

PREFACE

Coordination chemistry is a fascinating field in inorganic chemistry. Coordination compounds are of great practical importance. Coordinating agents are used in metal-ion sequestration or removal, solvent extraction, dyeing, leather tanning, electroplating, catalysis water splitting and other industrial processes. In fact, new practical applications for them are found almost daily. They are of tremendous importance in biochemistry. For example vitamin B₁₂ is a coordination compound of cobalt, the hemoglobin of human blood is coordination compound of iron, the haemocyanin of invertebrate animal blood is a coordination compound of copper and the chlorophyll of green plants is a coordination compound of magnesium. The scope and application of coordination compounds have been giving excitement, inspiration and challenge to inorganic chemists. Even though a large number of coordination compounds are reported, the exploration is still going on at a fast pace. This fast exploration is to obtain the structural information and the biological applications of the complexes, which will be obtained from spectral, magnetic and other physicochemical studies. The reaction tendencies of the complexes with various reagents can also provide useful information regarding the donor-acceptor relationship between various donor atoms and the central metal ion. This knowledge will help to understand the nature of bonding, type of hybridization involved, extent of quenching of paramagnetism, symmetry of the compound formed etc.

The transition metal complexes of heterocyclic ligands, especially those containing nitrogen and sulfur have diverse applications in various fields of science and technology. Metal complexes of N and S donor ligands are known to possess antimicrobial, antiviral, antifungal anticonvulsant, anti carcinogenic and anti herbicidal activities. Many of these ligands are also used as powerful pesticides and insecticides. Metal chelates of certain multidentate Schiff bases have been used for the purification of metals due to their high volatility and solubility in non-polar solvents. The metal complexes

with Schiff bases find various industrial applications also. Metal complexes of 1, 2, 4-triazole derivatives have been extensively investigated.

Another important application of coordination chemistry is the introduction of organic reagents into analytical chemistry. Chelate complexes of sulfur containing ligands are more stable and selective than other donor centres. Quantitative analytical procedures based on the uses of absorption spectra are generally simple, fast, accurate and easily acquired and lend themselves to routine measurements. The subject of metallic corrosion has gained considerable importance during last few decades because of the increasing awareness of the enormous loss caused by corrosion damage. Economic factor is the prime consideration for much of the current research in this field. The second reason is the need for conservation of depleting natural metal resources. The use of inhibitors is one of the most practical methods for protecting metals against corrosion and is becoming increasingly popular. A large number of investigations have been carried out on the corrosion behavior of various materials in mineral acids and on the inhibition of corrosion of these materials using both organic and inorganic compounds. It is well known that a particular inhibitor which gives a very high efficiency for a particular metal in a specific media may not work with the same efficiency for other metals in the same media. In recent years, considerable efforts have been taken to find novel and efficient corrosion inhibitors with oxygen, sulfur and/or nitrogen containing molecules. Most of these inhibitors form a protective film on the surface of the metals through either adsorption or complex formation. Researchers have concluded that adsorption depends mainly on the physicochemical properties of the inhibitor group, such as functional groups, electronic density at the donor atom, Π -orbital character, and the molecular electronic structure. The triazoles, benzotriazoles and their derivatives, for instance, are excellent corrosion inhibitors for mild steel and copper in a wide variety of water solutions, temperature and pH ranges. Quantum chemical calculations are found to be a very powerful tool for studying inhibition mechanisms.

The present investigation therefore, is an attempt to understand the properties and applications of some new Schiff base ligands and its metal complexes. It also aims at investigating the suitability of some of these Schiff base ligands as spectrophotometric agents and corrosion inhibitors.

The chapter wise content of the thesis is summarized as

Chapter I

This is an introductory chapter divided in to three sections. Part A provides an introduction to spectrophotometry and deals with the importance of spectrophotometry as an analytical tool, its sensitivity, accuracy, precision, applications and limitations. Part B deals with an introduction to nitrogen donor heterocycles and their metal complexes. Metal complexes of S and N donor Schiff base ligands, their reactivity, bonding and applications are discussed. It also provide a brief introduction to Pre ADMET, a web based study of pharmacokinetic properties of new generation compounds. Part C gives a brief introduction to corrosion inhibition studies and application of computational methods in predicting the corrosion inhibition behavior of organic molecules.

Chapter II

This chapter describes a simple and highly sensitive spectrophotometric method for the determination of trace amount of osmium(VIII) using ethylene thiourea (ETU) [Figure 1] as a chromogenic reagent. The method is based on the formation of an instantaneous purple colored complex at room temperature by the reaction of osmium(VIII) with ETU in acidic (pH=1) solution having absorption maximum at 490 nm and is confirmed using derivative spectrophotometry. Linear calibration graphs are obtained for 0.03-3 $\mu\text{g/ml}$ of the analyte. Sandell's sensitivity

($1.13 \times 10^{-3} \mu\text{gcm}^{-2}$), molar absorptivity ($16.87 \times 10^4 \text{ Lmol}^{-1} \text{ cm}^{-1}$), detection limit (0.0291 $\mu\text{g/ml}$) and quantitation limit (0.0833 $\mu\text{g/ml}$) are also calculated. The method is optimized and different analytical parameters are evaluated. The stoichiometry of the complex is found to be 1:3 by Job's method and mole ratio

method. The stoichiometry of the complex is further confirmed by synthesizing the solid compound and characterizing it by various physicochemical methods.

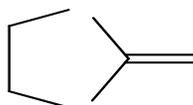


Figure 1 Structure of Ethylene thiourea (ETU)

Chapter III

This chapter describes the synthesis and characterization of a series of transition metal complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Pt(IV) and Pd(II), with three Schiff base ligands (E)-4-(4-methoxybenzylideneamino)-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2H)-one(MMTDT), (E)-4-(2-chlorobenzylideneamino)-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2H)-one(CBMTDT) and (E)-4-(1-(2-hydroxyphenyl)ethylideneamino)-6-methyl-3-thioxo-3,4-dihydro-1,2,4-triazin-5(2H)-one(HEMTDT) [Figure 2]. The nature of ligands, its coordination sites and the structure of the metal complexes are ascertained by elemental analysis, spectral, magnetic susceptibility, thermal and computational studies. The ligands coordinate to the metal ions as bidentate through nitrogen and sulfur atoms. Electronic spectra, magnetic susceptibility measurements and molecular modeling studies support octahedral geometry around the Co(II), Ni(II), Pt(IV) ions, square planar around Cu(II), Pd(II) and tetrahedral geometry around Zn(II), Cd(II) and Hg(II) ions. The presence of coordinated water in Co(II), Ni(II) and Pt(IV) complexes was confirmed by thermal and IR data of the complexes. Fukui indices are used for predicting the electrophilic and nucleophilic centers in the Schiff base using DFT calculations. In addition, total energy, heat of formation and other related parameters were calculated theoretically by semi empirical PM3 method. The 'rule of five' and complementary criteria of pharmacokinetic properties were determined to predict whether these complexes are orally bioavailable or not.

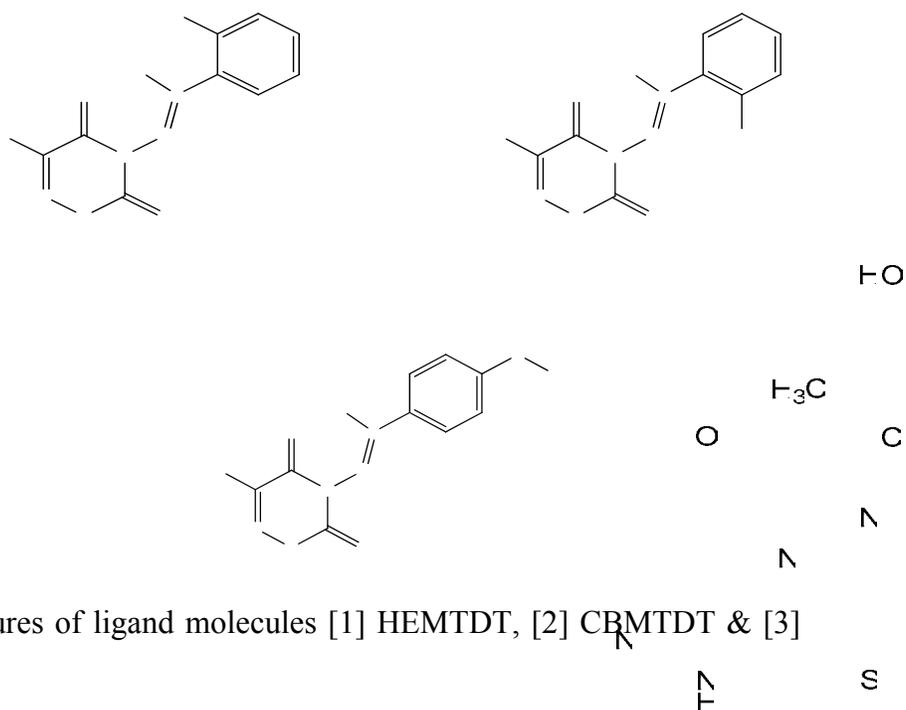


Figure 2. Structures of ligand molecules [1] HEMTDT, [2] CBMTDT & [3] MMTDT

[1]

Chapter IV

This chapter provides an overview of materials and various methods used for corrosion inhibition studies. The features of the experiment, corrosion cell and basic information about various methods are also included in this chapter.

Chapter V

This chapter illustrates the inhibition of copper corrosion in 1 M HNO₃ by (E)-(4-(4-methoxybenzylideneamino)-4H-1, 2, 4-triazole-3, 5-diyl) dimethanol (MBATD) [Figure3]. Analytical techniques like potentiodynamic polarization, electrochemical impedance, adsorption studies, quantum chemical calculations, molecular dynamics methods and surface morphological studies have been used for this. Polarization studies showed that MBATD acts as mixed type inhibitor. Adsorption followed the Langmuir isotherm with negative value of free energy. Various thermodynamic and kinetic parameters were calculated to understand the energy changes associated during the inhibition process. The correlation between inhibitive effect and molecular structure is ascertained by quantum chemical calculations using density functional theory and Fukui functions. The

H₃C

N

molecular dynamics method has also been used to simulate the adsorption of inhibitor molecule on the metal surface.

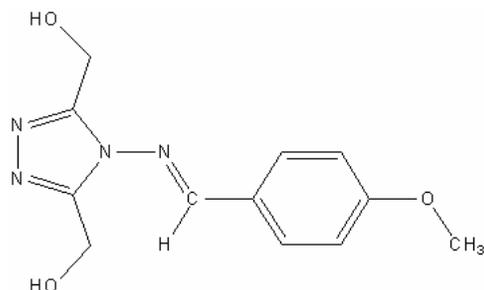


Figure 3. Structure of the inhibitor molecule (MBATD)

Chapter VI

This chapter describes the inhibition effect of ethylene thiourea (ETU) [Figure1] on the corrosion behavior of mild steel in 1N HCl using potentiodynamic polarization, linear polarization resistance (LPR), electrochemical impedance spectroscopy (EIS) and adsorption studies. The effect of inhibitor concentration, temperature, corrosion rate and surface coverage are investigated. The corrosion rate and other parameters are evaluated for different inhibitor concentrations and the probable mechanism is also proposed. The results show that ETU possess excellent inhibiting effect for the corrosion of the MS and the substance acts as a mixed type inhibitor. The high inhibition efficiency of ETU was due to the adsorption of inhibitor molecule on the metal surface. The decrease of surface area available for electrode reactions to take place is due to the formation of a protective film. Activation energies and enthalpies of activation in the presence and absence of ETU were obtained by measuring the temperature dependence of the corrosion current.

Chapter VII

This chapter describes the corrosion inhibition behavior of (E)-4-(4-methoxybenzylideneamino)-4H-1, 2, 4-triazole-3, 5-diol) dimethanol (MBATD)[Figure 3] towards mild steel in 1M HCl at various concentrations (10, 50, 100 & 200 ppm) and temperatures (303,313 & 323 K) using

polarization, electrochemical impedance spectroscopy (EIS), quantum chemical calculations and surface morphological studies. The thermodynamic functions and activation parameters for the adsorption process were calculated and discussed. In addition, an attempt was also made to investigate the adsorption of MBATD molecule on the Fe (110) surface using molecular dynamics simulations.

Chapter VIII

This chapter explains the influence of (E)-4-(2-chlorobenzylideneamino)-6-methyl-3-thioxo-3, 4-dihydro-1,2,4-triazin-5(2H)-one (CBMTDT) [Figure2] towards mild steel corrosion in 1M HCl. The work strategy includes the conventional weight loss method, potentiodynamic polarization studies (Tafel), linear polarization studies (LPR), electrochemical impedance spectroscopy (EIS), adsorption studies and quantum chemical calculations. Results showed that the corrosion rate decreases and inhibition efficiency increases with inhibitor concentration. The results of polarization studies reveal that the additive acts as a mixed type inhibitor. The surface adsorption of the inhibitor molecules decreases the double layer capacitance and increases the polarization resistance. The adsorption process is spontaneous and follows Langmuir adsorption isotherm model. The optimized structure of the inhibitor, energies of LUMO, HOMO and other physical parameters are calculated by computational quantum chemical methods.

Fully unsaturated six-membered nitrogen heterocycles, such as pyridine, pyrazine, pyrimidine and pyridazine, have stable aromatic rings. Oxygen and sulfur analogs are necessarily positively charged, as in the case of 2,4,6-triphenylpyrylium tetrafluoroborate. From heat of combustion measurements, the aromatic stabilization energy of pyridine is 21 kcal/mole. This reagent adds to Schiff bases in the presence of catalysts such as aluminum chloride, zinc iodide or trisacetylacetonate aluminum, to give α -cyano-N-trimethyl-silylamines which are not isolated but are converted by neutral hydrolysis into α -amino nitriles in high yield (80-90%). Alternatively, the cyanotrimethylsilyl adducts can be converted by acidic hydrolysis directly into α -amino acids. Schiff bases lacking hydrogen atoms $\hat{\pm}$ to the carbon-nitrogen double bond react with Grignard and organolithium reagents (alkyl and aryl) analogously to carbonyl compounds to give adducts which on hydro Schiff bases have remarkable complex-forming properties and serve as excellent chelating ligands and have been used as analytical reagents for the spectrophotometric determination of metal ions [14,15]. For the abovementioned properties, and in continuation of our program in synthesis of biologically active heterocyclic compounds [16-26], we decided to use 2,3-diaryloxirane-2,3-dicarbonitrile derivatives 1a-c as a key starting material for the purpose of preparing some novel heterocyclic compounds by reaction with different nitrogen and carbon nucleophiles whereby we synthesized pyrazoles, oxa