



A Review Of Effect Of Metal Complexation On Biological Activity

¹Hemant Kumar, ²Dr. M. Z. Shahzada

¹Research Scholar, Magadh University, Bodh Gaya

²Associate Professor, Department of Chemistry, K.L.S. College Nawada (M.U. Bodh Gaya)

Abstract : Metal complexes with nitrogenous Schiff bases are becoming increasingly relevant for their biochemical, analytical and antimicrobial activities. On viewing the metallo-elements, there are certain metallo-elements without which the normal functioning of the living organism is inconceivable. Of these metallo-elements, the so called ‘metals of life’, four members form an ‘island’. These are Na, Mg, K and Ca, amongst the transition elements V, Cr, Mn, Fe, Co, Ni, Cu, and Zn. These elements are present in trace or ultra-trace quantities and known to form Schiff base complexes.

Key Words : Metal complexes, Schiff bases

Introduction : It has been found that the activity of the biometals is attained through the formation of complexes with different bio-ligands. Certain drugs play a vital role as bio-ligands in the biological systems. Similarly, nitrogen containing bases such as derivative of pyrrole, pyridine, pyrimidine, pyrazine and purine amines such as histamine, carbohydrates such as glucose, and different vitamins such as ascorbic acid are well recognized-bioligands. The role of metal ions in the virus replication process is extremely important. A virus can penetrate into the host’s cell only when it is mediated by some suitable metal ions. As a matter of fact, for virus replication, copper and zinc are essentially required, hence by increasing or decreasing their concentration, viral growth may be controlled. Interaction of various metal ions with antibiotics may enhance or suppress their antimicrobial activity but usually in many cases, the pharmacological activity of antibiotics, after complexation with metals, is enhanced as compared to that of the free ligands.

Many of the well-known antibiotics, penicillin, streptomycin, bacitracin, tetracycline etc are chelating agents and their action is improved by the presence of small amount of metal ions. In chelates, metal is firmly held by a number of ligand atoms usually nitrogen, oxygen or sulphur



through co-ordinate covalent bonds. Some of the chelates are model analogues of certain metallo-enzymes. Further, some of the chelates develop considerable antimicrobial activity. The biological activity of chelating compounds is enhanced on chelating with a metal atom. The antitumour activity of some Schiff bases has been attributed to their ability to chelate with trace transition metal. Generally, it has been observed that transition metal complexes have greater activity and less toxic effects.

METALLO-ELEMENTS UNDER INVESTIGATION

Copper is a member of the group IB elements along with gold and silver. Thus, although in some ways a typical transition metal, it is distinct in its properties. Copper can exist under normal conditions in four oxidation states 0,1,2,3. The most common oxidation state is +2. The cuprous compounds easily get oxidized to cupric state. Cupric ion (Cu^{+2}) is characterized by $3d^9$ configuration. Its complexes are often distorted resulting in unequal bond lengths, inter bond angles and a large variety of possible geometries. When Cu^{+2} is placed in an octahedral or tetrahedral environment, Jahn-Teller distortion is possible. The extent of Jahn-Teller distortion affects the stereochemistry of the complex. All the octahedral complexes are tetragonally distorted. As the distortion becomes maximum, the configuration becomes square planar.

Complexes of the type M_2CuX_4 are examples of tetrahedral complexes which are distorted [M = Univalent cation, $\text{X} = \text{Cl}^-$ or Br^-]. Distorted tetrahedral and trigonal bipyramidal structures are also reported for Cu^{+2} complexes. Only in few cases, the symmetry is D_{3h} , while in most cases, the structure is distorted. Waters et al studied the absorption spectra of a variety of complexes of copper (II). Almost all complexes were found to be either green or blue. In some cases, the complex was brown or red due to the interference of the charge transfer band in the visible region. $\text{Cu}(\text{II})$ ion subjected to Jahn-Teller distortion is never expected to form a regular octahedral complex. This fact is highly reflected in spectral and magnetic properties. The energy level diagram for ligand fields of D_{4h} symmetry predicts three transitions, $2\text{B}_{1g} \rightarrow 2\text{A}_{1g}$, $2\text{B}_{1g} \rightarrow 2\text{B}_{2g}$ and $2\text{B}_{1g} \rightarrow 2\text{E}_g$. But, due to the overlap of these bands, only one band is observed in a number of cases. The magnetic moments of simple $\text{Cu}(\text{II})$ complexes are generally in the range of 1.8 - 2.20 BM, irrespective of the stereochemistry. Copper (II) forms a number of polynuclear compounds with magnetic anomalies. In these compounds, the magnetic moments indicate



significant interaction between two adjacent copper atoms. As a result, the magnetic moment will be lowered and the value is temperature dependant. Detailed studies were carried out with Copper(II) carboxylates to interpret these magnetic anomalies.

The highest coordination number of nickel is six. The electronic absorption spectra of octahedral complexes of Ni(II) are characterized by three transitions which are due to $3A_{2g} \rightarrow 3T_{2g}$, $3A_{2g} \rightarrow 3T_{1g}(F)$ and $3A_{2g} \rightarrow 3T_{1g}(P)$, all the three being allowed transitions. Octahedral complexes of Ni(II) have two unpaired electrons and show magnetic moments ranging from 2.9 to 3.4 BM, depending on the magnitude of orbital contribution. Square pyramidal and trigonal bipyramidal five coordinate complexes of Ni(II) have been reported with high spin and low spin magnetic moments[59-61]. For a true trigonal bipyramidal structure the symmetry must be D_{3h} , but in many complexes of Ni(II), the symmetry lowers to C_{3v} as is supported by electronic spectra. The stereochemistry of the other five-coordinated complexes which do not contain “tripod” ligands is trigonal bipyramidal. A few square pyramidal complexes are also possible.

Tetrahedral complexes of Ni(II) with stoichiometries $[NiX_4]^{2-}$, $[NiX_3L]^-$, $[NiL_2X_2]$ and $[Ni(L-L)_2]$ (X = halogen, L-L bidentate ligand) are possible. However, strict tetrahedral symmetry is expected only in the complexes $[NiX_4]^{2-}$. In many cases, the dihedral angle differs from 90° , so that the resultant geometry is between tetrahedral and square planar. The extent of distortion will be reflected in the magnetic properties, as tetrahedral complexes are paramagnetic and square planar complexes are diamagnetic. For tetrahedral Ni(II) complexes, the ground state is $3T_1(F)$ and the electronic absorption spectrum is characterized by the transition, $3T_1(F) \rightarrow 3T_1(P)$, which falls in the visible region. A strictly tetrahedral Ni (II) complex should have a magnetic moment of about

Octahedral and tetrahedral complexes differ in their magnetic properties also. For the high spin complexes of Co(II), the ground state of $4T_1g$ provides an unquenched orbital contribution to the magnetic moment. For octahedral complexes, the effective magnetic moments at room temperature are in the range, 4.7-5.2 BM. This value is much higher than the spin only value. For tetrahedral complexes of Cobalt (II), the value of the magnetic moment ranges from 4.3 to 4.7



BM. Low spin Co(II) octahedral complexes are rare. In this case, the electronic configuration is t_{2g}

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