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COORDINATION COMPOUNDS

You have come across compounds like $\text{Na}[\text{Ag}(\text{CN})_2]$ and $\text{Na}_2[\text{Zn}(\text{CN})_4]$. Such compounds are referred to as coordination compounds or complex compounds. Coordination compounds play an important role in the chemical industry and in life itself. For example, the Ziegler-Natta catalyst which is used for polymerization of ethylene, is a complex containing the metals aluminum and titanium. Metal complexes play important role in biological systems. For example, chlorophyll, which is vital for photosynthesis in plants, is a magnesium complex and hemoglobin, which carries oxygen to animal cells, is an iron complex. These are the compounds that contain a central atom or ion, usually a metal, surrounded by a number of ions or molecules. The complexes tend to retain their identity even in solution, although partial dissociation may occur. Complex ion may be cationic, anionic or nonionic, depending on the sum of the charges of the central atom and the surrounding ions and molecules.

In this lesson you will study about the complexes including their nomenclature and nature of bonding in them.



OBJECTIVES

After reading this lesson, the learner will be able to,

- state the postulates of Werner's theory;
- define ligands, coordination number and coordination sphere;
- name simple complexes by IUPAC system;
- explain valence bond theory;
- apply VB theory to explain hybridization, shape and magnetic behavior of the following complexes $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Cr}(\text{NH}_3)_6]^{2+}$, $[\text{NiCl}_4]^{2-}$, $[\text{Ni}(\text{CO})_4]$ and $[\text{Ni}(\text{CN})_4]^{2-}$ and



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- explain Crystal Field Theory (CFT);
- explain the colour and magnetic behaviour of coordination compounds on the basis of CFT.
- explain the isomerism in coordination compounds;
- explain the applications of coordination compounds in extraction of metals, medicine and qualitative analysis.

22.1 WERNER'S COORDINATION THEORY

Coordination compounds were known in eighteenth century. It was a mystery for the chemist, of those days to understand as to why a stable salt like CoCl_3 reacts with varying number of stable molecules or compounds such as ammonia to give several new compounds: $\text{CoCl}_3 \cdot 6\text{NH}_3$, $\text{CoCl}_3 \cdot 5\text{NH}_3$ and $\text{CoCl}_3 \cdot 4\text{NH}_3$; and what are their structures? These compounds differed from each other in their chloride ion reactivity. Conductivity measurements on solutions of these compounds showed that the number of ions present in solution for each compound are different. Several theories were proposed, but none could satisfactorily explain all the observable properties of these compounds and similar other series of compounds which had been prepared by then. It was only in 1893 that Werner put forward a set of ideas which are known as Werner's coordination theory, to explain the nature of bonding in complexes. His theory has been a guiding principle in inorganic chemistry and in the concept of valence. The important postulates of **Werner's theory** are:

1. Metals exhibit two types of valence:
 - (a) Primary valence (ionizable)
 - (b) Secondary valence (non-ionizable).

Primary or ionizable valence is satisfied by negative ions and corresponds to oxidation state of the metal. The secondary or non-ionizable valence, which is satisfied by negative, positive or neutral groups, is equal to the coordination number of metal ion.

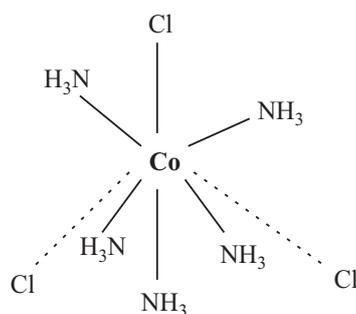
Every metal tends to satisfy both its primary and secondary valence.

2. The secondary valence is directed toward fixed positions in space i.e. this has spatial arrangement corresponding to different coordination number.

For the complexes $\text{CoCl}_3 \cdot 6\text{NH}_3$, $\text{CoCl}_3 \cdot 5\text{NH}_3$ and $\text{CoCl}_3 \cdot 4\text{NH}_3$, the number of ionizable ions in these complexes are three, two and one, respectively. It has been proved by precipitation reactions and conductivity measurements. On the basis of Werner's postulate these compounds are formulated as:

$[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ and $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, respectively, the species inside the square brackets being the complex ion and outside the square brackets the ionisable ions.

On the basis of Werner's theory the structure of $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ is:



Primary valence (ionizable) (-----)

Secondary valence (non-ionizable) (———)

One of the three chloride ions satisfy both primary and secondary valence.

He also postulated that octahedral, tetrahedral and square planar shapes are more common for coordination compounds of transition elements. Six coordinated complexes such as $[\text{Ni}(\text{NH}_3)_6]^{2+}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$ are octahedral whereas four coordinated such as $[\text{NiCl}_4]^{2-}$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are tetrahedral and square planar, respectively.



INTEXT QUESTIONS 22.1

1. Explain primary valence.
2. Explain secondary valence.
3. What is the number of the secondary valence in the following: $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ and $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$?
4. What is shape associated with a six-coordinated complex?
5. How many types of shapes are possible for four-coordinate complexes?

22.2 DEFINITION OF SOME IMPORTANT TERMS

There are certain terms, which are normally used in dealing with coordination compounds. Some of these important terms are defined below:

Ligand: the molecules or ions that are attached to the metal in a complex ion are called ligands. The interaction between a metal atom and the ligands can be thought

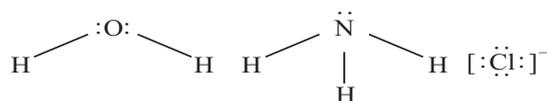


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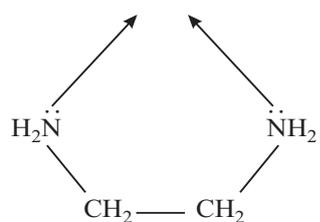
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of as Lewis acid-base reaction. As you know a Lewis base is a substance capable of donating one or more electron pairs, every ligand has at least one unshared pair of valence electron. Few examples are shown below:



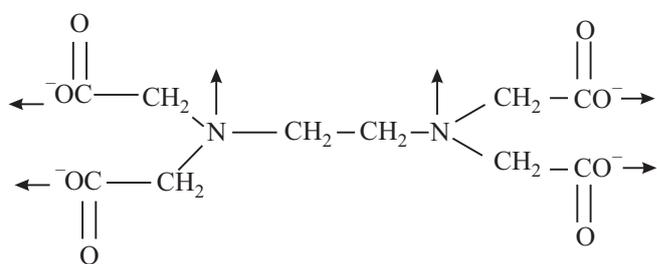
The atom in the ligand that is bound directly to the metal atom is known as the donor atom. For example, nitrogen is the donor atom and Cu^{2+} is the acceptor atom in the $[\text{Cu}(\text{NH}_3)_4]^{2+}$ complex ion.

Depending on the number of the donor atoms present, ligands are defined as monodentate, bidentate or polydentate. H_2O and NH_3 are monodentate ligands with only one donor atom in each. Ethylenediamine (en) is a bidentate ligand.



Ethylenediamine

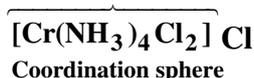
The two nitrogen atoms can coordinate with a metal atom. Bidentate and polydentate ligands are also called chelating agents because of their ability to hold the metal atom like a claw (from the Greek Chele, meaning “claw”) one example is ethylenediaminetetraacetate ion (EDTA), a polydentate (hexadentate) ligand.



Ethylenediaminetetraacetate ion

Coordination number: The coordination number in coordination compounds is defined as the number of ligand (donor) atoms/ions surrounding the central metal atom in a complex ion. For example, the coordination number of cobalt in $[\text{Co}(\text{NH}_3)_6]^{3+}$ is six. Similarly the coordination number of Ag^+ in $[\text{Ag}(\text{NH}_3)_2]^+$ is 2, that of Cu^{2+} in $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is 4, and that of Fe^{3+} in $[\text{Fe}(\text{CN})_6]^{3-}$ is 6.

Coordination sphere: The central metal atom and the ligands which are directly attached to it are enclosed in a square bracket and are collectively termed as coordination sphere. The ligands and the metal atom inside the square brackets behave as single constituent unit.



Oxidation number: Another important property of coordination compounds is the oxidation number of the central metal atom. The net charge on a complex ion is the sum of the charges on the central atom and its surrounding ligands. In the $[\text{PtCl}_6]^{2-}$ ion for example, each chloride ion has an oxidation number of -1 , so the oxidation number of Pt must be $+4$. If the ligands do not bear net charges the oxidation number of the metal is equal to the charge of the complex ion. Thus in $[\text{Cu}(\text{NH}_3)_4]^{2+}$ each NH_3 is neutral, so the oxidation number of copper is $+2$.



INTEXT QUESTIONS 22.2

- What is the coordination number of the metal ion in the following?
 - $[\text{Co}(\text{NH}_3)_5\text{Cl}]^+$
 - $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$
 - $[\text{NiCl}_4]^{2-}$
- What is the oxidation state of the metal ion in the following?
 - $[\text{MnCl}_6]^{4-}$
 - $[\text{Fe}(\text{CN})_6]^{3-}$
 - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
 - $[\text{Ni}(\text{en})_3]^{2+}$
- Give an example of a chelate ligand.
- Give one example of each monodentate, bidentate and polydentate ligand.
- What is the oxidation and coordination number of Co in this $[\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{CN}]^{2+}$ complex ion Which ligand is bidentate in the above complex?

22.3 RULES OF NOMENCLATURE OF COORDINATION COMPOUNDS

We have already discussed about the ligands and oxidation number of metal, our next step is, to learn how to name these coordination compounds. The rules for naming coordination compounds as recommended by IUPAC are as follows:



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1. The cation is named before the anion, as in other ionic compounds. The rule holds regardless of whether the complex ion bears a net positive or a negative charge. For example, in $K_3[Fe(CN)_6]$ and $[Co(NH_3)_4Cl_2]Cl$ compound, we name the K^+ and $[Co(NH_3)_4Cl_2]^+$ first, respectively.
2. Within a complex ligands are named first, in alphabetical order, and the metal ion is named last.
3. The name of anionic ligand ends with the letter 'O', whereas a neutral ligand is usually called by the name of the molecule. The exceptions are H_2O (aqua), CO (carbonyl) and NH_3 (ammine). The table given below lists some common ligands:

Table 22.1: Some Common Ligands

Ligand	Name of the ligand in coordination compounds
Fluoride (F^-)	Fluro
Chloride (Cl^-)	Chloro
Bromide (Br^-)	Bromo
Hydroxide (OH^-)	Hydroxo
Sulphate (SO_4^{2-})	Sulphato
Oxide (O^{2-})	Oxo
Carbonate (CO_3^{2-})	Carbonato
Oxalate ($C_2O_4^{2-}$)	Oxalato
Thiocyanate (SCN^-)	Thiocyanato
Cyanide (CN^-)	Cyano
Isothiocyanate (NCS^-)	Isothiocyanato
Ethylenediamine ($NH_2CH_2CH_2NH_2$)	Ethylenediamine
Ammonia (NH_3)	Ammine
Water (H_2O)	Aqua
Carbon monoxide (CO)	Carbonyl
EDTA	Ethylenediamineteracetato

4. When several ligands of a particular kind are present, we use the Greek prefix di, tri- tetra etc to name them. Thus the ligands in cation $[Co(NH_3)_4Cl_2]^+$ are named as "tetraammine dichloro" (note that prefixes are ignored when alphabetizing ligands). If the ligand itself contains a Greek prefix, we use the prefixes *bis*, *tris* and *tetrakis* etc to indicate the number of ligands present. For example, the ligand ethylenediamine already contains di, therefore, if two such ligands are present the name is *bis*(ethylenediamine).

- The oxidation number of the metal is written in roman numerals following the name of the metal. For example, the roman numeral III is used to indicate the +3 oxidation state of chromium in $[\text{Cr}(\text{NH}_3)_4\text{Cl}_2]^+$, which is named as tetraamminedichlorochromium (III) ion.
- If the complex is an anion, its name ends in -ate. For example, in $\text{K}_4[\text{Fe}(\text{CN})_6]$ the anion $[\text{Fe}(\text{CN})_6]^{4-}$ is called hexacyanoferrate(II) ion. Note that the numeral (II) indicate the oxidation state of iron. Table given below gives the name of anions containing metal atoms (Table 22.2).
- If the complex is either a cation or is neutral, no change is required in the name of the central metal ion. For example $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Ni}(\text{CO})_4]$ are named as hexaamminecobalt(III)ion and tetracarbonyl nickel(0), respectively.

Table 22.2: Some anions containing metal atoms

Metal	Name of metal in anionic state
Copper	Cuprate
Zinc	Zincate
Aluminum	Aluminate
Chromium	Chromate
Tin	Stannate
Cobalt	Cobaltate
Nickel	Nickelate
Gold	Aurate
Silver	Argentate
Lead	Plumbate
Rhodium	Rhodate
Iron	Ferrate
Manganese	Manganate

A. few examples are given below:

$[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_3$	hexaaquacobalt(III) chloride
$\text{K}_2[\text{PtCl}_6]$	potassium hexachloroplatinate(IV)
$[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$	diamminetetrachloroplatinum(IV)
$[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$	dichlorobis (ethylenediamine)cobalt(III) chloride.



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INTEXT QUESTIONS 22.3

- Write down the name of the following complexes:
 - $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]^+$
 - $(\text{NH}_4)_3[\text{Cr}(\text{NCS})_6]$
 - $\text{Ni}(\text{CO})_4$
 - $\text{K}_4[\text{Fe}(\text{CN})_6]$
 - $[\text{Cr}(\text{en})_3]\text{Cl}_3$
- Write down the formula of the following:
 - Tetrachloronickelate(II)
 - Pentaamminenitrocobalt(III) ion
 - Potassium hexacyanoferrate(III)
 - Dichlorobis(ethylenediammine) chromium(III) ion

22.4 VALENCE BOND THEORY

Linus Pauling of the California Institute of Technology developed the valence bond theory. He was awarded the Nobel prize in chemistry in 1954. Pauling's ideas have had an important impact on all areas of chemistry. He applied valence bond theory to coordination compounds. This theory can account reasonably well for the structure and magnetic properties of metal complexes.

The basic principles, which are involved in the valence bond treatment of coordination compounds are:

- Hybridization of valence orbitals of the central metal/ ion
- Bonding between ligand and the metal ion/atom.
- Relation between the type of bond and the observed magnetic behaviour.

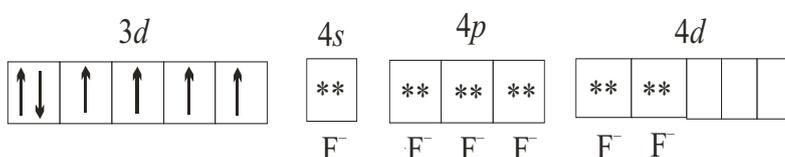
Six Coordinate Complexes

Let us explain by taking simple examples such as $[\text{CoF}_6]^{3-}$ and $[\text{Co}(\text{NH}_3)_6]^{3+}$. Although in both the complexes, the oxidation state of cobalt is +3, but $[\text{CoF}_6]^{3-}$ is paramagnetic and $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic, why? The formation of a complex may be considered as a series of hypothetical steps. First the appropriate metal ion is taken e.g. Co^{3+} . Cobalt atom has the outer electronic configuration $3d^74s^2$. Thus Co^{3+} ion will have the configuration $3d^6$ and the electrons will be arranged as:



Co^{3+} ion forms both paramagnetic (outer orbital) and diamagnetic (inner orbital) complexes depending upon the nature of ligands as illustrated below.

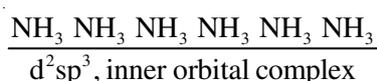
As Co^{3+} ion combines with six fluoride ligands in $[\text{CoF}_6]^{3-}$, empty atomic orbitals are required on the metal ion to receive the coordinated lone pair of electrons. The orbitals used are one $4s$, three $4p$ and two $4d$. These are hybridized to give a set of six equivalent sp^3d^2 hybrid orbitals. A ligand orbital containing a lone pair of electron forms a coordinate bond by overlapping with an empty hybrid orbital on the metal ion. In this way a σ bond is formed with each ligand. The d -orbitals used are the $4d_{x^2-y^2}$ and $4d_{z^2}$. It is shown below:



sp^3d^2 , outer orbital complex

Since the outer $4d$ orbitals are used for bonding, this is called an outer orbital complex. The energy of these orbitals is quite high, so the complex will be reactive. This complex will be high-spin paramagnetic, because it has four unpaired electrons.

An alternative octahedral arrangement in $[\text{Co}(\text{NH}_3)_6]^{3+}$ is possible when the electrons on metal ion are rearranged as shown below:

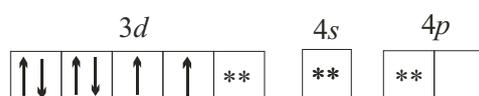


Since inner d -orbitals are used this is called an inner orbital complex. There is no unpaired electron, the complex will be low-spin diamagnetic.

The metal ion can also form 4-coordinate complexes. For such complexes two different arrangements are possible i.e. tetrahedral (sp^3) and square planar (dsp^2):



tetrahedral sp^3



square planar dsp^2



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About such complexes you will study later.

Let us illustrate six coordinate complexes with more examples:



The electronic configuration of only 3d, 4s and 4p orbitals are taken into account. The following steps are involved. The electronic configuration of Cr atom and Cr^{3+} ion are given in (i) and (ii) below:

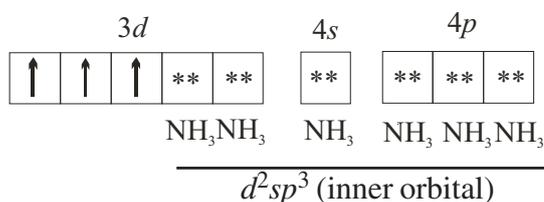
(i) Cr ground state:



(ii) Cr^{3+}



(iii) $[\text{Cr}(\text{NH}_3)_6]^{3+}$



The 12 electrons for bond formation come from six ligands, each donating a lone pair of electrons. The resulting complex will be paramagnetic because it has three unpaired electrons. Its magnetic moment will be:

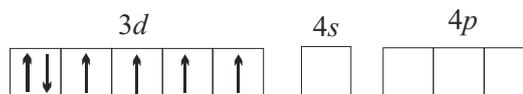
$$\sqrt{n(n+2)} = \sqrt{3(\sqrt{3+2})} = \sqrt{15} = 3.87\text{B.M}$$

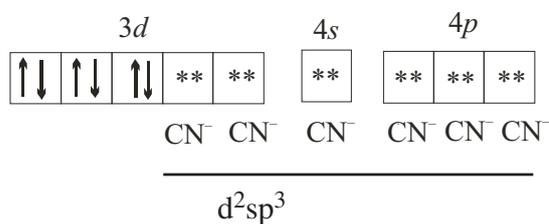


(i) Fe



(ii) Fe^{2+}

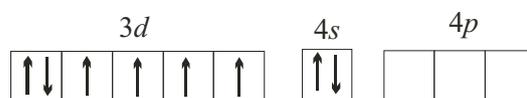


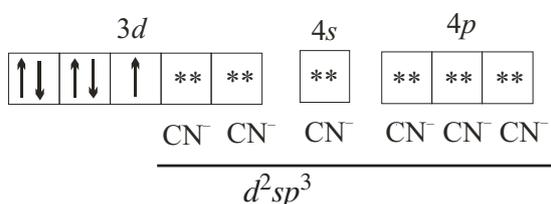
(iii) $[\text{Fe}(\text{CN})_6]^{4-}$


The resulting complex is inner orbital, octahedral and due to the absence of unpaired electron, it will be diamagnetic.

 3. $[\text{Fe}(\text{CN})_6]^{3-}$

(i) Fe


 (ii) Fe^{3+}

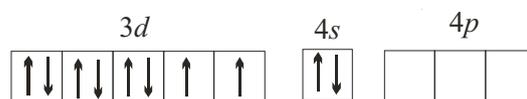
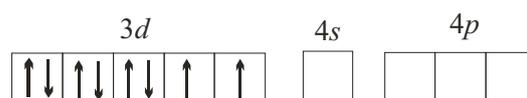
 (iii) $[\text{Fe}(\text{CN})_6]^{3-}$


The resulting complex is inner orbital, octahedral. Due to presence of one unpaired electron, it will be paramagnetic.

Four coordinate complexes:

 1. $[\text{NiCl}_4]^{2-}$

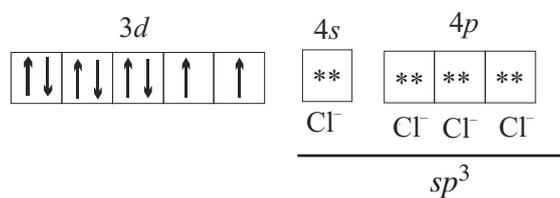
(i) Ni


 (ii) Ni^{2+}


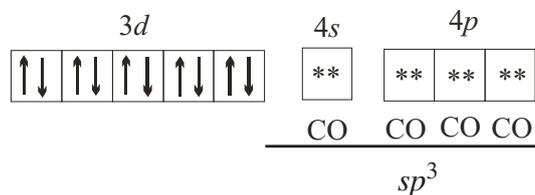
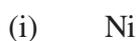
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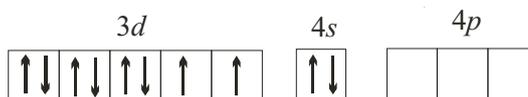
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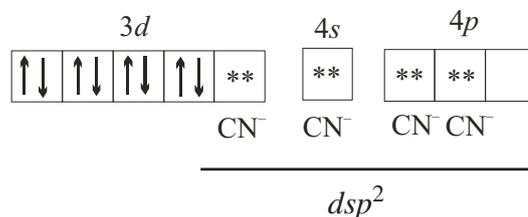


The resulting complex will be tetrahedral with two unpaired electrons. It will be paramagnetic.



The resulting complex will be tetrahedral. It has no unpaired electrons and will be diamagnetic.





The resulting complex is square planar and diamagnetic.

22.5 CRYSTAL FIELD THEORY

Although valence bond theory explains the bonding and magnetic properties of complexes, it is limited in two important ways. First, the theory cannot easily explain the color of complexes. Second, the theory is difficult to extend quantitatively. Consequently, another theory—crystal field theory—has emerged as the prevailing view of transition-metal complexes. This theory has been given by Bethe and van Vlack.

Crystal field theory is a model of the electronic structure of transition-metal complexes that considers how the energies of the d orbitals of a metal ion are affected by the electric field of the ligands. According to this theory, the ligands in a transition-metal complex are treated as point charges. So a ligand anion becomes simply a point of negative charge. A neutral ligand, with its electron pair that it donates to the metal atom, is replaced by a partial negative charge, representing the negative end of the molecular dipole. In an electric field of these negative charges, the five d orbitals of the metal atom no longer have exactly the same energy. The result, as you will see, explains both the paramagnetism and the color observed in certain complexes.

Effect of an Octahedral Field on the d Orbitals

All five d orbitals of an isolated metal atom have the same energy. But if the atom is brought into the electric field of several point charges, these d orbitals may be affected in different ways and therefore may have different energies. To understand how this can happen, you must first see what these d orbitals look like. You will then be able to picture what happens to them in the crystal field theory of an octahedral complex.

Figure 22.1 shows the shapes of the five d orbitals. The orbital labeled dz^2 has a dumbbell shape along the z -axis, with a collar in the x - y plane surrounding this dumbbell. Remember that this shape represents the volume most likely to be occupied by an electron in this orbital. The other four d orbitals have “cloverleaf” shapes, each differing from one another only in the orientation of



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the lobes in space. The “cloverleaf” orbital $dx^2 - y^2$ has its lobes along the x -axis and the y -axis. Orbitals dxy , dxz , and dyz have their lobes directed between the two sets of axes designated in the orbital label. Orbital dxy , for example, has its lobes lying between the x - and y -axes.

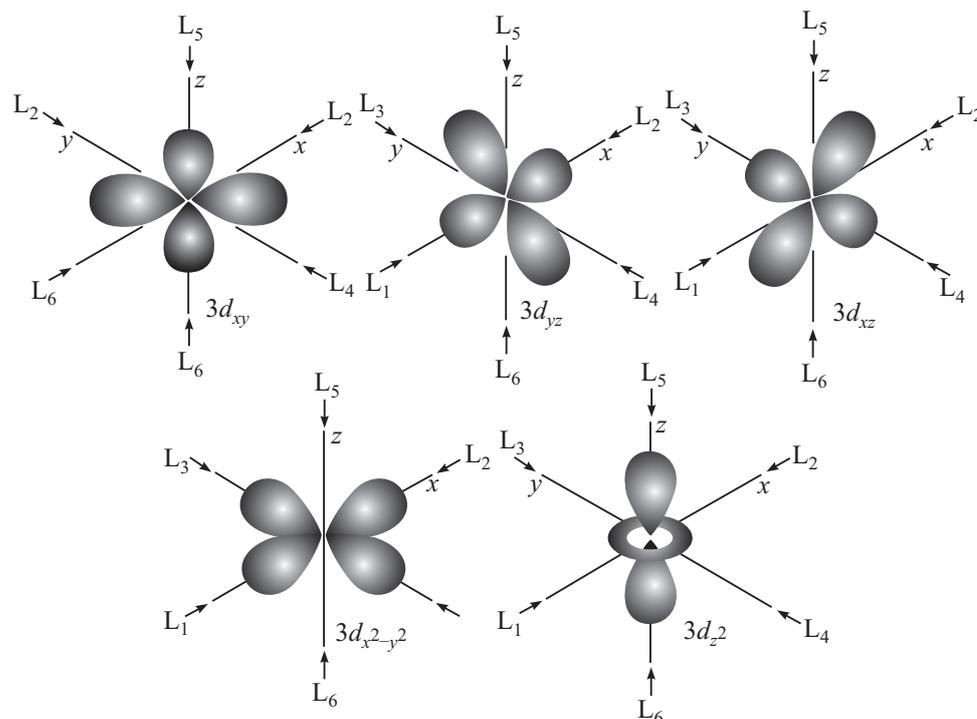


Fig. 22.1: Shapes of d orbitals

A complex ion with six ligands will have the ligands arranged octahedrally about the metal atom to reduce mutual repulsion. Imagine that the anionic ligands are replaced by point negative charges and the neutral ligands are replaced by the partial negative charge from the molecular dipoles. The six charges are placed at equal distances from the metal atom, one charge on each of the positive and negative sides of the x -, y -, and z -axes.

Fundamentally, the bonding in this model of a complex is due to the attraction of the positive metal ion for the negative charges of the ligands. However, an electron in a d -orbital of the metal atom is repelled by the negative charge of the ligands.

When ligands approach along the x , y , and z axes, electrons in the $3d$ orbital will be repelled but as can be seen from above diagrams the effect will be greater for the $3dz^2$ and $3dx^2 - y^2$ orbitals since these two orbitals have lobes lying along the line of approaching ligands. The net result is that the energy of the $3dz^2$ and $3dx^2 - y^2$ orbitals is raised relative to the energy of the $3dxy$, $3dxz$, and $3dyz$ orbitals i.e. the degeneracy of the $3d$ orbitals is now destroyed.

The 3d levels are split into an upper group of two (doubly degenerate and labeled e_g) and a lower group of three (triple degenerate and labeled t_{2g}), the splitting of the levels is represented by the symbol Δ . If we reckon the zero of energy as the state of affairs that would obtain if each of the five 3d orbitals had interacted equally with the six ligands, then each of the upper two orbitals is raised by $\frac{3}{5} \Delta$ while each of the three lower orbitals is lowered by $\frac{2}{5} \Delta$ (Δ collectively). As shown in diagram.

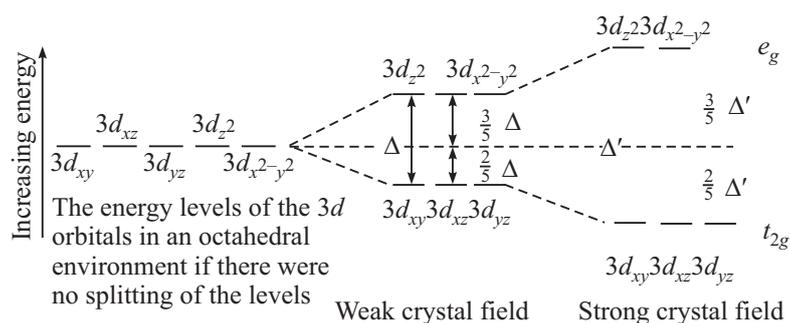


Fig. 22.2: The splitting of the 3d levels in an octahedral environment of ligands.

If we now consider the example of a transition metal ion with only one 3d electron surrounded octahedrally by six ligands, e.g. $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, then this single 3d electron will normally occupy one of the three degenerate lower levels (t_{2g}). In order to transfer this electron into an upper level (e_g) radiation of the appropriate frequency must be supplied. Transition metal ions are coloured because radiation in the visible spectrum is of the right frequency to promote this electronic transition, and in particular $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ions are purple because green light (wavelength about 500 nm) is absorbed, i.e. white light minus green light gives purple light. The relationship between Δ and the frequency of light absorbed is given by the usual expressions-

$$\Delta = h\nu$$

Where h is Planck's constant and ν is the frequency absorbed.

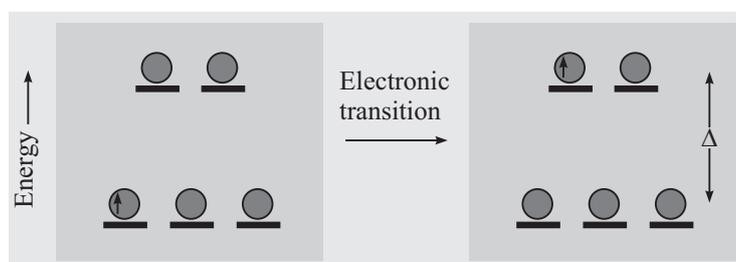


Fig. 22.3: The electronic transition responsible for the visible absorption in $\text{Ti}(\text{H}_2\text{O})_6^{3+}$. An electron undergoes a transition from a lower-energy d orbital to a higher-energy d orbital. The energy change equals the crystal field splitting Δ .



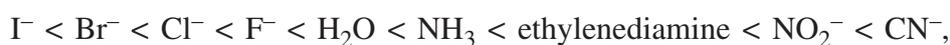
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Similar considerations apply to complexes in which the central transition metal ion has more than one 3d electrons although needless to say the presence of more than one electron in the 3d orbitals leads to slight complications.

It is found experimentally that for a given transition series (in the case of first transition series) the value of Δ depends upon (a) the charge carried by the central transition metal ion, (b) the nature of the ligand and, (c) the transition metal ion itself. In general, for a given ligand, the crystal field splitting is greater for M^{3+} octahedral complexes compared to that in Mn^{2+} octahedral complexes, while for transition metal ions carrying the same charge, the value of Δ increase in the order,



where the above ions and neutral molecules are the ligands which may surround the transition metal ion. This order is known as the spectro chemical series.

Since small changes in the values of Δ can significantly affect the colour of the light absorbed by transition metal ions, it is not surprising that transition metal ions can show a wide range of colour in different environment.

Magnetic Properties

In order to explain why the same transition metal ion can often display two widely different degrees of paramagnetism in different environments. It is necessary to consider the spectrochemical series. For instance, the CN^- ion produces a greater crystal field splitting than other ligands.

Consider, for example, the octahedral complexes $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$ (Figure). The electron configuration of Fe^{3+} is $[Ar]3d^5$, and there are two possible ways to distribute the five d electrons among the d orbitals.

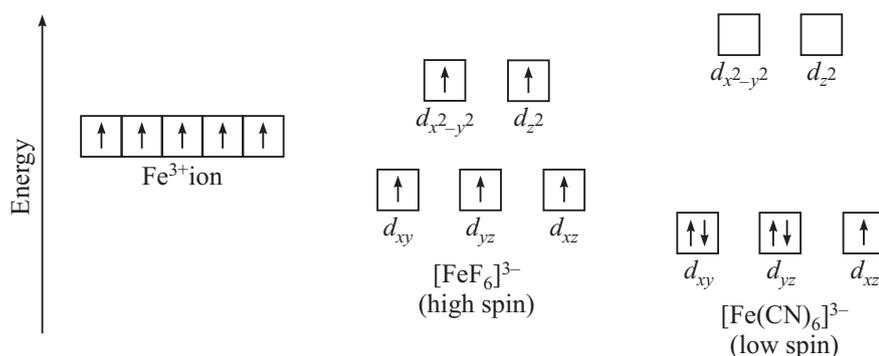


Fig. 22.4: Energy-level diagrams for the Fe^{3+} ion and for the $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$

As discussed earlier the d orbitals are split into two groups i.e. t_{2g} and e_g . If the value of Δ is small then high-spin complex is formed but if value of Δ is large then complex will be of low spin type.

High-spin complexes are more paramagnetic than low-spin complexes. d^4 , d^5 , d^6 and d^7 electronic configuration form low and high spin complexes. It is not possible to differentiate d^1 , d^2 , d^3 , d^8 and d^9 systems on the basis of magnetic moments.

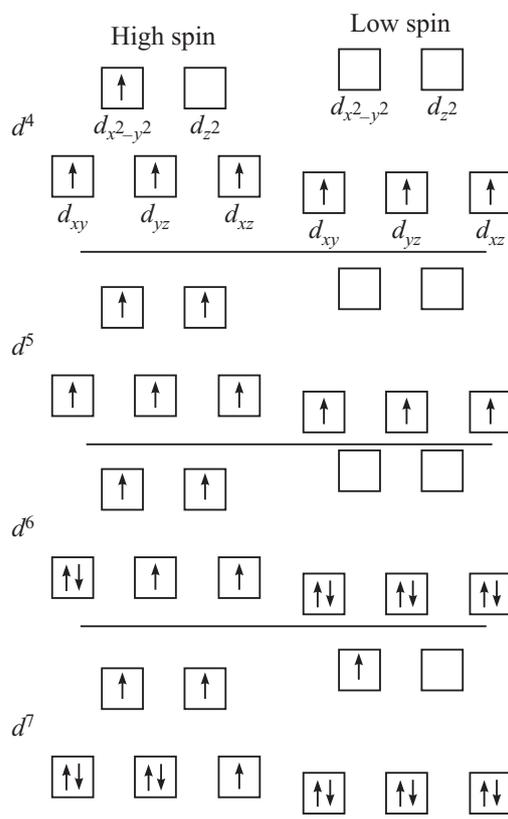


Fig. 22.5: Orbital diagrams for the high spin and low spin octahedral complexes corresponding to the electron configuration d^4 , d^5 , d^6 , and d^7 .



INTEXT QUESTIONS 22.4

- Name the type of hybridization present in: $[\text{Co}(\text{NH}_3)_6]^{3+}$.
- $[\text{Fe}(\text{CN})_6]^{3-}$ is diamagnetic or paramagnetic?
- $[\text{NiCl}_4]^{2-}$ and $\text{Ni}(\text{CO})_4$ have sp^3 or dsp^2 hybridization?
- Which one is diamagnetic: $[\text{Ni}(\text{CN})_4]^{2-}$ or $[\text{NiCl}_4]^{2-}$?
- What type of hybridization is shown by (i) inner and (ii) outer orbital complexes?
- $[\text{FeF}_6]^{4-}$ is paramagnetic but $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic. explain by CFT.
- Which is strong field ligand F^- or CN^- .



Notes

22.6 ISOMERISM

Compounds which have the same molecular formula, but different structural formulae are said to be isomers. There are many types of isomerism possible. The isomerism can be classified as:

Isomerism

Structural isomerism	Stereo isomerism
(a) Ionisation	(a) Geometrical
(b) Hydrate	(b) Optical
(c) Coordination	
(d) Linkage	

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- Structural isomerism.** This may be subdivided into sub-classes; for example:
 - Ionization isomerism, when the compounds yield different ions in solution, e.g. $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}\text{SO}_4^{2-}$ and $[\text{Co}(\text{NH}_3)_5\text{SO}_4]^+\text{Br}^-$.
 - Hydration isomerism. These compounds show different conductivities in solution, and they precipitate different amounts of silver chloride from cold silver nitrate solution. e.g. $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (violet), $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (light green), and $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (dark green).
 - Coordination isomerism, when cation and anion both are complexes. e.g. $[\text{Co}(\text{NH}_3)_6]^{3+}[\text{Cr}(\text{C}_2\text{O}_4)_3]^{3-}$ and $[\text{Cr}(\text{NH}_3)_6]^{3+}[\text{Co}(\text{C}_2\text{O}_4)_3]^{3-}$.
 - Linkage Isomerism: Complexes in which linkages of ligand is different for example $[\text{Co}(\text{NH}_3)_5\text{SCN}]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$.
- Geometrical isomerism.** These are isomers in which the composition of the first coordination sphere is the same, but the geometrical arrangement of the ligands varies. This is often called *cis-trans* isomerism, referring to the relative positions of two selected ligands. This isomerism is only possible for coordination numbers greater than or equal to four, e.g. *cis* and *trans* $\text{PtCl}_2(\text{NH}_3)_2$.
- Optical isomerism.** Any molecule which contains no plane or centre of symmetry may exist in two forms which are non-superimposable mirror images of one another. These have identical chemical and physical properties except that they rotate the plane of plane-polarized light equally but in opposite directions, and they react differently with other optically active compounds. Such compounds are normally obtained as a 50:50 mixture (called a racemic mixture) of the two optical isomers (called enantiomers, or enantiomorphs), which is therefore optically inactive, such as $[\text{Co}(\text{en})_3]^{3+}3\text{Cl}^-$.

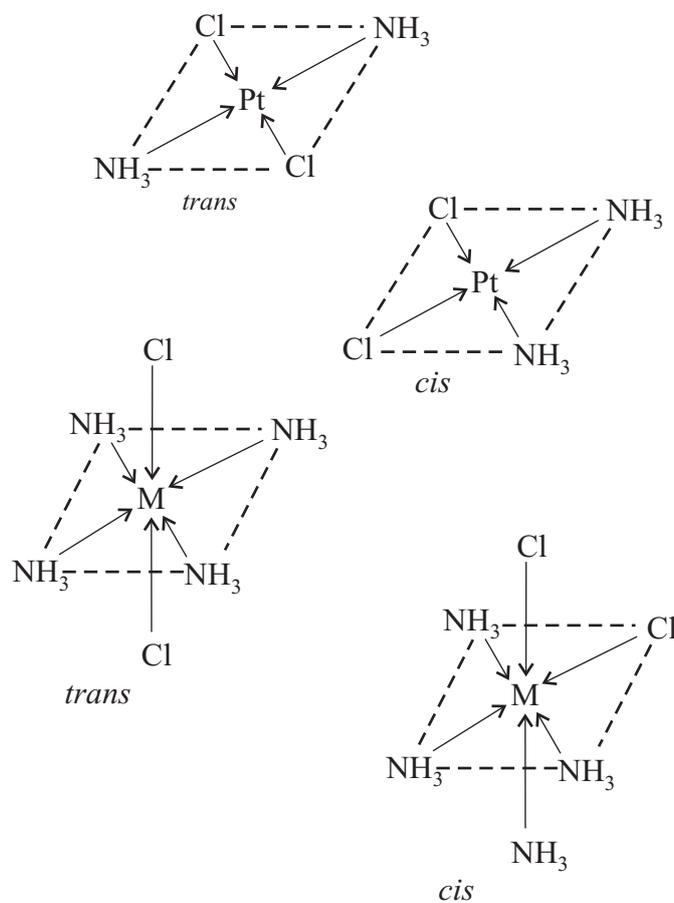
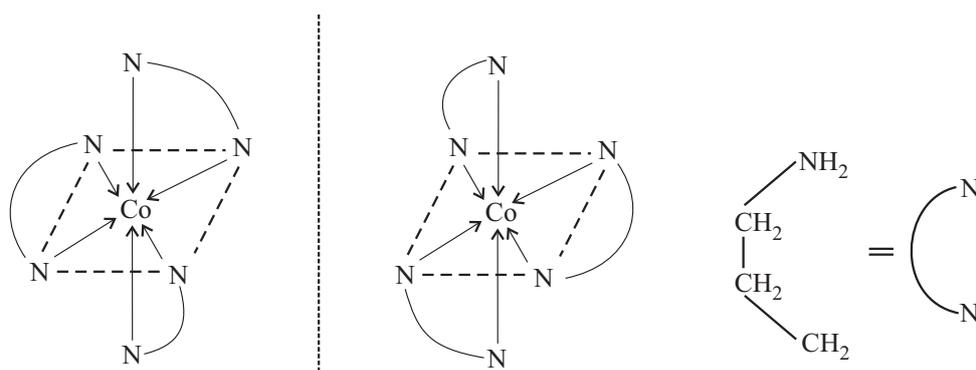

 Two examples of *cis-trans* isomers


Fig. 22.6: The enantiomers of $[\text{Co}(\text{en})_3]^{3+}$ (*en* = ethylenediamine), also called 1,2-di-aminoethane.

22.7 APPLICATIONS OF COORDINATION COMPOUNDS

Coordination compounds are found in living systems and have many uses in the home, in industry and in medicines. A few examples are given below:

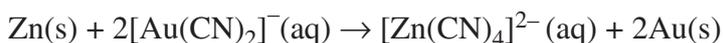


Notes



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Extraction of metals: cyanide ions are used for the extraction of gold and silver. The crushed ore is heated with an aq. cyanide solution in the presence of air to dissolve the gold by forming the soluble complex ion $[\text{Au}(\text{CN})_2]^-$.

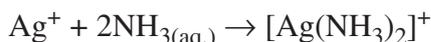


Complex formation is also useful for the purification of metals. Nickel is purified by converting the metal to the gaseous compound $\text{Ni}(\text{CO})_4$ and then decomposing the latter to pure nickel.

Medicines: EDTA is a chelating agent which is used in the treatment of lead poisoning. Cis platin $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ is used in the treatment of cancer. Sodium nitroprusside, $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$ is used to lower blood pressure during surgery.

Qualitative Analyses: complex formation is useful for qualitative analyses.

(a) Separation of Ag^+ from Pb^{2+} & Hg^{2+}



Soluble

(b) Separation of IIA and IIB groups: The cations of IIB group form soluble complex with yellow ammonium sulphide.

(c) Cu^{2+} ion forms complex on addition of ammonia $[\text{Cu}(\text{NH}_3)_4]^{2+}$.

(d) Fe^{2+} forms a blue complex with $\text{K}_3\text{Fe}(\text{CN})_6$, i.e. $\text{K Fe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$.

(f) Cobalt(II) gives color with HCl due to the formation of complex $[\text{CoCl}_4]^{2-}$.

(g) Nickel forms a red complex $[\text{Ni}(\text{DMG})_2]$ with dimethylglyoxime (H_2DMG).



INTEXT QUESTIONS 22.5

1. Name two elements which are extracted by complexation.
2. What is the use of EDTA in medicine?
3. Name the compound of platinum which is used as anticancer agent?
4. Give two uses of complexes in qualitative analyses
5. Write down geometrical isomers of $\text{Pt}(\text{NH}_3)\text{Cl}_2$.
6. $[\text{Co}(\text{NH}_3)_5\text{SCN}]^{2+}$ and $[\text{Co}(\text{NH}_3)_5\text{NCS}]^{2+}$ is the example of

**WHAT YOU HAVE LEARNT**

- Coordination compounds are compound in which a central metal ion is attached to a group of surrounding ligands by coordinate covalent bond. Ligands can be monodentate or polydentate, depending upon the number of donor atoms attached to the metal. Polydentate ligands are also called chelating agents. They form complexes that have rings of atoms known as chelate rings.
- The number of donor atoms bonded to a metal is called the coordination number of the metal. Common coordination number and geometries are 2 (linear), 4 (tetrahedral and square planar), and 6 (octahedral).
- Systematic names for complexes specify the number of ligands of each particular type, the metal, and its oxidation state.
- Valance Bond Theory describes the bonding in complexes in terms of two-electron, coordinate covalent bonds resulting from the overlap of filled ligand orbitals with vacant metal hybrid orbitals that point in the direction of the ligands; sp (linear), sp^3 (tetrahedral), dsp^2 (square planar) and d^2sp^3 or sp^3d^2 (octahedral).
- Colour and magnetic behaviour of the complexes by using Crystal Field theory.
- Structural isomension i.e. ionisation, hydrate, coordination and Linkage Stereoisomerism, Geometrical and optical.
- Complexes are very useful in qualitative analyses and in medicine.

**TERMINAL EXERCISE**

1. Define the following:
 - (i) Coordination number
 - (ii) Coordination sphere
 - (iii) Oxidation number
2. Define ligands. Give one example of each of monodentate, bidentate and polydentate ligands.
3. Write the postulates of Werner's theory of coordination compounds.



Notes



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4. Write down the name of the following complexes:
 - (i) $\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$
 - (ii) $[\text{Co}(\text{NH}_3)_2(\text{H}_2\text{O})_2\text{Cl}_2]^+$
 - (iii) $[\text{Pt}(\text{en})_2]^{2+}$
 - (iv) $[\text{NiCl}_4]^{2-}$
 - (v) $[\text{Fe}(\text{CN})_6]^{4-}$
5. Write down the formulae of the following complexes:
 - (i) Tris(ethylenediamine)platinum(IV)
 - (ii) Tetraaquadibromocobalt(III) ion
 - (iii) Sodium tetraiodozincate(II)
 - (iv) Tetracyanonickelate(II) ion
 - (v) Dichlorotetrathiocyanatochromium(III) ion
6. Give the salient features of VB theory for complexes. What do you mean by inner and outer orbital complexes?
7. $[\text{NiCl}_4]^{2-}$ and $\text{Ni}(\text{CO})_4$ are tetrahedral but differ in magnetic behaviour, explain.
8. $\text{Ni}(\text{CO})_4$ and $[\text{Ni}(\text{CN})_4]^{2-}$ are diamagnetic but have different geometry, explain.
9. $[\text{NiCl}_4]^{2-}$ is paramagnetic whereas $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic, explain.
10. Explain the types of hybridization and magnetic behaviour of the following complexes on the basis of VB theory:
 - (i) $[\text{Fe}(\text{CN})_6]^{4-}$
 - (ii) $[\text{Cr}(\text{NH}_3)_6]^{2+}$
 - (iii) $[\text{Fe}(\text{CN})_6]^{3-}$
 - (iv) $[\text{NiCl}_4]^{2-}$
 - (v) $\text{Ni}(\text{CO})_4$
11. Explain the application of complexes in extraction of elements, medicines and qualitative analyses.
12. Write down geometrical and optical isomeric of $[\text{Co}(\text{Cu})_2\text{Cl}_2]^+$.
13. $[\text{Co}(\text{NH}_3)_6]^{3+}$ is yellow in colour but $[\text{CoF}_6]^{3-}$ is blue. Why?
14. $\{\text{Fe}(\text{H}_2\text{O})_6\}^{3+}$ shows magnetic moment is 5.9 BM but magnetic moment of $[\text{Fe}(\text{CN})_6]^{3+}$ is 1.82 BM. Explain on the basis of CFT.



ANSWERS TO INTEXT QUESTIONS

22.1

1. Primary valence corresponds to the oxidation state of the central metal ion. It is satisfied by negative ions only.
2. Secondary valence of the metal corresponds to coordination number and is satisfied by negative ions or neutral molecules.
3. In both secondary valance is 6.
4. Octahedral.
5. Two i.e. Tetrahedral or square planar.

22.2

1. (i) 6
(ii) 6
(iii) 4
2. (i) +2
(ii) +3
(iii) +3
(iv) +2
3. EDTA
4. NH_3 , ethylenediammine and EDTA
5. +3, 6, Ethylenediammine.

22.3

1. (i) Tetraamminedichlorocobalt (III) ion
(ii) Ammonium-hexaisothiocyanatochromate (III)
(iii) Tetracarbonylnickel (0)
(iv) Potassium-hexacyanoferrate (II)
(v) Tris(ethylenediamine) chromium (III) chloride
2. (i) $[\text{NiCl}_4]^{2-}$
(ii) $[\text{Co}(\text{NH}_3)_5\text{NO}_2]^{2+}$



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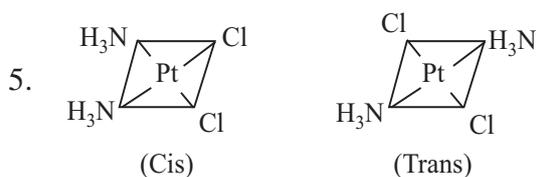


22.4

1. d^2sp^3
2. $[Fe(CN)_6]^{3-}$ is paramagnetic because it has one unpaired electron.
3. Both the complexes have sp^3 (tetrahedral) hybridization.
4. $[Ni(CN)_4]^{2-}$ is diamagnetic because it is square planar (dsp^2 hybridization). It has no unpaired electron.
5. Inner – d^2sp^3 , outer – sp^3d^2
6. F^- is weak field ligand therefore electron will be filled $t_{2g}^4e_g^0$ (i.e. four unpaired electron) therefore paramagnetic but CN^- is strong field ligand so electronic configuration will be $t_{2g}^6e_g^0$ (no unpaired electron)
7. F^- weak field CN^- strong field ligand.

22.5

1. Gold and silver are extracted by cyanide process.
2. EDTA forms soluble complex with elements. It is used in the treatment of lead poisoning.
3. Cis-platin
4. $[Cu(NH_3)_4]^{2+}$ & $[Ni(DMG)_2]$



6. Linkage isomerism

