

Transition Metals

classmate

Date _____

Page 1

Introduction:

Those elements in which the last electron enter the $(n-1)d$ orbital are called d-block elements. Transition elements have general characteristics properties intermediate between the elements of s-block and p-block elements of the periodic table. Transition elements are those elements that have partially filled d-subshells in their elemental or common oxidation states. Although three atoms (Zn, Cd and Hg) have completely filled d-subshell in their elemental and common oxidation state.

Characteristics of transition metals:

1. All the transition elements are metals. Transition metals are hard, malleable and ductile due to presence of strong metallic bonds.
2. Transition metals usually have very high value of melting and boiling points due to presence of strong metallic bonds.

3. Many compounds of transition elements are coloured in contrasts to those of s and p block elements.
4. They exhibit variable oxidation state except zinc.
5. Most of the metals have great tendency to form complex compounds.
6. Most of them are paramagnetic in nature.
7. They exhibit catalytic property for hydrogenation, oxidation, dehydration, etc.
8. They form alloys with each other due to their comparable size.
9. Their general electronic configuration is $(n-1)d^{1-10} ns^{1-2}$.

Oxidation state of transition metals:

Most of the transition elements show variable oxidation states in their compounds which are related to their electronic configuration. The outermost electronic configuration of the transition metals is $(n-1)d^{1-10} ns^{1-2}$. Since the energy levels of $(n-1)d$ and ns orbitals are quite close to each other, hence both the $(n-1)d$ and ns orbitals are available for bonding purposes. Therefore the number of oxidation states shown by these metals depend upon the number of d -electrons and s -electrons they have.

The study of common oxidation states gives the following conclusion:

1. The variable oxidation state shown by the transition metals are due to outer ns and inner $(n-1)d$ electrons in bonding.

2. The most common oxidation state shown by the metals of first transition series is +2, except Sc. This oxidation state arises from the loss of two 4s electrons. This means that after Sc, d-orbitals become more stable than the s-orbital.
3. The highest oxidation state shown by any transition metal is +8. It is shown by ruthenium (Ru) and osmium (Os).
4. The transition metals in the +2 and +3 oxidation states mostly form ionic bonds. In compounds of the higher oxidation states, the bonds are essentially covalent. For example, in permanganate ion (MnO_4^-), all bonds formed between Mn and oxygen are covalent.
5. Oxidation state increases on moving down the group. For example, Fe shows the common oxidation state of +2 and +3 but Ru and Os in the

same group form compounds in the $+4$, $+6$ and $+8$ oxidation state.

6. Transition metal also form compounds in low oxidation states such as 0 and $+1$. For example, Ni in $\text{Ni}(\text{CO})_4$ has 0 oxidation state.

Complex ions and metal complexes:

Transition metals are well known for complex compound formation. These metals and their ions show a strong tendency for complex formation. The tendency of transition metals to form complexes is due to two factors:—

1. These ions are very small in size and therefore has high positive charge density which facilitates acceptance of lone pair of electrons from certain molecule (CO , NO , NH_3 , H_2O , etc) or with ions (F^- , Cl^- , CN^- , etc) called ligands.

2. They have vacant orbitals and these orbitals accept lone pairs of electrons donated by ligands to form coordinate covalent bonds.

Shapes of complex ions:

Complex ions have a definite geometrical shape. It is due to that the bond between central metal and ligand is directional in nature. Transition metals can have any of four possible ion complex shapes. ~~Five~~ linear, square planar, tetrahedral and octahedral.

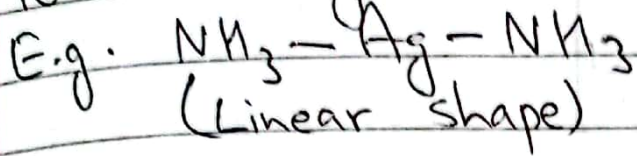
The shape of the complex ion depends upon:-

- (i) Number of ligands (coordination number)
- (ii) Types of hybridization

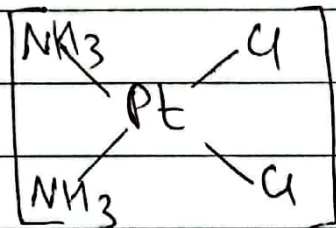
The four possible shapes of complex ions are:-

1. **Linear**: The complex ion in which central metal ion is forming two coordinate covalent bonds or attached

to two ligands has linear geometry.

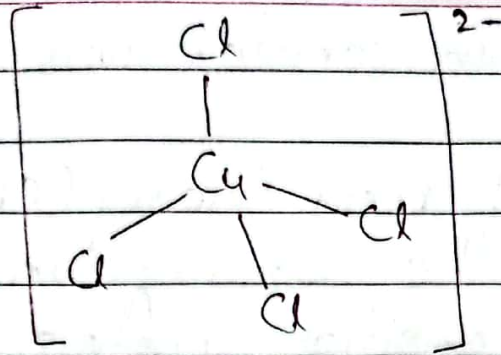


2. Square planar: The complex ion in which central metal ion is forming four coordinate covalent bonds or attached to four ligands, among which two ligands are pointing up and two ligands are pointing down has square planar geometry. E.g. $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$.



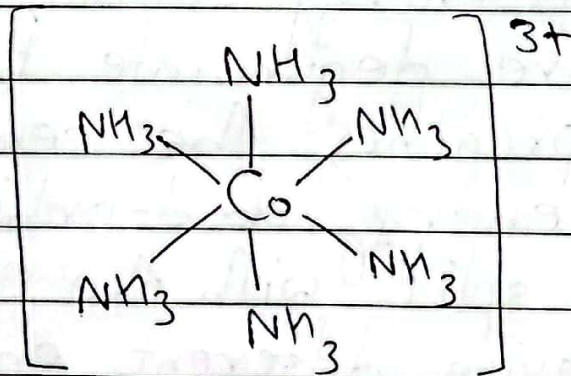
Dichloro diamine platinum (II)

3. Tetrahedral: The complex ion in which central metal ion is forming four coordinate covalent bonds or attached to four ligands, among which one ligand is pointing up, one ligand is pointing down and two are pointing front and back has tetrahedral geometry. E.g. $[\text{CuCl}_4]^{2-}$



Tetrachloro copper(II) ion

4. Octahedral: The complex ion in which central metal ion is forming six coordinate covalent bonds or attached to six ligands, among which four ligands are in one plane, one above the plane and one below the plane has octahedral geometry. E.g. $[\text{Co}(\text{NH}_3)_6]^{3+}$

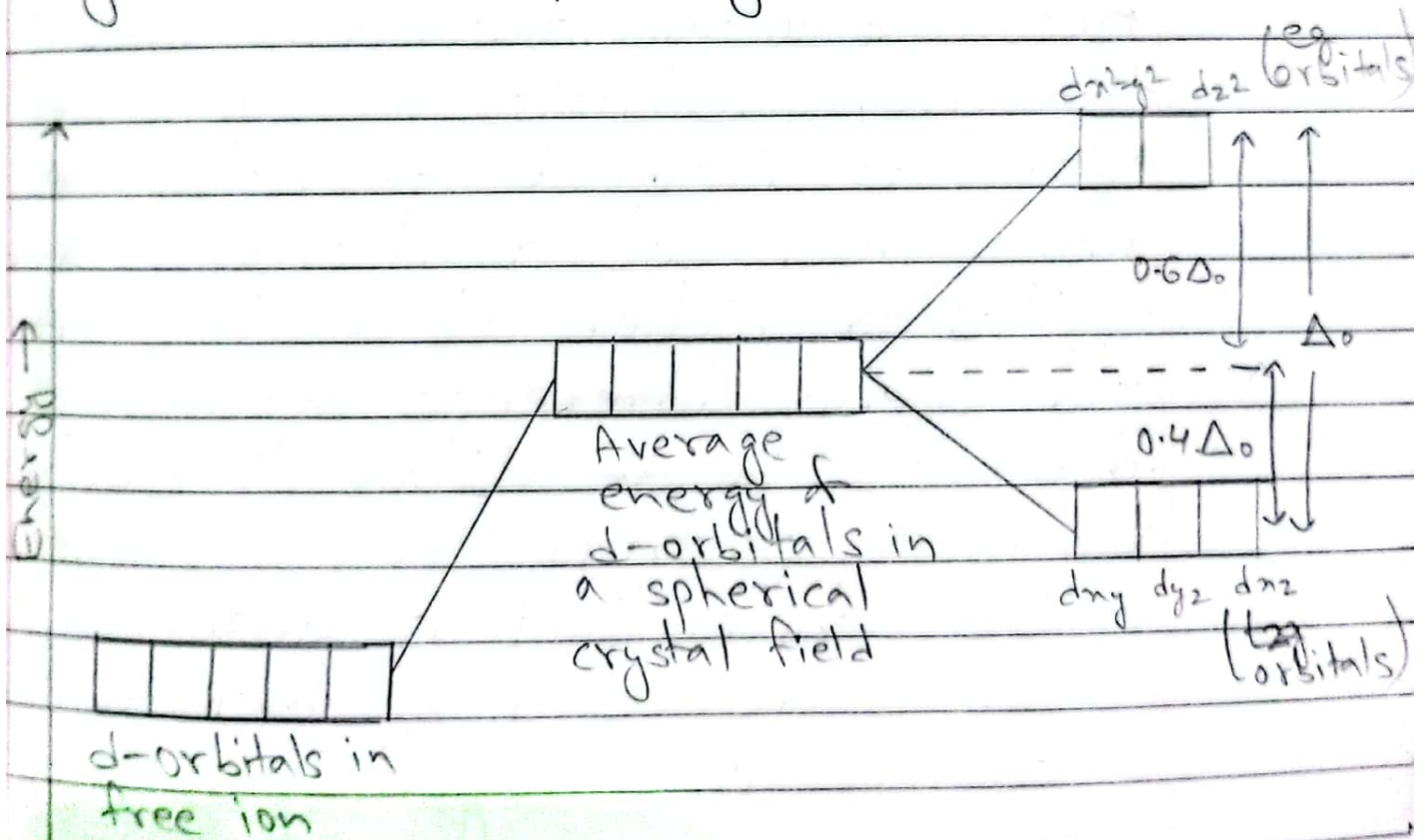


Hexamine cobalt(III) ion

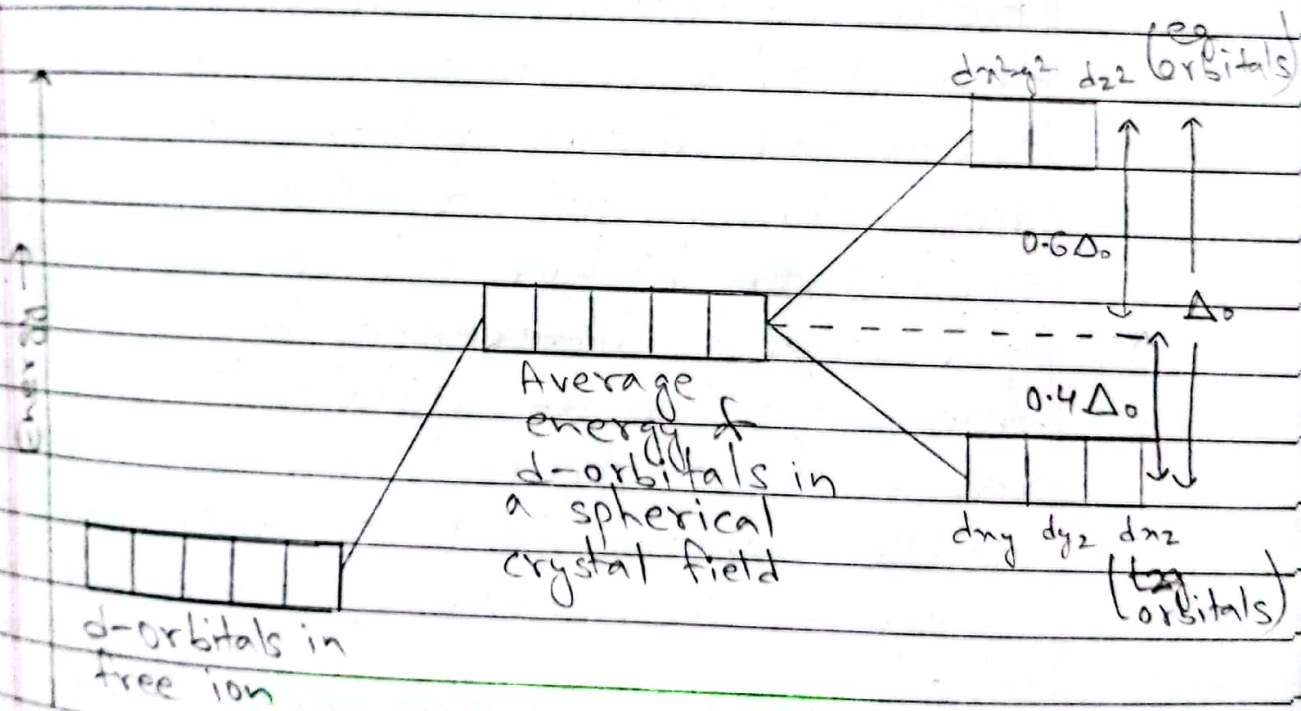
d-orbitals in complex ions for octahedral complex:

The crystal field theory (CFT) is the model for the bonding interaction between transition metals and ligands. When the ligands approach the central metal ion, the electrons in the d-orbitals and those in the ligand repel each other due to repulsion between like charges. Thus the d-electrons closer to the ligands will have a higher energy than those further away which results in the d-orbitals splitting in energy. Initially, the d-orbitals are degenerate but as the ligand approaches the central metal ion, the energy of d-orbitals increases and they split into the e_g and t_{2g} subsets having different energy. The e_g set has $d_{x^2-y^2}$ and d_{z^2} orbitals that lie along the axes. Since they lie along the axes, they experience greater repulsion and have higher energy than average energy. Similarly, the t_{2g} set has d_{xy} , d_{yz} and d_{zx}

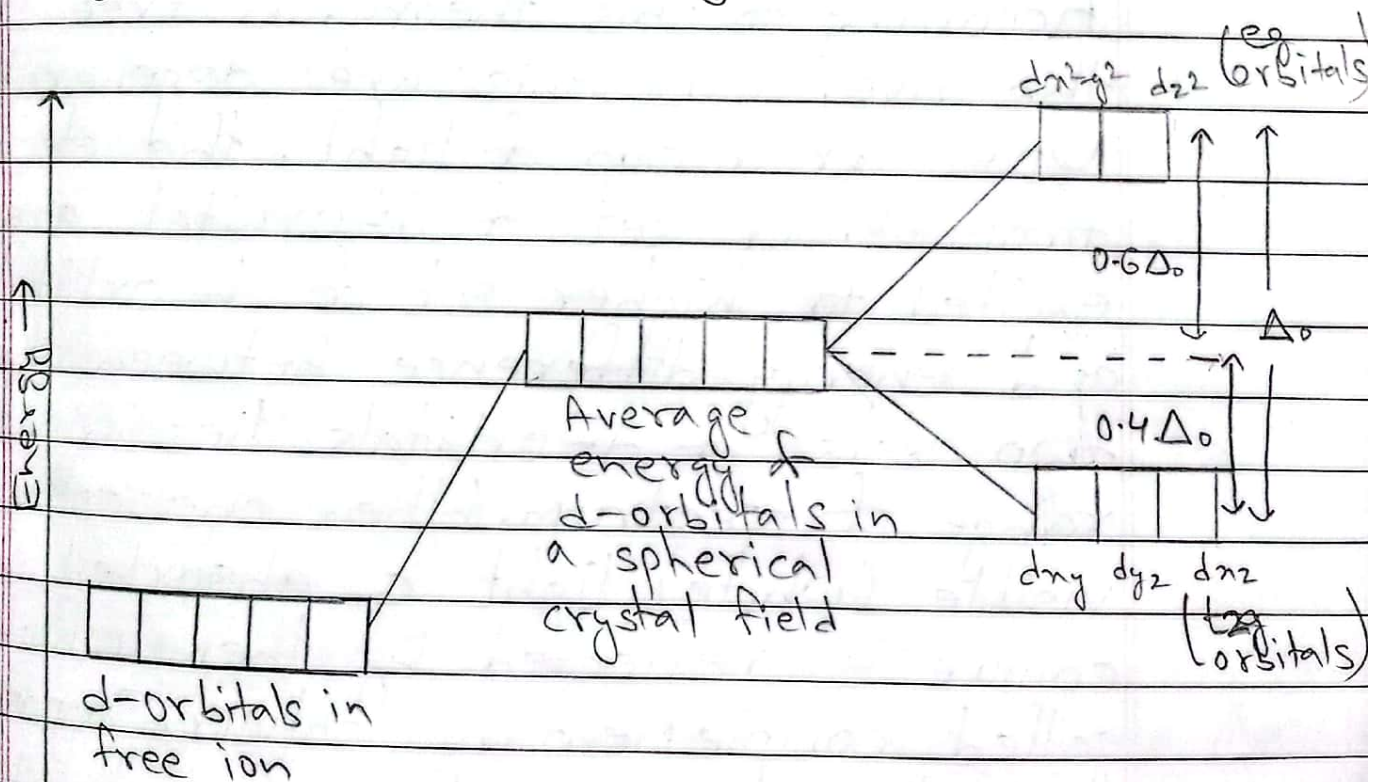
orbitals that lie between the axes. Since, they lie between the axes, they experience lower repulsion and have lesser energy than average energy. This splitting of degenerate orbitals in the presence of a ligand is known as crystal field splitting.



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Reason for the colour of transition metal compounds:

The colour of the transition metal complex is due to incompletely filled d-orbitals and d-d electronic transition based on crystal field splitting theory. According to this theory, in free state, the five d-orbitals are degenerate. Upon irradiation of light, the electron from lower set of d-orbitals are excited to higher set of d-orbitals and energy difference between these two sets of d-orbitals lies in visible range of spectrum. When one colour of visible (white) light is absorbed, another colour is reflected by them which is called complementary colour. Suppose, that the energy gap in the d-orbitals of the complex ion corresponds to the energy of yellow light, then yellow light would be absorbed and its energy promotes the electron and leaves the complementary colour i.e. dark blue colour and is observed. This is the

reason why the complexes of transition metal ions are usually colourful.

Catalytic properties of the transition metal:

Transition metals show catalytic properties due to the following reasons:-

- (i) Some transition metals and their compounds provide a large surface area on which the reactants can absorb and come closer for the reaction. The property of occlusion of some metals makes them act as a catalyst in several reactions.
- (ii) These metals have vacant d-orbitals and show variable oxidation states. These elements can form an unstable intermediate compound with suitable reactants providing alternative paths with lower activation energy and therefore increase the rate of reaction. The intermediate compound decomposes readily to form the final product and catalyst.