CHAPTER 8

CHEMISTRY

Doctoral Theses

084. AMBIKA
Isolation and Chemical Studies of Active Constituents From Selected Medicinal Plants.
Supervisor : Prof. S. M. S. Chauhan
Th 15633

Abstract

Picrorhiza kurron, an important demicinal plant used in traditonal and modern medicine, for liver disorder, fever, asthma and jaundice and is known to possess hepatoprotective, immunomodulatory, and antiasthamatic activities. The main iridoid glycoside reported from the methanol extract from the roots and rhizomes of P. kurroa is "kutkin", which is a mixture of picroside-I and picroside-II. Gentiana kurroo is a small perineal herb. The roots and rhizomes are used as a bitter tonic for improving appetite and to increase the gastric secretions to cure fever and urinary complaints. The isolation of active constituents from the roots and rhizomes of G. kurroo and structural characterization has been examined to find out the most active constituents from the above plant. The isolation of anthraquinone derivatives are carried out from Rubia cordifolia and Rheum emodi. Synthesis of selected covalenty linked isoalloxazines has been undertaken to understand the orientation and role of the two flavins in NADPH-Cytochrome P450 reductase. Brief surveys of naturally occuring bisflavins and their covalent modifications and their characterization have also been undertaken.

Contents

4. Quinones as antimalarials from medicinal plants and their interaction with haem. 5. A brief survey of naturally occurring bisflavins and their covalent modifications and their characterization. Summary and Publications.

085. ARORA (Reema)
Development of Synthetic Methodologies.
Supervisor : Prof. J. M. Khurana
Th 15789

Abstract

Reports some novel synthetic methods developed for (i) synthesis of 7,11-diary1-2-,4-diazapiro(5.5)undecne-1,5,9-triones: a new series of spiroheterocycles, (ii) microwave assisted solvent free oxidation of hydrobenzoins, benzoins and alcohols with N-bromosuccinimide-neutral alumina, (iii) chemoselective deprotection of benzyl esters with nickel boride, and (iv) oxidation of sulphides, selenides, tellurides, sulphoxides, selenoxides and telluroxides with MoO_5.Py.HMPA complex.

Contents

086. ARYA (Sunil Kumar)
Preparation, Characterization and Application of Some Monolayers to Cholesterol Biosensor.
Supervisors : Prof. Monika Datta and Dr. B. D. Malhotra
Th 15630

Abstract

It is an attempt towards the preparation, charaterization and application of some SAMs [11-amino-undecanethiol (AUT), N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (AEAPTS), dithiobis-(succinimidy1 propionate) (DTSP), octadecanethiol (ODT) and ply03-hexylthiophene) (P3Ht)] for the immobilization of enzymes [cholesterol oxidase (ChOx), cholesterol esterase (ChEt) and horseradish peroxidase (HRP)] for development of cholesterol biosensor.

Contents

1. Introduction. 2. Materials and experimental techniques. 3. Self-assembled monolayer based cholesterol biosensors for estimation of free cholesterol. 4. Self-assembled monolayer based cholesterol biosensors for estimation of total cholesterol. 5. Self-assembled monolayer based cholesterol biosensors for estimation of cholesterol using surface plasmon resonance technique. 6. Future prospects and summary.

087. BANSAL (Vikas)
Green Approaches for Compounds of Industrial Importance.
Supervisor : Prof. M. Kidwai
Th 15628

Abstract

Develops bioactive bis(4-hydroxycounmarin) using molecular iodine in water. Catalytic activity of molecular iodine is further evaluatd by the preparation of pharmacologically important 1, 3-diazepines derivatives. As water is a solvent of choice for many industries, thus biodynamic substituted imidazoles were prepared using $InC1_3$ in water. Prepared versatile biologically important quinolines using $InCl_3$ and microwave technology. Prepared industrially important 2-arybenzoxazole, alcohols by reduction, and propargylamines using metal nanoparticles. Methodology is a step ahead in the area of green chemistry for the preparation of industrially important compounds.

Contents

1. Introduction. 2. Molecular iodine : A highly efficient catalyst for the synthesis of Bis(4-Hydroxycoumarins) methanes in water. 3. Indium chloride catalyzed one-pot synthesis of 2,4, 5,-Trisubstituted and 1,2,4,5-Tetrasubstituted imidazole in water. 4. (a) One-pot regioselective green synthesis of novel quinolines using a neat reaction technology. (b) an environmentally benign indium (III) chloride catalysed one-pot synthesis of quinolines. 5. Molecular iodine : A highly efficient catalyst for the synthesis of 7-Arylbenzopyrono(1,3) diazepines in non-protic solvents. 6. (a) Ni-nanoparticles : An efficient green catalyst for chemoselective reduction of aldehydes. (b) Cu-nanoparticles : an efficient green catalyst for the oxidative cyclization of schiff' bases. 7. (a) the first au-nanoparticles catalyzed green synthesis of propargylamines Via three-component coupling reaction

of Aldehyde, Alkyne and Amine. (b). Cu-nanoparticles catalyzed A^3 coupling Via C-H activation. Summary.

088. BISHT (Gopal Singh)
Designing, Synthesis and Characterization of Antimicrobial Peptides and Study of their Biological Activity.
Supervisors : Dr. Diwan S. Rawat and Dr. Santosh Pasha
Th 15641

Abstract

Deals with designing and synthesis of peptide-based antibiotics. The general aim of this thesis is designing, synthesis characterization of antimicrobial peptides and study of their biological acitivity.

Contents

1. An overview of cationic antimicrobial peptides. 2. Designing, synthesis and characterization of synthetic cationic amphipathic antimicrobial peptides. 3. Designing, synthesis and characterization of synthetic hybrid peptides. 4. Designing, synthesis and characterization of short amino terminal modified tetra peptides. 5. Biological activity of cationic amphipathic peptides, hybrid peptides and modified short peptides. 6. Biophysical studies of antimicrobial peptides. Summary and Publications.

089. GAUTAM (Archana)
Spectral and Structural Studies on Transition Metal Complexes of Polydentate Ligands.
Supervisor : Dr. Sulekh Chandra
Th 15635

Abstract

Deals with the study of growth of corodination chemistry, historical background of macrocycles, macrocyclic design, their synthesis and synthesis and characterization of ligands. Describes antimicrobial screening of Mn(II), Co(II), Ni(II), Pd(II), Pt(IV) and Cu(II) complexes with tetraazamacrocyclic ligands viz. L_2, L_3, L_4 and L_5. the antifungal and antibacterial screening are carried out using Agar Plate and Disc Diffusion Method respectively. Five macrocyclic ligands : L_1, L_2, L_3, L_4 and L_5 are prepared by 2+2 condensation of precursor molecules.

Contents

1. Introduction, Synthesis and characterization of ligands. 2. Chromium (II), $3d^3$. 3. Manganese(II), $3d^5$. 4. Cobal(II), $3d^7$. 5. Nickel(II), $3d^8$, Palladium(II), $4d^8$ and platinum(IV), $5d^6$. 6. Copper(II), $3d^9$, 7. Biological screening. Summary.

090. GIRI (Nand Gopal)
Chemical Studies of Functional Porphyrins and Related Compounds.
Supervisor : Dr. S. M. S. Chauhan
Th 15640

Abstract

Porphyrins and realted tetrapyrrolic macrocycles are an important class of biologically relevant molecules that have found a broad spectrum of applications in various fields such of bacterial photosynthetic systems and important groups of enzymes such as cytochrome P, cytochrome C and oxygen carries (hemoglobin) etc. The biomedical applications of porphyrins include treatment of psoriasis and viruses, gene regulation therapy and drug targeting. Deals with catalysis and self-assembly (by hydrgen bonding and coordination); the two important fields of applications of porphyrins and metalloporphyrins chemistry.

Contents

1. The oxidation of polynuclear aromatic hyrocarbons with H_2O_2 catalyzed by 5,10,15,20-tetraaryliron(III)porphyrins in different reaction conditions. 2. Synthesis of functional zinc porphyrins and their applications in self-assembly by coordination. 3. Synthesis of iron(III)benzoporphyrins and their applications in the oxidation of chlorophenols in different reaction conditions. 4. Synthesis of selected functional porphyrins and their uses in hetero and homocomposite hydrogen bondings. 5. Synthesis of selected mono-2-hetero-21-carbaporphyrins, their aromatic character and metal bindings. Synopsis.

091. GUPTA (Meenakshi)
Study of Some Substituted Anilines as Corrosion Inhibitors for Mild Steel in Acidic Medium
Supervisor : Prof. Gurmeet Singh
Th 15627

Abstract

Desbribes the use of N-substituted anilines as corrosion inhibitors for mild steel in sulphuric acid. The compounds studied are N,N-Dimethylaniline (NNDMA), N,N-Diethylaniline (NNDEA), N,N-Dibutylailine (NNDBA), N-Benzyl N-Ethylaniline (NBNEA), N-Ethyl N-Hydroxy Ethylaniline (NENHEA) and N-Methyl Formanilide (NMF).

Contents

092. JOSHI (Penny)
Synthesis of Phidolopin and Cyanuric Acid Analogues as Bio-dynamic Agents.
Supervisor : Dr. Diwan S. Rawat
Th 15643

Abstract

Synthesizes substituted phidolopin analogues. Some of these compounds were screened against gram-positive and gram-negative bacteria, and have shown very weak activity. Designes theophylline or coumarin triazole conjugates using copper sulphate and sodium ascorbate as catalyst and t-BuOH/ H_2O as solvent via click chemistry approach. Some of these compounds are screened for anti microbial and anti malarial activity. Deals with the synthesis of triazine based macromol ecules, which contains trizines, triazoles, xanthine and coumarines. Some of these compounds have been screend for antimicrobial activity.

Contents

093. MANOJ PRASAD
Selective Recognition of DNA by Synthetic Ligands.
Supervisor : Dr. Shrikant Kukreti
Th 15632

Abstract

Attempts to invetigate the interactions between a series of small molecules with various DNA sequences in order to gain insight into how these DNA sequences can be effectively targeted in a sequence and structure-specific manner, and to provide the basis of design of new molecules which will bind with improved with DNA triplexes provide the basic idea to understand the effect of intracellular molecular crowding on DNA structures and their stabilities using in vitro conditions.

Contents

1. Introduction. 2. Experimental. 3. Biophysical and biochemical of deoxyoligonucleotides and ligands. 4. DNA-Ligand interactions. 5. Effect of synthetic polymers on DNA stability in solutions tion. 6. Conclusions. Bibliography.

094. MISHRA (Anurag)
Synthesis and Characterization of Novel Heterometallic Complexes Utilizing Coordination Complexes as the Building Block.
Supervisor : Dr. Rajeev Gupta
Th 15637

Abstract

Provides an alternate general procedure for the synthesis of the desired heterobimetallic complexes where a coordination complex has been used as the building block. Shows the utilization of simple pyridine - amide based ligands to selectively coordinate a central/primary metal ion and arranging the peripheral functional groups to generate a molecular cleft capable of binding a secondary metal ion(s) thus generating desired heterobimetallic complex. Also show the synthesis and characterization of $\{M_1^{n+}\text{-}M_2^{m+}\}$ and $\{M_2^{m+}\text{-}M_1^{n+}\text{-}M_2^{m+}\}$ heterobimetallic complexes, where M_1^{n+} and M_2^{m+} metal ions selectively take central and peripheral positions, respectively.

Contents

1. Overview of the corodination chemistry with pyridine amide

ligands. 2. Synthesis and characterization of cobalt(III) complexes with bidentate pyridine-amide ligands (HL^{1-3}). 3. Synthesis and characterization of cobal(III) complexes with tridentate pyridine-amide ligands (H_2L^{4-6}). 4. (a) Synthesis and characterization of $\{Co^{3+}\text{-}Zn^{2+}\}$ heterobimetallic complexes. (b) Applications $\{Co^{3+}\text{-}Zn^{2+}\}$ heterobimetallic complexes int he beckmann rearrangement reactions. 5. Synthesis and characterization of $\{Co^{3+}\text{-}Cd^{2+}\}$ and $\{Co^{3+}\text{-}Hg^{2+}\}$ heterobimetallic complexes. Future scope of the work and Summary.

095. MISHRA (Nidhi)

Synthesis and Characterisation of Biologically Active Chalcones and Flavonoids.

Supervisor : Dr. Satish K. Awasthi

Th 15631

Abstract

Deals with synthesis of several substituted flavone derivatives. Different flavonoids are able to act in each level of the cancer process. This work involves the synthesis of Oxygencontaining heterocyclic compounds. Seven aminoflavone derivatives have been synthesized and evaluated. The LPS induced SO production on rat peritoneal macrophages has been performed. Described the design strategy of chalcones with different substitution on A and B rings. The compounds were designed with an aim to show anti-malarial and anti-microbial profile. Around twenty two compounds with different substitution have been synthesized in this series. The anti-malarial and antimicrobial activity has been discussed. The synthesized compounds that possessed properties like high solubility in polar solvents are tested for binding with calf thymus DNA using fluorescence spectrometry 3-(4-methoxypheny1)-1-(4-(pyrrolidin-1-yl)phenyl)prop-2-en-1-one has shown intramolecular charge transfer phenomenon and binding with ct-DNA. Such molecules can be used as fluorescence probes.

Contents

096. SANE (Shalini)
Corrosion Inhibition of Nickel in Acidic Medium by Some Organic Inhibitors.
Supervisor : Prof. Gurmeet Singh
Th 15639

Abstract

A special class of organic inhibitors, called green inhibitors, find a great applicability as their usage does not harm the environment. The work studies the influence of certain amino acids namely, L-Methionine, L-Tryptophan and L-Phenylalanine. The aim is to ascertain the role of these inhibitors during the anodic dissolution of Nickel and the cathodic reduction of Oxygen and Hydrogen. The effectiveness of these inhibitors arestudied by carrying out the following analysis : Galvanostatic polarization studies, Potentiostatic polarization studies, Temperature kinetic studies, Electrochemical impedance studies, Infrared spectroscopy studies, Scanning electron microscopy studies and Quantum chemical studies analysis.

Contents

097. SINGH (Pradeep Pratap)
Chemical Studies of Biologically Active Heterocycles and Related Compounds.
Supervisor : Prof. S. M. S. Chauhan
Th 15634

Abstract

Ricinus communis L is a widely cultivated shrub. The leaves of R. communis L are food for the Eri silkworm (Philosemia ricini or Attacus ricini). The isolation and antioxidant ectivity of the active constitutents have been studied. Arnebia benthamii is small herb used a santidermatophytic, antibacterial and antitumor. The isolation of colouring matters from roots and rhizomes form organic solvents and supercritical CO_2 are undertaken, their chemical characterizatuib abd tgeur ubteractuibs wutg ctckidextrubs gave veeb examined. Rheum

emodi (Polygonaceae) is commonly known as Indian rhubarb. the roots and rhizomes of R. emodi are widely used in Ayurvedic preparations and Herbal medicines. The compounds isolated from roots and rhizomes of Rheum emodi were also analyzed for the antioxidant activity against 2,2'-Azinobis(3-ethylbenzthiazoline-6-sulfonic acid) ($ABTS^{\bullet+}$). Swertia chirata (Gentianaceace) is a small herb, which is used as an antimalarial, a bitter stomachic and to cure certain types of mental disorders. A brief literature survey of the isolation and biological activity of the active constituents have been described.

Contents

098. SINGH (Rajiv Kumar)
Synthesis, Characterization and Charge Transport of Poly (3-hexylthiophene) and its Composites with functionalized Single Walled Carbon Nanotubes for Photovoltaic Applications.
Supervisors : Dr. Rama Kant and Dr. Ramadhar Singh
Th 15636

Abstract

Aims to understand and develop semiconducting organic polymer (poly(3-hexylthiophene)), from the point of view of optimal synthesis and processing parameters to obtain good electronic grade polymer and its composite with carbon nanotubes to use for fabrication of organic photovoltaic device. Describes synthesis of a polymer at low cost; in-depth analysis of pristine and doped P3HT performed for understanding structural, morphological, physical, electronic and electrical behavior. The single walled carbon nano tubes are chemically modified to achieve homogeneous dispersion and self-assemble with pristine P3HT polymer matrix. Attempts to evolve a low cost chemical polymerization route for the synthesis of P3HT.

Contents

1. Introduction to conducting polymers. 2. Synthesis and doping of poly(3-hexylthiophene). 3. Structural, photophysical, morphological characterizations of pristine and doped poly(3-hexylthiophene). 4. DC charge transport of pristine and doped poly(3-hexylthiophene). 5. Dielectric behavior and AC conductivity of pristine and doped poly (3-hezylthiophene). 6. Solublization of single walled carbon nanotubes and its composite with poly(3-hexylthiophene). 7.P3HT-FSWCNTS solar cell. Concluding remarks.

099. UPADHYAY (Sunil Kumar)
Synthesis, Spectral and Oxidase Studies of Some Copper Complexes with Multidentate Diamide and Tetra Amide Ligands Carrying Pendant Benzimidazolyl Groups.
Supervisor : Prof. Pavan Mathur
Th 15642

Abstract

Describes the synthesis and characterization of Copper(II) complexes with novel multidentate bis benzimidazole diamide and tetrakisbenzimidazole tetraamide ligands. These ligands are N,N'-bis(2-benzimidazolylethyl) hexane diamide [a tetradentate N_2O_2donor], N,N'-bis (2-benzimidazolylethyl)-2,2'-thiadiethanamide [a pentadentate N_2O_2S donor] and Ethylenediamine-N,B,N',N'-tetrakis[(2-benzimidazolylmethyl)-acetamide] [an octadentate N_4O_4 donor]. The ligands comprise of two biologically important groups i.e. amide and benzimidazole. Amide group being the basic unit in many biomolecules. Imine-N atom of benzimidazole is similar to that of histidine nitrogen which is known to be the coordinating atom in several copper containing metalloenzymes. Benzimidazoles are therefore good mimies of Histidines; these novel multidentate ligands therefore provide a local coordinating environment similar to that existent in the metalloenzymes.

Contents

1. Introduction. 2. Theory of techniques uitlized in the identification of ligands and their copper complexes. 3. Synthesis and characterization of ligands : analytical data, UV, IR, and ^1H NMR studies. 4. Synthesis, spectral and electrochemical studies of copper(II) complexes with diamide and tetra amide based ligands. 5. Characterization of copper(II) compounds synthesized in

reverse micellar media and oxidase studies of some copper(II) complexes.

100. VERMA (Hemant)
Novel Polyurethane-Based Tri-Block Copolymers Through Atom Transfer Radical Polymerization.
Supervisor : Dr. K. Tharanikkarasu
Th 15629

Abstract

Deals with the synthesis of novel poly (methy1 methacrylate)-block-polyurethane-block-poly (methye methacrylate) (PMMA-b-PU-b-PMMA) tri-block copolymers through reserse ATRP. This is example of the synthesis of tri-block copolymer through reverse ATRP. Tetraphenylethane based polyurethane (PU-TPE) is used as a macroinferter, cupric halides ($CUBr_2$, CuCl2) are used as the catalyst and N, N, N', N', N"-pentamethyldiethylenetriamine is used as a ligand. All macroinitiators (Br-PU-Br, $BrMe_2C$-PU-CMe_2Br, Br_3-PU-Br_3, PU-TPE) which have been used further to synthesize noel tri-block copolymers have been thoroughly studied and characterized using spectral and thermal analysis, viz. ^1H NMR, ^{13}CNMR, FT-IR, GPC, TGA and DSC.

Contents

101. VERMA (Shweta)
Synthesis, Structure, Magnetism and Biological Studies of Transition Metal Complexes Containing New Macrocyclic Ligands.
Supervisor : Dr. Sulekh Chandra
Th 15626

Abstract

Five macrocyclic ligands : L^1, L^2, L^3, L^4 and L^5 are prepared by 2+2 condensation of precursor molecules. The synthesized novel

macrocyclic ligands are as follows : 5,6,13,14-dibenzo [1,4,8,11]dioxadiaza-5,7,11,13-cyclotetradecin (L^1), 1,2,7,9-tetraaza-2,8-dithia-4,10-dimethy1-6,12-diphynylcyclododeca-4,6,10,12-tetraene (L^2), 1,5,11,15,21,22-hexaaza-2,14 dimethy-14,12 -diphenyltricyclo-[15.3.1.I(7-11)]docosane [1,4,6,8,10 (22),11,14,16,18,20(21)] (L^3), 1,9,12,20-tetraaza- 1,8,13,19-tetraone-5,16-dithiacyclodocosane (L^4), 1,9,13,21-tetraaza-2,8,14,20-tetraone- 5,17-dithiacyclotetracosane (L^5). The transition metal ions, used for complexation are Mn(II), Co(II), Ni(II), Pd(II), Pt(IV) and Cu(II). The complexes are characterized by elemental analyses, magnetic susceptibility measurements, molar conductance, IR, electronic and EPR spectral studies. The ligands and their complexes are screened in vitro against two pathogenic fungi (F.moniliformae and R. solani) to assess their growth inhibiting potential.

Contents

102. ZAIDI (Sheza)
Curtius and Schmidt Rearrangements of Some Acyl Azides : A DFT Mechanistic Study.
Supervisor : Prof. Rita Kakkar
Th 15638

Abstract

Explores the synthetically important organic reaction, the Curtius reaction, and its acid-catalyzed counterpart, the Schmidt reaction, from a mechanistic point of view using state-of-the-art DFT calculations with a fairly large basis set. The calculations have revealed important mechanistic details of the Curtius reaction.

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