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Analysis on Transition Metal Hydrazone Complexes and Coordination of Organometallic Compounds

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Abstract* – *Complexes of transition metal ions with multidentate organic ligands have been the subject of intensive research because they not only have interesting spectral and magnetic properties, but they also possess a diverse spectrum of biological activities. These complexes often possess remarkable and unique spectroscopic, photo physical and electrochemical properties, which may be exploited in sensory and diagnostic applications, and there have been a number of reviews on the utilization of transition metal complexes as ion and molecular sensors. Based on the widely diverse coordination environment of the transition metal complexes, and variation in the identities of the coordinating ligands, synthesis of such complexes with desired molecular geometry can be realized.

Keywords: Chemical, Complexes, Metal

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1. INTRODUCTION

“While the knowledge of coordination chemistry is essential to the understanding of the structural and functional features of various biomolecules like metalloproteinase, its medical application ranges from the development of MRI contrasting agents, radiopharmaceutical chemotherapeutics to the treatment of metal toxicity” (Holm and O′Connor, 1967). Studies on the complex formation of metal ions with a number of biomolecules or biologically active ligands have, in fact, attracted a lot of interest during the last few years because they act as models for the interactions of metallo enzymes (Ettling, 1840) and other complicated proteins (Ettling, 1840). in the biological systems. Thus, the bioinorganic chemistry of nickel is a topic of increasing interest (Hennig, 1971) because the study of the interactions of Ni (II) with nucleotides offers an unique opportunity for understanding various properties of Ni(II) complexes such as the carcinogenicity of some nickel compounds (Hennig, 1971) and the antineoplastic activity recently detected in some nickel complexes (Lindoy, 1971).

Furthermore, development in the field of bioinorganic chemistry has also led to an increased interest in complexes of N, O-donor ligands since it has been recognized that many of these complexes may serve as models for biologically important species having N and O as bonding sites (Calligaris, *et. al.,* 1972). Amino acids and their derivatives are extensively studied as typical N, O-donor ligands. In the N-protected amino acids, the introduction of a substituent such as acetyl, benzoyl or benzoyl carbonyl group directly on the amino group could reduce the ligand field of the in-plane donor thus diminishing the affinity of the amino group for the metal ion and permitting a variety of coordinating type. Aroyl hydrazones derived from amino acids and N-protected amino acids are of special interest in that they not only possess many potential donor sites but there is also possibility of keto- enol tautomeric which may lead to varied bonding and stereo chemical behavior in the complexes in which they act as neutral or mono-negative or even as diamniotic ligands depending on the aroyl substituents and the reaction conditions (Ya. L. *et. al.,* 1972). Their chemistry has also been intensely investigated owing to their cooperative capability (Abstracts of the 29th International Conference on Chemistry, 1992), their pharmacological activity (Calligaris, *et. al.,* 1972) and their use in analytical chemistry as metal extracting agents (Heravi, *et. al.,* 2007). The interest in the study of these compounds arose from their tendency to form chelates with transition metals, lanthanides, and main group metals, and their interactions have served as model systems for the study of many biomolecules and metalloproteinase.

“To understand the complexion reactions of metals, complex formation ability of the ligands and the activities of the complexes formed, it is necessary to have a detailed knowledge about the thermodynamic and solution equilibria involved in these reactions. The extent to which a ligand binds to a metal ion is normally expressed in terms of the stability constants and the information about the concentration of a metal complex in equilibrium mixture can be predicted on the basis of their formation constants in solution. Most of the reported studies on the formation and stability constants of the metal complexes are carried out in aqueous or mixed aqueous organic solvent media. Although there are reports (Abstracts of the 29th International Conference on Chemistry, 1992) on the effect of micelles in the reacting systems of many chemical reactions, not enough attention has been given to understand the role of micelles in the metal complexation reactions. Since micelles represent a multiphase system where a species may be distributed in both the bulk aqueous phase and on the micelle's surface, study of the metal-ligand complexation reactions in micellar media would assume a critical significance in view of the fact that reaction behavior observed at surfactant interfaces are expected to be more representative of many biological reactions than are reactions studied in dilute aqueous solutions" (Maurya and Rajput, 2007).

2. REVIEW OF LITERATURE

"An extensive literature survey reveals that there are a number of reports on the synthesis, characterization and physicochemical properties of a number of metal complexes of various N, O-donor ligands, and mention may be made here of only the transition metal complexes of N, O-donor Schiff bases and determination of stability constants of the transition metal complexes. Although an effort has been made to make an exhaustive survey of the existing literature on the reports on the study of the various physicochemical constants like stability constant and thermodynamic parameters, only the abstracts that appeared in the last ten years in the above fields and relevance to the present work are given below."

Binary and ternary Co(II), Ni(II), Cu(II) and Zn(II) complexes of the type MY and MXY [X = *N*-(2-hydroxy-1-naphthylidene)-2,6-diisopropylaniline and Y = *N*- (2-hydroxybenzylidene)-2,3-dimethylaniline] had been examined pH-metrically (Heravi, *et. al.,* 2007) at 27±0.5oC and 0.1 M ionic strength in 75:25 % (v/v) 1,4-dioxane-water medium. The values of stability constants for binary and ternary systems were calculated.

Tayade *et al* (Ya. L. *et. al.,* 1972). synthesized 2-amino-4-hydroxy-6-methylpyrimidine and 1-(4-hydroxy-6-methyl pyrimidino)-3-phenylthiocarbamide and the interactions of Cu2+, Cd2+, Cr2+ ions with both the ligands were studied at 0.1 M ionic strength in 70 % dioxane-water mixture by Bjerrum method (Abstracts of the 29th International Conference on Chemistry, 1992) as adopted by Calvin and Wilson (Maurya and Rajput, 2007). It is observed that these metal ions would form 1:1 and 1:2 complexes. The data obtained were used to estimate and compare the values of proton-ligand stability constant (pK) and metal-ligand stability constants (log k) and the effect of substituents were studied from estimated data.

Thermodynamic protonation constants of 5-aldehydosalicylic acid-aniline Schiff base, and o-, m-, p-Toluidine Schiff bases with 5-aldehydosalicylic acid were determined (Maurya and Rajput, 2007) by Calvin-Bjerrum pH titration technique (Heravi, *et. al.,* 2007) as used by Irving and Rossotti (Ozmen and Olgun, 2008). The thermodynamic formation constants of the chelates of Cu (II), Co (II), Ni (II), Zn (II), Cd (II) and Mg (II) with these four ligands were determined at four different temperatures in 50% (v/v) water-ethanol mixture; the stabilities of complexes follow the Irving-Williams order (Ozbek, *et. al.,* 2009).

Cr (III), Mn (II), Fe (III), Co (II), Ni (II), Cu (II) and Zn (II) complexes were prepared (Pouralimardan, *et. al.,* 2007) by template reaction of 5-acetyl 2,4-dihydroxyacetophenone (H2-ADA) and ethylenediamine in the presence of metal ions and characterized on the basis of elemental analyses, conductivity, magnetic moments, infrared and electronic spectral data. The Schiff base was reported to bind to metal ions in bis-multidentate ONNO mode leading to two-dimensional Schiff base polymers. All the complexes have been assigned octahedral stereochemistry.

Complexation of Cu(II) ion with dapsone in solution was studied spectrophotometrically (Lindoy, 1971). at absorption maximum of 680 nm at temperatures 250C, 450C and 600C. The stoichiometry of the complex was determined using mole ratio and Job's continuous variation methods. The data showed that Cu(II) and dapsone combined in 1:1 molar ratio at pH 7.4 with ionic strength maintained at O.1 M using KNO3. The stability constants were 0.086 x 103, 0.090 x 103 and 0.137 x 103, 0.142 x 103 at 250C and 450C, respectively.

The complexation equilibria of L-norvaline (Nva) and ferulic acid (FA) were studied (Heravi, *et. al.,* 2007) in aqueous solutions at 298 K and in fixed ionic strength (0.15 mol·dm−3 NaNO3) by means of potentiometry and spectrophotometry techniques. The complexing capacities of Nva and FA with Fe3+, Cr3+ and Cu2+ ions and their overall stability constants in aqueous solutions were obtained by the HYPERQUAD 2008 program (Ozbek, *et. al.,* 2009) from the potentiometric data. The concentration distributions of the various complex specia in solution were evaluated and discussed. The spectroscopic UV−visible measurements were carried out to give qualitative information about the confirmation of the complexes formed in these solutions.

The complex formation between a new Schiff base and Ni2+, Co2+, Cu2+, and Zn2+ ions in ethanol, dimethylformamide (DMF), and acetonitrile (AN) was studied (Naskar, *et. al.,* 2007) spectrophotometric ally using rank annihilation factor analysis (RAFA). According to molar ratio data and Job's plots, the stoichiometry of complexation between the Schiff base and the cations was 1:2, and that between the Schiff base and Cu2+ in all solvents and Zn2+ in AN was 1:1. Formation constants of these complexes were derived using RAFA on spectrophotometric data. The effect of surfactants such as sodium dodecyl sulfate, cetyltrimethylammonium bromide and Triton X-100 on the complex formation constant of Cu2+ with the Schiff base in DMF was investigated.

3. COORDINATION AND ORGANOMETALLIC COMPOUNDS:

"Transition metal complexes act as homogeneous catalysts in many industrially important reactions such as hydrogenation, hydrosilation, hydroformylation, polymerisation, isomerisation, acylation and oxidative hydrolysis of olefins. Binuclear transition metal complexes have also received much attention in recent years as they may serve as model for variety of biological reactions such as oxygen transport, oxygen activation, photosynthesis water reduction, electron transfer process, metal-metal interactions and multi centered catalysis."

"Transition metal ions with different oxidations state have a strong role in redox enzyme systems and may provide the basis of models for active sites. To mention a few, nickel is an essential component in at least 4 types of enzymes viz. urease, carbon monoxide dehydrogenase (CODH) or acetyl coenzyme A synthase, hydrogenase and methyl-S-coenzyme M reductase. Some polydentate Co(II) complexes with ligands capable of intercalation into DNA strands are capable of inducing DNA cleavage under photochemical conditions. Since the recognition of Vitamin B12 and synthesis of cobalmines, responsible for erythrocytes (RBC) formation in human body, there has been much study of model systems. Copper complexes are known to play important role in the active site of many copper proteins in vivo as well as in homogeneous and heterogeneous catalysis for organic chemical reactions. A large body of evidence indicates that copper chelation is an effective method to inhibit tumor growth and copper chelators have become promising agents in the treatment of cancer. It has been found that some copper chelators acquire more effective or novel bioactivity after forming complexes. Recent studies indicated that Cu2+ was critically needed for PDTC induced apoptosis in HL-60 cells and the copper complex of salicylaldehyde benzoylhydrazone (SBH) derivatives showed increased potency of growth inhibition in several cancer cell lines, compared with the metal-free organics. Copper-SBH complexes were significantly more cytotoxic than complexes of other transitional metals (Cu > Ni > Zn > Mn > Fe > Cr > Co) in MOLT-4 cells, an established human T-cell leukaemia cell line. It was noted that SBHs, especially their copper complexes appeared to be unusually potent inhibitors of DNA synthesis and cell growth in a variety of human cancer cell lines, including the human lung epithelial cancer cell line, SKMES-1 and rodent cancer cell lines. A series of, novel salicylaldehyde pyrazole hydrazone (SPH) derivatives were found capable of inhibiting the growth of A549 lung carcinoma cells."

Hydrazones

"The architectural beauty of coordination complexes arises from the interesting ligand systems containing different donor sites. Among the ligand systems, hydrazide and hydrazone occupy special place because complexes of these compounds with transition metals are nowadays extensively used for the treatment of several diseases, in synthetic and analytical chemistry as novel heterogeneous catalysts in oxido-reduction processes and various chemical and photochemical reactions as well as numerous industrial applications of science and technology" (Naskar, *et. al.,* 2007).

4. TRANSITION METAL HYDRAZONE COMPLEXES:

"The coordination chemistry of hydrazones as ligand is an intensive area of study and numerous transition metal complexes of them have been investigated. Earlier, investigations on the hydrazone complexes were focused mainly on the synthesis and structural characterization, but nowadays these metal complexes were reported to serve some applications in various fields like non-linear optics, sensors, medicine" etc.

In bioactivities:

"Metal complexes containing site-specific substructures and multiple reactive sites constitute a group of promising candidates for nuclease activity because of their electronic and structural advantages. Most of the first row transition metals either alone or in their complex form are biologically essential with a number of known bioactivities. Among them, nickel, cobalt and copper are especially notable as they involve in many biological processes. It is well known that cancer is currently the second leading cause of death in industrialized countries, accounting for roughly a quarter of total numbers. Hence, development of new anticancer therapies is one of the fundamental goals in medicinal chemistry. The interactions between bio macromolecules and drugs have attracted special interest among both chemistry and biology researchers recently. DNA is one of the main molecular targets in the design of anticancer compounds and the interaction between nucleic acids and other molecules is a fundamental issue in life science that relates the replication, transcription, mutation of genes and related variations of species in character, origin of some diseases and mechanism of interaction of some DNA-targeted drugs. Further, it has been demonstrated that free radicals can damage proteins, lipids and DNA of bio-tissues leading to increased rates of cancer and fortunately antioxidants can prevent this damage due to their free radical scavenging activity. Hence, it is very important to develop compounds with strong DNA binding, antioxidant and cytotoxic properties for effective cancer therapy. As known well, serum albumins are the class of proteins involved in the transport of metal ions and metal complexes along with drugs through the blood stream. Many drugs, including anticoagulants, tranquilizers, anti-inflammatory and general anaesthetics are transported in the blood via combination with albumin. The nature and magnitude of drug-albumin interaction significantly influence the pharmacokinetics of drugs and thus the binding parameters are useful in studying protein-drug binding as they greatly influence absorption, distribution, and metabolism and excretion properties of typical drugs.

In molecular sensors”

Recently, the development of molecular sensors has attracted lot of research activities for their use in processes that include food, clinical, environmental analysis and analytical applications. It was reported that a potentiometric aluminium sensor based on N,N'-bis(salicylidene)-1,2-cyclohexanediamine as a neutral carrier in poly(vinyl chloride) matrix was successfully applied for direct determination of aluminium (III) in biological, industrial and environmental samples 68 in the pH range of 2.0-9.0. It has been used as an indicator electrode in potentiometric titration of aluminium ion with EDTA. The Schiff base, N,N′,N″,N‴-1,5,8,12-tetraazadodecane-bis (salicylaldiminato), has been used as an ionophore for preparing Mn2+ selective sensorover a number of alkali, alkaline and heavy metal ions for the determination of manganese in various samples by direct potentiometry (Naskar, *et. al.,* 2004).

In non-linear optical devices:

Non-linear optics (NLO) deals with the interactions of applied electromagnetic fields materials to generate new electromagnetic fields, altered in frequency, phase, or other physical properties. Such materials that are able to manipulate photonic signals efficiently are of importance in optical communication, optical computing and dynamic image processing.70-74 In this connection, transition metal complexes have emerged as potential building blocks for nonlinear optical materials due to various excited states present in these systems as well as their ability to tailor metal-ligand interactions. Compared to the more common organic molecules, metal complexes offer a large variety of novel structures, the possibility of enhanced thermal stability and a diversity of tunable electronic behaviours by virtue of the coordinated metal center and hence they may find use as NLO materials with unique magnetic and electrochemical properties.81-83 Investigations on NLO properties of metal complexes are being pursued by several research groups.84-90 Di Bella and co-workers reported that bis(salicylaldiminato) metal Schiff base complexes exhibit good second order NLO properties.

Based on the above facts, studies on the chelating properties of hydrazone ligands and the effect of coordination of them on the composition and geometry of the complexes containing cobalt (II), nickel (II) and copper (I/II) ions were undertaken as the subject of the present work. Additionally, comparison on the biological properties of hydrazone complexes with respect to DNA / BSA interactions, free radical scavenging and cytotoxicity under in vitro conditions have been carried out.

CONCLUSION:

There are reports on the synthetic, magnetic and spectral studies of transition metal complexes of a number of hydrazones in aqueous and organic media. Amidst the abundant literature on the transition metal complexes of various N, O-donor ligands, a considerable number of reports appear on the determination of the stability constants and thermodynamic parameters of the transition metal complexes. However, most of the studies reported were carried out in aqueous and/or mixed solvent media.

There are a few reports on the complexes of N-benzoylglycine hydrazide and its hydrazones with transition metal ions (Mishra, *et. al.,* 2007) and copper ions (Armstrong, *et. al.,* 2003).

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