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BINARY AND TERNARY COMPLEXES OF SOME TRANSITION METAL IONS WITH NITROGEN AND OXYGEN DONOR LIGANDS

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ABSTRACT

Buildings of transition metal ions with multidentate natural ligands have been the subject of escalated examination since they have fascinating ghostly and attractive properties, as well as have an assorted range of organic exercises. These buildings frequently have wonderful and special spectroscopic, photophysical and electrochemical properties which might be abused in tactile and analytic applications and there have been various surveys on the utilization of transition metal edifices as ion and atomic sensors. In view of the generally assorted coordination environment of the transition metal buildings, and variation in the characters of the organizing ligands, amalgamation of such edifices with sought atomic geometry can be figured it out. It is surely understood that few metal chelates have been appeared to hinder tumor development. and

a few medications even show expanded movement when directed as metal edifices. Therefore, the investigation of the coordination of transition metal ions with various sorts of ligands has been opened up by the late advancements in the field of bioinorganic science and medications. The rich differing qualities of transition metal coordination science, consequently, gives energizing prospects to the outline of novel coordination ligands having exceptional structures and important functional attributes. and noteworthy endeavors coordinated toward the configuration of particular designs framed by the self-get together procedures have been completed in various fields of engineered science.. Much of the time, transition metal ions and their buildings assume a focal part in controlling the reactivity and instrument of the chemical reactions of hobby. The remarkable capacity of transition metal ions and their edifices to control the science of natural, modern, and organic procedures has expanded the significance of illuminating their unthinking conduct in straightforward and complex chemical procedures.

INTRODUCTION

While the learning of chemistry is fundamental to the comprehension of the basic and functional components of different biomolecules like metalloproteins, its therapeutic application ranges from the advancement of MRI differentiating specialists, radiopharmaceutical chemotherapeutics to the treatment of metal harmfulness.. Thinks about on the mind boggling formation of metal ions with various biomolecules or organically dynamic ligands have, truth be told, pulled in a considerable measure of enthusiasm amid the most recent couple of years since they go about as models for the interactions of metalloenzymes. and other confused proteins. in the natural frameworks.

Therefore, the bioinorganic science of nickel is a subject of expanding interest in light of the fact that the investigation of the interactions of Ni(II) with nucleotides offers a special open door for comprehension different properties of Ni(II) buildings, for example, the cancer-causing nature of some nickel mixes. and the antineoplastic movement as of late identified in some nickel edifices.

Besides, advancement in the field of bioinorganic science has additionally prompted an expanded enthusiasm for buildings of N, O-contributor ligands since it has been perceived that a hefty portion of these edifices might serve as models for naturally critical species having N and O as holding destinations.. Amino acids and their subordinates are broadly concentrated on as average N, O-contributor ligands. In the N-secured amino acids, the introduction of a substituent, for example, acetyl, benzoyl or benzylo carbonyl gathering straightforwardly on the amino gathering could lessen the ligand field of the in-plane contributor therefore decreasing the liking of the amino gathering for the metal ion and allowing an assortment of planning sort. Aroyl hydrazones got from amino acids and N-secured amino acids are of exceptional enthusiasm for that they have numerous potential contributor locales as well as probability of ketoenol toutomerism which might prompt shifted holding and stereochemical conduct in the buildings in which they go about as nonpartisan or mononegative or even as dianionic ligands relying upon the aroyl substituents and the reaction conditions.. Their science has likewise been seriously examined inferable from their helpful capacity., their pharmacological action. and their utilization in logical science as metal separating specialists.. The enthusiasm for the investigation of these mixes emerged from their inclination to shape chelates with transition metals, lanthanides, and fundamental gathering metals, and their interactions have served as model frameworks for the investigation of numerous biomolecules and metalloproteins. To comprehend the complexation reactions of metals, complex formation capacity of the ligands and the exercises of the edifices shaped, it is important to have a point by point information about the thermodynamic and solution equilibria included in these reactions. The degree to which a ligand ties to a metal ion is regularly communicated regarding the strength constants and the information about the concentration of a metal complex in balance blend can be anticipated on the premise of their formation constants in solution. A large portion of the reported studies on the formation and security constants of the metal edifices are done in watery or blended fluid natural dissolvable media.

Despite the fact that there are reports. on the impact of micelles in the responding frameworks of numerous chemical reactions, insufficient attention has been given to comprehend the part of micelles in the metal complexation reactions. Since micelles speak to a multiphase framework where an animal groups might be dispersed in both the mass fluid stage and on the micelle's surface, investigation of the metal-ligand complexation reactions in micellar media would accept a basic criticalness in perspective of the way that reaction conduct saw at surfactant interfaces are relied upon to be more illustrative of numerous organic reactions than are reactions considered in weaken watery solutions.. A broad writing review uncovers that there are various reports on the union, characterization and physicochemical properties of various metal buildings of different N, O-contributor ligands, and mention might be made here of just the transition metal edifices of N, O-benefactor Schiff bases and determination of solidness constants of the transition metal buildings. In spite of the fact that an exertion has been made to make a comprehensive review of the current writing on the reports on the investigation of the different physicochemical constants like soundness steady and thermodynamic parameters, just the edited compositions that showed up in the most recent ten years in the above fields and pertinence to the present work are given underneath. Parallel and ternary Co(II), Ni(II), Cu(II) and Zn(II) buildings of the sort MY and MXY [X = N-(2-hydroxy-1-naphthylidene)- 2,6-diisopropylaniline and Y = N-(2-hydroxybenzylidene)- 2,3-dimethylaniline] had been analyzed pH-metrically. at 27±0.5 o C and 0.1 M ionic quality in 75:25 % (v/v) 1,4-dioxane-water medium. The estimations of dependability constants for parallel and ternary frameworks were figured.

Thermodynamic protonation constants of 5-aldehydosalicylic corrosive aniline Schiff base, and o-, m-, p-Toluidine Schiff bases with 5-aldehydosalicylic corrosive were resolved. by Calvin-Bjerrum pH titration method. as utilized by Irving and Rossotti.. 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 resolved at four distinct temperatures in half (v/v)water-ethanol blend; the strong qualities of buildings take after the Irving-Williams request.. Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) edifices were readied. by layout reaction of 5-acetyl 2,4-dihydroxyacetophenone (H2-ADA) and ethylenediamine in the vicinity of metal ions and described on the premise of natural investigations, conductivity, attractive minutes, infrared and electronic unearthly information. The Schiff base was accounted for to tie to metal ions in bis-multidentate ONNO mode prompting two dimensional Schiff base polymers. All the edifices have been relegated octahedral stereochemistry. Patil et al. combined a progression of Co(II), Ni(II) and Cu(II) buildings of the sort ML2 with Schiff bases got from methylthiosemicarbazone and 5-formyl-6-hydroxy coumarin/8-formyl-7-Hydroxy-4-methylcoumarin. The edifices were non-electrolytes in nature.

Complexes of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) with 4-[2'-hydroxy salicylidene 5' (2"-thiozlylazo] chlorobenzene were synthesized and characterized. by elemental analysis, molar conductance, magnetic susceptibility, spectral studies, IR, electronic, ESR and X-ray diffraction studies. The metals coordinate with Schiff base nitrogen atom, azo nitrogen atom and phenolic hydroxyl oxygen atom of the ligand. The ONN donor ligand acts as a tridentate ligand in all complexes. The spectral analysis indicated tetrahedral geometry for Co(II), Ni(II), Zn(II) and Cd(II) complexes while distorted tetrahedral geometry for Cu(II) complex. The X-ray powder diffraction of some complexes suggested tetragonal crystal system. The ligand and complexes had been screened for their antimicrobial activity against some bacterial and fungal activity. Stability constants of some metal complexes of 1-Phenyl-2-[2-hydroxy-3- sulfo-5-

nitrophenylazo] butadione-1,3 synthesized from benzoylacetone were determined. by potentiometric and conductometric titrations. The stability of these complexes decreased in the following order: Fe > Cu > UO2 > Ni > Co > Zn > Cd > Mn > Mg > Ca.

Reddy et al. synthesized Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of a dibasic bis-chelating ligand, 5-acetyl 2,4-dihydroxy acetophenone semicarbazone (H2-ADAS) and characterized on the basis of their elemental analyses, conductivity, magnetic moments, IR and electronic spectral data. Metal to ligand ratio in all the chelates had been found to be 1:1. The Schiff base behaves in a dibasic pentadentate manner with OO and ONN donor atoms. All the complexes had been assigned octahedral stereochemistry. The ligand H2-ADAS forms polymeric metal complexes with first row divalent transition metal ions.

Hankare et al. synthesized and characterized Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes of a Schiff base obtained by condensation of 5-(2'-thiazolylazo) salicylaldehyde and p-methoxy aniline by elemental analysis, magnetic susceptibility, molar conductance, IR, electronic spectra, ESR and thermal analysis (TGA). The ONN environment of the metal ion was realized in the complexes by involvement of the -N=N- group in coordination. The analysis of magnetic moment and electronic spectral data indicated tetrahedral geometry for the complexes except Cu(II) complex which had a distorted tetrahedral geometry.

Kabir et al. determined the stability constants (D log K) of the ternary Cu(II) and Ni(II) complexes of folic acid and some amino acids such as tryptophane, tyrosine, dipicolinic acid and adenosine triphosphate by pontentiometric method and their redox behavior had been examined by cyclic voltammetric method. A statistical increased in the value of mixed ligand formation constants was observed by small negative or positive value of _ log K. The pontentiometric and cyclic voltammetric study showed that Ni(II) complexes were more stable than Cu(II) complexes.

Garg et al carried out the chemical-speciation and molecular modelling studies for accessing the interactions of metal ions with some amide containing ligands by using the BEST program. and method of Bjerrum and 32 Calvin. as modified by Irving and Rossoti. has been used to find out the values of stability constants. The order of stability constants is found to be fairly in agreement to Irving-Williams order.. Molecular modelling studies have been carried out to determine the ideal site for metal binding to the ligands PCPAH and PCBAH.

Equilibrium-based computer models on eight Schiff base complex systems, viz. Co(II)/Ni(II)/Cu(II)/Zn(II)-2-pyridinecarboxaldehyde(A)-L-threonine (thr) 37 and L-glutamin (gln) (B) systems demonstrated [122] the formation of Schiff base complexes having the stoichiometry MAB, MA2B and Ma2B2. The Schiff base (AB) binds the metal ion in a tridentate manner. Tetrahedral geometry for CoAB and NiAB, square-planar geometry for CuAB and octahedral geometry for M(AB)2 complexes are indicated. Transition metal complexes of furfurylidene(N-benzoyl)glycyl hydrazone, FBzGH, of the formulae [M(FBzGH)2Cl(H2O)]Cl (M = Mn, Cu, Zn, Cd, Hg), [Co(FBzGH)2]Cl2·H2O and [Ni(FBzGH)2Cl2]·H2O were isolated from acidic solutions and the complexes [M(FBzG)2 (H2O)2] (M = Co, Ni, Cu), from neutral solutions.

Elemental analyses, molar conductances, magnetic susceptibilities, electronic, pH-metric, ESR, IR, and NMR studies had been carried out on these complexes to illuminate the ligational behavior of FBzGH toward the divalent metal ions. Formation constants of the metal chelates were determined pH-metrically in aqueous-dioxane. Bidentate nature of the hydrazone coordinating as a neutral species in the adducts and as a uninegative one in the neutral complexes was suggested. 1H NMR spectra indicated the presence of two different conformers of the ligand at room temperature even after complexation which would coalescent at a temperature higher than 340 K indicating that one of the conformers was stabilized. A highly shielded chemical shift value of 113Cd NMR showed a strongly bound but weakly coordinated Cd2+ ion.

The literature survey reveals the following noteworthy points:

1. There are reports on the synthetic, magnetic and spectral studies of transition metal complexes of a number of hydrazones in aqueous and organic media.
2. 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.
3. There are a few reports on the complexes of N-benzoylglycine hydrazide and its hydrazones with transition metal ions and lanthanide ions.
4. There is no report in the literature till date on the complexation reactions, stability constants and thermodynamic data of the transition metal complexes of Schiff bases derived from N-benzoylglycine hydrazide in aqueous, organic and/or aqueous-micellar media.

It is thereof, synthesized two novel Schiff bases from the condensation of N-benzoylglycine hydrazide with two carbonyl containing compounds, 4-dimethylaminobenzaldehyde and 3-aminoacetophenone, and carried out a detailed study on the interactions of the transition metal ions with the two bases employing potentiometric titration and various physico-chemical techniques. Proton - ligand and metal - ligand formation constants of the bases and their Ni(II), Cu(II) and Cd(II) complexes along with the thermodynamic parameters associated with the protonation and complexation reactions have been evaluated. The Cu(II), Ni(II) and Cd(II) complexes are also isolated and characterized. Studies have also been made on the spectral properties of the complexes.

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