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Department of Chemistry

L.S COLLEGE MUZAFFARPUR

B. R. A. BIHAR UNIVERSITY

Dr. Priyanka

TOPIC:- **THE COMPLEXES OF THE FIRST TRANSITION SERIES ELEMENTS, THEIR COORDINATION NUMBER AND GEOMETRY**

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The elements of first transition (3d) series fulfill all conditions of complex formation and thus are most suitable for this purpose. The general representation for the complexes is as follows:

$[M \leftarrow L_n]^{x\pm}$ where n represents the number of lone pairs accepted by the central metal atom/ion from the ligands (L) and x is the charge on the metal complex which may be positive or negative or even zero in neutral complexes. All the elements of this series form complexes with a variety of ligands, e.g. $[CrCl_2(H_2O)_4]^+$, $[Fe(CN)_6]^{3-}$, $[Ni(NH_3)_6]^{2+}$, $[Co(H_2O)_6]^{2+}$, $[Co(NH_3)_3(SCN)_3]$, $[Cu(NH_3)_4]^{2+}$, $[Ag(NH_3)_2]^+$ etc. The elements of this series form stable complexes with N, O, and halogen donor ligands.

Coordination Number (CN)

The number of ligands (monodentate only) directly attached to the central metal atom / ion or more appropriately the number of lone pairs of electrons accepted by the central metal atom / ion from the ligands (mono as well as polydentate) in the process of the formation of the complexes (molecules or ions), is known as the coordination number (C.N.) of the metal. In the above examples, the C.N. of Ag^+ ion is 2, that of Cu^{2+} ion is 4, for Cr^{3+}, Ni^{2+}, Co^{3+}, Co^{2+} and Fe^{3+} ions it is 6. The central metal atom / ion and attached ligands are kept within the square brackets called coordination sphere. With the polydentate ligands the metal atom / ions form ring type complexes known as **chelates** (meaning claw).

Geometry of the Complexes

The coordination number of the central metal atom/ion of the complex is intimately related with its geometry. The relationship may be shown as follows:

C.N. Geometry of the complex

2 Linear: Cu^+ and Ag^+ complexes, e.g. $[Ag(NH_3)_2]^+$

4 Tetrahedral: Mn^{2+}, Co^{2+}, Fe^{2+}, Ni^{2+}, Cu^{2+} complexes with weak ligands *viz*. H_2O, Cl^-, Br^-, I^- etc., e.g. $[MnCl_4]^{2-}$, $[MnBr_4]^{2-}$, $[NiCl_4]^{2-}$, $[CuCl_4]^{2-}$, $[FeCl_4]^{2-}$ etc.

Square planar: Ni^{2+}, Cu^{2+} complexes with strong ligands viz. CN^-, NH_3, en, dmg etc., e.g. $[Ni(dmg)_2]$, $[Cu(en)_2]^{2+}$, $[Cu(NH_3)_4]^{2+}$, $[Ni(CN)_4]^{2-}$ etc.

6 Octahedral: Cr^{2+}, Cr^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+},Co^{2+}, Co^{3+}, Ni^{2+} complexes with weak and strong field ligands, e.g. $[Cr(H_2O)_6]^{3+}$, $[Mn(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$, $[Co(NH_3)_6]^{3+}$, $[Co(en)_3]^{3+}$ etc.

It may be recalled that octahedral complexes of the metal ions with weak field ligands are outer orbital (also called high spin) complexes involving sp^3d^2 hybridisation and those with strong field ligands are inner orbital (also known as low spin) complexes, the central ion undergoing d^2sp^3 hybridisation.

SUMMARY

In contrast to main group elements, the last electron in the atoms of d-block elements enters the (n-1)d-subshell which influences the characteristics and periodicity in properties of transition elements. Hence, the text material of this unit is related with characteristic properties in general of d-block elements such as their electronic configuration, variable oxidation states, complex formation tendency, magnetic properties, formation of coloured ions / compounds, catalytic activity, formation of interstial and non-stoichiometric compounds, alloy formation, metallic character, melting and boiling points, atomic and ionic radii, ionization energies, reactivity, standard electrode (reduction) potential and reducing properties. The above properties have also been discussed for the elements of the first transition (3d) series in brief giving examples where ever possible. A brief but concrete account of binary compounds of elements of 3d-series along with relative stability of their oxidation states, their complexes, coordination number and geometry of the complexes has also been given.