SYNTHESIS AND CHARACTRIES OF SOME METAL COMPLEXES

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Abstract: There are many physical and chemical properties, which may, in principle, be used to detect the formation of complexes in solution and to measure the stability constant of complexes. The excellent monograph on metal ammines by Bjerrum published in 1941. Stimulated investigations on the stepwise equilibrium in complex forming reactions in' solution, Mention must also be' made of the work Leden and Schwarzenbach and their associates who were also pioneers in this field. In studying the formation of complexes in solution.

Keywords: Chemical, metal complexes, Ionization energies, equilibrium

Introduction

The classification of all chemical compounds in to so called simple (atomic) and complex (molecular) compounds was made after the ideas about valence developed compounds. The compounds which did not fit in an usual category of simple compounds were denoted by the term "molecular compounds". In later cases union of entire molecules was involved and these molecules did not under go any significant change structures in the process of union. Literature reveals that although extensively studies have been carried out on formation constants of 3d metal complexes of various oxygen, nitrogen and sulphur donor ligands, but no systematic study on stability constant has been made on the peptides. Which received considerable attention during recent years because of their wide applications in various biological processes. In view of the current biochemical interest, an attempt has been made to study the binary and mixed ligand stability constants of borne bivalent metals. Most of the present day methods for studying ionic equilibria in aqueous solution were introduced before or around 1900. The development however, was slow, perhaps because of the tendency of workers always to strive for equilibrium constants at infinite dilution. The acceleration of the work in this field was started in the last twenty years. The e.m.f. Methods for measuring individual metal ion concentrations was introduced by Nemst and applied by Goodwin for measuring solubility products.

Factors affecting the stabilty of metal complexes

A number of factors affect the stability of metal complexes. Some of these factors depend on the nature of the central ion, nature of the ligand, the medium and the chelate effect.

(A) Nature of the central metal ion

With respect to the nature of the central metal ion, the following factors are important :

(i) Charge and Size

In general, the metal ion with larger charge and smaller size form more stable complexes. A smaller but more highly charged cation permits a more closer approach of the ligands and large electrostatic attraction and thus forming a more stable complex. Stability (or stability constant) increases with decreasing size of the metal ion (r) i.e., K generally varies as 1/r. charge/radius ratio for the central ion called ionic potential or polarizing power of the cation is important. A large value of charge/radius ratio for a central ion means that the central ion will be forming more stable complexes. The ions with high polarazibility give complexes with higher stability constants. Thus, Cu (1) complexes have higher K values than the similar sized Na^+ complexes.

Stabilities of high spin complexes of the ions between Mn (II) and Zn (II) with a given ligand frequently vary in order :-

Mn (II) < Co (II) < Ni (II) < Cu (II) > Zn (II)

This order which is called natural order (sometimes called the Irving Williams order) (85) of stability is consistent with charge -to-radius ratio concept.

Ionization energies or Ionization potential

The electro negativity, covalent nature and ionic radii can all be related to the ionization energies of the atoms. It is found that the stability constants for the metal complexes with a ligand increase with the ionization energies of the metallic species.

Class a and Class b Metal

Chatt and Ahrland have classified the metals into three categories. On the basis of their electron acceptor properties. Class a metals are the hydrogen, the alkali and alkaline earth metals, the elements from Sc to Cr, Al to CI, Zn to Br, etc. Class b metals are Rh, Pd, Ag, Ir, Pt, Au, Hg and borderline metals - from Mn to Cu, TI to Po, Mo, Te, Ru, W, Re, Os, Cd.

Class a .metals . form more stable complexes with ligands having the coordinating atoms from the second period elements (e.g. N,O,F).The most stable complexes of class b metals are formed with ligands like PMe_3, S^{2-}, F, CO, CN etc. for borderline metals, the stability constants do not display either class a or class b behaviour unequally.

According to Bjerrum the formation of a complex in solution proceeds by the stepwise addition of the Hg and to the metal ion. Thus, the formation of the complex MLn (M = central metal ion, L = ligand and n = maximum coordination number of the metal ion M for the ligand L, n varies from one ligand to another for the same metal ion), may be supposed to take place by the following n consecutive steps and equilibrium constants.

$$M + L \xrightarrow{K1} ML, \qquad K1 = \frac{[ML]}{[M][L]}$$

$$ML + L \xrightarrow{K2} ML2, \qquad K2 = \frac{[ML_2]}{[ML][L]}$$

These equilibrium constants, K1, K2 characterises the stability of the complexes are usually called stability constants. The equilibrium constants K1, K2 ... Kn are called stepwise stability constants or stepwise formation constants.

The formation of complex MLn may also be expressed by the following steps and the equilibrium constants

$$M + L \xrightarrow{\square 1} ML, \qquad \square 1 = \frac{[ML]}{[M][L]}$$

$$M+2L \xrightarrow{\square 2} ML2, \qquad \square 2 = \frac{[ML_2]}{[M][L]^2}$$

$$MnL \xrightarrow{\square n} MLn, \qquad \square n = \frac{[ML_n]}{[M][L]^n}$$

The equilibrium constants □□□□□**2,** □**n** are called overall (or cumulative) formation constants or overall (or cumulative) stability constants. □n is termed as n^{th} overall (or cumulative) formation constant or overall (or cumulative) stability constants.

As ligand is added to the solution of metal ion, ML is first formed more rapidly than any other complex in the series. As addition of ligand is continued, the ML2 concentration rises rapidly, while the ML concentration drops, then ML3 becomes dominant and so for the until the highest complex MLn is formed.

APPLICATIONS OF COMPLEX FORMATION EQUILIBRIUM

The development of the chemistry of complex equilibrium initiated research work on the other fields of coordination chemistry. This led to important discoveries on the nature of the chemical bond and on the structure and reactivity of compounds.

Knowledge of the principles of complex equilibria in solution, especially in aqueous solutions are important for a better understanding of numerous analytical applications. Complexation equilibria of transition metal ions with amino acids and small peptides have attracted considerable interest in recent years as many of these offer simple models for the complex metalloenzymes.

Chemistry of complex ions, which contain transition metal as nuclei, has been intensively studied and this is an active area of theoretical and experimental research. Use of complex formation as an analytical tool has provided simple titration method for determining trace - amounts of many polyvalent cations. There has been considerable investigation of equilibria involving reactions of metal ions with molecules of biochemical interest. Complex formation involving ore - forming metals has been recognized as important in geo - chemical ore - deposition.

Knowledge of stability constant value is of considerable importance in analytical chemistry, since these provide information about the concentration of various complexes formed by a metal in specified equilibrium mixtures.

ROLE OF METALS IN BIOLOGICAL PROCESSES

Various biological phenomenon are dependent on the role of metal ions, which themselves constitute many biological materials, or affect the progress of reactions. Kohn reported that drugs like tetracycline and naturally occurring macromolecules, may be linked together by divalent cations, which suggests a mechanism by which tetracycline inhibit the growth of microorganism. Earlier classification of the trace elements into essential, non - essential and toxic groups are neither true nor accurate. All the essential elements become toxic at sufficiently high intakes and the margin between level that are beneficial and those that are harmful may be small. It would thus not be surprising, that trace elements classically regarded as toxic elements were later found to be beneficial or essential.

Considerable attention has been paid to the role of metals in biology and medicines. Among the transition metals, the first row 3d - transition metals are mostly present in our body. The metals ions Cu (II), UO2 (II), Ni (II), Co (II), Zn (II), and Cd (II). Selected for the present study, playa vital role in a number of biological processes. These metals are known as essential and trace metals whose presence either in small or large amount is essential for our life processes.

The last decade has been significant advances in the area of precise metabolic roles of the trace elements. It seems established that metal ions function in catalysis, synthesis and stabilization of the structure of proteins and transport. It should be appreciated that the physico - chemical properties of many of the metals, which are essential to the function of metalloenzymes, i.e. mostly those of the first transition series, are capable of probing their environments.

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