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Study of stability of metal complexes with reference to the nature of metal ion and ligand and factors affecting the stability

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Abstract : The stability of compounds means in a most general sense, the compounds exist under suitable conditions may be stored for a long period of time. However when the formation of complexes in solution is studied, two types of stabilities, thermodynamic stability and kinetic stability are considered. In the language of thermodynamics, the equilibrium constants of a reaction are the measure of the heat released in the reaction and entropy change during reaction. The greater amount of heat evolved in the reaction, the most stable are the reaction products. Secondly, greater the increase in entropy during the reaction, greater is the stability of products. The kinetic stability of complexes refers to the sped with which transformation leading to the attainment of equilibrium will occur.

The factors that affect the stability of complexes.

a. Ligand factors

i. Size and charge of ligand.

If a ligand is small, it can approach the metal ion more closely forming a stable bond. Similarly, a highly charged ligand would also form a strong bond with the metal. Thus the high charge and small size of a ligand leads to the formation of stable complexes. For example the stability of the complexes of a given metal ion with halide ions used as ligands is in the order; $F^- > C1^- > Br^- > I^-$. This order is applicable for class a metals. When class b metals such as Pd, Ag, Pt, Hg etc are used the order is reversed that is for class b metals the order is $F^- < C1^- < Br^- < I^-$.

ii. Chelate effect

A chelating ligand is symmetrical if the two coordinating atoms are the same. In case the coordinating atoms are different it is unsymmetrical. All types of bi-dentate, tri-dentate and poly-dentate ligands can act as chelating ligands.

The stability of complexes is greatly increased by chelating ligand. This is known as chelate effect. The more the rings present in a complex the more is the stability it acquires. Chelating ligands forms more stable complexes than does non chelating ligands. This can be readily explained in terms of thermodynamic factors. Large value of stability constant K are favored by large negative enthalpy and positive entropy changes.

For example, in the reaction: $[M(H_2O)_6]^{2+} + en \rightarrow [M(H_2O)_4en]^{2+} + 2H_2O$ Two H_2O are replaced by the bi-dentate en ligand. This process increases the number of particles in the system and hence its disorder and entropy. Thus, $[M(H_2O)_4en]^{2+}$is more stable than $[M(H_2O)_6]^{2+}$.
This supports the fact that the stability of complexes increases with the increase of entropy.

Larger the number of the chelate rings in a complex, the greater is its stability. Chelates with 5 membered rings including the metal atom are more stable if they do not contain double bonds and the ligands are saturated. On the other hand, chelates with six membered rings are more stable if the ligands contain conjugate double bonds. eg: acetylacetanato complexes.

iii. Steric effect

When a bulky group is either attached to or is present near a donor atom of a ligand, repulsion between the donor atom of the ligand and the bulky group is produced and this mutual repulsion weakens the metal-ligand bonding and hence makes the complex less stable. The effect of the presence of bulky group on the stability of a complex is commonly called steric hindrance.

iv. basicity of ligand

The more basic is the ligand, more easily it can donate electron pairs to the central ion and hence more easily it can form complexes of greater stability. The ligands that bind H^+ firmly form stable complexes with metal ions. Thus F^- should form more stable complexes than Cl^-, Br^- or I^- and NH_3 should be better ligand than H_2O which in turn should be better than HF. This behavoiur is observed for alkali, alkaline earth and other electropositive metals like the first row transition elements.

b. Metal factors

i. Charge and size of metal ion.

For a given ligand, the stability of complexes of metallic ions having the same charge on them decreases with the increase of the size of the central metal ion. Thus the stability of complexes given by the cations belonging to the same group and having the same charge decrease as we proceed from top to bottom in the group, since the size of the metallic cations increases in the same order. Also for a given ligand, the stability of the complexes of the metallic ions having almost the same size but different charges on them decreases with the decrease of the charge on them.

ii. Class a and class b metals-Ahrland and chatt classification.

Chatt and Ahrland have classified the metals into three categories: a, b and borderline, on the basis of their electron-acceptor properties. This classification is shown below.

(a) Class a metals: H, the alkali and alkaline earth metals, the elements Sc, Cr, Al, Cl, Zn, Br, In, Sn, Sb and I, the lanthanides and actinides.
(b) Class b metals: Rh, Pd, Ag, Ir, Pt, Au and Hg.
(c) Borderline metals: the elements Mn, Cu, Ti, Po, Mo, Te, Ru, W, Re, Os and Cd.

Class a metals form more stable complexes with ligands having the coordinating atoms from the second period elements (e.g., N, O, F) than those of an analogous ligand in which the donor atom is from third or later period (e.g, P, S, Cl). Class b metals have the relative stabilities reversed. If the ligand contains the heavier donor atoms, class a and b metals are characterized by the stability order.

Class a metals stability order: $F^- > C1^- > Br^- > I^-$
Class b metals stability order: $F^- < C1^- < Br^- < I^-$

Class b metals are characterized by the presence of a number of d-electrons beyond an inert gas core. These d-electrons are used to form π-bond with ligand atoms. It is believed that the stability of the complexes of class b metals results from covalent contribution to metal-ligand bond and from the transfer of electron density from the metal to the ligand via π-bonding. The most stable complexes of class b metals are formed with ligands like PMe_3, S^{2-} and I^- which have vacant d-orbitals or like CO, CN^- which have vacant molecular orbitals of low energy.

iii. CFT and Irvin-Williams stability order

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

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

This order was found to hold for a wide variety of ligands

The ionic radius is expected to decrease regularly for Mn^{2+} to Zn^{2+}. This is the normal periodic trend and would account for the general increase in stability.

The Crystal Field Stabilization Energy (CFSE) increases from zero for manganese(II) to a maximum at nickel(II). This makes the complexes increasingly stable. CFSE for zinc(II) is zero.

Although the CFSE of copper(II) is less than that of nickel(II), octahedral copper(II) complexes are subject to the Jahn-Teller effect, which affords a complex extra stability.

Crystal Field Theory is based on the idea that a purely electrostatic interaction exists between the central metal ion and the ligands. This suggests that the stability of the complexes should be related to the ionic potential; that is, the charge to radius ratio. In the Irving-Williams series, the trend is based on high-spin M(II) ions, so what needs to be considered is how the ionic radii vary across the d-block.

For high-spin octahedral complexes it is essential to consider the effect of the removal of the degeneracy of the d-orbitals by the crystal field. Here the d-electrons will initially add to the lower t_{2g} orbitals before filling the e_g orbitals since for octahedral complexes, the t_{2g} subset are directed in between the incoming ligands whilst the e_g subset are directed towards the incoming ligands and cause maximum repulsion.

For the sequence Mn(II) to Zn(II), the crystal field (q/r) trend expected would be:

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

Apart from the position of Cu(II), this corresponds to the Irving-Williams series. The discrepancy is once again accounted for by the fact that copper(II) complexes are often distorted or not octahedral at all. When this is taken into consideration, it is seen that the Irving-Williams series can be explained quite well using Crystal Field Theory.

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