DEPARTMENT OF CHEMISTRY, SATAVAHANA UNIVERSITY

Syllabus for Ph.D. Course Work

Paper- II : Inorganic Chemistry Specialization

Bonding in metal complexes, Spectroscopic Applications, Supramolecular, Organometallic and Bio-inorganic Chemistry

Unit-I: Bonding in metal complexes,

Molecular Orbital Theory of Metal Complexes: Symmetry Classification of Metal and Ligand Orbitals in Cubic and Non-Cubic Environments: Octahedral, Tetrahedral, Square Planar, Square Pyramidal, Trigonal Bipyramidal Geometries – Concept of Ligand Group Orbitals – Construction of Molecular Orbital Energy Level Diagrams for Octahedral, Tetrahedral and Square Planar Metal Complexes with Sigma (σ) and Pi (π) Bonding Contribution from the Ligands.

Unit-II: Electron absorption Spectroscopy IR, Raman,

Electron absorption spectroscopy: Effect of weak cubic crystal fields on S,P,D and F terms- Orgel Diagrams. Selection Rules: Relaxation in Selection Rules – Nature of Electronic Spectral Bands: Band Widths, Band Intensities and Factors Influencing Band Shapes– Crystal Field Spectra of Oh and Td metal Complexes of 3dn Metal ions – Calculation of 10Dq Values, Racah Parameter.

IR and Raman: Symmetry Based Selection Rules of Infrared and Raman – Symmetry Requirements for Overtone, Binary and Ternary Combination Bands - Fermi Resonance Application of IR spectroscopy in the structural elucidation of inorganic compounds and metal complexes- Aquo, sulfato, carbonato , nitro and carbonyl metal complexes.

Unit-III: Multinuclear NMR and ESR

Multinuclear NMR: Characteristic Nuclear Properties of 1H, 13C, 19F, 31P and 15N – Reference standards- Ranges of Chemical Shifts –Use of Chemical Shifts and Coupling Constants for the structure determination of simple inorganic and Coordination Compounds containing one or more of 1H, 13C, 19F, 31P and 15N nuclei.Examples; (1)1H-NMR: Pt HCl(PEt3)2 , Pt (NH3)3(CH3)3, BH_4^- , [h7C7H7Mo(CO)3]+ , B2H6; (2) 19F- NMR: PF5, BF_4^-, SF4; (3) 31P-NMR: H3PO2, H3PO3, H3PO4, [Rh (PPh3)3 Cl3], [Mo(CO)3(PPh3)3], [Rh (PPh3)3 Cl] , ATP. (4) 13C-NMR: [h4 C8H8 Ru(CO)3], Fe(CO)5, Fe2(CO)9, Fe3(CO)12, [13C 15N Co(DH)2Pyridine].

ESR of Metal Complexes: Principle- Selection Rules –. g value and its significance, Interpretation of g in cubic , axial and rhombohedral geometries. Factors affecting g values. Calculation of g values with simple examples. Intensities of '$g_{\parallel}$ and $g_{\perp}$ peaks . Evidence for Metal-Ligand Bond Covalency-Cu(II)- Bis –Salicylaldimine. Co3(CO)9Se, [(NH3)5CoO2 Co

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(NH3)5]5+, Cu(II)- diethyldithio phosphinate, Vanadyl dithio phsphinate, Copper(II) tetraphenyl porphyrin, Co(II)- phthalocyanine, K2[IrCl6].

Unit-IV: Supramolecules and Organo metallic Catalysis

Supramolecular chemistryHost – Guest chemistry : Definition and different types of host and guests with examples – types of non covalent interactions – binding constants of host guest complex and thermo dynamics involved in it – designing principles of host. **Cation guest binding** – binding between metal cations and macro cycles – chelate and cryptate effects – relationship between cavity size of host and cation radius and stability of resultant complexes – binding of macro cycles having secondary binding sites – **Anion guest binding** – different hosts for anionic guests capable of binding through electro static interactions, hydrogen bonds, lewis acidic hosts – enhancement of binding strength using more than non covalent interactions – **Neutral guest binding** – binding of neutral guest using hydrogen bonding, π - π stacking, hydrophobic effect and charge transfer interactions – simultaneous binding of cation and anion guests – cascade approach, individual binding sites and zwitter ions approach –present and future applications – phase transfer agents – separation of mixtures – molecular sensors – switches and molecular machinery.

Catalytic role of Organometallic Compounds: Oxidative addition and Reductive Elimination : Stereochemistry and Mechanism of Oxidative Addition – Insertion Reactions – Hydrogenation of Olefins –Transfer Hydrogenation – Hydrosilation of Olefins – Isomerisation of Olefins – Ziegler – Natta Polymerization of Olefins – Oligomerization of Butadiene . Alkene Metathesis. Oxidation of Olefins to Carbonyl Compounds – Oxidation of Hydrocarbons to Alcohols and Acids – Oxidation of Aldehydes. Reactions of Carbon monoxide and Hydrogen : Hydroformylation – Carbonylation –Syngas-Water gas shift Reaction (WGS) – Reactions of Syngas. Applications of Metal Clusters in Catalysis : Hydroformylation of Ethylene using [HRu3(CO)11]– , Hydrogenation of Olefins. Use of [Fe6C(CO)16] as a model for Fischer – Tropsch process.

Unit-V: Bio inorganic Chemistry

Role of metal ions in biology – four basic principles in the biological selection of elements – brief survey of metal ions in biological system – effect of metal ion concentration and physiological effect.

Cobalt enzymes : chemistry, biochemistry and medicinal aspects of vit B12 – structure of vit B12 –various forms – Base 'On' and Base 'Off' and His 'On' or His 'Off' forms – complete and incomplete corrinoids – comparison of two biologically active forms of vit B12 – catalyzed reactions of vit B12 using coenzyme B and methyl cobalamin – biomethylation, methyl transfer to mercury and arsenic – vit B12 as drug transport vehicle – bio chemistry – functions of vit B12, symptoms and causes of vit B 12 deficiency, absorption and storage of vit B12 – historical events in the discovery of vit B 12.

Nickel enzymes : Urease – active site – mechanism of degradation of urea to carbon dioxide and ammonia.**Copper enzymes :** Substrate specific antioxidants – Cu, Zn superoxide dismutase – structure and catalytic mechanism. **Zinc enzymes :** Role of zinc in catalytic activities of carbonic

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hydrase, carboxy peptidase and alkaline phosphate. **Vit B6 :** Various forms – mechanism of catalysed reactions – Dunothan hypothesis – role of metal ions in B6 catalytic activity.

Platinum complexes in cancer therapy: Discovery, applications and structure effect Relationships. Cis platin(cis Pt(NH3)2Cl2) mode of action. Drug resistance and DNA repair mechanism.

Physical effects of metal complex: DNA binding, unwinding, shortening and bending of the double helix. Biological consequences of platinum –DNA binding. Transition metal complexes as donor acceptor pairs. Non classical platinum antitumor+ agents.

REFERENCES & SUGGESTED BOOKS:

1. Symmetry and Spectroscopy of Molecules, K. Veera Reddy, Second Edition, New Age International (P) Limited Publishers (2009)
2. Chemical Applications of Group Theory, F. A. Cotton, 3rd edition, Wiley NY (1990)
3. Symmetry and Group Theory In Chemistry, Mark Ladd, Harwood Publishers, London (2000)
4. Symmetry Through the Eyes of a Chemist, I. Hargittai and M. Hargittai, 2nd Edition, Plenum Press, NY (1995)
5. Molecular Symmetry and Group Theory, Robert L. Carter, John Wiley & Sons (1998)
6. Group Theory for Chemists, G. Davidson, Macmillan Physical Science Series (1991)
7. Molecular Symmetry, Schoenland
8. Electronic Spectroscopy, A. B. P. Lever
9. Introduction to Ligand fields, B. N. Figgis Infrared and Raman Spectroscopy of Inorganic and Coordination Compounds, K. Nakamoto
10. Infrared spectroscopy of Inorganic Compound, Bellamy
11. Physical Methods in Chemistry, R. S. Drago, W.B. Saunders Co., 1977.
12. Chemical Structure and Bonding, R.L. Decock and H.B. Gray.
13. Physical Methods for Chemists, Russell S. Drago Second edition, Saunders ,College Publishing, 1992.
14. Comprehensive Coordination Chemistry, Vol 6.
15. Modern Coordination Chemistry, Lewis and Wilkins.
16. Organometallics-A Concise Introduction, Ch.Eischeinbroich and Salzer-VCH
17. Organotransition Metal Chemistry Fundamental Concepts and Applications, John Akio Yamamato, Wiley & Sons.
18. Homogeneous Catalysis by Metal Complexes, M M Taqui Khan and A E Martel
19. Applied Homogenous Catalysis with Organo Metallic Compounds Vol I & II, Boy Cornills and W A Herrmann – VCH
20. Homogenous catalysis, G W Parshall, John Wiley & Sons, New York
21. Inorganic elements in the Chemistry of life, Wolfgang Kaim & Brigette Schwederdki.
22. Bio inorganic Chemistry, Bertini, Lippard and Valentine, University Science Books, California USA, 1994
23. Principles Bioinorganic Chemistry., S J Lippard and Berg University Science Books, California USA, 1994
24. Biological Chemistry of Elements, J. J.R. Franstodasilva and R.J.P. Williams, aoxford University Press 1991
25. Metal ions in Biological Systems (series) Ed.H. Sigel Marcel Dekkar, New York
26. Inorganic Biochemistry, J.A. Cowan, VCH publishers 1993

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DEPARTMENT OF CHEMISTRY, SATAVAHANA UNIVERSITY

Syllabus for Ph.D. Course work

Paper- II: Physical Chemistry Specialization

T-I : HETEROGENEOUS CATALYSIS

erogeneous catalysis: Broad categories of catalysts – metals, bimetals, semiconductors, ılators, zeolites, oxides and nano materials.

paration of metal catalysts: Supported metal catalysts and non- metallic catalysts.

aracterization of catalysts: Surface area by BET method. Determination of pore volume and e size distribution by BJH method. Pore size and specificity of catalysts. Surface acidity of alyst & determination of surface acidity by indicator method , IR spectroscopic method and D method.

ps in heterogeneous catalyzed reactions: Catalytic activity – the determining factors. ucture sensitive and structure insensitive catalysts. Mechanism of surface-catalyzed reactions. e Langmuir - Hinshelwood and the Eley- Rideal mechanisms. Rate constants and activation ergies of surface reactions.

roduction to Phase-transfer catalysis (PTC): Principles of phase-transfer catalysis. PTC ssification. Role of water in phase-transfer catalyzed reactions. Factors influencing the rate of C reactions. Inverse phase transfer catalysis.

NIT-II: FUNCTIONAL POLYMERS:

art materials –uses of smart materials in sensing devices and communication networks.

nducting polymers: Electrically conducting polymers and their uses (polyanilines, lypyrrole, polyacetylene and polythiophene). Photoconductive polymers. Liquid crystal lymers – smectic, nematic and cholesteric structures.

ic exchange polymers: Cationic and anionic exchange polymers and their uses. Eco-friendly lymers. Poly lactide from corn derived dextrose, PHB etc.

embrane separation. Filtration – micro, ultra and nanofiltration. Separation of gases – rmeselectivity and gas permeability of representative polymers. Liquid separation – dialysis, ectro osmosis and reverse osmosis. Fire retarding polymers, photonic polymers. Inter netrating networks (IPN), polymers in photo lithography.

lymers in biomedical applications – artificial organs and controlled drug delivery.

nerging polymers: PTTC- (poly tri methylene tetra phthalate), Nylon 4,6 (Stanyl) – their uctures, properties and uses.

NIT-III: ELECTRO CHEMISTRY :

lectrode-electrolyte interface : The electrical double layer. The Helmholtz-Perrin parallel-ate model, the Gouy-Chapman diffuse-charge model and the Stern model.

orrosion : Electrochemical mechanism of corrosion . Types of corrosion, various methods of rrosion control.

Polarography : Dropping mercury electrode-polarography Instrumentation-
ırogram.Types of limiting Currents : Adsorption, Diffusion, Kinetic. Ilkovic equation and its
sequences. Applications of polarography. Determination of stability constant of complex.
:lic Voltammetry : Principle, instrumentation, reversible and irreversible cyclic
:ammograms. Applications. Cyclic voltammetric study of insecticide parathion.
ctro-Organic synthesis : Electro chemical reduction of carboxylic acids, Electrochemical
uction of nitro compounds.
ɔdic oxidation of metals : Characteristics of anodic oxide films. Instrumentation –break
vn voltage. Industrial applications of anodic oxide films.

IT IV: MATERIALS SCIENCE AND MOLECULAR MODELING

:parative methods of inorganic solids: Ceramic, coprecipitation, sol-gel, chemical vapor
ısport.
aracterization techniques of inorganic solids: X-ray powder diffraction (XRD),
ısmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPES).
mposites: Classification, fiber reinforced composites- influence of fiber length.
nomaterials: preparation by sol-gel and hydrothermal methods, characterization by powder
:DScherer's equation and general applications.

IIT V: MOLECULAR MODELING
ɔlecular modeling: QSAR parameters – Physiochemical parameters- Lipophilicity –
:ctronic parameters, Steric parameters, effect of electronic and steric parameters on
ophilicity. Hansch analysis, significance of slopes and intercepts in Hansch analysis. QSAR-
, 3D. Case study – on Pyranenamine. Achievements of QSAR – Forecasting biological
:ivity, selection of proper substituents, bioisosterism, drug receptor interactions and
armacokinetic information – Introduction to database similarity Search–Alignment ;
ignment methods, – Pair-wise alignment ; Multiple Sequence Alignment – Homology
ɔdeling – Energy minimization methods – Active site Identification – Virtual Screening –
ıall molecule Building – Docking Algorithms – Docking Analysis

EFERENCES:
ıtalysis:

Principles of Heterogeneous Catalysis in practice, G. C. Bond, Oxford Publishing
Heterogeneous Catalysis, C. Satterfield, McGraw Hill
Catalysis, Principles and applications, edited by B. Vishwanathan, S. Sivasanker & A. V.
ama Swamy, Narosa Publishing House
Catalysis, J. C. Kuriacose, Macmillan
Phase Transfer Catalysis, Fundamentals, Applications and Industrial perspective, C. M. Stark,
.Liotta & M. Halpern, Academic Press
Phase Transfer Catalysis, E. V. Dehmlow & S. S. Dehmlow, Verlag Chemie, Weinheim
Phase Transfer Catalysis in Organic synthesis, W. P. Weber & G. W. Gokel, Springer

ctional Polymers:

extbook of Polymer Science, F. W. Billmeyer Jr, John Wiley & sons
olymer Science, V. R. Gowarikar, N. V. Viswanathan & J. Sreedhar, Wiley Eastern
Contemporary Polymer Chemistry, H. R. Alcock & F. W. Lambe, Prentice Hall
Physics and Chemistry of Polymers, J. M. G. Cowie, Blackie
demic and professional
Ploymer Chemistry, B. Vollmert
Physical Chemistry of Polymers, A. Tagers, Mir Publishers
Introduction to polymer Chemistry, By Charles E Carraher Jr (Taylor- Frncis)

ctro Chemistry:

Modern Electrochemistry 2A & 2B, J. O. M. Bockris & A. K. N. Reddy, Plenum publishers
Introduction to Electrochemistry, S. Glasstone
Industrial Electrochemistry, D. Pletcher, Chapman & Hall
Fundamental principles of Modern Electroplating, Lowenheim, John Wiley
Principles of Polarography, Heyrovsky.
Principles of Polarography, Kapoor.
Modern Electroanalytical methods, edited by C.Charlot, Elsevier Company.
Principles of Instyrumental analysis, Skoog, Holler and Nieman, Harcourt Asia PTE Ltd.
Analytical Chemistry-An Introduction, Skoog, West, Holler and Crouch, Saunders College
olishing.
Prinicples of Instrumental Analysis, Skoog and Leary, Saunders College Publishing.

terial Science:

. Solid state and its applications by A.R. West.
. New directions in solid state chemistry, J. Gopalakrishnan and C.N. R. Rao.
. Principles of the solid state by HV Keer.
. Materials science and engineering an introduction by W.D. Callister, Jr.

olecular modeling:

.Burger's medicinal chemistry and drug discovery. By Manfred E. Wolf.
. Introduction to Medicinal chemistry. By Patrick.
. Introduction to drug design. By Silverman
. Comprehensive medicinal chemistry. Vol 1-5 By Hanzsch.
. Principles of medicinal chemistry. By William Foye
. Biochemical approach to medicinal chemistry. By Thomas Nogrady.
. Pharmaceutical Chemistry and Drug synthesis By Roth and Kleeman
. Drug design By E.J. Arienes
. Jenkin's quantitative pharmaceutical chemistry By Knevel and Dryden
. Recent advances in Bioinformatics By I. A. Khan and A Khanum
. Computational chemistry By GH. Grant and WG. Richards
. Molecular modelling By Hans Dieter Holtje and Gerd Folkers

FACULTY OF SCIENCE
Pre. Ph.D. Examination

Subject: **CHEMISTRY**
Paper- I
(Common to all branches)

ıe: 3 Hours **Max. Marks : 100**

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(5 × 20= 100 Marks)

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FACULTY OF SCIENCE
Pre. Ph.D. Examination

Subject: **CHEMISTRY**
Paper- II

ne: 3 Hours **Max. Marks : 100**

te: Answer all questions .

(5 × 20= 100 Marks)

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T. Bharath
(Prof. T. Bharath)

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