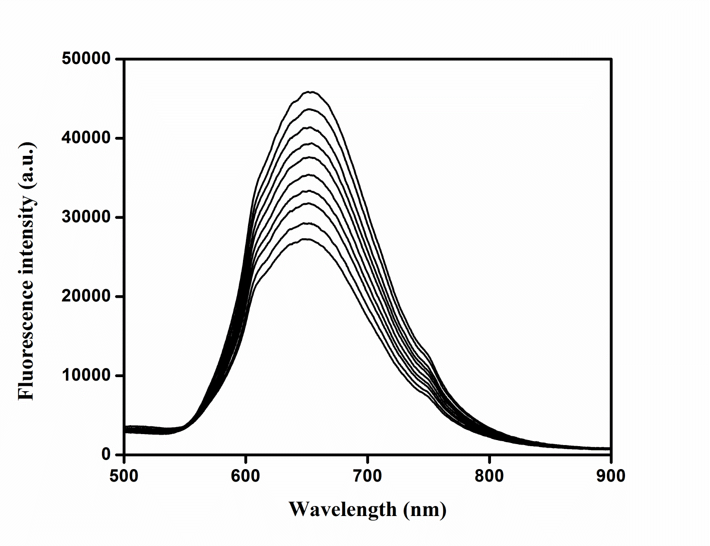

Figure 1 Fluorescence spectra of AuNCs in the presence of various concentrations of NE

In order to study the selectivity of the protein stabilized fluorescent probe towards NE, the emission intensity of AuNCs@BSA was measured in the presence of 4.76×10^{-7} Mconcentration of biologically important substances such as NE, epinephrine, creatinine, 3,4-dihyroxy phenylalanine, uric acid and ascorbic acid. Only NE induced a dramatic increase in the fluorescence intensity of AuNCs, whereas no obvious fluorescence changes were observed in the presence of other species. The practical application of the developed assay for the analysis of NE was tested by spiking the urine sample with a known amount of standard NE solutions and determining its recovery.

Conclusions

A simple of fluorescent platform was developed for the sensing of NE based on the fluorescence enhancement of BSA templated AuNCs.The AuNCs based sensing system exhibited a very low limit of detection as low as 8.55× 10^{-9}M. The developed turn on fluorescence sensor is simple, sensitive and was applied for the real sample analysis with satisfactory results.

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Multicomponent Synthesis of N-Substituted *Β*-Amino Carbonyl Scaffolds Using Nickel Sulphate as Catalyst

S. Arun[1], V.S. Shinu[2]
[1]Assistant Professor, Department of Chemistry, Christ College, Irinjalakuda
[2]Assistant Professor, Department of Chemistry, St.Joseph College, Devagiri
E-mail: arunkalazans@gmail.com, shinuvscalicut@gmail.com

Abstract

We report an efficient, mild and rapid approach for the synthesis of β-amino carbonyl scaffolds via three component coupling of aromatic aldehydes, enolizable ketones and nitriles in presence of acetyl chloride by using nickel sulphate as a new and highly effective catalyst under solvent free conditions. Our continuing interest in developing this methodology as a novel route to access highly functionalized structural scaffolds in a cost-effective, environmentally friendly and more importantly, a process requires less operational skill and conditions.

Key word: Multicomponent synthesis, Amido carbonyl compounds, Structural scaffolds.

Introduction

The traditional chemical industry was a hazardous and polluting one. It generated stoichiometric amounts of waste, causing much pollution of both air and water. Today, the escalating costs of petrochemicals and increasing energy and raw material consumption forcing a change. As a consequence, the industry demands from chemists the development of new reaction methodologies to obtain novel compounds in a fast, clean and efficient way. In this scenario, multicomponent reactions (MCRs) offer an alternative to the traditional synthesis mainly because it is based on available starting materials, operationally simple, easily automatable, resource effective, atom economical and ecologically benign. Mannich-Type products, specifically β-amino carbonyl compounds are useful chiral building blocks for the synthesis of β-amino acids, β-lactams, β-amino alcohols, and so forth. These class of compounds are generally synthesized by chiral Lewis acids assisted catalytic asymmetric reactions of imines derived from aldehydes and amines with enolate compounds.

Several efficient Lewis acids have been reported over the years and a recent attraction in this field is the development of the concept of bifunctional catalysis, wherein both partners of a bimolecular reaction are simultaneously activated, is very powerful for developing efficient asymmetric catalysts. Even though these chiral Lewis acids have proven to be efficient for many reactions, a major drawback is that most Lewis acids are unstable in presence of water and some of them are even moisture sensitive and also based on multi-step programme demands high synthetic skill. As an efficient alternative to the synthesis of Mannich-Type products, we and other groups have developed a one pot multicomponent protocol based on the coupling between an aldehyde, an enolizable ketone, and a nitrile molecule in the presence of an acid chloride and an acid catalyst. Several efficient catalysts have been reported by various research groups which includes $SnCl_4/SiO_2$, $Cu(OTf)_2$ and $Sc(OTf)_3$, $Mn(bpdo)_2Cl_2$/MCM-41, $CeCl_3 \cdot 7H_2O$, iron (III) chloride etc. Until recently, the scope of this three component process was limited to the synthesis of β-acetamido carbonyl compounds. Recent developments in this area, particularly from our laboratory, revealed that this process is highly useful for the one step synthesis of highly functionalized organic intermediates.

Our continuing interest in developing this methodology as a novel route to access highly functionalized structural scaffolds in a cost-effective, environmentally friendly and more importantly, a process requires less operational skill and conditions; we considered the possibility of performing this reaction in very mild conditions for the incorporation of a large variety of substrates. For this, we decided to follow this reaction in the presence of nickel sulfate.

Syntheses, Characterization and Second Order Nonlinear Optical Properties Of Dioxidomolybdenum(VI) Chelate of a Tridentate Aroylhydrazone

J. Bibitha[a], **M.R.P. Kurup**[b]
[a]*St. Joseph's college, Irinjalakuda*
[b]*Central University of Kerala, Kasaragod Kerala.*
E-mail: bibithajosephbj@gmail.com

***Keywords**: Aroylhydrazones, ONO donor ligand, second harmonic generation studies*

Abstract

Aroylhydrazone, 4-benzyloxy-2-hydroxybenzaldehyde-4-nitrobenzoylhydrazone dimethylformamidemonosolvate (H_2L) has been synthesized from the condenzation of 4-benzyloxy-2-hydroxybenzaldehyde and 4-nitrobenzoic hydrazide. Reactions of the hydrazone, H_2L with $MoO_2(acac)_2$in 1:1 molar ratio afforded the corresponding transition metal chelate. The Mo(VI) chelate was characterized by elemental analysis, single crystal XRD, molar conductance measurement, UV-Vis and IR spectra. The physico-chemical studies show that the complex is nonelectrolyte. In the complex, hydrazone coordinates in the dianioniciminolate form. The second harmonic generation studies indicate that the Mo(VI) chelate did not exhibit NLO property.

Introduction

Aroylhydrazones are a class of azomethines having the group –C=N–N– and are widely employed as ligands in coordination chemistry. These ligands are readily available, versatile and can exhibit various denticities and functionalities depending on the nature of the starting materials employed for their preparation[1-3].Among organic materials, hydrazones and their derivatives have recently attracted much attention due to their high tendency to crystallize in asymmetric structure and for their synthetic flexibility that can offer the modification of nonlinear properties. Nonlinear optical properties shown by some hydrazones and their metal complexes offer their use in optoelectronic devices [4].

Experimental

Materials

All the chemicals used in the present investigation were of the analytical reagent grade (AR). 4-Benzyloxy-2-hydroxybenzaldehyde(Sigma-Aldrich), 4-nitrobenzoic hydrazide (Sigma-Aldrich),and $MoO_2(acac)_2$(Sigma-Aldrich) were purchased and used as received. Solvent used were methanol and DMF.

Syntheses of [MoO_2LDMF]

Aroylhydrazone, H_2L is synthesized by refluxing 4-nitrobenzoic hydrazide (1 mmol) and 4-benzyloxy-2-hydroxybenzaldehyde (1 mmol) in DMF for 4 h. For the syntheses of [MoO_2LDMF], $MoO_2(acac)_2$ (1 mmol) in DMF was addedto a solution of H_2L (1 mmol) in DMF. The resultant solution was refluxed for 4 h. This was cooled and the orange colored crystalline complex formed was collected, washed with methanol followed by ether and dried over P_4O_{10}*in vacuo*. Orange block shaped crystals of [MoO_2LDMF] were obtained by recrystallization from DMF.

[MoO_2LDMF] : Yield: 67%, λ_m(DMF): 11 ohm^{-1} cm^2 mol^{-1}, Elemental Anal. Found (Calcd.) (%): C: 48.98 (48.82); H: 3.93 (3.76); N: 9.87 (9.49).

Results and Discussion

Molar conductivity and magnetic susceptibility measurements

The molar conductivity value for the complex is well below the range (65-90 ohm^{-1} cm^2 mol^{-1}) for uni-univalent electrolytes in the same solvent, indicating the non-electrolytic nature of the complex[5] . The magneticmoments of the complex is calculated from the magnetic susceptibility measurements at room temperature.Magnetic susceptibility measurements indicate the diamagnetic nature of these complexes and it is a clear evidence for the +6 oxidation state of molybdenum

Infrared and Electronic spectra

IR spectra give enough information regarding the coordination modes of the hydrazones. The aroylhydrazones show stretching bands attributed to ν(C=O), ν(C=N) and ν(N–H) at 1661, 1604 and 3186 cm^{-1} for H_2L. The bands due to ν(C=O) and ν(N–H) are absent in the complex, suggesting the occurrence of amido-iminoltautomerization followed by deprotonation of the ligands during complexation. The ν(C=N) absorption observed in the 1604 cm^{-1} region for the proligandis shifted to lower frequency in the complex indicating the coordination of azomethine nitrogen to the metal. The complex exhibit two bands in the903 and 940 cm^{-1} regions assigned to symmetric and asymmetric vibrations respectively of the *cis*-MoO_2 core[6]The electronic spectra of the hydrazone and complex showed bands in the region 28,970-36990 cm^{-1} due to n-π* and π-π* transitions. The complex show strong band at 23,340 cm^{-1}, assigned as charge transfer transition.

Crystal structure of [MoO_2LDMF]

A single crystal with approximate dimensions of 0.40 × 0.35 × 0.30 $mm^3$was mounted on a Bruker SMART APEXII CCD diffractometer equipped with a graphite crystal, incident-beam monochromator and a fine focus sealed tube with Mo Kα radiation (λ = 0.71073 Å) as the X-ray source. The unit cell dimensions were measured and the data collection was performed at 296 K.

The molecular structure of the complex with atom numbering scheme is shown in Fig. 1. The complex crystallizes into a triclinic space group $P\bar{1}$. The coordination geometry around molybdenum can be described as distorted octahedral with phenolate oxygen, imino nitrogen, iminolate oxygen and one oxo oxygen defining the equatorial plane and with DMF and the other oxo oxygen occupying axial positions. The hydrazone ligand is coordinated in its dianioniciminolate form which is evident from the C(15)–N(2) and C(15)–O(3) bond lengths with values of 1.292(4) and 1.316(3) Å respectively. In the complex, the dianionichydrazone ligand is bonded to the MoO_2 core in a planar fashion without changing its *E* configuration with respect to C(14)=N(1) bond. The atoms O(2), N(1), O(3) and O(6) in the complex define a plane with high degree of planarity and the Mo atom is displaced by 0.3264 Å from this plane. The tridentate hydrazone ligand coordinate to Mo atom in a meridional fashion forming five and six membered metallocycles involving the MoO_2^{2+} moiety. The coordination polyhedra present in a super cell is shown in Fig. 2 and the unit cell packing diagram of the complex viewed along *b*axis is shown in Fig. 3.

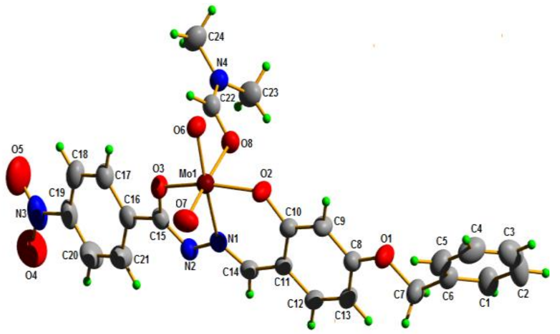

Fig. 1. The molecular structure of the complex with the atom numbering scheme. The solvent molecules are omitted for reasons of clarity.

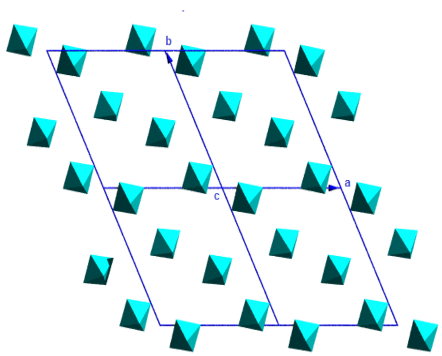

Fig. 2. Coordination polyhedra in a super cell.

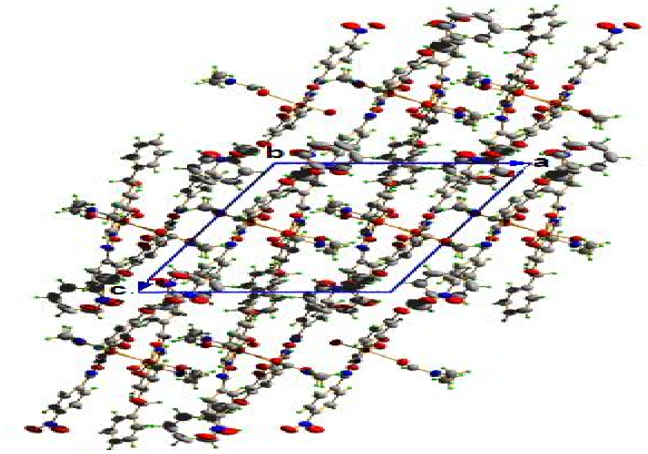

Fig. 3. Packing diagram of complex viewed along *b* axis

Second harmonic generation studies

The relative SHG efficiency of the Mo complex with respect to KDP was made by the Kurtz and Perry powder technique. The experimental arrangement for the nonlinear optical studies utilizes a Quanta-Ray DCR II Nd: YAG laser. The sample was illuminated by a laser beam of fundamental wavelength 1064 nm, with pulse width of 10 ns and repetition rate 10 Hz. The output from the sample was monochromated to collect the intensity of 532 nm components and the fundamental was eliminated. The second harmonic radiation generated by the randomly oriented sample was focused by a lens and detected by a photo multiplier tube. KDP was used as a reference material for the present measurements. The second harmonic generation studies indicate that the complex did not exhibit second order NLO property.

Conclusion

Preparation and characterization of Dioxidomolybdenum(VI) complex of4-benzyloxy-2-hydroxybenzaldehyde-4-nitrobenzoylhydrazone are reported. The MoO_2(VI) complex synthesized have got octahedral geometry and in the complex the hydrazone exist in the dideprotonated iminolate form. The second harmonic generation studies indicate that the Mo(VI) chelate did not exhibit NLO property.

Acknowledgment

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Synthesis, Characterization and Crystal Structure of a Copper(II) Bisazomethine Complex

Digna Varghese
PG and Research Department of Chemistry,
Christ College, Irinjalakuda, Thrissur-680125, Kerala
E-mail: dignavarghese@gmail.com

The binuclear bisazomethine copper(II) complex $[CuL]_2.11H_2O$ (where L is *N*,*N*′-bis(quinoxaline-2-carboxalidene)-1,2-diaminoethane) has been prepared and characterized by elemental analysis, conductivity measurements, IR, UV/Vis spectroscopy, TG−DTA and X-ray structure determination. The crystallographic study shows that the each copper(II) coordination sphere is distorted tetrahedral. The structure of the compound exhibits a novel three dimensional supramolecular network, formed by O−H…N intermolecular hydrogen bonding, π−π and CH…π stacking interaction.

Prussain Blue (PB)/ Multi Walled Carbon Nanotube (MWNT) Modified Glassy Carbon Electrode (GCE) Based Sensor

Laina A.L.[a], Krishnapillai Girish Kumar[b]
[a]Sacred Heart College, Chalakudy, [b]Department of Applied Chemistry, CUSAT, Kochi
E-mail: lainaal@gmail.com

Abstract

The electrochemical behavior of Hesperidin Methyl Chalcone (HMC) at a PB/ MWNT coated glassy carbon electrode was examined using various voltammetric methods. A systematic study of various experimental conditions was conducted by using differential pulse voltammetry (DPV). The number of electrons transferred was calculated by using cyclic voltammetric technique. Under the optimized conditions, the concentration of HMC showed excellent linear relationships with the reduction peak current, with a detection limit of 7.16×10^{-8} M.

Introduction

HMC supports and protects the integrity of the vascular system with particular activity in the capillaries and veins. HMC has been shown to help strengthen capillaries by increasing capillary resistance and decreasing capillary permeability. Increased venous motility, tone, and the ability of vessels to dilate are also enhanced by HMC. The methods available for the determination of HMC are thin layer chromatography [1] and high performance liquid chromatography [2]. As such these detection methods are limited in comparison to direct electroanalytical techniques by their expense, lack of portability, complex sample pre-treatment requirements and their inability to perform rapid in-field measurements. An attempt has been made to develop a convenient and sensitive method for the determination of HMC by DPV using PB/ MWNT modified GCE.

Prussain blue (PB), is an ancient coordination material and can be used as an electron transfer mediator. PB and its analogues are the prototype of a number of polynuclear transition-metal hexacyanometalates having an open, zeolite-like structure. Therefore, the study on a new method to fix chemically prepared PB without binders has great significance for expanding the application of the PB-modified electrode. The combination of PB and multiwalled carbon nanotubes (MWNTs) has received more attention [3-5]. CNTs are considered to be good mediators for PB-modified electrodes. Because of large specific surface area and good capability of electron transfer, MWNT opens a new door for electroanalytical chemistry field.

The PB/MWNT modified GCE was prepared by using drop drying method. At bare GCE, no voltammetric response was obtained. But on modification of GCE with PB/MWNT, a well defined and sensitive reduction peak was obtained at -972 mV for HMC. The developed sensor has also been successfully applied for the determination of HMC in pharmaceutical preparation and in urine sample.

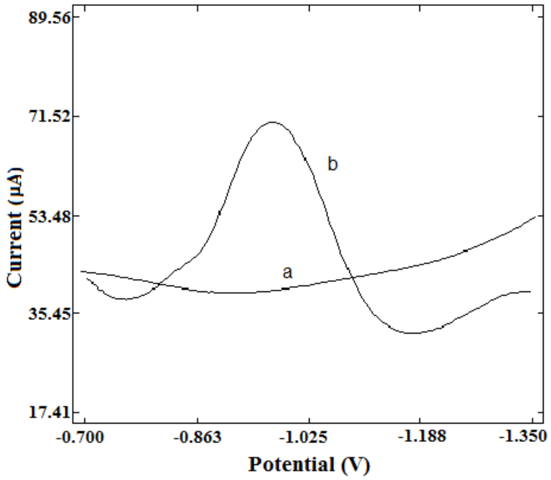

Figure 1: Differential pulse voltammmograms of 1x10^{-3} M HMC at (a) bare GCE (b) PB/MWNT modified GCE

Differential Pulse Voltammetry was applied to investigate the electrochemical behavior of HMC at the bare and modified GCE (Figure **1**). As can be seen, a well defined reduction peak at -972 mV with a peak current of 34.6532 µA appeared at PB/MWNT modified GCEs. These results undoubtedly proved the electrocatalytic activity of PB/MWNT modified GCE towards the oxidation of HMC.

The performance of the developed sensor depends on many analytical parameters including effect of supporting electrolyte and pH, effect of amount of the PB/MWNT dispersion, effect of scan rate, and interference of other materials. It was observed that the peak current is highest and the peak shape is well defined in acetate buffer of pH 2. Hence acetate buffer was chosen as the experimental medium for the voltammetric studies of HMC.

Electrochemical behaviors of HMC at different scan rates were also investigated on the surface of the PB/MWNT modified GCE by LSV and SWV (Figure **2**). A linear relationship was observed between the peak current and the scan rate in the range 20 to 280 mV/s in LSV and 20 to 220 mV/s in SWV, which revealed that the reduction of HMC was a diffusion controlled process.

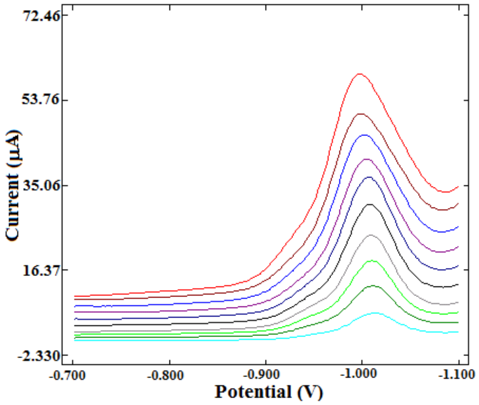

Figure 2: Overlay of Square Wave Voltammograms of 1x10^{-3} M HMC at PB/MWNT modified GCE in 0.1M acetate buffer at different scan rates (20 to 220 mV/s).

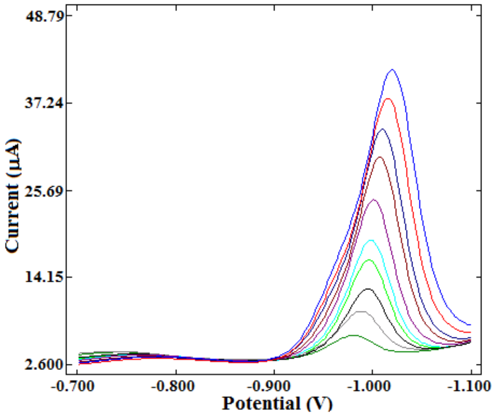

Figure 3: Differential pulse voltammograms of HMC at different concentrations, 10^{-3}- 10^{-7} M (top to bottom)

Dependence of peak current on the concentration of HMC was studied using DPV. Figure **3** shows DPV of HMC on PB/MWNT modified GCE at various concentrations (10^{-3} –

10^{-7}M). The results show that the cathodic peak current has a linear relationship with the concentration in the range 1.0×10^{-6}- 3.0×10^{-7} M.

Selectivity of the sensor was examined by studying the effects of foreign species on the determination of HMC. Up to 100-fold concentrations of urea, glucose, lactose, Na^+, K^+, Cl^- and SO_4^{2-} have no influences on 1×10^{-3} M HMC signals (deviation below 5%).

Conclusions

The electrochemical reduction behavior of HMC with acetate buffer on PB/MWNT modified GCE using CV, DPV, SWV and LSV is studied. Experimental data clearly confirms that HMC undergoes an irreversible diffusion controlled reduction process at the electrode surface. The PB/MWNT modified GCE showed electrocatalytic action for the reduction of HMC. Well-defined DP voltammograms are obtained in PB/MWNT modified GCE with high sensitivity and reproducibility.

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Corrosion Inhibition Investigations of 2-Pyridine Carbaldehyde 2-Aminophenol on Carbon Steel in 1M HCl

Sini Varghese C, Joby Thomas K*, Binsi M Paulson, Ragi K
Research Division, Department of Chemistry
St.Thomas' College (Autonomous) (University of Calicut) Thrissur, Kerala, India.
**Corresponding author: Associate Professor of Chemistry.*
Tel. /E-mail: +919847177695, drjobythomask@gmail.com

Introduction

Studies on carbon steel corrosion have become much important particularly in industrial and academic field during the past decade. Enormous use of hydrochloric acid for acid pickling, de-scaling and cleaning process of mild steel surface are the major reasons for the corrosion problems in the world. Increasing efforts have been made to study the corrosion behaviour of metals and mechanism of inhibition. The use of corrosion inhibitors is one of the most effective methods to protect metal surfaces against corrosion; especially in acid media The adsorption properties of organic molecules are responsible for their corrosion inhibition efficiency. Molecules containing nitrogen, oxygen, sulphur atoms and multiple bonds facilitate adsorption on the metal surface. It is reported that the adsorption of the organic inhibitors mainly depends on some physicochemical properties of the molecule which is related to its functional groups, possible sterric effects and electronic density of donor atoms. The availability of sophisticated computational tools and electrochemical techniques provide a better understanding of corrosion inhibitors and their mechanisms. In the present course of investigation, a heterocyclic derivative 2-Pyridine carbaldehyde-2-aminophenol (2PC2AP) was synthesized and characterized using various analytical tools and physicochemical studies. The corrosion inhibition efficiencies of the 2PC2AP on carbon steel in 1.0M HCl solutions using gravimetric methods, adsorption studies, electrochemical impedance studies and Tafel polarisation studies.

Experimental

Synthesis of the Schiff base

The heterocyclic compound 2PC2AP was synthesized by the condensation of equimolar mixture of 2-Pyridine carbaldehyde and 2-aminophenol in ethanol medium. The reaction mixture was refluxed for 4 hours, concentrated and cooled. The precipitated ligand was filtered, washed with ethanol water dried.

The aggressive solution of 1.0M HCl was prepared by the dilution of A.R grade (Merck) 37% of HCl with de-ionized water. Inhibitor solutions were prepared in the range 0.2mM-1mM concentrations.

Gravimetric studies on corrosion inhibition

The weight loss experiments were carried out under total immersion conditions in test solution maintained at 300K. Carbon steel specimens of 1.5x 2x 0.1 cm dimension were cut and abraded with various grades of silicon carbide papers (200, 400, 600, 800, 1000, 1200 and 2000). The exact area and thickness of each coupon were measured and washed. Specimens were then degreased with acetone and finally dried. After weighing, specimens were separately immersed in 50ml of 1.0M HCl solution in the absence and presence of the compound 2PC2AP. Weight loss of metal specimens was noted at every 24 h time interval. The experiments were carried out in duplicate and the average values were reported. The corrosion rate (ν) was calculated by the following equation

$$\nu = \frac{W}{St}$$

where W is the average weight loss of coupon, S is the total area of specimen, t is the time of treatment. The percentage of inhibition efficiency (η) can be calculated by the following equation

$$\eta_w \% = \frac{\nu_0 - \nu}{\nu_0} X100$$

where ν_0 and ν are the corrosion rates of uninhibited and inhibited specimens respectively.

Tafel polarisation studies

Polarization studies were conducted in the electrode potential range from -250 to +250mV Vs corrosion potential (E_{corr}) at a sweep rate of 1mV/sec. To obtain corrosion current densities, Tafel polarization analyses were done by extrapolating anodic and cathodic curves. The percentages of inhibition efficiency of molecules from polarisation measurements were calculated using corrosion current densities (I_{cor}).

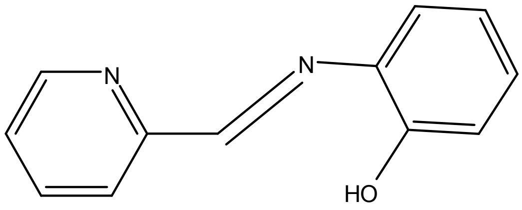
Results and Discussions

Characterization of the Schiff base

In the ^{1}H NMR spectrum of the imine a broad signal at 9.96δ was assigned to the OH proton. A weak signal was observed at 8.74 δ due to the presence of azomethine proton. The other aromatic protons exhibited their characteristic signals between 6.37-7.51 δ as multiplet._The $^{13}C_{nmr}$ spectrum of 2PC2AP gave characteristic signals for 12 different carbon atoms in different chemical environment. The azomethine carbon showed a peak at 136.84 δ. All the other 11 aromatic carbon atoms of pyridine ring and benzenoid ring showed different peaks between 114.33 -150.18 δ.

In the mass spectrum of 2PC2AP, the molecular ion peak appeared at m/z 198. The [M-1], [M-2] peak observed due to the loss of hydrogen atoms from the molecule. A peak was observed at m/z 183 due to the loss of oxygen atom from the molecule and formed the fragment $[C_{12}H_{11}N_2]^+$. The base peak appeared at m/z 120 for the fragment $[C_7H_6NO]^+$ due to the loss of pyridine ring. The peaks appeared at m/z 105 and 93 can be assigned to $[C_6H_5N_2]^+$ and $[C_6H_5O]^+$ respectively. The other peaks observed at m/z 79, 65 and 52 due to the formation of fragments $[C_5H_5N]^+$, $[C_5H_5]^+$ and $[C_4H_4]^+$ respectively.

The assignment of signals of 2PC2AP is provided in table 1.3. In the IR spectrum of 2PC2AP a broad peak of O-H observed at frequency of 3385cm^{-1} .The signals at 3061 cm^{-1} and 3008 cm^{-1} appeared due to the presence of stretching frequencies of aromatic and olefinic C-H respectively. A characteristic peak of azomethine was exhibited at 1590 cm $^{-1}$. The C-O stretching frequency was observed at 1387 cm$^{-1.}$ In the IR spectrum of 2PC2AP, two in plane deformation at 1102cm^{-1} and 1022cm^{-1} and one out of plane deformation at 747cm^{-1} was observed. In the uv – visible spectrum of 2PC2AP $\pi \rightarrow \pi^*$ signal observed at 38910cm^{-1} and $n \rightarrow \pi^*$ signal was at 28985cm^{-1}. Two significant electronic transitions were obtained. The spectral studies listed above and the CHNS data (C,71.84; H,4.49; N,13.55; %) suggest the following structure for the Schiff base 2PC2AP (Fig. 1).



(*E*)-2-(pyridin-2-ylmethyleneamino)phenol

Figure 1: Structure of 2PC2AP

Weight loss measurements

Weight loss studies were conducted to find out the variation of corrosion rate and inhibition efficiency with immersion time for a period of five days in the presence and absence of 2PC2AP. The rates of corrosion of the CS specimens decrease with increase in concentration of the 2PC2AP while the percentage of inhibition is markedly increased with increase in concentration which can be attributed to the increased adsorption of the 2PC2AP molecules on the metal surface. The increased surface coverage may partially hinder the reaction between metal and H^+ ions which in turn increase the percentage of inhibition. The inhibition efficiency showed a saturation value 85.16% at the inhibitor concentration 1.0mM in 1.0M HCl.

Adsorption isotherm and free energy of adsorption

Basic information on the interaction between inhibitors and metal surface can be provided using the adsorption isotherms. Different models of adsorption isotherms considered are Langmiur, Temkin, Frumkin, El-Awady, Flory-Huggin and Freundlich isotherms. For the evaluation of thermodynamic parameters it is necessary to determine the best fit isotherm with the aid of correlation coefficient (R^2). Among the isotherms mentioned above, the best description of the adsorption behaviour of 2PC2AP on CS specimens in 1M HCl is Langmuir adsorption isotherm which can be expressed as

Langmuir adsorption isotherm $\frac{C}{\theta} = \frac{1}{K_{ads}} + C$

where C is the concentration of the inhibitor, θ is the fractional surface coverage and K_{ads} is the adsorption equilibrium constant. The adsorption equilibrium constant K_{ads} is related to the standard free energy of adsorption $\Delta G^0_{ads,}$ by

$$\Delta G^0_{ads} = -RT\ln (55.5\ K_{ads})$$

where 55.5 is the molar concentration of water, R is the universal gas constant and T is the temperature in Kelvin [17]. The negative value of free energy of adsorption indicates the spontaneity of the process. In the present investigation 2PC2AP molecules showed ΔG^0_{ads}values as -34.23kJ/mol suggesting that the adsorption involves both physisorption and chemisorption [18].

Tafel polarisation

On examination of the Tafel plots and polarisation parameters of 2PC2AP it may be concluded that the corrosion potentials of carbon steel at various concentrations of 2PC2AP changes to cathodic and anodic directions and the inhibitive activity of this compound can be regarded as a mixed type i.e., 2PC2AP affect both cathodic and anodic process of corrosion more or less uniformly. Also the cathodic and anodic slopes of the Tafel curve changes in each scans, which can be taken as an additional supporting evidence for the above argument. Since the anodic and cathodic slopes of the Tafel lines changes from the blank, this molecule can also be regarded as the mixed type inhibitor. The corrosion inhibition efficiencies of 2PC2AP on the carbon steel metal surface were increases with increase in concentration. These results are in good agreement with the results obtained by weight loss analysis.

Conclusions

The corrosion inhibition efficiencies of the Schiff base 2PC2AP were studied in 1.0M HCl. The inhibitor exhibited higher inhibitive efficiency for carbon steel in 1M hydrochloric acid. The corrosion inhibition property of the imine increases with increase in concentration. It is believed that in HCl medium, the Cl^- ions are specifically adsorbed on the metal surface and creates an excess of negative charge on the surface which will favour the adsorption of protonated heterocyclic compound on the surface and hence reduce the dissolution of Fe to Fe^{2+}. Besides this electrostatic interaction between the protonated 2PC2AP and the metal surface, interactions of unshared electron pairs in the molecule with the metal or the interaction of π-electrons with the metal or a combination of the two are possible [19]. The π-electron cloud of the aromatic rings and the azomethine linkage also participate in the inhibition mechanism. Furthermore, the double bonds in the inhibitor molecule permit the back donation of metal d electrons to the π* orbital. Free energy calculations revealed that 2PC2AP molecules are adsorbed on the metal surface through both physisorption and chemisorption in HCl. The Schiff base obeys Langmuir isotherm in HCl. The Tafel polarisation studies also revealved that 2PC2AP act as mixed type inhibitor. From the above observations it is concluded that the inhibitor 2PC2AP exhibits a better corrosion inhibition performance in HCl medium.

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A Novel Method to Remove Fe^{3+} from Fresh Water using Ammonium Phosphomolybdate - Polyaniline Composite

Jisha Joseph and Jency Thomas*
Research & PG Department of Chemistry,
St. Thomas' College (Autonomous), Thrissur, Kerala
E-mail: jencythomas@stthomas.ac.in

Our fresh water sources are getting polluted day by day by quick-thriving industries. Unfortunately, presence of metal ions in fresh water samples lead to health issues as well as environmental problems. The removal of metal ions from solution can be done by chelation, ion exchange, adsorption, electrostatic attraction etc. In this context, composites of polyaniline have been employed for removal of heavy metal ions from solutions. Polyaniline/Palygorskite composite has been used for the removal of Cu(II), Ni(II), Cd(II) and Cr(IV) through adsorption [1]. Composite based on eucalyptus leaf and polyaniline was used for the adsorption of Pb^{2+} from aqueous solution. [2]. On the other hand, ammonium phosphomolybdate (APM) is inorganic salt of phosphomolybdic acid with remarkable porosity [3]. Therefore, in this present work, an attempt was made to synthesize and characterize composites of APM with polyaniline. Further the role of as-synthesized composites in the removal of Fe^{3+} from fresh water has been investigated and promising results were obtained.

Keywords: Ammonium phosphomolybdate, polyaniline, composite.

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Physico-Chemical Characteristics of Ground Water Samples from Different Areas of Thrissur District, Kerala State, India

Mity Thambi[1], Tom Cherian[2*], Anju Therese Jose[3], Sunaina Jamal[4]
[1]Department of Post Graduate Studies and Research in Chemistry, Baselius College, Kottayam.
[2,3,4] Department of Post Graduate Studies and Research in Chemistry, Christ College, Irinjalakuda, Thrissur-680 125, Kerala
E-mail: drtomcherian@gmail.com

The analysis of groundwater quality of important town areas of Thrissur district was carried out during the pre-monsoon period of 2014. The Physicochemical and biological parameters such as temperature, turbidity, electrical conductivity, total dissolved solid, pH, alkalinity, chloride, salinity, total harness, calcium, magnesium, iron, phosphate, sulphate, dissolved oxygen, biological oxygen demand, chemical oxygen demand, total coliform count and E. coli were determined. Most of the physicochemical parameters were observed above the desirable limit but below the permissible limit of drinking water standards of World Health Organization (WHO). Total coliform bacteria count values of different samples are within the permissible limit. The studies reveal that samples from Thrissur town (T), Guruvayoor (G) and Laloor (L) shows the presence of *E.coli* bacteria. All other samples were negative for *E.coli* bacteria. Dumping of wastes near road sides, flood due to heavy rains, improper waste management in hospitals, markets, flats etc increases the pollution of ground water. The results were compared with WHO guidelines, 2006 and Bureau of Indian Standards (IS: 10500, 1991) desirable limits for drinking water.

Key words: Physico-chemical characteristics, water quality parameters, ground water sample.

Synthesis, Characterisation and Antimicrobial Studies of Transition Metal Complexes of Schiff Base Ligand

Aby paul[1], Joby Thomas K[1,*], Vidhya Thomas K[1], Vinod P. Raphael[1],
Research Division, Department of Chemistry
[1]St. Thomas' College (Autonomous), Thrissur, Kerala
E-mail: drjobythomask@gmail.com

Introduction

Coordination compounds, especially Schiff base complexes, possess significant inhibitory activity towards the growth of different types of microbes.In the present work, the antimicrobial activity of the newly synthesized Schiff base ligand 3-formylindole-2-amino-5-nitrobenzoic acid (3FI2A5NBA) was screened on six different bacterial strains, such as *S. aureus, B. subtilis, B. thuringiensis, E. aerogenes, E. coli* and *P. vulgaris*. Transition metal complexes of these ligands prepared were also subjected to antibacterial studies on the same series of bacterial lines. For the comparison of the activity of the newly prepared compounds with the effect of standard antibiotics on the same types of bacteria, Erythromycin, Streptomycin, Gentamicin, Ampicillin and Pencillin-G were used.

Experimental

2-amino-5-nitrobenzoic acid (0.36g, 2 mM) was dissolved in hot ethanol and mixed with 3-formylindole (0.3g, 2 mM) in ethanol. The solution was refluxed for about 4h in a water bath. The resulting homogeneous mixture was concentrated, cooled in ice bath and kept overnight. The precipitate formed was filtered using a vacuum pump and washed with ethanol and dried over anhydrous $CaCl_2$. The melting point of Schiff base was found to be 220^0C.VO(II), Cr(III), Mn(II), Fe(III), Ni(II), Cu(II) and Zn(II) complexes of 3-formylindole-2-amino-5-nitrobenzoicacid(3FI2A5NBA) were prepared by mixing ethanolic solutions of metal acetate (2 mM), 2-amino-5-nitrobenzoicacid (2 mM) and 3-formylindole(2mM). The characterisation of ligand and its metal complexes were done by using different spectroscopic techniques like IR, UV, NMR, mass etc.

Antibacterial activity of the transition metal complexes and ligand was determined by the micro dilution method and Paper Disc Diffusion Method. Few drops (5-6drops) of sterilized water was taken in a test tube and with the help of inoculation loop, test organisms were taken off from the slant culture and diluted in the test tube. Using a sterile swab, the activated bacterial strains were spread over the entire surface of the Nutrient Agar plates in a uniform manner. Swab was Swab was used to obtain a continuous layer of microbe on the culture medium. This was then allowed to dry for 15-20 minutes. The paper discs which contained the samples were placed on agar plates using sterile forceps. The plates were incubated at 37^0C for 24 hours. The zone of inhibition was then measured around the disc using verniercaliper.

For antifungal screening, about 20ml of sterilized potato dextrose agar medium was poured into sterile petridishes and allowed to set. The culture of *Aspergillusniger* was spread on the medium using cotton swab method. Drug inoculation at four different concentrations (100, 200 and 500μgdisc^{-1}) was made in the discs. Also paper disc containing the solvent DMSO was tested. Ligand, complexes and standard antifungals were screened for their growth inhibition activity. Then the petridishes were incubated for one week in an incubator at 37^0C. Then the petridishes were taken and analysed for the fungal growth inhibition by measuring the diameter of inhibition zone.

Results and Discussions

The characterisation of newly synthesised ligand and its metal complexes was done by different analytical tools. The IR spectral data of the ligand 3FI2A5NBA contain a significant absorption frequency at 1629cm^{-1} and it can be attributed due to the stretching frequency of C=N group. The asymmetric and symmetric stretching frequencies of the carboxylate groups exhibited respectively at 1680cm^{-1} and 1494cm^{-1} . The ^{1}H NMR spectrum of the ligand showed a singlet at δ 9.63 due to the azomethine proton. Another singlet peak displayed by the Schiff base ligand in it'spmr spectrum at highly deshielded region (δ 12.15) can be assigned to the carboxylic acid proton. The ^{13}C NMR spectrum of the ligand possesses sixteen distinct peaks for sixteen carbon atoms at different chemical environments. Due to the presence of highly electron withdrawing oxygen atoms on the carboxylic group and also due to the π-electron anisotropic effect, this carbon exhibited a peak at 185ppm. The carbon atom of the azomethine moiety resonated at 128.69ppm. The molecular ion peak was absent in the mass spectrum, which shows that the molecular radical cation is quite unstable. A base peak observed at m/z 144 is due to the fragment

$[C_9H_7N_2]^+$. A significant peak at m/z 116 can be assigned to the indole moiety $[C_7H_6N]^+$ originated from the ligand. The electronic spectrum of the Schiff base 3FI2A5NBA showed three specific bands around 26700, 33600 and 40816cm^{-1}, characteristic of $n\rightarrow\pi^*$, $\pi\rightarrow\pi^*$ and $n\rightarrow\sigma^*$ transitions respectively.

Elemental analysis revealed that the complexes of Cr(III), Mn(II), Fe(III), Ni(II) and Cu(II) have 1:1 stoichiometry between the metal and the ligand while oxovanadium and zinc complexes possess 1:2 metal-ligand ratio. The magnetic moment of Cu(II) complex was seen at 1.26BM, corresponding to one unpaired electron. This value falls in the range observed for distorted octahedral geometry. Due to strong antiferromagnetic interaction of electrons, μ_{eff} value of Fe(III) complex exhibited lower magnetic moment (4.2BM) than the calculated value as per spin only formula. This supports a dimeric octahedral structure to Fe(III) complex. The effective magnetic moment of Cr(III) was 3.44BM, which is a clear evidence for octahedral geometry around the central metal ion. Ni(II) complex exhibited a μ_{eff} of 3.5BM, which is slightly higher than the expected magnetic moment calculated as per the number of unpaired electrons (d^8 configuration). This may be due to the slight orbital contribution and hence assigned an octahedral geometry to this complex. The oxovanadium complex showed anμ_{eff} value of 1.42BM and assumes a square pyramidal geometry. As expected Zn(II) complex behaved as a diamagnetic substance due the absence of unpaired electrons.

The symmetric and asymmetric stretching frequencies are well below the frequencies observed for the free Schiff base, γ_{COO}(asym) 1680cm^{-1} and γ_{COO}(sym) 1494cm^{-1}, indicating that the carboxylate part of the ligand is one of the coordination sites of the Schiff base. A significant shift to lower frequencies was observed for the bands of the azomethine part of the Schiff base in metal chelates which is a strong indicaton of the participation of the C=N part of the ligand. On close examination and comparison of the ^{1}H NMR spectrum of the ligand and chelates it was understood that the signal corresponds for the carboxylic acid proton (δ 12.15) was absent in all complexes, suggesting one of the coordination sites of the ligand is carboxylate moiety. Moreover the peak due to the imine hydrogen in the complexes showed downfield shift from δ 9.63 which is a clear evidence for the linkage of the Schiff base through azomethine group to the metal ion.From this spectroscopic analysis, we can plot the structure of newly synthesised ligand and its metal complexes.

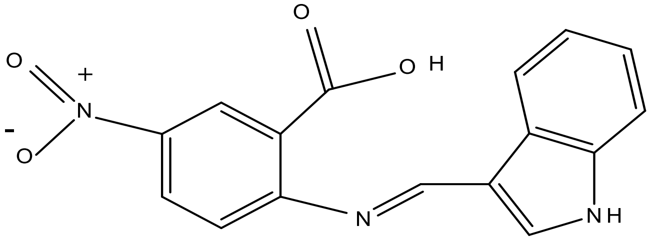

Fig 1: Structure of the Schiff base 3FI2A5NBA

The Schiff base, 3FI2A5NBA, and its transition metal complexes were screened for their antibacterial activity. It is evident from the results that the metal chelates show increased antibacterial activity than the corresponding Schiff base. Among the transition metal chelates of 3FI2A5NBA, Zn(II) and Ni(II) complex showed appreciable inhibition against all bacterial strains. At a concentration of 500µgdisc^{-1}, the nickel complex exhibited the diameter of inhibition zone 18mm, 22mm, 25mm and 23mm towards the growth of *S. aureus, B. subtilis, B. thurenginsis*and *P. vulgaris* respectively. Cu(II) complexalso exhibited much higher inhibition than the corresponding ligand. Generally poor inhibition was noted for Cr(III), Mn(II) and Cd(II) complexes. These complexes were totally inactive to the growth of *E. coli.*

From the antifungal studies it was concluded that Schiff base and its transition metal chelates were quite inactive against the growth of the fungus *A. niger* at all concentrations.

Fig 2: Antibacterial activity ofthe ligand 3FI2A5NBAon *S. aureus* at different concentrations

Overall studies revealed that the growth inhibitory power of the compounds increases upon chelation. Antibacterial activity of standard antibiotics like Erythromycin, Streptomycin, Gentamicin, Ampicillin and Pencillin-G and standard antifungals like Fluconazole and Amphotericin-B were also screened for comparison. Of course the growth inhibition ability of the parent compounds and solvents towards the studied bacteria and fungus were also screened. Even at very low concentration (100μgdisc^{-1}) Cd(II) complex of 3FI2A5NBA was found to be very active (18mm) of against the bacterial growth of *B. subtilis.* Although the mechanism of action of these complexes upon the growth inhibition of various bacterial species is not well explained, it is assumed that the azomethine moiety in the present chelates has a vital role. Also compared to the organic species, the metal derivatives possess increased cell permeability. Since the complexes possess increased delocalization of π electrons and the π electron back bonding, the lipophilicity of the complexes are high, which makes them to penetrate into the bacterial cells through their lipid layers.

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