Coordination Compounds - Part 3

Objectives

After going through this lesson, the learners will be able to understand the following

- Draw relation between the colour of coordination compounds and the wavelengths of the light in the visible range
- the special type of bond between metal carbonyls
- Learn the stability of coordination compounds
- Explain the applications of coordination compounds in extraction of metals, medicine and qualitative analysis

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- Introduction
- Colour in Coordination Compounds
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- Stability of Coordination Compounds
- Importance and Applications of Coordination Compounds/
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Introduction

Visible light is a very small portion of the electromagnetic spectrum that human eyes are sensitive to. It has a range of wavelengths that our eyes can detect. The colour of most objects depends upon the interaction between visible light and the electrons of atoms or molecules that make up the object. It is usually the result of a dynamic process on the molecular level: the absorption of light and the resulting change of a molecule's quantized energy. This absorption coloration mechanism is responsible for the colours of grass, blood etc. but not of the sky. The sky's colour is due to selective scattering of different wavelengths of sunlight by the molecules of nitrogen and oxygen in the atmosphere.

The perceived colour of an object has a complementary relationship with the colour of the visible light absorbed. First consider white light, a mixture of all visible wavelengths, impinging on a coloured object. The object absorbs some wavelengths of the light, the wavelengths of light that are not absorbed are transmitted or reflected to the observer's eye. A substance that appears blue is transmitting or reflecting blue light to the eye and absorbing other colors of the white light that are not blue, i.e. It would absorb red, orange, yellow, and violet light. The absorption spectrum would show high absorbance of all visible wavelengths, besides blue. The transmission or reflectance spectrum would have a maximum at a wavelength corresponding to blue light.

Colour in Coordination Compounds

One of the most distinctive properties of transition metal complexes is their wide range of colours. This means that some of the visible spectrum is being removed from white light as it passes through the sample, so the light that emerges is no longer white. The colour of the complex is complementary to that which is absorbed. The complementary colour is the colour generated from the wavelength left over; if green light is absorbed by the complex, it appears red. Table 1 gives the relationship of the different wavelengths absorbed and the colour observed.

Table 1 : Relationship between the Wavelength of Light absorbed and the Colour observed in some Coordination Entities

Coordinaton entity	Wavelength of light absorbed (nm)	Colour of light absorbed	Colour of coordination entity
$[CoCl(NH_3)_5]^{2+}$	535	Yellow 🟨	Violet 🟪
$[Co(NH_3)_5(H_2O)]^{3+}$	500	Blue Green 🟩	Red 🟥
$[Co(NH_3)_6]^{3+}$	475	Blue 🟦	Yellow Orange 🟧
$[Co(CN)_6]^{3-}$	310	Ultraviolet Not in visible region	Pale Yellow 🟨
$[Cu(H_2O)_4]^{2+}$	600	Red 🟥	Blue 🟦
$[Ti(H_2O)_6]^{3+}$	498	Blue Green 🟩	Violet 🟪

(Source: NCERT Chemistry Textbook of Class 12, page no. 259)

The colour in the coordination compounds can be readily explained in terms of crystal field theory. Consider, for example, the complex $[Ti(H_2O)_6]^{3+}$, which is violet in colour. This is an octahedral complex where the single electron (Ti^{3+} is a $3d^1$ system) in the metal d orbital is in the t_{2g} level in the ground state of the complex. The next higher state available for the electron is the vacant e_g level. If light corresponding to the energy of the blue-green region is absorbed by the complex, it would excite the electron from t_{2g} level to the e_g level ($t_{2g}^1 e_g^0 \rightarrow t_{2g}^0 e_g^1$). Consequently, the complex appears violet in colour (Fig. 1). The crystal field theory attributes the colour of the coordination compounds to d-d transition of the electron.

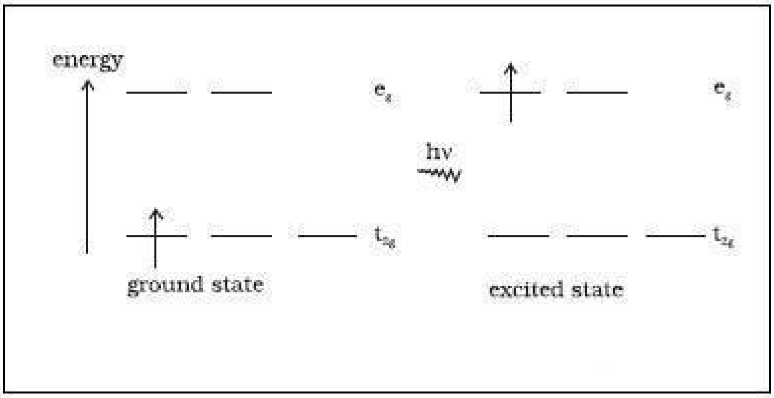


Fig 1: Transition of an electron in $[T_i(H_2O)_6]^{3+}$

(Source: NCERT Chemistry Textbook of Class 12, page no. 260)

It is important to note that in the absence of ligand, crystal field splitting does not occur and hence the substance is colourless. For example, removal of water from $[Ti(H_2O)_6]Cl_3$ on heating renders it colourless. Similarly, anhydrous $CuSO_4$ is white, but $CuSO_4.5H_2O$ is blue in colour. The influence of the ligand on the colour of a complex may be illustrated by considering the $[Ni(H_2O)_6]^{2+}$ complex, which forms when nickel(II) chloride is dissolved in water. If the bidentate ligand, ethane-1,2-diamine(en) is progressively added in the molar ratios en:Ni, 1:1, 2:1, 3:1, the following series of reactions and their associated colour changes occur:

$$[Ni(H_2O)_6]^{2+}(aq) + en\,(aq) \rightarrow [Ni(H_2O)_4(en)]^{2+}(aq) + 2H_2O$$

green pale blue

$$[Ni(H_2O)_4(en)]^{2+}(aq) + en\,(aq) \rightarrow [Ni(H_2O)_2(en)_2]^{2+}(aq) + 2H_2O$$

blue/purple

$$[Ni(H_2O)_2(en)_2]^{2+}(aq) + en\,(aq) \rightarrow [Ni(en)_3]^{2+}(aq) + 2H_2O$$

violet

This sequence is shown in Fig. 2.

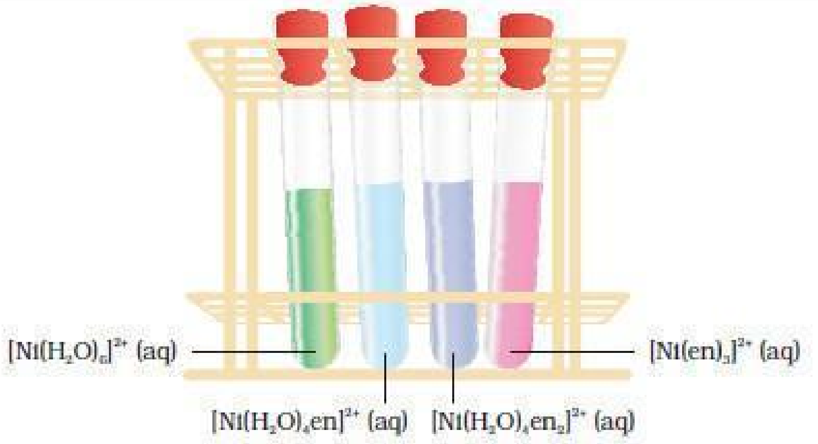


Fig 2: Aqueous solutions of complexes of nickel(II) with an increasing number of ethane-1, 2-diamine ligands

(Source: NCERT Chemistry Textbook of Class 12, page no. 260)

Colour of Some GemStones

The colours produced by electronic transitions within the *d* orbitals of a transition metal ion occur frequently in everyday life. Ruby [Fig.3 a] is aluminium oxide (Al_2O_3) containing about 0.5-1% Cr^{3+} ions (d^3), which are randomly distributed in positions normally occupied by Al^{3+} . We may view these chromium(III) species as octahedral chromium(III) complexes incorporated into the alumina lattice; *d–d* transitions at these centres give rise to the colourIn emerald [Fig.3 b], Cr^{3+} ions occupy octahedral sites in the mineral beryl ($Be_3Al_2Si_6O_{18}$). The absorption bands seen in the ruby shift to longer wavelengths, namely yellow-red and blue, causing emerald to transmit light in the green region.

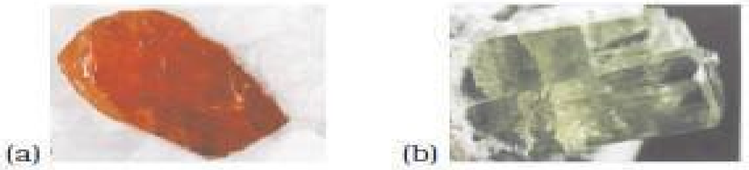


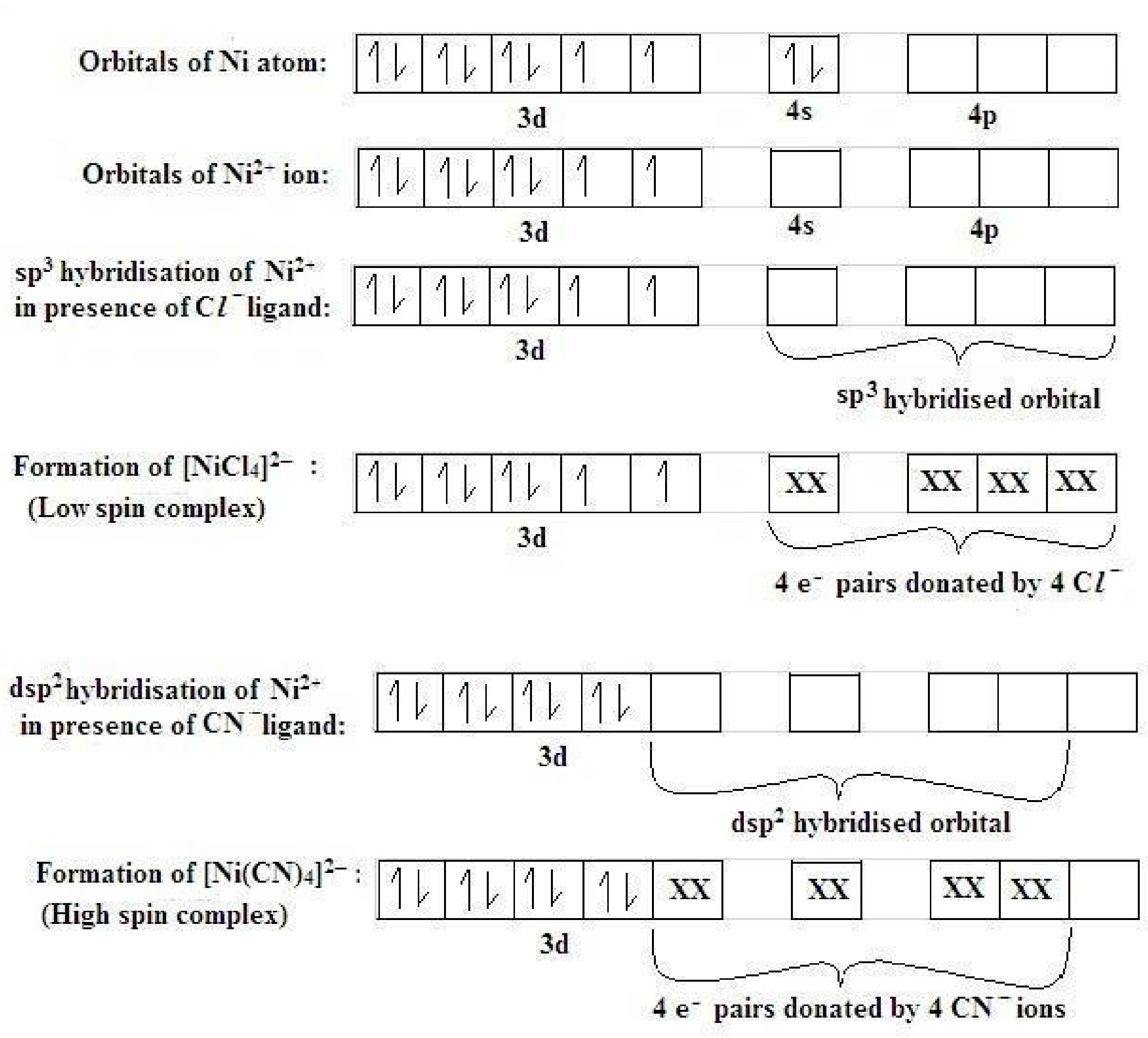
Fig. 3 (a) Ruby: this gemstone was found in marble from Mogok, Myanmar; (b) Emerald: this gemstone was found in Muzo, Columbia.

Limitations of Crystal Field Theory

Intext Questions

Problem 1: Explain on the basis of valence bond theory that $[Ni(CN)_4]^{2-}$ ion with square planar structure is diamagnetic and the $[NiCl_4]^{2-}$ ion with tetrahedral geometry is paramagnetic.

Solution: Nickel is in +2 oxidation state in$[Ni(CN)_4]^{2-}$ complex. The formation of $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$can be explained on basis of hybridization as below:



dsp^2 hybrid orbitals accommodate four pairs of electrons from four CN^- groups and the resulting square planar complex is diamagnetic since it does not contain any unpaired electrons. Ideally the complex should be following *sp*^{3} hybridisation but it is actually *dsp*^{2}, ie; the 2 unpaired 3*d* electrons pair up against Hund's rule before hybridization. This is on account of the following reasons:

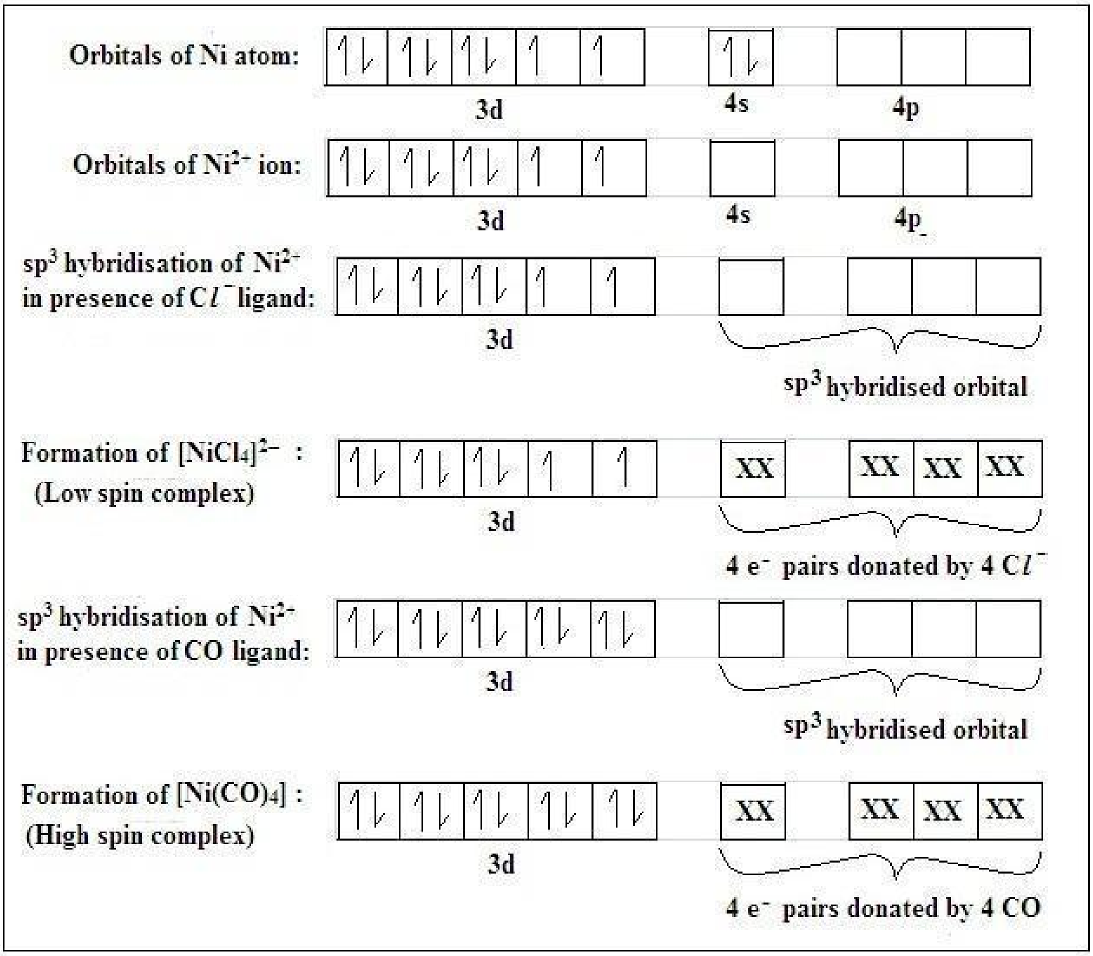
- If no pairing occurs the complex should be paramagnetic but it was actually found to be diamagnetic.

- CN^- is a strong ligand and as it approaches the metal ion, the electrons pair up.

On the other hand in $[NiCl_4]^{2-}$ Cl^- provides a weak ligand field. It is therefore unable to cause a pairing of the 3*d* unpaired electrons in Ni^{2+} ion. Hence, sp^3 hybridisation involving 4*s* and 4*p* orbitals takes place and the shape of the molecule is tetrahedral. This is paramagnetic in nature.

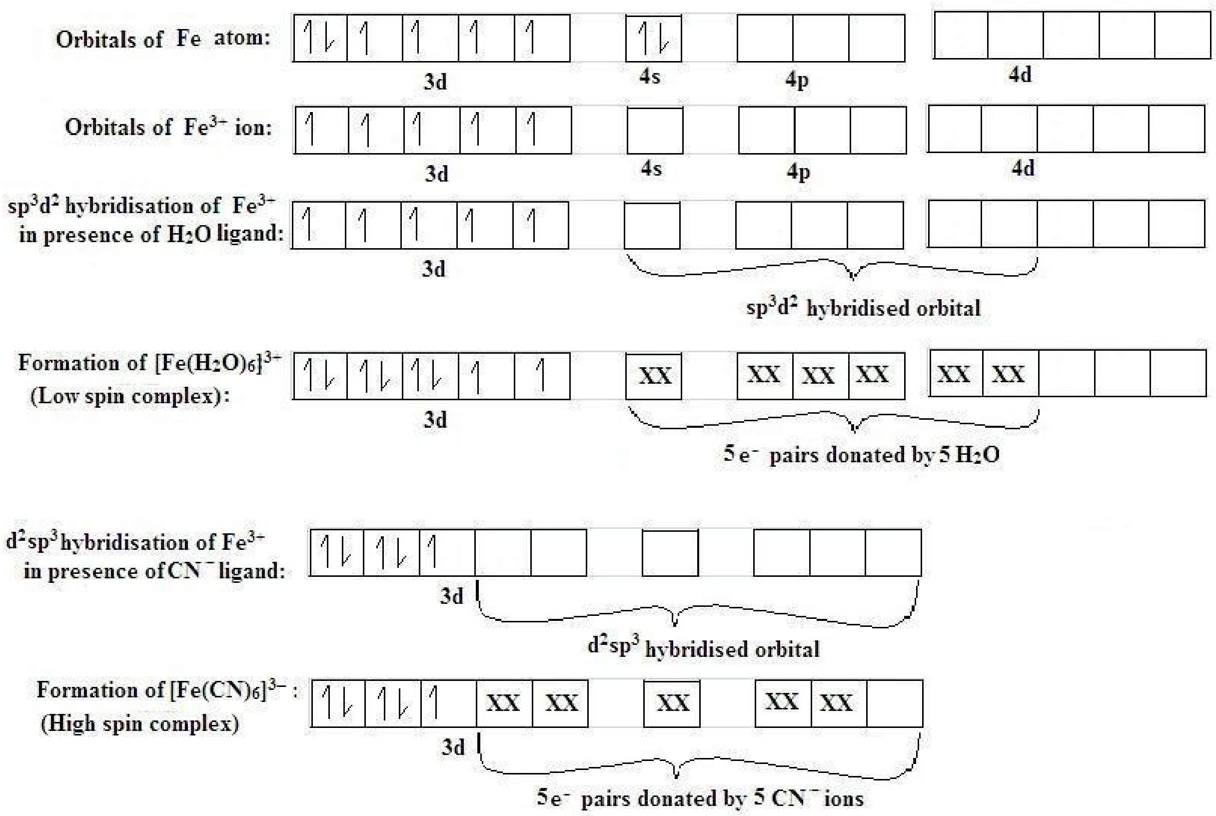
Problem 2: $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Why?

Solution: In $[NiCl_4]^{2-}$, Ni is in +2 oxidation state with the configuration $3d^8 4s^0$ and Cl^- provides a weak ligand field. It is therefore unable to cause a pairing of the 3*d* unpaired electrons in Ni^{2+} ion. Hence, sp^3 hybridisation involving 4*s* and 4*p* orbitals takes place and the shape of the molecule is tetrahedral. This is paramagnetic in nature. While in $[Ni(CO)_4]$, Ni is in zero oxidation state with the configuration $3d^8\ 4s^2$. In the presence of CO ligand which is a strong field ligand, the 4*s* electrons shift to 3*d* orbitals and pair up, thus there is no unpaired electron present in the molecule hence it is diamagnetic in nature. The formation of $[Ni(CO)_4]$complex can be explained as below:



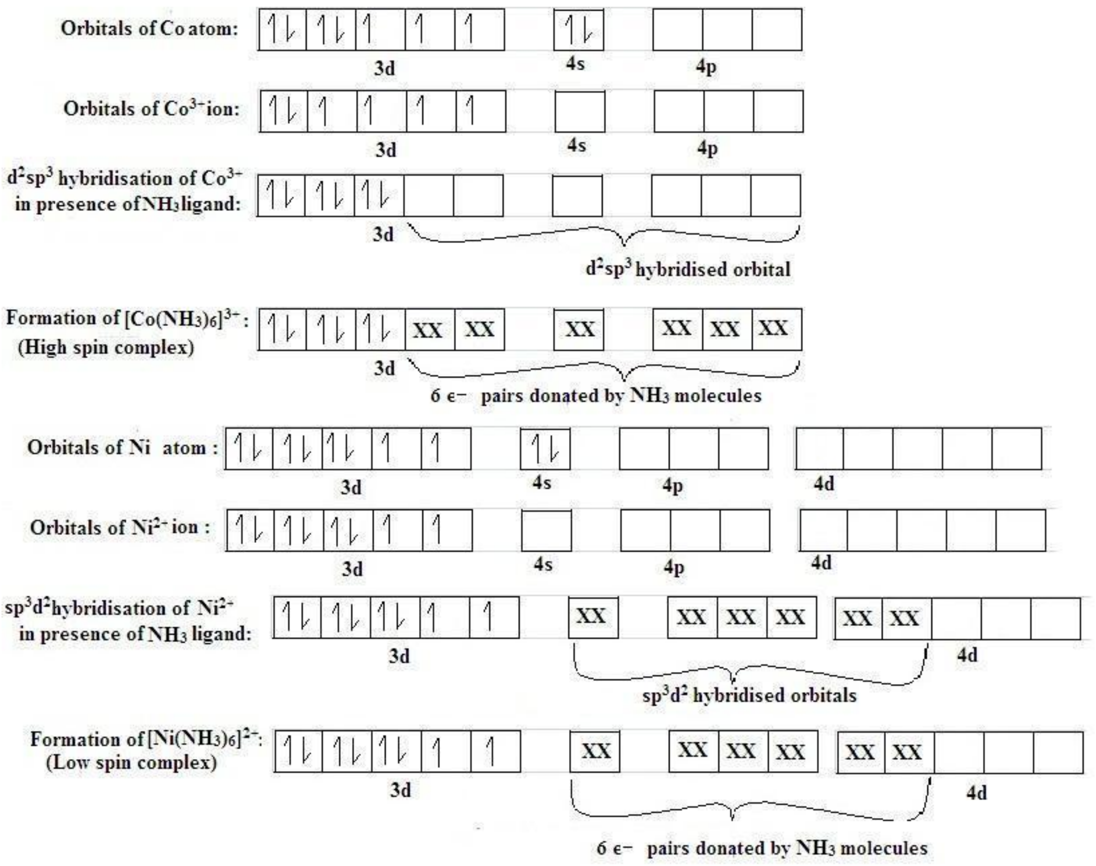
Problem 3: $[Fe(H_2O)_6]^{3+}$ is strongly paramagnetic whereas $[Fe(CN)_6]^{3-}$ is weakly paramagnetic. Explain.

Solution: In both the complexes Fe is in +3 oxidation state with the configuration $3d^5$, CN^- is a strong field ligand, hence in its presence the 3*d* unpaired electrons pair up leaving only 1 unpaired electron. The hybridization is d^2sp^3 forming an inner orbital complex. H_2O is a weak field ligand and hence in its presence the 3 *d* electrons do not pair up and the hybridization is sp^3d^2 forming an outer orbital complex with 5 unpaired electrons. Hence it is strongly paramagnetic. Formation of $[Fe(H_2O)_6]^{3+}$ and $[Fe(CN)_6]^{3-}$ is shown below:



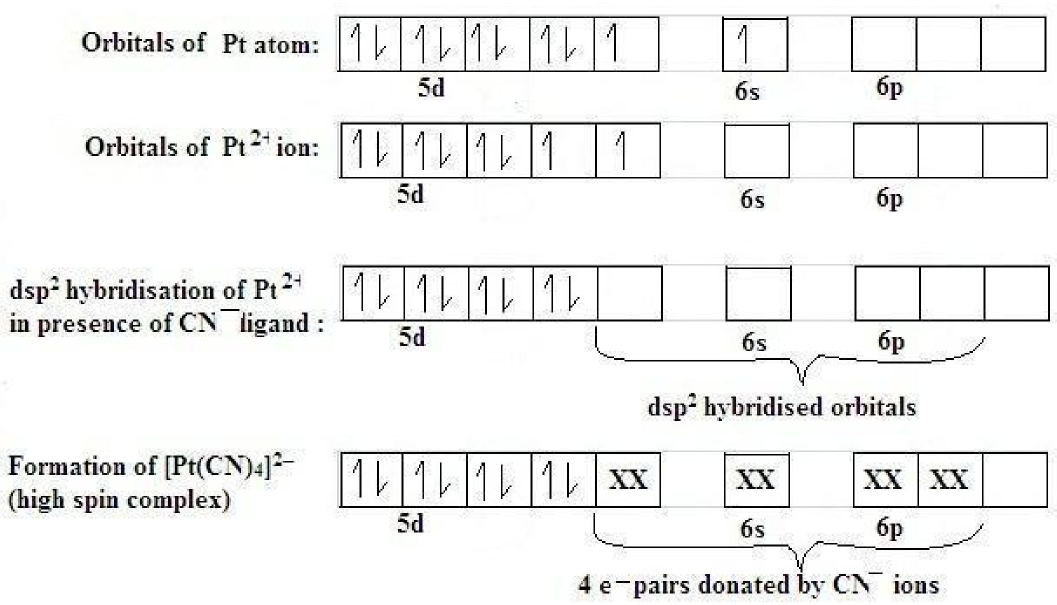
Problem 4: Explain $[Co(NH_3)_6]^{3+}$ is an inner orbital complex whereas $[Ni(NH_3)_6]^{2+}$ is an outer orbital complex.

Solution: In $[Co(NH_3)_6]^{3+,}$ Co is in +3 oxidation state with the configuration $3d^6$. In the presence of NH_3 $3d$ electrons pair up leaving two orbitals of $3d$ empty. Hence the hybridisation is d^2sp^3 forming an inner orbital complex. In $[Ni(NH_3)_6]^{2+}$, Ni is in +2 oxidation state with the configuration $3d^8$. In the presence of NH_3, the $3d$ electrons do not pair up. The hybridization involved is sp^3d^2 forming an outer orbital complex.



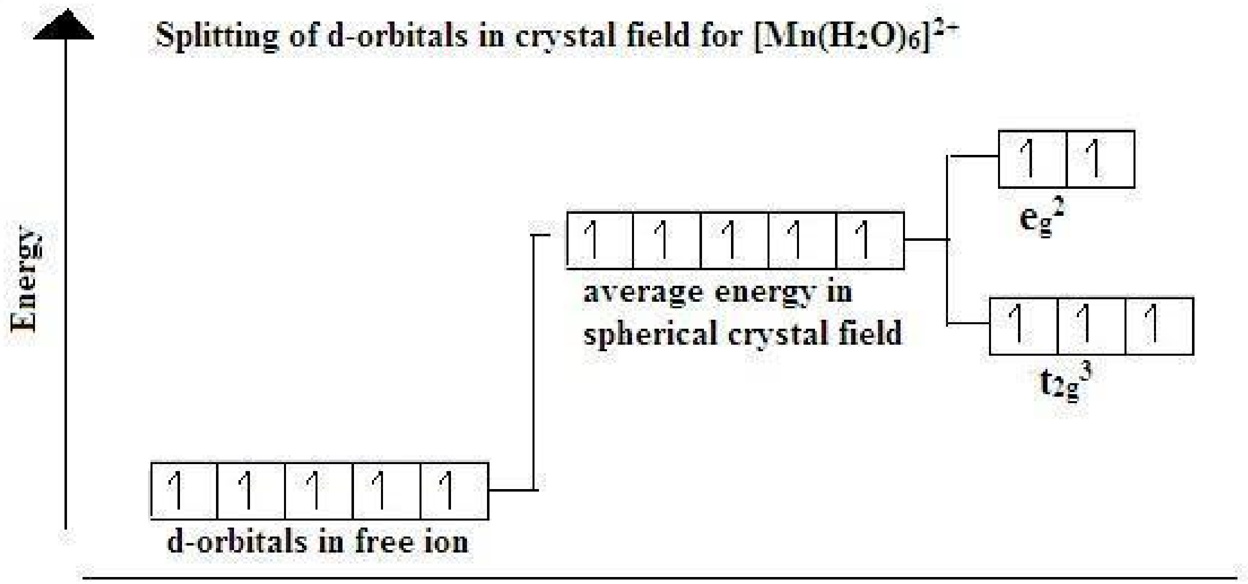
Problem 5: Predict the number of unpaired electrons in the square planar $[Pt(CN)_4]^{2-}$ ion.

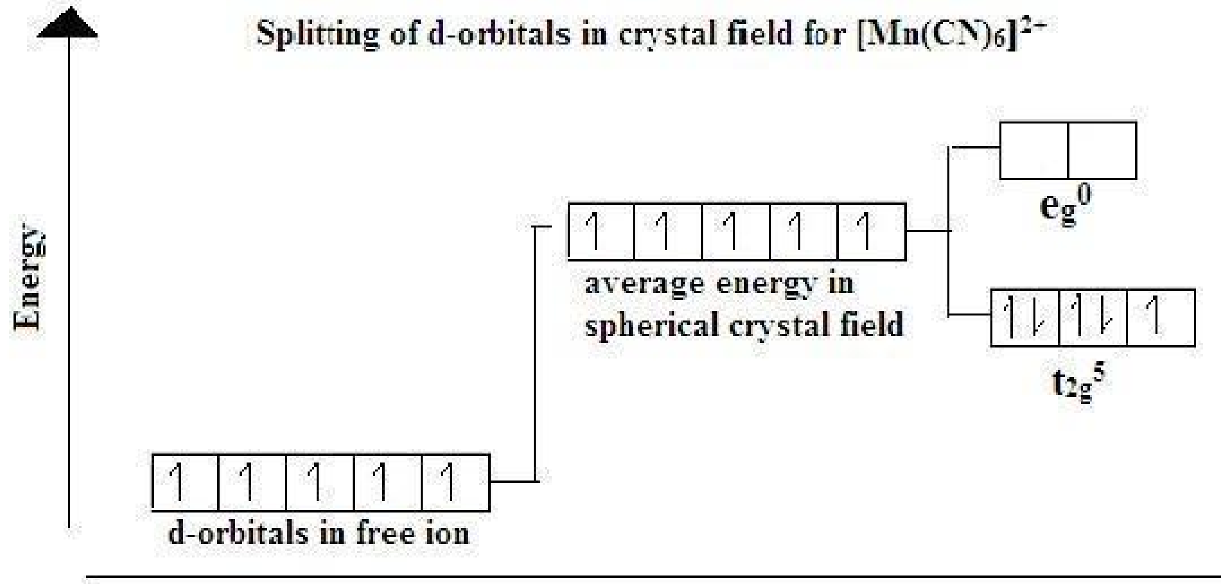
Solution: $_{78}Pt$ lies in group 10 with the configuration $5d^9\ 6s^1$. Hence, Pt^{2+} has the configuration $5d^8$. For square planar shape, the hybridization is dsp^2. Hence, the unpaired electrons in 5*d* pair up and thus there is one *d*-orbital empty, hence the hybridization dsp^2 is possible. Therefore there are no unpaired electrons in $[Pt(CN)_4]^{2-}$ ion.



Problem 6: The hexaaquamanganese(II) ion contains five unpaired electrons, while the hexacyanoiron contains only one unpaired electron. Explain using Crystal Field Theory.

Solution: The electronic configuration of Mn in +2 oxidation state is, $3d^5$. In the presence of H_2O ligands, the distribution of these five electrons becomes as; 3 electrons in 3-t_{2g} orbitals and 2 electrons in 2-e_g orbitals ($t_{2g}^3$and e_g^2). Thus, all electrons remain unpaired. In the presence of CN^- ligand, the distribution becomes as 5 electrons in 3-t_{2g} orbitals, therefore the pairing of electrons takes place with 5 electrons occupying 3-t_{2g} orbitals and none of the electrons occupy the 2-e_g orbitals, therefore 2-e_g orbitals remain empty. One t_{2g} orbital now has an unpaired electron while the other 2t_{2g} orbitals are completely filled with 2 electrons in each orbital.





Bonding in Metal Carbonyls

Metal carbonyls are a class of compounds involving carbon monoxide (CO) as a ligand. In homoleptic carbonyls the metal is attached to only CO ligands, the metal is generally in zero oxidation state. Tetracarbonylnickel(0), pentacarbonyliron(0) and hexacarbonylchromium(0) have tetrahedral, trigonal bipyramidal and octahedral structures respectively.Polynuclear carbonyls are also known. Decacarbonyldimanganese(0), $Mn_2(CO)_{10}$ has two $Mn(CO)_5$ units linked by a Mn – Mn bond. In octa carbonyl dicobalt(0), $Co_2(CO)_8$ there is a Co – Co bond and two carbonyl groups act as bridge between the two Co atoms (Fig. 4).

The metal_carbon bond in metal carbonyls possesses both sigma σ and pi π bond character. The M-C sigma bond is formed by donation of a lone pair of electrons on the carbonyl carbon to the vacant orbitals of the metal. The M-C pi bond is formed by donation of a pair of electrons from the filled d orbital of the metal into the vacant antibonding orbitals of the carbon monoxide. The metal ligand bonding creates a synergic effect which strengthens the bond between CO and the metal (Fig. 5).

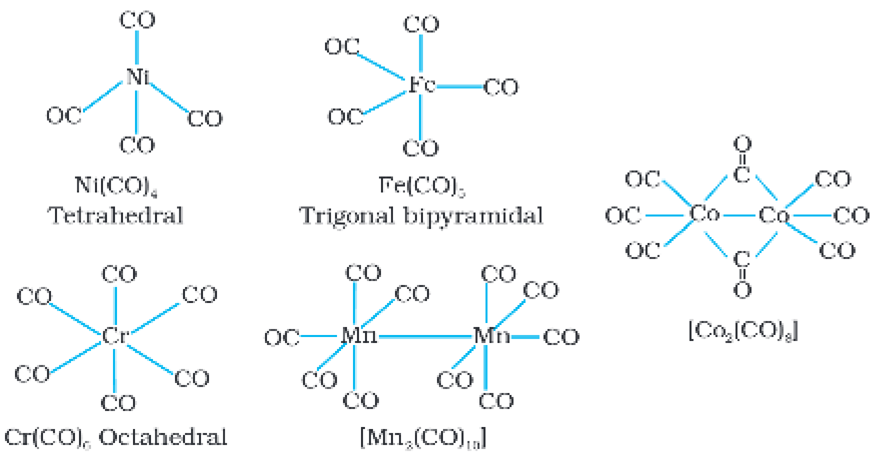


Fig. 4 Structures of some representative homoleptic metal carbonyls

(Source: NCERT Chemistry Textbook of Class 12, page no. 262)

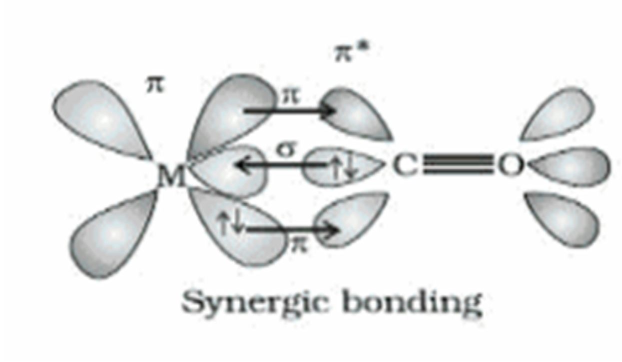


Fig. 5: Synergic Bonding

(Source: NCERT Chemistry Textbook of Class 12, page no. 262)

Stability of Coordination Compounds

The stability of a complex in solution refers to the degree of association between the two species involved in the state of equilibrium. The magnitude of the (stability or formation) equilibrium constant for the association, quantitatively expresses the stability. Thus, if we have a reaction of the type:

$$M + 4L \rightarrow ML_4$$

then the greater the stability constant, the higher is the proportion of ML_4 that exists in solution. Free metal ions rarely exist in the solution so that M will usually be surrounded by solvent molecules which will compete with the ligand molecules, L, and be successively replaced by them. For simplicity, we generally ignore these solvent molecules and write four stability constants as follows:

$M + L \rightarrow ML$ $\quad K_1 = [ML]/[M][L]$

$ML + L \rightarrow ML_2$ $\quad K_2 = [ML_2]/[ML][L]$

$ML_2 + L \rightarrow ML_3$ $\quad K_3 = [ML_3]/[ML_2][L]$

$ML_3 + L \rightarrow ML_4$ $\quad K_4 = [ML_4]/[ML_3][L]$

where K_1 , K_2 , etc., are referred to as stepwise stability constants. Alternatively, we can write the overall stability constant thus:

$M + 4L \rightarrow ML_4$ $\quad \beta_4 = [ML_4]/[M][L]^4$

The stepwise and overall stability constant are therefore related as follows:

$\beta_4 = K_1 \times K_2 \times K_3 \times K_4$ or more generally,

$\beta_n = K_1 \times K_2 \times K_3 \times K_4 \ldots\ldots\ K_n$

If we take as an example, the steps involved in the formation of the tetraamminecopper(II) ion, we have the following:

$Cu^{2+} + NH_3 \rightarrow Cu(NH_3)^{2+}$ $\quad K_1 = [Cu(NH_3)]^{2+}/[Cu^{2+}][NH_3]$

$Cu(NH_3)^{2+} + NH_3 \rightarrow [Cu(NH_3)_2]^{2+}$ $\quad K_2 = [Cu(NH_3)_2]^{2+}/[Cu(NH_3)]^{2+}[NH_3]$

where K_1, K_2 are the stepwise stability constants. The overall stability constant β_4 is represented as

$\beta_4 = [Cu(NH_3)_4]^{2+}/[Cu^{2+}][NH_3]^4$

The addition of the four ammonia molecules to copper shows a pattern found for most formation constants, in that the successive stability constants decrease. In this case, the four constants are: log $K_1 = 4.0$, log $K_2 = 3.2$, log $K_3 = 2.7$, log $K_4 = 2.0$ or log $\beta_4 = 11.9$

The instability constant or the dissociation constant of coordination compounds is defined as the reciprocal of the formation constant.

Intext Question

Problem 7: Calculate the overall complex dissociation equilibrium constant for the $[Cu(NH_3)_4]^{2+}$ ion, given that β_4 for this complex is 2.1×10^{13}.

Solution: The Overall stability constant (β_4) = $2.1 X 10^{13}$

The overall dissociation constant is the reciprocal of the overall stability constant. Hence, overall complex dissociation constant = $\frac{1}{\beta 4} = \frac{1}{2.1X10^{13}} = 4.7X10^{-14}$

Importance and Applications of Coordination Compounds

The coordination compounds are of great importance. These compounds are widely present in the mineral, plant and animal worlds and are known to play many important functions in the area of analytical chemistry, metallurgy, biological systems, industry and medicine.

These are described below:

- Coordination compounds find use in many qualitative and quantitative chemical analyses. The familiar colour reactions given by metal ions with a number of ligands (especially chelating ligands), as a result of formation of coordination entities, form the basis for their detection and estimation by classical and instrumental methods of analysis. Examples of such reagents include EDTA, DMG (dimethylglyoxime), α–nitroso–β–naphthol, cupron, etc.

- Hardness of water is estimated by simple titration with Na_2EDTA. The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The selective estimation of these ions can be done due to differences in the stability constants of calcium and magnesium complexes.

- Some important extraction processes of metals, like those of silver and gold, make use of complex formation. Gold, for example, combines with cyanide in the presence of oxygen and water to form the coordination entity $[Au(CN)_2]^-$ in aqueous solution. Gold can be separated in metallic form from this solution by the addition of zinc.

- Similarly, purification of metals can be achieved through formation and subsequent decomposition of their coordination compounds. For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel.

- Coordination compounds are of great importance in biological systems. The pigment responsible for photosynthesis, chlorophyll, is a coordination compound of magnesium. Haemoglobin, the red pigment of blood which acts as an oxygen carrier, is a coordination compound of iron. Vitamin B_{12}, cyanocobalamin, the anti–pernicious anaemia factor, is a coordination compound of cobalt. Among the other compounds of biological importance with coordinated metal ions are enzymes like carboxypeptidase A and carbonic anhydrase (catalysts of biological systems).

- Coordination compounds are used as catalysts for many industrial processes. Examples include rhodium complex, $[(Ph_3P)_3RhCl]$, a Wilkinson catalyst, is used for the hydrogenation of alkenes.

- Articles can be electroplated with silver and gold much more smoothly and evenly from solutions of the complexes, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ than from a solution of simple metal ions.

- In black and white photography, the developed film is fixed by washing with a hypo solution which dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^3$.

- There is growing interest in the use of chelate therapy in medicinal chemistry. An example is the treatment of problems caused by the presence of metals in toxic proportions in plant/animal systems. Thus, excess copper and iron are removed by the chelating ligands D–penicillamine and desferrioxamine B via the formation of coordination compounds. EDTA is used in the treatment of lead poisoning. Some coordination compounds of platinum effectively inhibit the growth of tumours. Examples are: cis–platin and related compounds.

Summary

The chemistry of coordination compounds is an important and challenging area of modern inorganic chemistry. During the last fifty years, advances in this area, have provided development of new concepts and models of bonding and molecular structure, novel breakthroughs in the chemical industry and vital insights into the functioning of critical components of biological systems. The first systematic attempt at explaining the formation, reactions, structure and bonding of a coordination compound was made by A. Werner. His theory postulated the use of two types of linkages (primary and secondary) by a metal atom/ion in a coordination compound. In the modern language of chemistry these linkages are recognised as the ionisable (ionic) and non-ionisable (covalent) bonds, respectively. Using the property of isomerism, Werner predicted the geometrical shapes of a large number of coordination entities. The Valence Bond Theory (VBT) explains with reasonable success, the formation, magnetic behaviour and geometrical shapes of coordination compounds. It, however, fails to provide a quantitative interpretation of magnetic behaviour and has nothing to say about the optical properties of these compounds. The Crystal Field Theory (CFT) to coordination compounds is based on the effect of different crystal fields (provided by the ligands taken as point charges), on the degeneracy of d orbital energies of the central metal atom/ion. The splitting of the *d* orbitals provides different electronic arrangements in strong and weak crystal fields. The treatment provides for quantitative estimations of orbital separation energies, magnetic moments and spectral and stability parameters. However, the assumption that ligands constitute point charges creates many theoretical difficulties. The metal–carbon bond in metal carbonyls possesses both σ and π character. The ligand to metal is σ bond and metal to ligand is π bond. This unique synergic bonding provides stability to metal carbonyls. The stability of coordination compounds is measured in terms of stepwise stability (or formation) constant (K) or overall stability constant (β). The stabilisation of coordination compounds due to chelation is called the chelate effect. The stability of coordination compounds is related to Gibbs energy, enthalpy and entropy terms. Coordination compounds are of great importance. These compounds provide critical insights into the functioning and structures of vital components of biological systems. Coordination compounds also find extensive applications in metallurgical processes, analytical and medicinal chemistry.