CHAPTER 8

CHEMISTRY

Doctoral Theses

076. ANGRISH (Chetna)
Self-Assembly of Selected Heterocycles and Polymerization of Olefins.
Supervisor : Prof. S. M. S. Chauhan
Th 14684

Abstract

Deals with an exhaustive review on the self-oranization of the molecular components of biological systems and the techniques used in the characterization of the self-assembled materials. A methodology to synthesize the functional phthalocyanines under mild conditions has been developed wherein the reaction of phthalonitriles in the presence of DBU and sugar has been carried out in methanol Metalloporphyrins serve as a chemical model catalyst for cytochrome P450 and other enzymes in the oxidation of various substrates carried out in organic and organized media their unique function to serve as a catalyst (or as an intiator in the polymerization reactions has been presented. Synthesis of copolymeric biomaterials using the biomimetic approach has been dealt with.

Contents

1. Self-Organization of the molecular components of biological systems. 2. Newer materials by self organization of the functional phthalocyanines. 3. Biomimetic polymerization of functional olefins in aqueous and/or organic media and ionic liquids and their applications in newer materials. 4. Synthetic biomaterials by copolymerization of selected monomers.

077. GUPTA (Archana)
Synthesis and Spectral Studies of Transition Metal Complexes with Macrocyclic Ligands.
Supervisor : Prof. K. K. Sharma
Th 14674

Abstract

Describes the synthesis and characterization of the transition metal complexes with some macrocyclic ligands. The following ligands were synthesized and characterized. (i) 2,7,9,14-Tetrapheny 1-1,3,6,8,10,13-hexaazacyclooctadecane (ii) 2,7,9,14-Tetrahydroxypheny1-1,3,6,8,10,13-jexaazaclooctadecane (iii)2,7,9,14-Tetracyclohexane-1,3,6,8,10,13-Hexaazacyclooctadecane (iv) 23,24-Dioxo-1,6,9,12,17,20-hexaazacyclotetracosa-1,5,12,16-tetraene (v) 25,26-Dioxo-1,6,12,17,23,24-hexaazacyclohexacosa-1,5,12,16-tetraene. The transition metal complexes with these ligands have been prepared and characteized by elemental analysis magnetic susceptibility measurement, molar conductance, IR, electronic and E P R, XRD spectral studies.

Contents

078. GUPTA (Rachna)
Spectral Studies on 3d and 4f Elements with Novel Macrocyclic Ligands.
Supervisor : Dr. Sulekh Chandra
Th 14672

Abstract

Describes the synthesis and characterization of 3dCr(III), Mn(II), Co(II), Ni(II) and Cu(II) and 4f elements (Ce(III),Eu(III) and Gd(III)with five hexadentate macrocyclic ligands. Following macrocyclic lighands have been prepared and characterized by elemental analysis, I.R. and mass spectral studies (i) 2,8,14,20.25.26,27,28 octaaza pentacyclo [19.31 $^{1.21}$.$1^{3.7}$.$1^{9.13}$.$1^{15.19}$] octacosa [1(25),2,7,9(27), 10,12,14,19,21, 23] decaene.[L^1] (ii)2,6,12,16,21,22 hexaaza tricyclo [15.3.$1^{1,17}$.$1^{11,7}$] dicosa 1,6,11,16 tetraene [L^2](iii) 2,5,11,14,19,20 hexaazatricyclo [13.3.1 ^{1,15}.$1^{6,10}$] cosa 1,5,10,14 tetraene [L^3] (iv) 3,4,12,13 Tetrafuran 2,5,11,14,19,20 hexaazatricyclo [13.3.$1^{1,15}$.$1^{6,10}$] cosa [2,4,6,8,10,11,13,15,17] nonene[L^4] (v) 2,7,13,18 tetramethyl 3,6,14,17,23,24 hexaazatricyclo[17.3.1.$1^{8,12}$] tetracosa 1(23), 2, 6, 8, 10, 12 (24), 13, 17, 19, 21Decaene [L^5] Cr(III),Mn(II), Co(II), Ni(II),Cu(II), Ce(III)< Eu(III) and Gd(III) complexes were synthesized with L^1, $L^{2,}$ L^3, L^4 and L^5Two methods has been adopted for the synthesis of complexes: (i). By using ligands (ii). By template method. The complexes were synthesized by lighands however in some cases where the ligand yield was too poor the

complexes were prepared by template method the complexes were characterized by elemental analysis molar conductance magnetic susceptiblility measurements I.R. electornic and EPR spectral studies.

Contents

079. GUPTA (Radha)

Experimental Studies Towards the Development of Sol-gel Based Optical Transducer for Biosensors.

Supervisor : Dr. S. Mozumdar and Dr. N. K. Choudhury

Th 14673

Abstract

Characterization of the internal environmet of a sol-gel matrix is an important area of investigation in optical biosensors. Different sol-gel compositions were prepared by varying the water (H_2O) to tetracthyl-orthosilicate (TEOS) ratios(R) 1,4,8,and 16 and the changes in the internal environment of the sol-gel both in bulk and thin films as a function of agaging (storage) were investigated using fluorescence spectroscopy. Focused on the fluorescence characteristics viz. emission and excited state lifetime of hoechst 33258 (H258), a bisbenzimidazole derivatiove which was used as fluorescence probe entrapped in the TEOS-derived sol-get bulk and thin films sol-gel derived bulk and thin films were prepared form differnet compositions at low $_pH$ (~2.0) containing varying concentration of ethanol form 15to60%(v/v) at constant H_2/TEOS molar ratio(R+4). The fluorescence microscopic and spectroscopic measurements on fluorescent probe, Hoechst 33258 (H258) entrapped in these compositions were carried out at different days of storage to monitor the effects of concentration of ethanol on the internal environment of the sol-gel materials. fluorescence microscopic observations on sol-gel thin films prepared by dip coating technique depicted uniform and cracked surface at withdrawal speed 1cm/min (highspeed) and 0.1 cm/min (low speed) respectively, which did not change during aging Sol-gel composition was prepared at water to tetraethyl-orthosilicate (TEOS) molar ratio R=32 with water only (wothout ethanol as solvent and TritionX-100 for preparation of sol-gel bulk and thin films. The sols were prepared at pH~6.0 by sonication and thin films were coated by dip coating technique at withdrawal speed

of 1cm/mim. Laser scanned images showed uniform thin films as observed by confocal microscop. Fluorescence spectroscopic studies have been undertaken to characterize the internal environment of sol-gel bulk and thin films under different storage conditions (at room temperature and 4^0C) using three different types of probes hoechst 33258 (H258), Pyranine(py), and 7-Azaindole(7-AI).This study mainlay emphasized on elucidation of the local environment using probes having different characteristics.

Contents

1. General Introduction. 2. Review of literature overview of biosensor. 3. Experimental procedures materials. 4. Effects of H_2O/TEOS molar ratios on internal environment of sol-gel bulk and thin films with aging. 5. Effects of ethanol variations on the internal environment of sol-Gel bulk and thin film with aging. 6. Characterization of the internal environment of sol-gel bulk and thin films under different aging conditions : A comparative study of multiple probes. Bibliography.

080. KHANDPUR (Namita)
Polyethoxyaniline as Doping Agent for Polymers for Corrosion Inhibition of Mild Steel.
Supervisor : Prof. Gurmeet Singh
Th 14681

Abstract

Studies the influence of certain polymers (Polyvinglpyrollidone-iodine compled (PVP-1), polyethylene glycol nonyl pheny1 ether (PEGNPE) polyoxyethylene N,N,N 1,3 diamino propane (POENN') polysorbate 20(Poly-20) as inhibitors on acid corrosion of mild steel. Also the effect of a conductiong polymer i.e. polyethoxyaniline on the corrosion inhibition efficiency has been studied. Ascertains the role of these inhibitors during anodic dissolution of mild steel and cathodic reduction of oxygen and hydrogen. Concludes that all these inhibitors reatard corrosion at lower temperature but enhance it at higher temperatures. This shows that they belong to putilova's 1st category of inhibitors.When the conducting polymer solution is mixed with the polymer solution the inhibition efficiency increases. These inhibitors show no appreciable shift of Ecorr indicating that they are mixed type of inhibitors. Irregular trends in Tafel slope values indicaties that adsorption of the inhibiting species is assisted by some other ions present in the solution. The charge transfer resistance values in presence of the

inhibitor are higher and Cdi values are lower as compared to that in acid. All the inhibitors follow different adsorption isotherm patterns. The values of heat of adsorption (Qads) and effective activation energies (Eeff) indicate that all the inhibitors are physiosorbed on the metal surface.

Contents

1. Introduction. 2. Literature survey. 3. Experimental techniques.4.Weight loss studies. 5. Galvanostatic polarization studies. 6. Impedance measurements. 7. Temperture kinetic studies. 8. Potentiostatic polarization studies. 9. Infrared spectroscopic studies. 10. Scanning electron microscopy. 11. Quantum chemical calculations. Bibliography.

081. MISHRA (Ajay Kumar)
Synthesis and Characterization of Some Thiohydrazide Thiodiamine and Thiohydrazone Transition Metal Complexes.
Supervisor : Prof. N. K. Kaushik
Th 14675

Abstract

Describes the synthesis, characterization, thermal biological and corrosion studies of Pt(IV), Pd(II), Co(II), Ni(II) and Cu(II) metal complexes with nitrogen and sulphur donor ligands. the ligands are thiohydrazides thiodiamines and thiodiamines and thiohydrazones.

Contents

1. Introduction. 2. Experimental. 3. Results and discussion. Bibliography.

082. MUKHERJEE (Chandrani)
Synthetic Biocatalytic Resolution and Biological Activity Evaluation Studies on O/N- Containing Heterocyclic Compounds.
Supervisor : Dr. Ashok Kumar Prasad
Th 14683

Abstract

Heterocyclic compounds are widely distributed in nature and are essential to life. They play a vital role in the metabolism of all living cells. There are also a vast number of pharmacologically active heterocyclic compounds many of which are in regular clinical use some of these are of natural origin e.g. alkaloids

and glycosides. However a large majority are synthetic heterocycles which have found widespread uses like anticancer agents, anesthetics analgesics sedatives hypnotics antihypertensice agents etc and in agrochemicals as pestivides insecticides rodenticides herbicides and fungicides. The work thesis involves the synthesis of four different classes of pharmacologically active O-orN- containing heterocyclic compounds i.e. 3,5-bisarylidene-4piperidones, 2-acetoxyethy1-1,4-benzoxazin-3-ones,4-(3/4-Acetoxyary1)-3,4-dihydropyrimidin-2-ones and aminoalcohols i.e. ehty1 4-[4'-(2"-hydroxy-3 aminoalky1-propoxy) ary1]-6-methy1-3,4-dihydropyrimidin-2-one-5-carboxylates.

Contents

1. Synthesis and bioevaluation of novel 3,5-bisarylidene-4-piperidone derivatives as anticancer agents. 2. Part-1.Synthesis biocatalytic resolution and activity evaluation studies on methyI(=)-2-(2-acetoxyethyI)-4-arylmethy 1-3-oxo-3,4-dihydro-2H-1,4-benzoxazin-6-carboxylates. 3.Part-2. Synthetic and lipase-catalyzed enantioselective deacetylation studies on 4-ary1-3,4-dihydropyrimidin-2-ones. 4. Part-3. Synthesis of ethyI 4-[4'-(2"-hydroxy-3'-aminoalkyI-propoxy)aryI]-6-methyI-3,4-dihydropyrimidin-2-one-5-carboxylates Summary

083. PANDEY (Maneesha)
Effect of Size of Ions (Alkali Salts) on Amino Acid Interaction in Aqueous Medium at 310.15K
Supervisor : Dr. Man Singh
Th 14677

Abstract

Focusses on the effect of size of cations on amino acids (glycine, DL-alanine and DL-leucine along with a peptide (glycylglycine) in aqueous medicum. due to the charged end centers, and also methylene groups of amino acids, they have both hydrophilic and hydrophobic interactions with water. Due to hydrophobic species, the water in a hydration co-sphere is more structured than of in the bulk. the overlap of hydration co-sphere of two such hydrophohic species involving hydrophobic-hydrophobic interactions results in a part of (more structured) water form the overlapping region to relax to the bulk. On the other hand, the presence of hydrophilic charged species restricts the free movement of water molecules, held in primary hydration sheath in its immediate vicinity due to charged-dipole interactions. There may also be second layer of water molecules (secondary

hydration sheath) around it. For species (dipolar/zwitterions/ amino acids) involving hydrophilichy-drophilic interactions (electrostriction) lead to a decrease in the hydrogen-bonded water structure of water in the co-sphere of hydrophilic ions than in the bulk. the overlap of co-spheres of two such hydrated species also relaxes some solvation water to bulk but water so released in these interaction is less structured (less in volume) than the corresponding case involving hydrophobic-hydrophobic interactions.

Contents

1. Introduction. 2. Literature review. 3. Theory. 4. Experiment, chemicals and claculations. 5. Result and discussion. Summary and Bibliography.

084. PATHAK (Mallika)
Theoretical Study of the Structure and Unimolecular Decomposition Pathways of Pyruvic Aid
Supervisor : Prof. Rita Kakkar
Th 14682

Abstract

Deals with some of the applications of quantum chemistry to the study of unimolecular rearrangements. It is concerned with a study of the structures of isomers their relative stabilities and interconversions for a biochemically important molecule pyruvic acid in aqueous solution the preferred keto conformer becomes the one with the two carbony group dipole vectors pointing in the same direction moreover the separation in energies between the keto and enol forms also reduces and both forms should exist in solution. This makes decarboxylation to viny1 alcohol via the enol tautomer also possible contrary to expectations based on dipole moment considerations. The transition state for decarboxyation to acetaldehyde is not stabilized in aqueous solution and the activation barrier in fact increases. This emphasizes the need for the catalytic mechanism even in solution.

Contents

1. Introduction. 2. Computational methods. 3. Structures of pyruvic acid isomers and their vibrational spectra.4. Unimolecular decomposition of pyruvic acid. 5. Stabilities of products and barriers to intramolecular rearrangements. 6. Ef-

fect of aqueous solvation on the structures of pyruvic acid isomers and their reactions in solution. 6. Conclusions, perspectives and Bibliography.

085. RUCHI SINGH

Chemical and Biochemical Investigations on Synthetic Nanoparticles in Gene Delivery.

Supervisor : Prof. N. K. Kaushik

Th 14679

Abstract

Aqueous core of reverse micellar droplets can be effecatively used to carry out the synthesis of these nanoparticles doped with plasmid DNA. Preparatory method is simple easy and carried out in mild conditions so that the biomolecules are not denatured. The size of the nanoparticles can be modulated by adjusting the size of the host aqueous reverse micellar droplets(Wo). Plasmid DNA can be effectively entrapped within calcium phosphate nanoparticles and chitosan nanoparticles. Such DNA doped nanoparticles can be used as a nonviral vector for gene delivery. Transgene expression is quite signigicant for the plasmid DNA encapsulated nanoparticles. The entrapped plasmid DNA remains in the blood circulation for longer duration resulting in prolonged transgene expression. Bile duct infusion of the nanoparticles in rat model results in the effective liver directed gene delivery.

Contents

086. SABA AZAMI

Recovery and Recycling of the Metals From Industrial and Other Waste Waters using Various Chelating Resins : A Green Chemistry Approach

Supervisor : Prof. B. S. Garg

Th 14676

Abstract

Describes the synthesis and applications of chelating resins for selective separation and preconcentration of CU(II) CR(III) Co(II), Ni(II) and Mn(II). Assesses the potential of silica gel chemically modified by covalently linking acenaphthenequinone on aminopropylated silica gel for the separation and preconcentration of Cu(II),Ni(II) and Co(II). This chelating resin exhibits relatively higher absorption capacities for Cu(II), Ni(II) and Co(II) using the newly synthesized chelating resin. The enrichment of Cu(II), Ni(II) and Co(II) from natural water samples and other samples has been successfully carried out. The RSD values are low. The short time required for loading of metal ions onto the newly synthesized matrix is an advantage. The repeated use of chelating silica gel is feasible. It can be regenerated by washing the column with 2M HCI Silica gel modified with GBH has been used for enrichment of Cr(III), Cu (II) and Co(II) prior to their determination by atomic absorption spectrometry (AAS) Silica gel functionalized with acenaphthenequinonemonoxime was successfully applied for the extraction of Cr(III), Cu(II) and Co(II) from aqueous solution. Amberlite XAD-16 modified with GBH and AQM has been used for the enrichment of Cr(III)Cu(II) Co(II), NI(II) and mn (II) prior to their determination by atomic absorption spectroscopy (AAS). The optimun Ph for quantitative adsorption on amberlite XAG+16-GBHWas found between 5.0To9;0 whereas form amberlite Xad-16-AQM between 4.0 and 9.0 2MHCI was found to be suitable for desorbing the metal ions form both the resins the newly synthesized chelation resin exhibit relatively higher sorption capacities forCu(II) Co(II) and Cr(III) and quite selective for these cations for preconcentration and separation from waste water samples. All the methods described in the thesis are greener analytical methods.

Contents

087. SANJAY KUMAR

Hplc Monitored Protein Interactions in Aqueous Ketonic Polymer Solutions.

Supervisor : Dr. Man Singh

Th 14680

Abstract

The physicochemical characterization of such solutions has been made as a function of composition and thermal state. Notably the techniques of HPLC along with densimetry and viscometry have been found excellent to give a qualitative and quantitative estimation for these properties to assist characterization of binary and ternay solutions.Concludes the PVP and BSA decrease hydrodynamic volume of each other. Reduced viscosity decrease with PVP concentration for extremely dilute solutions while for dilute solutions increase. PVP and BSA molecules remain in different conformational state at different temperatures. The mutual compositions of them strengthen the hydrophobic interactions. The cage moderl of water becomes a key control over hydrophobic interactions to compensate the compositional impacts. The magnitudes of ΔS function elucidate a prominent reorientation ofsuch molecules in aqueous medium at p^H 7.0. Hydrogen bonding interactions made through oxygen of water with positively charged site of the BSA/ Amino acid increase the electron acceptance ability (EPA) of water thereby stabilize the PVP-BSA complex. Negatively chaged sites interact via hydrogen of water and decrease EPA of water that leads to destabilization of PVP-BSA complex.

Contents

088. SAXENA (Anjali)

Design and Synthesis of Some Novel Spiro and Bis-spiro [Indol-benzoxazines] by Molecular Modification and Phytochemical Studies of Piper Sylvaticum.

Supervisor : Prof. S. C. Jain

Th 14685

Abstract

Drugs from higher plants continue to occupy a unique niche in the modern therapeutic armamentarium and appear to remain so into the forseeable future. If one analyze the various strategies used in drug discovery one will find that as far as therapeutic agents from higher plants are concerned, the most successful strategy revolves around inverstigation of medicinal palnts of various cultures. As part of the on going progammes to isolate biologically active compounds from plant sources, piper sylvaticum for phytochemical investigation . has been selected extracted together leaves and stems of the plant, first with cold dichloromethane:methanol (1:1) and then with hot dichloromethane:methanol (1:1) in order to obtain two extracts containing different compounds. However, these solvent free extracts of P. sylvaticum (leaves and stems) showed similar behaviour on TLC in different solvent systems and hence were mixed. The combined extract was chromatographed using silica gel as an adsorbent. The column was eluted with solvent of varying polarity and number of fractions was collected. From the fractions using repeated column charomatography & crystallization techniques, have isolated thirteen compounds in pur form which were characterized as : octadecan-1-01, 9Z,12Z-octadecadienoic acid, cycloart-23-en-3-one, tetratriacontanoic acid, benzy1 benzoate, stigmast-4,7-dien-14-hydroxy-3-one, stigmast-5-en3β-OL,N-isobuty1-2E,4E-decadienamide, N-isobuty 1-5-(3,4-methlenedioxypheny1)-2E,4E-pentadienamide, N-[5-(3,4-methylenedioxpheny1)-2E,4E-pentadienoy1] piperidine, 7-methy1-5H-benzo[g]-1,3-benzodioxolo[6,5,4-de]quinoline-5,6-(7H)-dione, stigmast-5-en-3-O-b-D-galactopyranoside and 4-amino-3 methoxybenzoic acid are new natural products and have not been reoported form any natural source so far. This is also the first report of isolation of stigmast-5-en-3-O-b-D- galactopyranoside form the genus piper. All these compounds have heen fully characterized on the basis of their detailed spectral studies such as IR.1HNMR,13CNMR and Mass spectrum.

Contents

089. SHYAM KISHOR

Electronic Structure and Conduction Properties of Biopolymers and Conduction Polymers.

Supervisor : Prof. A. K. Bakhshi

Th 14816

Abstract

Design and investigates systematically the electronic structures and conduction properties of model copolymers belonging to the class of both Type-II staggered and Type-II misaligned superlattices respectively using the Negative Factor Counting (NFC) method in tight binging approximation. For each class three system have been studied in these three systems one component (homopolymer B) is common while the second component (homopolymer A) has different alignments with respect to component B provided the pair belongs to the same class Type-II staggered or Type-II misaligned as the case may be. The trends in the electronic structures and conduction properties of copolymers $(A_mB_n)x$ as a function of the (i) block size nof A; (ii)block size n of B; (iii) composition(m/n), (iv) arrangement of the units (periodic or aperiodic) in the copolymer chain and (v) Band discontinuity ratio($\Delta E_a/\Delta E_i$) were studied.

Contents

090. SONI (Sheetal)

Studies on the Trafficking of Smart Nanoparticles Across Blood Brain Barrier

Supervisors : Prof.Amarnath Maitra and Dr. Rakesh Kumar Sharma

Th 14705

Abstract

Explores the possiblility of using surface modified nanoparticles

to be targeted across the Blood-Brain Barrier. Nanoparticles are solid colloidal particles, ranging in size form 1 to 1000nm, consisting of various macromolecules in which therapeutic drugs can be adsorbed, entrapped, or covalently attached. One utility of nanoparticles is to serve as novel drug delivery carriers to tissues throughout the body. This is accomplished by masking the membrane barrier, limiting characteristics of the therapeutic drug molecule, as well as retaining drug stability, with that of the properties of the colloidal drug carrier. Deals with the delivery of inorganic nanoparticles encapsulation DNA across the blood-brain barrier. Some ceramic particles of nanodimension have beeen prepared encapsulating or in conjugation with DNA with the purpose of using these inorganic nanoparticles were coated with polysorbate 80. To know the distribution pattern of the calcium phosphate nanopartivales in brain, the nanopartivles were loaded with FITC dextran which would act as a marker molecule. The FITC loaded nanoparticles were sacrificed at predetermined time intervals. the tissues were removed and the homogenised. The fluorescence was measured in the homogenate. The fluorescence data showed increased uptake of the nanoparticles on coating with polysorbate 80.

Contents

091. TYAGI (Richa)

Study of Vinyl Polymers for Drug Delivery and Capping Agents for Nanorods Synthesis.

Supervisor : Dr. Subho Mozumdar

Th 14678

Abstract

Explores the possibility of using viny1 polymers in the biomedical field of drug delivery and their applications in the synthesis of advanced nanomaterials. Arjunglucoside I and anti

leishmaniasis drug, is hydrophobic in nature. A suitable drug delibvery system which could encapsulate this poorly water soluble drug with high entrapment efficiency and coluld also release this drug in a controlled release fashion was prepared. Copolymeric miceller nanoparticles of N-isopropylacrylamide (NIPAAM) with N-vinylpyrrolidone (VP) crosslinked with N,N'-methylene bis acrylamide (MBA) were prepared. On the front of advanced nanotechnology, polymers have also attracted attention in the synteresis of metal nanoparticles, semiconductors, nanorods and nanowires. These nanoscale metal particles have aroused interest because of their unusual size-dependent optical and electronic properties which have found wide applications in the dield of information technology, biosensors and catalysis. Synthesized the silver nanorods by a simple polyol process using polyviny1 pyrrolidone as a capping agent. The mechanism of formation of silver nanorods was observed using a transmission electron microscope. It was suggested that the nanorods resulted due to the aggregation of previously formed silver nanoparticles. The XRD and SEM results gave us the conclusive idea of the structure of the silver nanorods.

Contents

M.Phil Dissertations

092. MISHRA (Anupama)
Synthesis and Characterization of Copper (ii) Complexes of Amide-Amine Based Tri-Asa Macrocyclic Ligend having Potential of Synthetic Rotamase Activity.
Supervisor : Dr. Rajeev Gupta