Comprehensive Review of The Stability Behaviour of Metal Complexes

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Asma Parween
Mukhtar Shaikh

Abstract

The stability of metal complexes plays a crucial role in understanding their chemical reactivity, structural characteristics and functional applications in coordination chemistry, catalysis and bioinorganic systems. This review presents an overview of the key factors influencing complex stability, including the nature of the metal ion, the type of ligand, solvent effects and thermodynamic as well as kinetic considerations. The discussion also highlights methods used for determining stability constants and examines the impact of electronic configuration and chelation on overall stability.

Keywords: *Coordination compounds, ligand, metal complexes, stability of metal complexes.*

1. Introduction

The stability constant for the formation of metal complexes serves as a measure of the interaction strength between ligands. This process results in the formation of two types of metal complexes: supramolecular complexes, also referred to as host-guest complexes and anion-containing complexes. In solution, it provides and calculate the necessary information regarding the concentration of metal complexes. Characteristics such as solubility, light absorption, conductance, partitioning behaviour and chemical reactivity distinguish these complexes from their individual components. Various numerical and graphical methods are employed to determine the equilibrium constants. This determination is based on a specific

Asma Parween
Department of Chemistry, New Arts, Commerce and Science College, Ahmed Nagar, Maharashtra., *Email: asmaparween219@gmail.com*
Mukhtar Shaikh
Department of Chemistry, New Arts, Commerce and Science College, Ahmed Nagar, Maharashtra.
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quantity known as the complex formation function. During the displacement process that occurs during metal complex formation, certain ions are removed, leading to the establishment of bonds between metal ions and ligands. This phenomenon may be attributed to the displacement of a proton from a ligand species or ions or molecules, which results in a decrease in the pH values of the solution. A technique for calculating the stability constant, known as the potentiometric technique, was developed by Irving and Rossotti [1, 2].

To find out the stability constant, Bjerrum employed a straightforward approach known as the metal salt solubility method. In contrast, for the investigation of a broader range of polycarboxylic acid-, oxime and phenol-containing metal complexes, Martel and Calvin utilized the potentiometric technique to compute the stability constant. Additionally, uncharged ligands were also analysed, with their stability constant calculations being influenced by the constraints associated with the ligand solubility method. A comparison is made between the limitations of the metal salt solubility method and the outcomes derived from solubility methods. Examples of metal-ligand bonding include M-L, MLM, and (M_3) L. A common characteristic among all these types of metal complexes is the presence of a single ligand [1, 3].

The design of ligands for the formation of metal complexes plays a important role in catalysis, materials synthesis, photochemistry and biological systems. This process relies on the overlapping of s, d, and f block orbitals, with elements exhibiting distinct characteristics. Among these, d-block metals are more prevalent due to their variable oxidation states and low-lying orbitals. The chelate and macrocyclic effects serve as factors for assessing the stability of metal complexes. The size of the chelate rings formed by open-chained polyamine ligands influences the stability of ions, with stability decreasing as the ring size increases from 5 to 6 members. A metal complex with a cyclic polydentate ligand demonstrates greater thermodynamic stability compared to one with a non-cyclic ligand [4, 5]. Certain inorganic elements involved in metal complex formation, such as the dioxygen molecule O_2, which interacts with transition metals, can undergo reduction of its single or double bonds. Enzymatic catalysts, resembling proteins that are linked through peptide bonds, function as a medium within the solvent. This interaction diminishes ionic attraction and repulsive forces, facilitating the formation of a protein complex [6, 7]. This review is focussing the characteristics of metal complexes and factors affecting on the stability of metal complexes.

2. Materials and Methods

A total of nine electronic databases were searched from 2011 to 2024, without any language restrictions. These databases include PubMed, Science Direct, Scopus,

Web of Science, Springer Link, Sci Finder and Google Scholar. The keywords utilized in the search incorporate "Metal complex and Ligand", "Metal complex and Stability", among others. This review analyses and summarizes all eligible studies.

3. Characteristics of Metal Complexes and Metal-Based Compounds

Metal complexes and metal-based compounds have the capacity to coordinate with ligands in a three-dimensional arrangement, thus enabling the functionalization of groups that can be tailored to specific molecular targets [8].

3.1 Structure and Bonding

Metal complexes have the ability to aggregate into a diverse array of coordination geometries, resulting in unique shapes. The bond length, bond angle, and coordination site differ based on the specific metal and its oxidation state. Furthermore, metal-based complexes can undergo structural modifications to form various distinct molecular species, which provide a broad range of coordination numbers and geometries [8,9].

3.2 Charge Variation

In a solution of water, metal ions are present as species with a positive charge. Based on the current coordination environment, the charge may be altered to produce species that can be cationic, anionic or neutral. Most significantly, they create positively charged ions in aqueous solution that have the ability to bind to negatively charged biological molecules [10].

3.3 Metal-Ligand Interaction

Various types of metal–ligand interactions are present; nevertheless, these interactions typically result in the creation of complexes that differ from those formed by individual ligands or metals. The thermodynamic and kinetic characteristics of metal–ligand interactions affect ligand exchange reactions. The capacity of metals to participate in these reactions provides numerous benefits, allowing metals to engage and coordinate with biological molecules [11].

3.4 Redox Activity

Numerous transition metals frequently engage in oxidation and reduction reactions. The oxidation state of these metals is a crucial factor in the formulation of coordination compounds. In biochemical redox catalysis, metal ions typically function to activate coordinated substrates and to take part in redox-active sites for charge accumulation [12,13].

4. The Factors that Affect the Stability of Complexes

4.1 Ligand Factor

4.1.1 Size and Charge effect

If a ligand is small, it can approach the metal ion more closely, resulting in

the formation of a stable bond. Likewise, a ligand with a high charge would also establish a strong bond with the metal. Therefore, the combination of a high charge and small size of a ligand contributes to the creation of stable complexes. For instance, the stability of complexes formed between a specific metal ion and halide ions acting as ligands follows this order: $F^- > Cl^- > Br^- > I^-$. This sequence is relevant for class A metals. Conversely, when class B metals such as Pd, Ag, Pt, and Hg are involved, the order is inverted; for class B metals, the sequence becomes $F^- < Cl^- < Br^- < I^-$ [13].

4.1.2 Chelate effect

A chelating ligand is considered symmetrical when both coordinating atoms are identical. Conversely, if the coordinating atoms differ, it is classified as unsymmetrical. All varieties of bi-dentate, tri-dentate, and poly-dentate ligands can function as chelating ligands. The presence of a chelating ligand significantly enhances the stability of complexes, a phenomenon referred to as the chelate effect. The stability of a complex increases with the number of rings it contains. Chelating ligands form more stable complexes compared to non-chelating ligands, which can be easily understood through thermodynamic principles. A high stability constant K is associated with a large negative enthalpy and positive entropy changes [13]. For instance, in the reaction: $[M(H_2O)_6]^{+2} + en \rightarrow [M(H_2O)_4en]^{2+} + 2H_2O$, two water molecules are substituted by the bi-dentate ligand. This substitution results in an increase in the number of particles within the system, thereby enhancing its disorder and entropy. Consequently, $[M(H_2O)_4en]^{2+}$ exhibits greater stability than $[M(H_2O)_6]^{2+}$. This observation reinforces the notion that the stability of complexes is positively correlated with an increase in entropy [13].

The greater the number of chelate rings in a complex, the higher its stability. Chelates featuring five-membered rings, which include the metal atom, demonstrate enhanced stability when they lack double bonds and the ligands are saturated. In contrast, chelates with six-membered rings exhibit greater stability when the ligands possess conjugated double bonds, such as in acetylacetanato complexes [13].

4.1.3 Steric effect

When a large group is either connected to or located close to a donor atom of a ligand, a repulsive force arises between the donor atom of the ligand and the large group. This mutual repulsion diminishes the strength of the metal-ligand bond, resulting in a less stable complex. The influence of a bulky group on the stability of a complex is typically referred to as steric hindrance [14].

4.1.4 Basicity of ligand

The simpler the ligand, the more readily it can donate electron pairs to the central ion, thereby facilitating the formation of more stable complexes. Ligands that strongly bind H+ create stable complexes with metal ions. Consequently, F^- is expected to form more stable complexes than Cl^-, Br^-, or I^-, and NH_3 is anticipated to be a superior ligand compared to H_2O, which in turn is better than HF. This behaviour is noted for alkali metals, alkaline earth metals, and other electropositive metals, including the first row of transition elements [14].

4.2 Metal Factors

4.2.1 Charge and size of metal ion

For a specific ligand, the stability of complexes formed by metallic ions with identical charges diminishes as the size of the central metal ion increases. Consequently, the stability of complexes formed by cations within the same group and possessing the same charge decreases as one moves from the top to the bottom of the group, due to the increasing size of the metallic cations in that order. Additionally, for a particular ligand, the stability of complexes involving metallic ions that are nearly the same size but have varying charges decreases as the charge on them decreases [15].

4.2.2 Class a and class b metals-Ahrland and chatt classification

Chatt and Ahrland have categorized metals into three distinct groups: class a, class b, and borderline, based on their electron-acceptor characteristics. This classification is detailed below.

(a) Class a metals include H, the alkali and alkaline earth metals, as well as the elements Sc, Cr, Al, Cl, Zn, Br, In, Sn, Sb, and I, along with the lanthanides and actinides.

(b) Class b metals consist of Rh, Pd, Ag, Ir, Pt, Au and Hg.

(c) Borderline metals are represented by the elements Mn, Cu, Ti, Po, Mo, Te, Ru, W, Re, Os and Cd.

Class metals tend to form more stable complexes with ligands that have coordinating atoms from the second period elements (e.g., N, O, F) compared to analogous ligands where the donor atom is from the third or later periods (e.g., P, S, Cl). In contrast, class b metals exhibit the opposite trend in relative stabilities. When the ligand features heavier donor atoms, the stability order for class a and b metals is defined as follows.

Stability order for class a metals: $F^- > Cl^- > Br^- > I^-$

Stability order for class b metals: $F^- < Cl^- < Br^- < I^-$

Class b metals are distinguished by the presence of several d-electrons beyond an inert gas core. These d-electrons participate in forming ð-bonds with ligand atoms. It is posited that the stability of class b metal complexes arises from a covalent contribution to the metal-ligand bond and the transfer of electron density from the metal to the ligand through ð-bonding. The most stable complexes of class b metals are formed with ligands such as PMe_3, S_2^{-}, and I^{-}, which possess vacant d-orbitals, or with CO and CN^{-}, which have low-energy vacant molecular orbitals[15].

4.3 CFT and Irvin-Williams stability order

The Irving-Williams Series pertains to the relative stabilities of complexes formed by metal ions. For high-spin complexes involving the divalent ions of first-row transition metals, the stability constant for complex formation adheres to the following order:

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

This sequence has been observed to be consistent across a diverse range of ligands. It is anticipated that the ionic radius will consistently decrease from Mn^{2+} to Zn^{2+}. This trend aligns with the normal periodic behaviour and accounts for the overall increase in stability. The Crystal Field Stabilization Energy (CFSE) rises from zero for manganese(II) to a peak at nickel(II), thereby enhancing the stability of the complexes. The CFSE for zinc(II) remains at zero.

Despite the CFSE of copper(II) being lower than that of nickel(II), octahedral copper(II) complexes experience the Jahn-Teller effect, which provides an additional layer of stability.

Crystal Field Theory posits that a purely electrostatic interaction exists between the central metal ion and the ligands. This implies that the stability of the complexes should correlate with the ionic potential, defined as the charge to radius ratio. In the context of the Irving-Williams series, the trend is derived from high-spin M(II) ions, necessitating consideration of how the ionic radii fluctuate across the d-block.

For high-spin octahedral complexes, it is crucial to account for the impact of the crystal field on the degeneracy of the d-orbitals. In this scenario, the d-electrons will first occupy the lower t_2g orbitals before filling the eg orbitals, as the t_2g subset is oriented between the incoming ligands while the eg subset points directly at the incoming ligands, resulting in maximum repulsion.

For the series from Mn(II) to Zn(II), the anticipated crystal field (q/r) trend would be: Mn(II) < Fe(II) < Co(II) < Ni(II) > Cu(II) > Zn(II).

With the exception of the position of Cu(II), this aligns with the Irving-Williams series. The inconsistency is again explained by the tendency of copper(II) complexes to exhibit distortion [16].

5. Conclusion

The formation constant of metal complexes is influenced by their structure, bonding characteristics and the structure of ligands. The stability of these complexes is related to the size and charge of the ions, in accordance with the hard and soft acid-base theory. Complexes are frequently formed using ligands, drugs and nucleic acids. Metal ions have significant biological roles within living systems.

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