CO–ORDINATION COMPOUNDS

1 TRANSITION ELEMENTS

Three series of elements are formed by filling the 3d, 4d and 5d–subshells of electrons. Together these comprise the d–block elements. *They are often called 'transition elements' because their position in the periodic table is between the s–block and p–block elements*. Their properties are transitional between the highly reactive metallic elements of the s–block, which typically forms ionic compounds and the elements of the p–block, which are largely covalent. In the s and p–blocks, electrons are added to the outer shell of the atom. In the d–block, electrons are added to the penultimate shell, expanding it from 8 to 18 electrons. Typically the transition elements have an incompletely filled d–level. Group 12 (the zinc group) has a d^{10} configuration and since the d–subshell is complete, compounds of these elements are not typical and show some differences from the others. The transition elements make up three complete rows of ten elements and an incomplete fourth row.

Thus, the transition elements are defined as those elements, which have partly filled d–orbitals, as elements and in any of their important compounds.

The general electronic configuration of the d–block elements can be represented as,

$(n-1)d^{1-9}ns^{1-2}$

Depending on the subshell getting filled up the transition elements form three series. The first transition series contain the elements from Sc (Z = 21) to Zn (Z = 30) and the 3d–orbital gets filled up in this series. In the second series, the 4d–orbital gets filled up from Y (Z = 39) to Cd (Z = 48). The 5d–orbital from La (Z = 57) to Hg (Z = 80) gets filled up for the elements of the third series. The fourth series starting with Ac is incomplete.

Group No.	3	4	5	6	7	8	9	10	11	12
At. No. (Z)	21	22	23	24	25	26	27	28	29	30
Symbol	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
At. No. (Z)	39	40	41	42	43	44	45	46	47	48
Symbol	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
At. No. (Z)	57	72	73	74	75	76	77	78	79	80
Symbol	La *	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
At. No. (Z)	89									
Symbol	Ac *									

14 Lanthanide elements
14 Actinide elements

Unlike the s and p–block elements of the same period, the d–block elements do not show much variation in properties, both chemical and physical. This is because these elements differ only in the number of electrons in the penultimate d–shell. The number of electrons in the valence shell remains the same, ns^2, for most of the elements.

2 METALLIC CHARACTER

In the d–block elements, the penultimate shell of electrons is expanding. Thus, they have many physical and chemical properties in common. Thus, all the transition elements are metals. They are good conductors of heat and electricity, have a metallic luster and are hard, strong and ductile. They also form alloys with other metals. Copper exceptionally is both soft and ductile and relatively noble.

3 VARIABLE OXIDATION STATE

One of the most striking features of the transition elements is that the elements usually exist in several different oxidation states and the oxidation states change in units of one.
For example: Fe^{3+} and Fe^{2+}, Cu^{2+} and Cu^{+} etc.

The oxidation states shown by the transition elements may be related to their electronic configurations. Calcium, the s–block element preceding the first row of transition elements, has the electronic configuration:

$$\text{Ca }(Z = 20):\quad 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 : \ [Ar]4s^2$$

It might be expected that the next ten transition elements would have this electronic arrangement with from one to ten d–electrons added in a regular way: $3d^1$, $3d^2$, $3d^3$…$3d^{10}$. This is true except in the cases of Cr and Cu. In these two cases, one of the s–electrons moves into the d–subshell, because of the additional stability of the exactly half–filled or completely filled d–orbital. Since the energies of (n–1) d and ns–orbitals are nearly equal, the transition elements exhibit variable oxidation states. The oxidation states of the d–block elements are listed below.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Electronic configuration	$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^4 4s^2$ $3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^9 4s^2$ $3d^{10} 4s^1$	$3d^{10} 4s^2$
Oxidation states				I					I	
	II	II	II	II	II	II	II	II	II	II
	III	III	III	III	III	III	III	III	III	
		IV	IV	IV	IV	IV	IV	IV		
			V	V	V	V	V			
				VI	VI	VI				
					VII					

Thus, Sc could have an oxidation state of (II) if both s–electrons are used for bonding and (III) when two s and one d–electrons are involved. Ti has an oxidation state (II) when both s–electrons are used for bonding, (III) when two s and one d–electrons are used and (IV) when two s and two d–electrons are used. Similarly, V shows oxidation numbers (II), (III), (IV) and (V). In the case of Cr, by using the single s–electron for bonding, we get an oxidation number of (I); hence by using varying number of d–electrons, oxidation states of (II), (III), (IV), (V) and (VI) are possible. Mn has oxidation states (II), (III), (IV), (V), (VI) and (VII). Among these first five elements, the correlation between electronic configuration and minimum and maximum oxidation states is simple and straight forward. In the highest oxidation states of these first five elements, all of the s and d–electrons are being used for bonding. Thus, the properties depend only on the size and valency.

Once the d^5 configuration is exceeded, i.e. in the last five elements, the tendency for all the d–electrons to participate in bonding decreases. Thus, Fe has a maximum oxidation state of (VI).

However, the second and third elements in this group attain a maximum oxidation state of (VIII), as in RuO_4 and OsO_4. This difference between Fe and the other two elements (Ru and Os) is attributed to the increased size and decreased attraction with the nucleus.

The oxidation number of all elements in the elemental state is zero. In addition, several of the elements have zero–valent and other low–valent states in complexes. Low oxidation states occur particularly with π–bonding ligands such as carbon monoxide and dipyridyl.

Some other important features about the oxidation states of transition elements

1. In group 8 (the iron group), the second and third row elements show a maximum oxidation state of (VIII) compared with (VI) for Fe.
2. The electronic configurations of the atoms in the second and third rows do not always follow the pattern of the first row. The configurations of group 10 elements (the nickel group) are:

   Ni (Z = 28) : $3d^8 4s^2$
   Pd (Z = 46) : $4d^{10} 5s^0$
   Pt (Z = 78) : $5d^9 6s^1$
3. Since a full shell of electrons is a stable arrangement, the place where this occurs is of importance in the transition series. The d–levels are complete at copper, palladium and gold in their respective series.

Ni	Cu : $3d^{10}4s^1$	Zn :	$3d^{10}4s^2$
Pd : $4d^{10}5s^0$	Ag : $4d^{10}5s^1$	Cd :	$4d^{10}5s^2$
Pt	Au : $5d^{10}6s^1$	Hg :	$5d^{10}6s^2$
4. Even though the ground state of the atom has a d^{10} configuration, Pd and the coinage metals Cu, Ag and Au behave as typical transition elements. This is because in their most common oxidation states, Cu(II) has a d^9 configuration and Pd(II) and Au(III) have d^8 configurations, that is they have an incompletely filled d–level. However, in zinc, cadmium and mercury, the ions Zn^{2+}, Cd^{2+} and Hg^{2+} have a d^{10} configuration. Because of this, these elements do not show the properties characteristic of transition elements.

Compounds are regarded as stable if they exist at room temperature, are not oxidized by the air, are not hydrolysed by water vapour and do not disproportionate or decompose at normal temperatures. Within each of the transition metals of groups 3–12, there is a difference in stability of the various oxidation states that exist. In general, the second and third row elements exhibit higher co–ordination numbers and their higher oxidation states are more stable than the corresponding first row elements. Stable oxidation states form oxides, fluorides, chlorides, bromides and iodides. Strongly reducing states probably do not form fluorides and/or oxides, but may well form the heavier halides. Conversely, strongly oxidizing states form oxides and fluorides, but not iodides.

Oxides and halides of some elements of the first row:

		Cr	**Mn**	**Fe**
II	O	CrO	MnO	FeO
	F	CrF_2	MnF_2	FeF_2
	Cl	$CrCl_2$	$MnCl_2$	$FeCl_2$
	Br	$CrBr_2$	$MnBr_2$	$FeBr_2$
	I	CrI_2	MnI_2	FeI_2
III	O	Cr_2O_3	Mn_2O_3	Fe_2O_3
	F	CrF_3	MnF_3	FeF_3

Cl	$CrCl_3$	–	$FeCl_3$
Br	$CrBr_3$	–	$FeBr_3$
I	CrI_3	–	–
IV O	CrO_2	MnO_2	–
F	CrF_4	MnF_4	–
Cl	$CrCl_4$	–	–
Br	$CrBr_4$	–	–
I	CrI_4	–	–
V F	CrF_5	–	–
VI O	CrO_3	–	–
F	CrF_6	–	–
VII O	–	Mn_2O_7	–

4 ATOMIC AND IONIC RADII

The covalent radii of the elements decrease from left to right across a row in the transition series, until near the end when the size increases slightly. On passing from left to right, extra protons are placed in the nucleus and extra orbital electrons are added. The orbital electrons shield the nuclear charge incompletely (d–electrons shield less efficiently than p–electrons, which in turn shield less effectively than s–electrons). Because of this poor screening by d–electrons, the nuclear charge attracts all of the electrons more strongly, hence a contraction in size occurs.

The elements in the first group in the d–block (group 3) show the expected increase in size Sc $\longrightarrow$ Y $\longrightarrow$ La. However, in the subsequent groups (4–12) there is an increase in radius of 0.1 $\longrightarrow$ 0.2 Å between the first and second member, but hardly any increase between the second and third elements. This trend is shown both in the covalent radii and in the ionic radii. Interposed between lanthanum and hafnium are the 14 lanthanide elements, in which the antipenultimate 4f–subshell of electrons is filled.

There is a gradual decrease in size of the 14 lanthanide elements from cerium to lutetium. This is called the "***lanthanide contraction***". The lanthanide contraction cancels almost exactly the normal size increase on descending a group of transition elements. Therefore, the second and third row transition elements have similar radii. As a result they also have similar lattice energies, solvation energies and ionization energies. Thus, the differences in properties between the first row and second row elements are much greater than the differences between the second and third row elements. The effects of the lanthanide contraction are less pronounced towards the right of the d–block. However, the effect still shows to a lesser degree in the p–block elements that follow.

Covalent radii of the transition elements (in Å)

K 1.57	Ca 1.74	Sc 1.44	Ti 1.32	V 1.22	Cr 1.17	Mn 1.17	Fe 1.17	Co 1.16	Ni 1.15	Cu 1.17	Zn 1.25
Rb 2.16	Sr 1.91	Y 1.62	Zr 1.45	Nb 1.34	Mo 1.29	Tc –	Ru 1.24	Rh 1.25	Pd 1.28	Ag 1.34	Cd 1.41
Cs 2.35	Ba 1.98	La * 1.69	Hf 1.44	Ta 1.34	W 1.30	Re 1.28	Os 1.26	Ir 1.26	Pt 1.29	Au 1.34	Hg 1.44

14 Lanthanide elements

5 DENSITY

The atomic volumes of the transition elements are low compared with elements in neighbouring groups 1 and 2. This is because the increased nuclear charge is poorly screened and so attracts all the electrons more strongly. In addition, the extra electrons added occupy inner orbitals. Consequently, the densities of the transition metals are high. Practically, most of the elements have a density greater than 5 g cm^{-3}. (The only exceptions are Sc: 3.0 g cm^{-3} and Y and Ti: 4.5 g cm^{-3}). The densities of the second row elements are high and third row values are even higher. The two elements with the highest densities are osmium: 22.57 g cm^{-3} and iridium: 22.61 g cm^{-3}. Thus, iridium is the heaviest element among all the elements of the periodic table.

6 MELTING AND BOILING POINT

The melting and boiling points of the transition elements are generally very high. Transition elements typically melt above 1000°C. Ten elements melt above 2000°C and three melt above 3000°C (Ta: 3000°C, W: 3410°C and Re: 3180°C). There are a few exceptions. **For example**, La and Ag melts just under 1000°C (920°C and 960°C respectively). Other notable exceptions are Zn(420°C), Cd(320°C) and Hg, which is liquid at room temperature and melts at –38°C. The last three behave atypically because the d–subshell is complete and d–electrons do not participate in metallic bonding.

7 IONISATION ENERGY

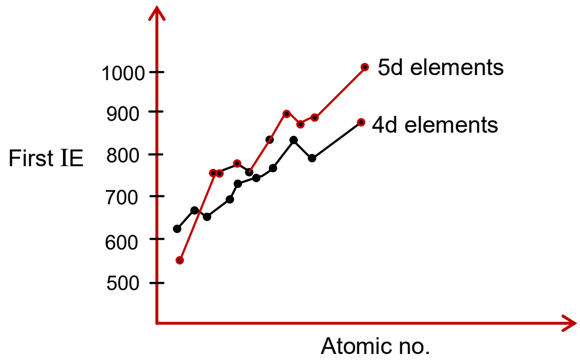
In a period, the first ionization energy gradually increases from left to right. This is mainly due to increase in nuclear charge. Generally, the ionization energies of transition elements are intermediate between those of s and p–block elements. The first ionization potential of the 5d–elements are higher than those of 3d and 4d–elements due to the poor shielding by 4f–electrons.

From 3d $\longrightarrow$ 4d series, general trend is observed but not from 4d $\longrightarrow$ 5d series because of incorporation of the 14 lanthanides elements between La and Hf. Third period of transition elements have the highest ionisation energy. This reflects the fact that increase in radius due to addition of extra shell is compensated by the decrease in radius due to lanthanide contraction.

As the radius of 4d and 5d–elements more or less remains the same, due to which Z_{eff} of elements of 5d series is higher, which results in high ionization energy of the 5d–elements of transition series.

The ionisation energy values (in kJ/mole) of the transitions elements are given in the table below:

3d series	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
First I. E	631	656	650	652	717	762	758	736	745	906
4d series	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
First I. E	616	674	664	685	703	711	720	804	731	876
5d series	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
First I. E	541	760	760	770	759	840	900	870	889	1007



8 REACTIVITY OF METALS

Many of the metals are sufficiently electropositive to react with mineral acids, liberating H_2. A few have low standard electrode potentials and remain unreactive or noble. Noble character is favoured by high enthalpies of sublimation, high ionization energies and low enthalpies of solvation. The high melting points indicate high heats of sublimation. The smaller atoms have higher ionization energies, but this is offset by small ions having high solvation energies. This tendency to noble character is most pronounced for the platinum metals (Ru, Rh, Pd, Os, Ir, Pt) and gold.

9 FORMATION OF COMPLEX COMPOUNDS

The transition elements have characteristic tendency to form co–ordination compounds with Lewis bases, that is with groups that are able to donate an electron pair. These groups are called ***ligands***. A ligand may be a neutral molecule such as NH_3, or an ion such as Cl^- or CN^-. Cobalt forms more complexes than any other element and forms more compounds than any other element after carbon.

$$Co^{3+} + 6NH_3 \rightleftharpoons [Co(NH_3)_6]^{3+}$$

$$Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$$

This ability to form complexes is in marked contrast to the s– and p–block elements, which form only a few complexes. The reason transition elements are so good at forming complexes is that they have small, highly charged ions and have vacant low energy orbitals to accept lone pairs of electrons donated by other groups or ligands. Complexes where the metal is in the (III) oxidation state are generally more stable than those where the metal is in the (II) state.

Some metal ions form their most stable complexes with ligands in which the donor atoms are N, O or F. Such metal ions include group 1 and 2 elements, the first half of the transition elements, the lanthanides and actinides and the p–block elements except for their heavier members. These metals are called "***class–a acceptors***" and correspond to ***'hard' acids***. In contrast the metals Rh, Ir, Pd, Pt, Ag, Au and Hg form their most stable complexes with the heavier elements of groups 15, 16 and 17. These metals are called "***class–b acceptors***" and correspond to ***'soft' acids***. The rest of the transition metals and the heaviest elements in the p–block, form complexes with both types of donors and are thus 'intermediate' in nature.

Classification of elements on the basis of type of acceptors

Li (a)	Be (a)											B (a)	C (a)	N (a)	O –
Na (a)	Mg (a)											Al (a)	Si (a)	P (a)	S (a)

K (a)	Ca (a)	Sc (a)	Ti (a)	V (a)	Cr (a)	Mn (a)	Fe (a/b)	Co (a/b)	Ni (a/b)	Cu (a/b)	Zn (a)	Ga (a)	Ge (a)	As (a)	Se (a)
Rb (a)	Sr (a)	Y (a)	Zr (a)	Nb (a)	Mo (a)	Tc (a/b)	Ru (a/b)	Rh (b)	Pd (b)	Ag (b)	Cd (a/b)	In (a)	Sn (a)	Sb (a)	Te (a)
Cs (a)	Ba (a)	La (a)	Hf (a)	Ta (a)	W (a)	Re (a/b)	Os (a/b)	Ir (b)	Pt (b)	Au (b)	Hg (b)	Tl (a/b)	Pb (a/b)	Bi (a/b)	Po (a/b)
Fr (a)	Ra (a)	Ac (a)													
			Ce (a)	Pr (a)	Nd (a)	Pm (a)	Sm (a)	Eu (a)	Gd (a)	Tb (a)	Dy (a)	Ho (a)	Er (a)	Tm (a)	Yb (a)
			Th (a)	Pa (a)	U (a)	Np (a)	Pu (a)	Am (a)	Cm (a)	Bk (a)	Cf (a)	Es (a)	Fm (a)	Md (a)	Mo (a)

Common Co-Ordination Number Shown by Transition Elements of First Row

(i) Scandium

Sc^{3+} forms complexes with co–ordination number of 6. Examples of such complexes are $[Sc(OH)_6]^{3-}$, $[ScF_6]^{3-}$ etc.

(ii) Titanium

Ti^{4+} forms complexes with a co–ordination number of 6. For example, $[TiCl_6]^{2-}$, $[Ti(SO_4)_3]^{2-}$ etc.

(iii) Vanadium

V^{2+} forms mostly octahedral complexes (co–ordination number = 6), for example $[V(H_2O)_6]^{2+}$, $K_4[V(CN)_6].7H_2O$. But $K_4[V(CN)_7].2H_2O$ is also known with a pentagonal bipyramidal structure (co–ordination number = 7).

V^{3+} forms octahedral complexes such as $[V(H_2O)_6]^{3+}$.

V^{4+} is known to form square pyramidal complexes with a co–ordination number of 5. Example of such complexes are $[VOX_4]^{2-}$, $[VO(OX)_2]^{2-}$, $[VO(bipyridyl)_2Cl]^{+}$ etc.

(iv) Chromium

Cr^{2+} forms octahedral complexes, such as $[Cr(H_2O)_6]^{2+}$ and $[Cr(NH_3)_6]^{2+}$ with co–ordination number 6.

Cr^{3+} forms octahedral complexes, such as $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_5Cl]^{2+}$ with co–ordination number 6.

(v) Manganese

Mn^{2+} forms octahedral complexes such as $[MnCl_6]^{4-}$ and $[Mn(en)_3]^{2+}$ with co–ordination number 6.

Mn^{3+} forms octahedral complexes such as $K_3[Mn(CN)_6]$ with co–ordination number 6.

Mn^{4+} forms octahedral complexes such as $K_2[MnF_6]$ and $K_2[Mn(CN)_6]$ with co–ordination number 6.

(vi) Iron

Fe^{2+} forms mostly octahedral complexes like $[Fe(H_2O)_6]^{2+}$ but few tetrahedral halides with co–ordination number 4 like $[FeX_4]^{2-}$ are also known.

Fe^{3+} is known to form octahedral complexes such as $[Fe(H_2O)_6]^{3+}$.

(vii) Cobalt

Co^{2+} is known to form both tetrahedral like $[Co(H_2O)_4]^{2+}]$ and octahedral such as $[Co(H_2O)_6]^{2+}$ complexes.

Co^{3+} forms octahedral complexes. For example, $[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$.

(viii) Nickel group

Ni^{2+} commonly forms octahedral and square planar complexes. Few tetrahedral, trigonal bipyramidal and square based pyramidal structures are also formed.

Pd^{2+} and **Pt^{2+}** are all square planar.

Ni^{3+} forms octahedral compounds. For example, $K_3[NiF_6]$ and $[Ni(en)_2Cl_2]Cl$.

Pd^{4+} forms a few octahedral complexes like $[PdX_6]^{2-}$, where X = F, Cl or Br. These are generally reactive. Halide complexes are decomposed by hot water, giving $[PdX_4]^{2-}$ and halogen. In contrast Pt^{4+} forms large number of very stable octahedral complexes like $[PtCl_6]^{2-}$.

(ix) Copper, silver and gold

Cu^+ forms tetrahedral complexes with Cl (for example, $[Cu(Cl)_4]^{3-}$) and linear complexes like $[CuX_2]^-$.

Cu^{2+} forms complexes both of co–ordination number 4 (like $[CuX_4]^{2-}$) and of co–ordination number 6 {like $[Cu(en)_3]^{2+}$, $[Cu(H_2O)_3(NH_3)_3]^{2+}$}.

Ag^+, Au^+ forms complexes with co–ordination number 2 like ($[M(CN)_2]^-$.

(x) Zinc and cadmium

Zn^{2+} and Cd^{2+} forms both tetrahedral and octahedral complexes. For example, $[MCl_4]^{2-}$, $[M(NH_3)_2Cl_2]$, $[M(NH_3)_4]^{2+}$, $[M(H_2O)_6]^{2+}$ etc.

10 COLOUR OF COMPLEX COMPOUNDS

Many ionic and covalent compounds of transition elements are coloured. In contrast compounds of the s– and p–block elements are almost always white. When light passes through a material, it is deprived of those wavelengths that are absorbed. If wavelength of the absorption occurs in the visible region of the spectrum, the transmitted light is coloured with the complementary colour to the colour of the light absorbed. Absorption in the visible and UV regions of the spectrum is caused by changes in electronic energy. Thus, the spectra are sometimes called electronic spectra.

Colour may arise from an entirely different cause in ions with incomplete d or f–subshells. This source of colour is very important in most of the transition metal ions.

In a free isolated gaseous ion, the five d–orbitals are degenerate that is they are identical in energy. In actual practice, the ion will be surrounded by solvent molecules if it is in solution, by other ligands if it is in a complex, or by other ions if it is in a crystal lattice. The surrounding groups affect the energy of some d–orbitals more than others. Thus, the d–orbitals are no longer degenerate and at their simplest they form two groups of orbitals of different energy. Thus, in transition element ions with a partly filled d–subshell it is possible to promote electrons from one d–level to another d–level of higher energy. This corresponds to a fairly small energy difference and so light it absorbed in the visible region. The colour of a transition metal complex is dependent on how big the energy difference is between the two d–levels. This in turn depends on the nature of the ligand and on the type of complex formed. Thus, the octahedral complex $[Ni(NH_3)_6]^{2+}$ is blue, $[Ni(H_2O)_6]^{2+}$ is green and $[Ni(NO_2)_6]^{4-}$ is brown–red. The colour changes with the ligand used. The colour also depends on the number of ligands and the shape of the complex formed.

The source of colour in the lanthanides and the actinides is very similar, arising from f $\longrightarrow$ f transitions. With the lanthanides, the 4f–orbitals are deeply embedded inside the atom and are well–shielded by the 5s and 5p–electrons. The f–electrons are practically unaffected by complex formation. Hence, the colour remains almost constant for the particular ion regardless of the ligand.

Some compounds of the transition metal are white, for example Cu_2Cl_2, $ZnSO_4$ and TiO_2. In these compounds, it is not possible to promote electrons within the d–level. Cu^+ and Zn^{2+} has a d^{10} configuration and the d–level is completely filled. Ti^{4+} has a d^0 configuration and the d–level is empty. In the series Sc(III), Ti(IV), V(V), Cr(VI) and Mn(VII), these ions may all be considered to have an empty d–subshell; hence d–d spectra are impossible and they should be colourless. However, as the oxidation state increases, these states become increasingly covalent. Rather than forming highly charged simple ions, they form oxoions like TiO^{2+}, VO_2^+, VO_4^{3-}, CrO_4^{2-} and MnO_4^-. VO_2^+ is pale yellow, but CrO_4^{2-} is strongly yellow coloured and MnO_4^- has an intense purple colour in solution, though the solid is almost black. The colour arises by charge transfer mechanism.

In MnO_4^-, an electron is momentarily transferred from O to the metal, thus momentarily changing O^{2-} to O^- and reducing the oxidation state of the metal from Mn(VII) to Mn(VI). Charge transfer requires the energy levels on the two different atoms to be fairly close. Charge transfer always produces more intense colours than the colours generated due to d–d transitions. Charge transfer is also possible between metal–ion and metal–ion as seen in prussian blue, $Fe_4[Fe(CN)_6]_3$.

The s and p–block elements do not have a partially filled d–subshell, so there cannot be any d–d transitions. The energy required to promote an s or p–electron to a higher energy level is much greater and corresponds to ultraviolet light being absorbed. Thus, compounds of s and p–block elements are typically not coloured.

11 MAGNETIC PROPERTIES

Compounds of the transition elements exhibit characteristic magnetic behaviour. Those, which are attracted by a magnetic field, are termed as paramagnetic. Those, which are repelled by a magnetic field, are called diamagnetic. Paramagnetic species have unpaired electrons in their electronic configuration. Diamagnetic substances are those in which electrons are fully paired. In a simple situation, where one may consider aquo complex ions, we have the following formulation.

Metal ion	Electronic configuration	No. of unpaired e^-'s	Metal ion	Electronic configuration	No. of unpaired e^-'s
Sc^{3+}	$3d^0$	No unpaired electrons	Ti^{3+}	$3d^1$	1 unpaired electron
V^{3+}	$3d^2$	2 unpaired electrons	Cr^{3+}	$3d^3$	3 unpaired electrons
Mn^{3+}	$3d^4$	4 unpaired electrons	Fe^{3+}	$3d^5$	5 unpaired electrons
Mn^{2+}	$3d^5$	5 unpaired electrons	Fe^{2+}	$3d^6$	4 unpaired electrons
Co^{2+}	$3d^7$	3 unpaired electrons	Ni^{2+}	$3d^8$	2 unpaired electrons
Cu^{2+}	$3d^9$	1 unpaired electron	Cu^+	$3d^{10}$	No unpaired electrons
Zn^{2+}	$3d^{10}$	No unpaired electrons			

Unpaired electrons in any species have, each, a spin angular momentum, which can be vectorially added to yield a resultant spin angular momentum. This gives rise to a magnetic moment. Actually, there are two contributions to the magnetic moment i.e., the magnetic moment due to orbital angular momentum and the spin magnetic moment. In many situations, the environment in which a species is located has the effect of quenching out the orbital contribution.

Thus, in such cases, only the spin magnetic moment is measured; in units of Bohr magneton. The spin magnetic moment is given by $\mu_s = \sqrt{n(n+2)}$ in BM, where n is the number of unpaired electrons.

Note : Bohr magneton has the value; BM = $\frac{eh}{4\pi m_o c}$ where e = magnitude of electronic charge, m_o = rest mass of the electron and c = speed of light in vaccum. Typical values are Ti^{3+}, $3d^1$, $\sqrt{1\times 3}$ BM = 1.73 BM and this agrees with the measured value. In many cases, the observed and calculated values in the spin magnetic moment are in fair agreement. In fact, determination of spin magnetic moment helps us to know the number of unpaired electrons in the complex/complex ion, which leads us to the bonding and structure elucidation of the complex/complex ion.

12 CATALYTIC PROPERTIES

Transition metals and their compounds act as good catalysts for a variety of reactions. The presence of empty d–orbitals enables them to form various intermediates during a reaction, thus providing a reaction path with lower activation energy for the reaction.

Many transition metals and their compounds have catalytic properties. Few of them are listed in the table below:

$TiCl_3$	Used as the Ziegler–Natta catalyst in the production of polythene.
V_2O_5	Converts SO_2 to SO_3 in the contact process for making H_2SO_4.
MnO_2	Used as a catalyst to decompose $KClO_3$ to give O_2.
Fe	Promoted iron is used in the Haber–Bosch process for making NH_3.
$FeCl_3$	Used in the production of CCl_4 from CS_2 and Cl_2.
$FeSO_4$ and H_2O_2	Used as Fenton's reagent for oxidizing alcohols to aldehydes.
Pd	Used for hydrogenation (e.g. phenol to cyclohexanone)
Pt/PtO	Adams catalyst, used for reductions.
Pt	Formerly used for $SO_2 \longrightarrow SO_3$ in the contact process for making H_2SO_4.
Pt/Rh	Formerly used in the Ostwald process for making HNO_3 to oxidize NH_3 to NO.
Cu	Is used in the manufacture of $(CH_3)_2SiCl_2$ used to make silicones.
$CuCl_2$	Deacon process of making Cl_2 from HCl.
Ni	Raney nickel is used in numerous reduction processes (e.g. manufacture of hexamethylenediamine, production of H_2 from NH_3, reducing anthraquinone to anthraquinol in the production of H_2O_2).

13 NON – STOICHIOMETRIC COMPOUNDS

A unique feature of the transition elements is that they sometimes form non–stoichiometric compounds. These are compounds of indefinite structure and proportions. For example, iron(II) oxide (FeO) should be written with a bar over the formula, $\overline{FeO}$ to indicate that the ratio of Fe and O atoms is not exactly 1 : 1. Analysis shows that the formula varies between $Fe_{0.94}O$ and $Fe_{0.84}O$. Non–stoichiometry of FeO is caused by defects in the solid structure.

Vanadium and selenium form a series of compounds ranging from $VSe_{0.98}$ to VSe_2. These are given the formulae:

$$\overline{VSe} \quad (VSe_{0.98} \longrightarrow VSe_{1.2})$$
$$\overline{V_2Se_3} \quad (VSe_{1.2} \longrightarrow VSe_{1.6})$$
$$\overline{V_2Se_4} \quad (VSe_{1.6} \longrightarrow VSe_2)$$

Non–stoichiometry is shown particularly among transition metal compounds of the group 16 elements (O, S, Se, Te). It is mostly due to the variable valency of transition elements. For example, copper is precipitated from a solution containing Cu^{2+} by passing in H_2S. The sulphide is completely insoluble, but this is not used as a gravimetric method for analyzing Cu because the precipitate is a mixture of CuS and Cu_2S.

14 INNER TRANSITION ELEMENTS

f–block elements are also referred as *"inner transition elements"*. These are two series of elements, formed by the filling of 4f and 5f–subshells. The elements in which 4f–subshell is filled are called *lanthanides* and the elements in which 5f–subshell is filled are called *actinides*.

15 ELECTRONIC CONFIGURATION

(i) Lanthanides :

Ce (Z=58) to Lu (Z=71) – (6^{th} period)

Atomic No. (Z)	58	59	60	61	62	63	64	65	66	67	68	69	70	71
Symbol	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

Electronic Configuration: $[Xe]\ 4f^{1-14}\ 5d^{0-1}\ 6s^2$

(ii) Actinides :

Th (Z = 90) to Lr (Z = 103) – (7^{th} period)

Atomic No. (Z)	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Symbol	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Electronic Configuration: $[Rn]\ 5f^{1-14}\ 6d^{0-1}\ 7s^2$

16 VARIABLE OXIDATION STATES OF LANTHANIDES AND ACTINIDES

Lanthanides exhibit (III) oxidation state (some elements show (II) and (IV) also). Many of the compounds are coloured. In the lanthanide elements, there is regular decrease in the radius as the period is traversed. This is known as ***"Lanthanide Contraction"*.** In case of actinides, it is called "***Actinide Contraction***". In these elements, the electrons are added to the anti–penultimate shell. The addition of each electron to the 4f–orbitals results in a concomitant increase in atomic number. Since, the addition of electrons is to the anti–penultimate shell, there is no significant change in the ultimate and penultimate shells. As a result of the increasing nuclear charge, there is a regular decrease in the radius along the period.

Electronic structures and oxidation states for lanthanide series

Element	**Symbol**	**Outer electronic configuration**	**Oxidation states**		
Lanthanum	La	$[Xe]5d^1 6s^2$		**III**	
Cerium	Ce	$[Xe]4f^1 5d^1 6s^2$		**III**	IV
Praseodymium	Pr	$[Xe]4f^3 6s^2$		**III**	(IV)
Neodymium	Nd	$[Xe]4f^4 6s^2$	(II)	**III**	
Promethium	Pm	$[Xe]4f^5 6s^2$	(II)	**III**	
Samarium	Sm	$[Xe]4f^6 6s^2$	(II)	**III**	
Europium	Eu	$[Xe]4f^7 6s^2$	II	**III**	
Gadolinium	Gd	$[Xe]4f^7 5d^1 6s^2$		**III**	
Terbium	Tb	$[Xe]4f^9 6s^2$		**III**	(IV)
Dysprosium	Dy	$[Xe]4f^{10} 6s^2$		**III**	(IV)
Holmium	Ho	$[Xe]4f^{11} 6s^2$		**III**	

Erbium	Er	$[Xe]4f^{12}6s^2$		**III**	
Thulium	Tm	$[Xe]4f^{13}6s^2$	(II)	**III**	
Ytterbium	Yb	$[Xe]4f^{14}6s^2$	II	**III**	
Lutetium	Lu	$[Xe]4f^{14}5d^1 6s^2$		**III**	

Electronic structures and oxidation states for actinide series

Element	**Symbol**	**Outer electronic configuration**	**Oxidation states**					
Actinium	Ac	$6d^1 7s^2$		**III**				
Thorium	Th	$6d^2 7s^2$		III	**IV**			
Protactinium	Pa	$5f^2 6d^1 7s^2$		III	IV	**V**		
Uranium	U	$5f^3 6d^1 7s^2$		III	IV	V	**VI**	
Neptunium	Np	$5f^4 6d^1 7s^2$		III	IV	**V**	VI	VII
Plutonium	Pu	$5f^6 7s^2$		III	**IV**	V	VI	VII
Americium	Am	$5f^7 7s^2$	**II**	**III**	IV	V	VI	
Curium	Cm	$5f^7 6d^1 7s^2$		**III**	IV			
Berkelium	Bk	$5f^9 7s^2$		**III**	IV			
Californium	Cf	$5f^{10} 7s^2$	II	**III**				
Einsteinium	Es	$5f^{11} 7s^2$	II	**III**				
Fermium	Fm	$5f^{12} 7s^2$	II	**III**				
Mendeleviu m	Md	$5f^{13} 7s^2$	II	**III**				
Nobelium	No	$5f^{14} 7s^2$	**II**	**III**				
Lawrencium	Lr	$5f^{14} 6d^1 7s^2$						

The most important oxidation states (generally the most abundant and stable) are shown in bold. Other well–characterized but less important states are shown in normal type. Oxidation states that are unstable or in doubt are given in parentheses.

17 CO-ORDINATION COMPOUNDS SOME BASIC TERMS

SIMPLE SALTS

These are produced as a result of neutralisation of an acid by a base. For example,

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

When dissolved in water, they produce ions in the solution. Depending on the extent of neutralisation of the acid or base, simple salts are further classified as normal, acid or basic salts.

MIXED SALTS

These salts contain more than one acidic or basic radicals. For example, $NaKSO_4$

MOLECULAR OR ADDITION COMPOUNDS

When solutions containing two or more simple stable salts in stoichiometric proportions are allowed to evaporate, addition compounds are formed. For example,

$$KCl + MgCl_2 + 6H_2O \longrightarrow \underset{\text{(Carnalite)}}{KCl.MgCl_2.6H_2O}$$

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow \underset{\text{(Alum)}}{K_2SO_4.Al_2(SO_4)_3.24H_2O}$$

$CuSO_4 + 4NH_3 + H_2O \longrightarrow [Cu(NH_3)_4]SO_4.H_2O$
(Complex)

$4KCN + Fe(CN)_2 \longrightarrow K_4[Fe(CN)_6]$
(Potassium ferrocyanide)

Addition compounds are of two types:

(a) Double salts (Lattice compounds):

Addition compounds, which exist as such in crystalline state only and lose their identity in solution are called double salts. For example,

$FeSO_4.(NH_4)_2SO_4.6H_2O \longrightarrow Fe^{2+}(aq) + 2NH_4^+(aq) + 2SO_4^{2-}(aq) + 6H_2O$

(b) Co–ordination compounds:

The addition compounds that results from the combination of two or more simple stable salts and retain their identity in the solid as well as in dissolved state are called complex compounds. e.g.

$K_4[Fe(CN)_6] \longrightarrow 4K^+ + [Fe(CN)_6]^{4-}$

A complex compound contains a simple cation and a complex anion or a complex cation and a simple anion or a complex cation and a complex anion or a neutral molecule. Examples are $K_4[Fe(CN)_6]$, $[Cu(NH_3)_4]SO_4$, $[Co(NH_3)_6]$ $[Cr(CN)_6]$ and $Ni(CO)_4$ respectively. Thus, a complex ion is defined as "an electrically charged radical, which consists of a central metal atom or ion surrounded by a group of ionic or neutral species.

LIGANDS

The neutral molecules or ions (usually anions) which are linked directly with the central metal atom/ion are called ligands. In most of the complexes, ligands act as donor of one or more lone pairs to the central metal atom/ion. It should be noted that in metallic carbonyls, the ligand, CO, acts as both donor and acceptor $(M \rightleftarrows CO)$.

CO–ORDINATION NUMBER (OR LIGANCY)

The total number of atoms of ligands that can coordinate to the central metal atom/ion is called co–ordination number. For example, in $[Fe(CN)_6]^{4-}$, the co–ordination number of Fe^{2+} ion is 6.

CO–ORDINATION SPHERE

The central metal ion and the ligands that are directly attached to it, are enclosed in a square bracket, called co–ordination sphere or first sphere of attraction.

EFFECTIVE ATOMIC NUMBER (EAN)

Sidgwick extended the Lewis theory to account for the bonding in the co–ordination compounds. He introduced the term co–ordinate bond for a shared electron pair if it initially belonged to one atom (donor atom) only. In this case, the donor atom acts as a Lewis base and the metal ion acts as a Lewis acid. The metal ion accepts the electron pairs till it achieves the next inert gas configuration. This is called the effective number rule.

The total number of electrons, which the central metal atom appears to possess in the complex, including those gained by it in bonding, is called effective atomic number of central metal ion. When the EAN was 36 (Kr), 54 (Xe) or 86 (Rn), the EAN rule was said to be followed.

For example, in $[Co(NH_3)_6]^{3+}$ cobalt has an atomic number 27. In Co^{3+} number of electrons is 24. Each ammonia molecule donates a pair of electrons. So, EAN becomes $24 + (2 \times 6) = 36$.

In many cases it was found EAN in a complex should be equal to number of electrons present in next noble gas.
There are exceptions as well. For example,
EAN of $[Ni(NH_3)_6]^{+2}$ is 38 and $[Cr(NH_3)_6]^{3+}$ is 33.

The EAN of metals in some metal complexes

Metal complex	Atomic number of metal	Electrons on metal ion	Electrons donated by the ligands	EAN
$[Co(NO_2)_6]^{3-}$	Co (27)	24	$6 \times 2 = 12$	$24 + 12 = 36$
$[Cd(NH_3)_4]^{2+}$	Cd (48)	46	$4 \times 2 = 8$	$46 + 8 = 54$
$[PtCl_6]^{2-}$	Pt (78)	74	$6 \times 2 = 12$	$74 + 12 = 86$
$[Cr(CO)_6]$	Cr (24)	24	$6 \times 2 = 12$	$24 + 12 = 36$
$[Ni(CO)_4]$	Ni (28)	28	$4 \times 2 = 8$	$28 + 8 = 36$
$[Ag(NH_3)_2]Cl$	Ag (47)	46	$2 \times 2 = 4$	$46 + 4 = 50$
$K_4[Fe(CN)_6]$	Fe (26)	24	$6 \times 2 = 12$	$24 + 12 = 36$
$[Cu(NH_3)_4]SO_4$	Cu (29)	27	$4 \times 2 = 8$	$27 + 8 = 35$
$K_2[Ni(CN)_4]$	Ni (28)	26	$4 \times 2 = 8$	$26 + 8 = 34$
$K_2[PtCl_6]$	Pt (78)	74	$6 \times 2 = 12$	$74 + 12 = 86$
$K_3[Cr(C_2O_4)_3]$	Cr (24)	21	$6 \times 2 = 12$	$21 + 12 = 33$
$K_2[HgI_4]$	Hg (80)	78	$4 \times 2 = 8$	$78 + 8 = 86$

As a theory, EAN rule is of no importance as it merely emphasizes the importance of the inert gas shell stability in compounds. Even though metal carbonyls and related compounds seem to obey this rule, many exceptions exist that invalidate the usefulness of the rule.

18 CLASSIFICATION OF LIGANDS

There are two ways ligands can be classified:

(I) Classification based on donor and acceptor properties of the ligands

(i) Ligands having one or more lone pair(s) of electrons are further classified as

(a) Ligands containing vacant π–type orbitals can receive back donated π–electrons from the metal ion in low oxidation state. Examples of such ligands are CO, NO, CN^- and unsaturated organic molecules. Such ligands have filled donor orbitals in addition to vacant π– acceptor orbitals. Thus, in the complexes formed by such ligands, both metal and the ligand act as donors and acceptors ($M \underset{\sigma}{\overset{\pi}{\rightleftharpoons}} L$).

(b) Ligands, which have no vacant orbitals to get back donated electrons from the metal. e.g. H_2O, NH_3, F^- etc.

(ii) Ligands having no lone pair of electrons but π–bonding electrons. e.g. C_2H_4, C_6H_6 $C_5H_9^{\ominus}$ etc.

(II) Classification based on the number of donor atoms present in the ligands:
Such ligands are of following types:

(i) Monodentate or unidentate ligands

The ligands that can co–ordinate to the central metal ion at one site only are called monodentate ligands. Such ligands may be neutral molecules, negatively or positively charged ions. For example,

F^-, Cl^-, CN^-, OCN^-, H_2O, NH_3, $\bar{N}O_2$, NO^+, $NH_2NH_3^+$ etc.

A monodentate ligand having more than one lone pair of electrons may simultaneously co–ordinate with two or more atoms and thus acts as a bridge between the metal ions. In such a case, it is called a bridging ligand and the complex thus formed is known as bridged complex. For example,

OH^-, F^-, NH_2^-, CO, O^{2-}, SO_4^{2-} etc.

(ii) Bidentate ligand

Ligands, which have two donor atoms and have the ability to co–ordinate with the central atom/ion at two different sites are called bidentate ligands. For example,

$H_2\ddot{N}–(CH_2)_2–\ddot{N}H_2$ (ethylenediamine)

(iii) Tridentate ligands

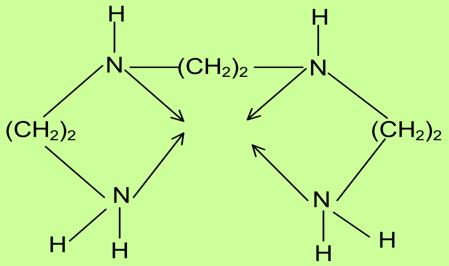
The ligands having three coordination sites are called tridentate ligands. For example,

e.g., $H_2\ddot{N} – CH_2 – CH_2 – \ddot{N}H – CH_2 – CH_2 – \ddot{N}H_2$

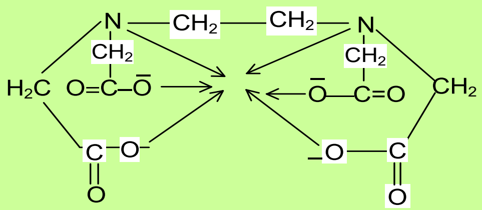
Diethylenetriamine

(iv) Polydentate ligands

The ligands having four or more co-ordination sites are called polydentate ligands. For example,



Triethylenetetramine (trine)



Ethylenediamine tetraacetate ion (EDTA)

(v) Ambidentate ligands

They have two or more donor atoms but, while forming complexes only one donor atom is attached to the metal ion. The examples of such ligands are CN^-, NO_2^-, NCS^-, NCO^- etc.

(vi) Chelating ligands

When a bidentate or a polydentate ligand is attached through two or more donor atoms to the same metal ion forming a ring structure, the ligand is called chelating ligand.

The chelating ligands form more stable complexes than ordinary unidentate ligands.

19 IUPAC NOMENCLATURE OF COMPLEXES

The following rules are used for naming all types of complexes.

(1) In case of ionic complexes, cation is named first followed by the anion, irrespective of the fact, whether cation or anion or both are complex. Simple cation and anion are named just like naming a simple salt.

(2) Number of cations and anions are not mentioned while writing its name.

(3) There has to be a gap between the cation's name and anion's name. The gap should not exist anywhere else and the name of cation and anion should be written in one continuous text.

(4) Within a complex ion, the ligands are named first in the alphabetical order followed by name of the metal ion, which is followed by the oxidation state of metal ion in Roman numeral in parentheses except for zero.

(5) Name of all negative ligands ends with 'o' while the name of all positively charged ligands ends with 'ium'. Neutral ligands have no special ending.

Name of Negative Ligands

Ligand	Name	Ligand	Name
H^-	hydrido	HS^-	mercapto
O^{2-}	oxo	NH_2^-	amido
O_2^{2-}	peroxo	NH^{2-}	imido
O_2H^-	perhydroxo	NO_3^-	nitrato
OH^-	hydroxo	ONO^-	nitrito
F^-	fluoro	NO_2^-	nitro
Cl^-	chloro	N^{3-}	nitrido
Br^-	bromo	P^{3-}	phosphido
I^-	iodo	N_3^-	azido
CO_3^{2-}	carbonato	CNO^-	cyanato
$C_2O_4^{2-}$	oxalato	NCO^-	isocyanato
$CH_3CO_2^-$	acetato	SCN^-	thiocyanato or thiocyanato–S
CN^-	cyano	NCS^-	isothiocyanato or thiocyanato–N
SO_4^{2-}	sulphato	HCO_3^-	hydrogencarbonato
SO_3^{2-}	sulphito	$S_4O_6^{2-}$	tetrathionato
S^{2-}	sulphido	EDTA $(^-O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2^-)_2$	ethylenediaminetetraacetato
HSO_3^-	hydrogensulphito	$NH_2CH_2CO_2^-$	glycinato
$S_2O_3^{2-}$	thiosulphato	$C_5H_5^-$	cyclopentadienyl

Ligands whose names end in –"ite" or –"ate" become –"ito" or –"ato", i.e., by replacing the ending –e with –o.

Name of Neutral Ligands

Ligand	Name	Abbreviation	Ligand	Name	Abbreviation
H_2O	aqua/aquo	–	$NH_2(CH_2)_2NH_2$	ethylenediamine	(en)
NH_3	ammine	–	CH_3NH_2	methylamine	–
CO	carbonyl	–	C_6H_6	benzene	–
NO	nitrosyl	–	N_2	dinitrogen	–
CS	thiocarbonyl	–	O_2	dioxygen	–
NS	thionitrosyl	–	Ph_3P	triphenylphosphine	–
C_5H_5N	pyridine	(py)	CH_3COCH_3	acetone	–

Name of Positive Ligands

Ligand	Name

NO^+	nitrosonium
NO_2^+	nitronium
$NH_2NH_3^+$	hydrazinium

(6) If the number of a particular ligand is more than one in the complex ion, the number is indicated by using Greek numbers such as di, tri, tetra, penta, hexa, etc for number of ligands being 2, 3, 4, 5 and 6 respectively.

However, when the name of the ligand includes a number, for example, dipyridyl, ethylenediamine, then bis, tris, tetrakis etc. are used in place of di, tri, tetra etc. The ligands for which such prefixes are used, their names are placed in parenthesis.

(7) For deciding the alphabetical order of ligands, the first letter of the ligand's name is to be considered and prefixes di, tri, tetra, bis, tris, tetrakis etc. are not considered.

(8) Neutral and positive ion complexes have no special ending but complex negative ion ends with the suffix 'ate' attached to English names of the metal but in some cases 'ate' is attached to the Latin names of the metal.

Element	Metal as named in anionic complex
Cobalt	Cobaltate
Nickel	Nickelate
Chromium	Chromate
Iron	Ferrate
Copper	Cuprate
Silver	Argentate
Lead	Plumbate

Co–ordination sphere is named in continuum.

(9) For those complexes containing solvent of crystallization, it is indicated as: first write the cation's name, followed by anion's name (obviously after a gap) followed by a gap and then write the number of solvent molecules in Arabic numeral followed by a hyphen which is followed by solvent's name.

Coordination compounds containing complex cationic ion	
$[Pt(NH_3)_6]Cl_4$	Hexaammineplatinum(IV) chloride
$[Co(NH_3)_4(H_2O)Cl]Cl$	Tetraammineaquochlorocobalt(II) chloride
$[Cu(en)_2]SO_4$	*Bis*(ethylenediamine)copper(II) sulphate
$[Cr(H_2O)_4Cl_2]^+$	Tetraaquodichlorochromium(III) ion
$[Fe(H_2O)_4(C_2O_4)]_2SO_4$	Tetraaquooxalatoiron(III) sulphate
$[Cr(NH_3)_4(ONO)Cl]NO_3$	Tetraamminechloronitritochromium(III) nitrate
$[Ag(NH_3)_2]Cl$	Diamminesilver(I) chloride
$[Co(NH_3)_5(NCS)]Cl_2$	Pentaammineisothiocyanatocobalt(III) chloride
$[\{(C_6H_5)_3P\}_3Rh]Cl$	Tris(triphenylphosphine)rhodium(I) chloride

Coordination compounds containing complex anionic ion	
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)

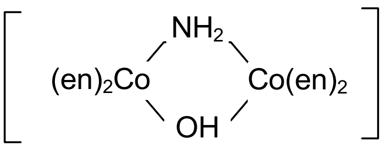
$K_3[Fe(CN)_6]$	Potassium hexacyanoferrate(III)
$K_3[Cr(C_2O_4)_3]$	Potassium trioxalatochromate(III)
$K_3[Co(C_2O_4)_2Cl_2]$	Potassium dichlorodioxalatocobaltate(III)
K_2HgI_4	Potassium tetraiodomercurate(II)
$K_2[PtCl_6]$	Potassium hexachloroplatinate(IV)
$Na[Ag(CN)_2]$	Sodium dicyanoargentate(I)
$[Ni(CN)_4]^{2-}$	Tetracyanonickelate(II) ion
$Na_3[Co(NO_2)_6]$	Sodium hexanitrocobaltate(III)
$K_3[Fe(CN)_5NO]$	Potassium pentacyanonitrosylferrate(II)

Coordination compounds containing complex cationic and anionic ions:	
$[Cr(NH_3)_6]\,[Co(CN)_6]$	Hexaamminechromium(III) hexacyanocobaltate(III)
$[Pt(NH_3)_4]\,[CuCl_4]$	Tetraammineplatinum(II) tetrachlorocuprate(II)
$[Cr(NH_3)_6][Co(C_2O_4)_3]$	Hexaamminechromium(III) trioxalatocobaltate(III)
$[Pt(py)_4]\,[PtCl_4]$	Tetrapyridineplatinum(II) tetrachloroplatinate(II)

Non–ionic coordination compounds	
$Fe(CO)_5$	Pentacarbonyliron(0)
$[Co(NO_2)_3(NH_3)_3]$	Triamminetrinitrocobalt(III)
$Cu(Gly)_2$	Diglycinatocopper(II)
$Ni(DMG)_2$	Bis(dimethylglyoximato) nickel(II)

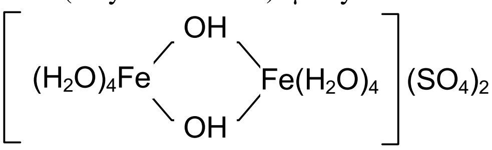
(10) Naming of the bridging ligands of the bridged polynuclear complexes:

Complexes having two or more metal atoms are called polynuclear complexes. In these complexes, the bridging group is indicated by separating it from the rest of the complex by hyphen and adding the prefix μ–before the name of each different bridging group. Two or more bridging groups of the same type are indicated by di–μ–, tri–μ–etc. When a bridging ligand is attached to more than two metal atoms or ions, this is indicated by a subscript to μ.



$(SO_4)_2$ is named as

Bis(ethylenediamine)cobalt(III)–μ–amido–μ–hydroxo–bis(ethylenediamine)cobalt(III)sulphate or μ–amido–tetrakis (ethylenediamine)–μ–hydroxo–dicobalt (III) sulphate

The complex 

is named as: Tetraaquoiron(III)–di–μ–hydroxo–tetraaquoiron(III) sulphate

The stable oxidation states of some of the transition metals of the three series are given below. These would be helpful to find the oxidation states of the metal ions while naming complexes having cation and anion both as complex species.

(i) First transition series

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+3	+2, +3, +4	+2, +3, +4, +5	+2, +3, +6	+2, +3, +4, +7	+2, +3	+2, +3	+2, +3	+1, +2	+2

(ii) Second transition series

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
+3	+4	+3, +5	+6	+4, +6, +7	+3	+3	+2, +4	+1	+2

(iii)Third transition series

La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
+3	+4	+5	+6	+4, +6, +7	+3, +4, +6	+1, +3, +4	+2, +4	+1, +3	+1, +2

20 WERNER'S CO-ORDINATION THEORY

Several theories were proposed to explain the observed properties of Co(III) ammines and of other similar compounds like Pt(IV) ammines which had been prepared by then. It was only in 1893, that Werner presented a theory known as Werner's coordination theory which could explain all the observed properties of complex compounds. Important postulates of this theory are

(i) Most elements exhibit two types of valencies: (a) primary valency and (b) secondary valency.

(a) Primary valency

This corresponds to the oxidation state of the metal ion. This is also called principal, ionisable or ionic Valency. It is satisfied by negative ions and its attachment with the central metal ion is shown by dotted lines.

(b) Secondary or auxiliary valency

(i) It is also termed as coordination number (usually abbreviated as CN) of the central metal ion. It is non-ionic or non-ionisable (i.e coordinate covalent bond type). This is satisfied by either negative ions or neutral molecules. The ligands, which satisfy the coordination number are directly attached to the metal atom or ion and are shown by thick lines. While writing down the formulae, these are placed in the coordination sphere along with the metal ion. These are directed towards fixed positions in space about the central metal ion, e.g. six ligands are arranged at the six corners of a regular octahedron with the metal ion at its centre. This postulate predicted the existence of different types of isomerism in coordination complexes and after 19 years, Werner actually succeeded in resolving various coordination examples into optically active isomers.

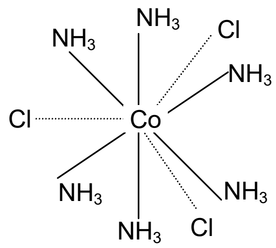
(ii) Every element tends to satisfy both its primary and secondary valencies. In order to meet this requirement a negative ion may often show a dual behaviour, i.e., it may satisfy both primary and secondary valencies (since in every case the fulfilment of coordination number of the central metal ion appears essential).

In all the ammine cobalt complexes, cobalt shows secondary valency (i.e., coordination number) of six and primary valency (i.e., oxidation state) of three.

Designation of formation of Co(III) Ammines

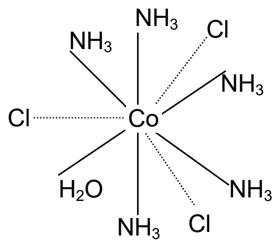
On the basis of postulates of his theory, Werner designated the ammines as given in figure and formulated them as described below

The molecule, $CoCl_3.6NH_3$ which is formulated as $\mathbf{[Co^{III}(NH_3)_6]^{3+}(Cl^-)_3}$ has six NH_3 molecules that satisfy the secondary valency of the metal ion, viz., Co^{3+} ion and their attachment with the central metal ion is shown by thick lines. The primary valency (i.e., oxidation state of +3) is satisfied by three Cl^- ions, which have been shown by dotted lines and are kept outside the coordination sphere. As all the three Cl^- ions are loosely bound, they are immediately precipitated as AgCl on the addition of $AgNO_3$ solution. Thus the solution of this compound should conduct current to give four ions in all viz. $[Co(NH_3)_6]^{3+}$ and $3Cl^-$, which has been confirmed by conductivity measurements.



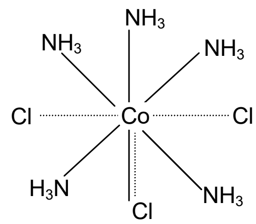
$CoCl_3.6NH_3$ or
$[Co^{III}(NH_3)_6]^{3+}(Cl^-)_3$

In the molecule, $CoCl_3.5\ NH_3.H_2O$ which is formulated as $\mathbf{[Co^{III}(NH_3)_5\ (H_2O)]Cl_3}$, five NH_3 molecules and one H_2O molecule satisfy the secondary valency (shown by thick lines in the designation). Primary valency is satisfied by three Cl^- ions. The solution of this compound also conducts current and gives in all four ions: one complex ion, $[Co^{III}(NH_3)_5(H_2O)]^{3+}$ and three simple ions, $3Cl^-$.



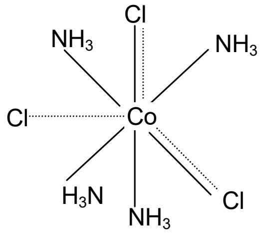
$CoCl_3.5NH_3.H_2O$ or
$[Co^{III}(NH_3)_5\ (H_2O)]^{3+}(Cl^-)_3$

In the molecule $CoCl_3{\cdot}5NH_3$ which is formulated as $\mathbf{[Co^{III}(NH_3)_5Cl]^{2+}(Cl^-)_2}$ on the basis of Werner's theory one Cl^- ion does the dual function, since it satisfies both primary and secondary valency. Werner, therefore, showed its attachment with the central metal ion by a combined dashed-solid line,—— . This Cl^- ion, being non-ionic, is not precipitated as AgCl by Ag^+ ions and hence it is different from the other two Cl^- ions and has been placed along with five NH_3 molecules and central metal ion in the coordination sphere as shown in its formulation. The other two Cl^- ions, being ionic, are precipitated as AgCl by Ag^+ ions and the total number of ions obtained is three: One complex ion, $[Co^{III}(NH_3)_5Cl]^{2+}$ and two simple ions, $2Cl^-$. Thus, $[Co^{III}(NH_3)_5Cl]^{2+}Cl_2$ satisfies both primary (+3) and secondary (Co–ordination number = 6) of Co^{3+}.



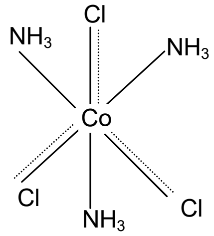
$CoCl_3{\cdot}5NH_3$ or
$[Co^{III}(NH_3)_5Cl]^{2+}(Cl^-)_2$

The formulation $\mathbf{[Co^{III}(NH_3)_4Cl_2]^+Cl^-}$ of $CoCl_3.\ 4NH_3$ shows that it has only one ionic Cl^- ion, which gets precipitated as AgCl by $AgNO_3$ solution. The conductivity measurements show that it has two ions in solution: $[Co^{III}(NH_3)_4Cl_2]^+$ and Cl^-.



$CoCl_3{\cdot}4NH_3$ or
$[Co^{III}(NH_3)_4Cl_2]^+ Cl^-$

The formulation $[Co^{III}(NH_3)_3Cl_3]^0$ of $CoCl_3.3NH_3$ has no ionic Cl^- ions and hence it behaves as a non–electrolyte.



$CoCl_3.3NH_3$ or $[Co^{III}(NH_3)_3 Cl_3]^0$

21 VALENCY BOND THEORY

The valence bond theory deals with the electronic structure of the central metal ion in its ground state, kind of bonding, geometry and magnetic properties of the complexes. This theory takes into account the hybridisation of vacant orbitals of central metal ion and was proposed by Linus Pauling, using hybridised orbitals. The main points of the valence bond theory are as follows.

1. The central metal loses requisite number of electrons and forms the cation. The number of electrons lost corresponds to the valency of the resulting cation.
2. The central metal ion makes available a number of empty s, p and d atomic orbitals equal to its coordination number.
3. These vacant orbitals hybridise together to form hybrid orbitals which are the same in number as the atomic orbitals hybridising together. These hybrid orbitals are vacant, equivalent in energy and have a definite geometry.
4. The non–bonding metal electrons occupies the inner orbitals and they do not take part in the hybridisation. The electrons are grouped in accordance with the Hund's rule of maximum multiplicity. However, under the influence of a strong ligand, they may be forced to pair up against the Hund's rule.
5. The d–orbitals involved in the hybridisation may be either inner (n–1) d–orbitals or outer nd–orbitals.
6. Each ligand (donor group) must contain a lone pair of electrons.
7. Vacant hybrid orbitals of the metal atom or ion overlap with the filled (for example, containing lone–pair of electrons) σ–orbitals of the ligands to form a covalent σ–bond represented as M $\xleftarrow{\sigma}$ L. The bond is also referred to as coordinate bond.
8. In addition to the σ–bond, a π–bond may be formed by overlap of a filled metal d–orbital with a vacant ligand orbital (M $\rightleftharpoons$ L). This usually happens in complexes of metal ions of low oxidation states.
9. If the complex contains unpaired electrons, the complex is paramagnetic in nature, whereas, if it does not contain any unpaired electron, the complex is diamagnetic in nature.

Difference between Inner and Outer Orbital Octahedral Complexes

Inner Orbital octahedral complex	*Outer orbital octahedral complex*
1. d^2sp^3 hybridisation	1. sp^3d^2 hybridisation
2. The inner orbital complexes are formed with covalent metal ligand bonds.	2. The outer orbital complexes are formed with ionic bond.
3. Low spin complexes	3. High spin complexes

VBT–OCTAHEDRAL COMPLEXES

On the basis of VBT, octahedral complexes are of two types:

1. Inner–orbital octahedral complexes, which result from d^2sp^3 hybridisation of the central metal atom/ion.
2. Outer orbital octahedral complexes, which result from sp^3d^2 hybridisation.

C.N.	Hybridisation	Geometry	Examples
2	sp (4s, $4p_x$)	Linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$, $[Cu(NH_3)_2]^+$
3	sp^2 (6s, $6p_x$, $6p_y$)	Trigonal planar	$[HgI_3]^-$
4	sp^3 (4s, $4p_x$, $4p_y$, $4p_z$)	Tetrahedral	$[NiCl_4]^{2-}$, $[Cu(CN)_4]^{3-}$, $[Ni(CO)_4]$, $[Zn(NH_3)_4]^{2+}$
4	dsp^2 ($3d_{x^2-y^2}$, 4s, $4p_x$, $4p_y$, $4p_z$)	Square planar	$[Ni(CN)_4]^{2-}$
5	dsp^3 ($3d_{z^2}$, 4s, $4p_x$, $4p_y$, $4p_z$)	Trigonal bipyramidal	$[Fe(CO)_5]^{3-}$, $[CuCl_5]^{3-}$
5	dsp^3 ($3d_{x^2-y^2}$, 4s, $4p_x$, $4p_y$, $4p_z$)	Square pyramidal	$[Ni(CN)_5]^{3-}$
6	d^2sp^3($3d_{x^2-y^2}$, $3d_{z^2}$, 4s, $4p_x$, $4p_y$, $4p_z$)	Inner orbital octahedral	$[Ti(H_2O)_6]^{2+}$, $[CrF_6]^{3-}$ uses (n–1) d–orbitals.
6	sp^3d^2(4s, $4p_x$, $4p_y$, $4p_z$, $4d_{x^2-y^2}$, $4d_{z^2}$)	Outer–orbital octahedral	$[Co(H_2O)_6]^{3+}$, $[Zn(NH_3)_6]^{2+}$, $[CoF_6]^{3-}$ uses nd–orbitals.

(a) Inner orbital octahedral complexes

The formation of these complexes can be explained on the basis of VBT by considering the complex ion, viz $[Co(NH_3)_6]^{3+}$.

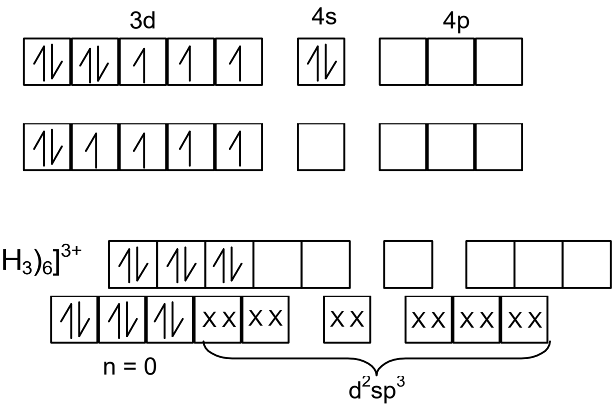
$[Co(NH_3)_6]^{+3}$

(a) Co atom ($3d^7 4s^2 4p^\circ$)

(b) Free Co^{3+} ion ($3d^6 4s^\circ 4p^\circ$) in ground state

(c) Co^{3+} ion in $[Co(NH_3)_6]^{3+}$

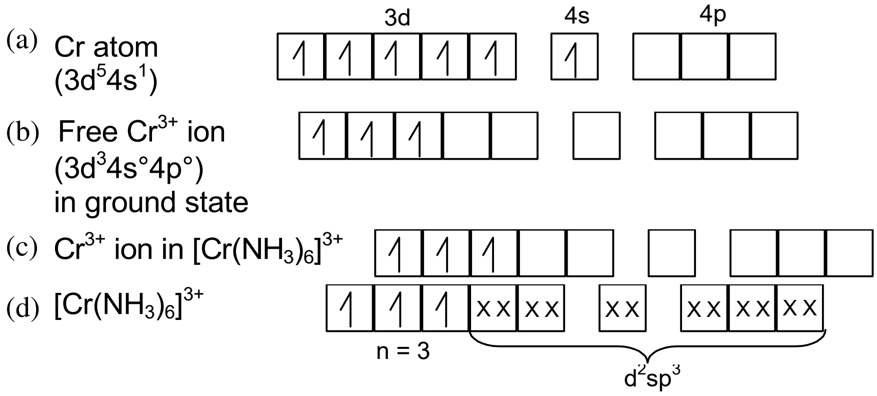
(d) $[Co(NH_3)_6]^{3+}$



Here n represents the number of unpaired electrons and 'XX' represents an electron pair donated by each of free six NH_3 ligands. The two electrons of the electron pair have opposite spin.The above complex ion is diamagnetic as all the electrons are paired.

In order to make 3d electrons paired, the two unpaired electrons residing in $3d_{z^2}$ and $3d_{x^2-y^2}$ orbitals are forced by the six NH_3 ligands to occupy $3d_{yz}$ and $3d_{zx}$ orbitals. By doing so, all the 3d electrons become paired and also at the same time, two 3d orbitals namely $3d_{z^2}$, $3d_{x^2-y^2}$, hybridise together with. 4s, $4p_x$, $4p_y$ and $4p_z$ orbitals to give six d^2sp^3 hybrid orbitals which, being empty accepts the six electron pairs donated by six NH_3 ligand molecules.

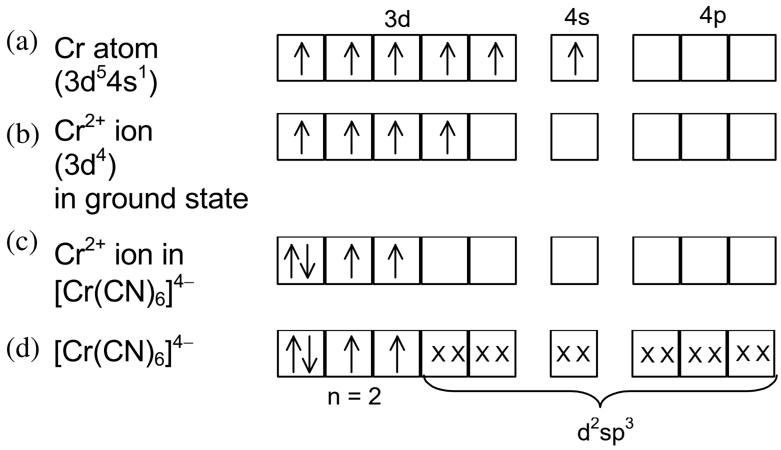
$[Cr(NH_3)_6]^{3+}$



The above complex ion is paramagnetic as there are three unpaired electrons.

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

$[Cr(CN)_6]^{4-}$



The above complex ion is paramagnetic since two unpaired electrons are present.

$$\mu = \sqrt{2(2+2)} = \sqrt{8}\ \text{B.M.}$$

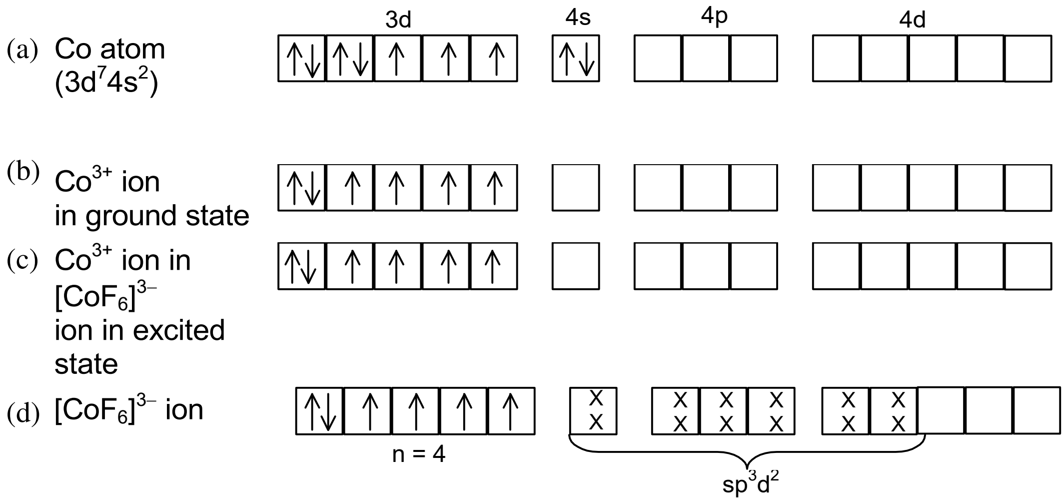
Other examples of inner orbital octahedral paramagnetic complexes are $[Ti(H_2O)_6]^{3+}$ (n=1), $[Mn(CN)_6]^{4-}$ (n = 1), $[Mn(CN)_6]^{3-}$ (n = 2), $[Fe(CN)_6]^{3-}$ (n =1), $[Co(CN)_6]^{4-}$ (n = 1 in 5s orbital) while the examples of inner orbital octahedral diamagnetic complexes are: $[Fe(CN)_6]^{4-}$, $[Co(CN)_6]^{3-}$, $[Co(H_2O)_6]^{3+}$, $[Co(NH_3)_6]^{3+}$, $[Co(NO_2)_6]^{3-}$, $[Pt(NH_3)_6]^{4+}$ etc.

All these complexes result from d^2sp^3 hybridisation of the central metal ion.

(b) Outer orbital octahedral complexes

Octahedral complexes resulted from sp^3d^2 hybridisation, using outer d– and outer s and p orbitals are called outer–orbital octahedral complexes.

$[CoF_6]^{3-}$



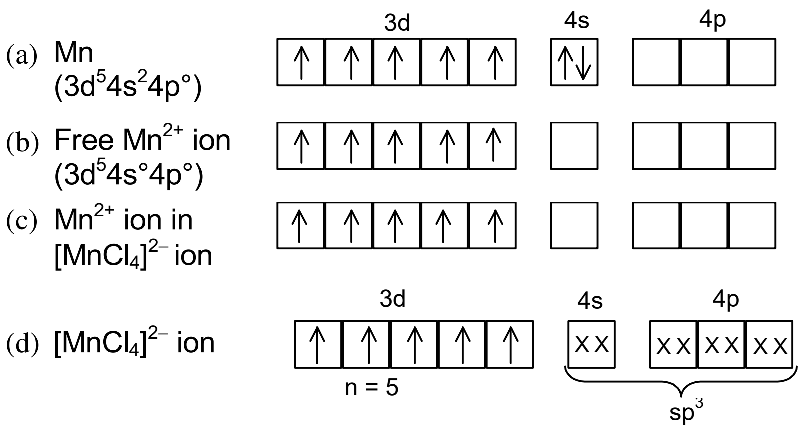
In this complex ion, it is $4d_{x^2-y^2}$ and $4d_{z^2}$ orbitals that mix with one 4s and three 4p orbitals to give six sp^3d^2 hybrid orbitals, which being empty, accept the six electron pairs denoted by each of the six F^- ligands. It is paramagnetic as there are four unpaired electrons.

$$\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} \text{ B.M.}$$

Some other examples of outer orbital octahedral paramagnetic complex are:
$[Cr(H_2O)_6]^{2+}$ (n = 4), $[Mn(H_2O)_6]^{2+}$ (n = 5), $[Fe(H_2O)_6]^{2+}$ (n = 4), $[Fe(NH_3)_6]^{2+}$ (n = 4)
$[Fe(H_2O)_6]^{3+}$ (n = 5), $[Fe(F)_6]^{3-}$ (n = 5), $[CoF_6]^{3-}$ (n = 4),
$[Co(NH_3)_6]^{2+}$ (n = 3)
$[Co(H_2O)_6]^{2+}$ (n = 3), $[Ni(NH_3)_6]^{2+}$ (n = 2),
$[Ni(H_2O)_6]^{2+}$ (n = 2), $[Ni(NCS)_6]^{4-}$ (n = 2),
$[Ni(NO_2)_6]^{4-}$ (n = 2), $[CuF_6]^{3-}$ (n = 2).
$[Zn(NH_3)_6]^{2+}$ (n = 0) is an example of outer orbital octahedral diamagnetic complex.

VBT–TETRAHEDRALCOMPLEXES(Co–ordination no. = 4, sp^3 hybridisation)

Tetrahedral complexes result from sp^3 hybridisation. In sp^3 hybridisation the s– and three p–orbitals should belong to the same shell. The formation of tetrahedral complexes by VBT can be explained by considering the complex ion like $[MnCl_4]^{2-}$. This complex ion is paramagnetic corresponding to the presence of five unpaired electrons and hence the configuration of Mn^{2+} ion in the free state and in the complex ion remains the same.



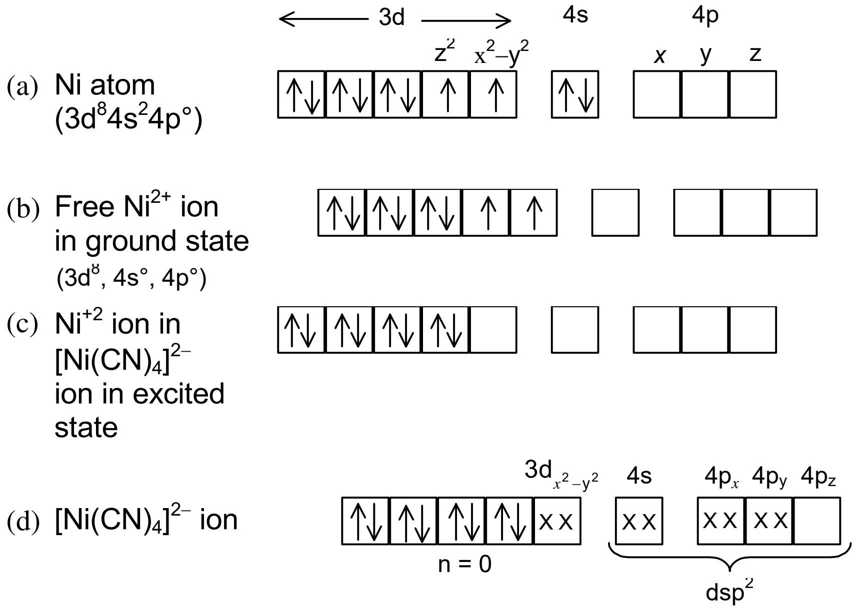
$$\mu = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35} \text{ B.M.}$$

Examples of some paramagnetic tetrahedral complexes are
$[NiCl_4]^{2-}$ (n = 2), $[Ni(NH_3)_4]^{2+}$ (n = 2)
$[MnBr_4]^{2-}$ (n = 5), $[FeCl_4]^{2-}$ (n = 4),

$[CoCl_4]^{2-}$ (n =3), $[CuCl_4]^{2-}$ (n = 1) etc.
While the examples of some diamagnetic tetrahedral complexes are:
$[Ni(CO)_4]$ (n = 0), $[Cu(CN)_4]^{3-}$ (n = 0), $[Zn(NH_3)_4]^{2+}$ (n = 0), $[ZnCl_4]^{2-}$ (n = 0), $[Cd(CN)_4]^{2-}$ (n = 0), etc. All these complexes result from sp^3 hybridisation of the central metal atom/ion.

VBT–SQUARE PLANAR COMPLEXES (Co–ordination no. = 4, dsp^2 hybridisation)

Square planar complexes result from dsp^2 hybridisation. In dsp^2 hybridisation, d–orbital should be $d_{x^2-y^2}$ orbital (belonging to the lower shell) while s and p orbitals should be from the higher shell. The two p–orbitals should be p_x and p_y orbitals. The selection of $d_{x^2-y^2}$, p_x and p_y orbitals is based on the fact that all these orbitals lie in the same plane. The formation of square planar complexes by VBT can be explained by considering the complex ion like $[Ni(CN)_4]^{2-}$. The measurement of magnetic moment value for $[Ni(CN)_4]^{2-}$ ion has shown that μ = 0 i.e. the complex ion has no unpaired electron and hence it is diamagnetic.



In order to make all the 3d–electrons paired, one unpaired electron residing in $3d_{x^2-y^2}$ orbital is forced by the four CN^- ligand to occupy $3d_{z^2}$ orbital. Now $3d_{x^2-y^2}$, 4s, $4p_x$, $4p_y$ orbitals mix together to form four dsp^2 hybrid orbitals which, being empty, accept the four electron pairs donated by the four CN^- ligand ions.

Examples of paramagnetic square planar complexes are:
$[Cu(CN)_4]^{2-}$ (n = 1), $[Cu(NH_3)_4]^{2+}$ (n = 1), $[CuCl_4]^{2-}$ derived from $(NH_4)_2[CuCl_4]$ (n = 1) etc. While the examples of diamagnetic square planar complexes are: $[Ni(CN)_4]^{2-}$ (n = 0), $[PtCl_4]^{2-}$ (n = 0), $[Pt(NH_3)_4]^{2+}$ (n = 0) etc.

Limitations of VBT

1. Although valence bond theory provides a satisfactory representation of the complex compound based upon the concept of orbital hybridisation, it cannot account for the relative stabilities for different shapes and coordination numbers in metal complexes.

2. VBT cannot explain as to why Cu(+2) forms only distorted octahedral complexes even when all the six ligands are identical.

3. The valence bond theory does not provide any satisfactory explanation for the existence of inner orbital and outer orbital complexes.

4. Sometimes the theory requires the transfer of electron from lower energy to the higher energy level, which is very much unrealistic in absence of any energy supplier. (For example, this happens in the case of $[CuX_4]^{-2}$).

5. The changes in the properties of the metal ion along with the ligands and the simple metal ions can not be explained. For example, the colour changes associated with electronic transition within d orbitals are affected on formation of complex, but the valence bond theory does not offer any explanation.

6. Sometimes the same metal acquires different geometry when formation of complex takes place with different ligands. The theory does not explain as to why at one time the electrons must be rearranged against the Hund's rule while, at other times the electronic configuration is not disturbed.

7. The energy change of the metal orbitals on formation of complex is difficult to be calculated mathematically.

8. VBT fails to explain the finer details of magnetic properties including the magnitude of the orbital contribution to the magnetic moments.

9. The VBT does not explain why certain complexes are more labile than the others.

10. It does not give quantitative interpretation of thermodynamic or kinetic stabilities of coordination compounds.

11. It does not make exact predictions regarding the tetrahedral and square planar structure of 4-coordinate complexes.

12. It does not tell about the spectral properties of coordination compounds.

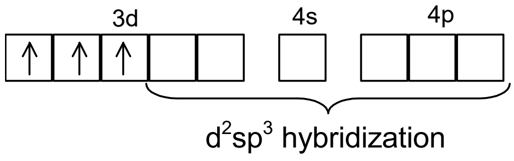
The above points may be made clear with the help of the following examples:

(i) *d^1, d^2, d^3 systems*

Ti(22) $\longrightarrow$ [Ar]$3d^2 4s^2$ $Ti^{3+} \longrightarrow$ [Ar]$3d^1$

V(23) $\longrightarrow$ [Ar]$3d^3 4s^2$ $V^{3+} \longrightarrow$ [Ar]$3d^2$

Cr (24) $\longrightarrow$ [Ar]$3d^5 4s^1$ $Cr^{3+} \longrightarrow$ [Ar]$3d^3$



In all the three systems two vacant 3d orbitals (n – 1) d orbitals are available for d^2sp^3 hybridisation. Hence, these systems may accept six lone pairs from six ligands and thus they form octahedral complexes: $[Ti(H_2O)_6]^{3+}$, $[V(H_2O)_6]^{3+}$, $[Cr(H_2O)_6]^{3+}$

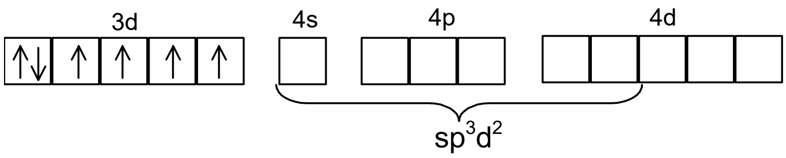
Since due to complexation, the unpaired electrons in (n – 1) d orbitals are not disturbed, the magnetic moment of free metal ions remains intact in octahedral complexes.

In addition to d^2sp^3 hybridisation, d^1, d^2, d^3 systems may undergo sp^3 or dsp^2 hybridization forming tetrahedral or square planar complexes respectively.

Since in sp^3 or dsp^2, the d–electrons are not disturbed, the magnetic moment of free metal ion remains intact in tetrahedral or square planar complexes.

(ii) *d^4, d^5 and d^6 systems*

Mn(III), Fe(III), Co(III), Fe(II)

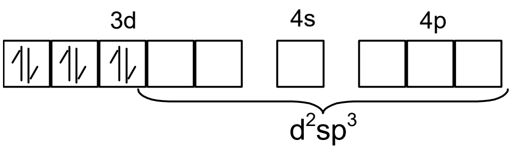


In d^4, d^5 and d^6 systems, in ground state two 3d orbitals are not vacant to participate in d^2sp^3 hybridization forming octahedral complexes. Hence, two d–orbitals of outer shell are involved in hybridisation and the complexes are formed as outer orbital octahedral complexes. The energies of the various orbitals are in the order: 4s < 3d < 4p < 5s < 4d. Since, the energy gap between 4s and 4d is large, the sp^3d^2 hybridisation is not perfect hybridization and hence outer orbital octahedral complexes are comparatively less stable.

Moreover, 4d orbitals are more extended in space than 3d orbitals and hence sp^3d^2 hybrid orbitals are also more extended in space than d^2sp^3 hybrids. So, bond length in outer orbital octahedral complexes is comparatively longer and so they are less stable.

In sp^3d^2 hybridisation, 3d electrons are not disturbed and hence magnetic moment of free metal ions remains intact in outer orbital octahedral complexes.

Other possibilities:



After maximum pairing of 3d electrons, two 3d orbitals may be made vacant for d^2sp^3 hybridisation forming octahedral complexes.

As two d–orbitals of inner shell are involved in hybridisation, complexes are said to be inner orbital octahedral complexes.

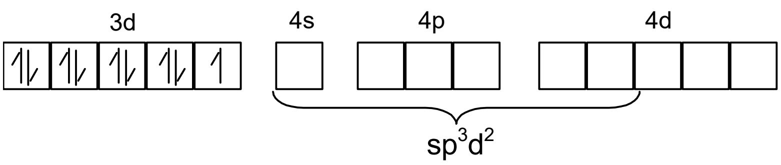
4s < 3d < 4p ; the energy of the orbitals involved in hybridisation is in continuation. The d^2sp^3 hybridisation is perfect and at the same time due to less extension of 3d orbitals in space, bond length is also short. So, inner orbital octahedral complexes are more stable than outer orbital octahedral complexes.

As the pairing of 3d electrons is forced in d^2sp^3 hybridisation in these systems (d^4, d^5 and d^6), hence *the magnetic moment of the free metal ion undergoes change on complexation.*

In addition to inner orbital octahedral and outer orbital octahedral complexes, d^4, d^5 and d^6 systems may also form tetrahedral and square planar complexes by sp^3 and dsp^2 hybridisation.

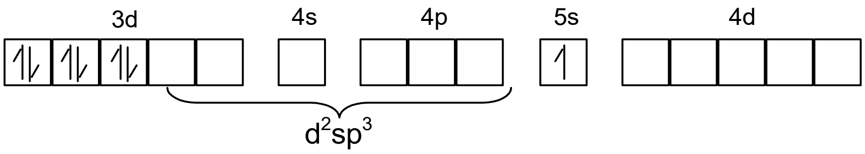
(iii) *d^7, d^8 and d^9 systems:*

Co(II), Ni(II), Cu(II)



In d^7, d^8 and d^9 systems, two vacant 3d orbitals cannot be made available for d^2sp^3 hybridization even after maximum pairing. So, there is no chance of the formation of inner orbital octahedral complexes by d^2sp^3 hybridisation. However, *these systems may undergo sp^3d^2 hybridization forming outer orbital octahedral complexes with same magnetic properties as in free metal. In d^7, d^8 and d^9 systems, sp^3 hybridizations can easily occur favouring the formation of tetrahedral complexes with unchanged magnetic character.*

Co^{2+}
under the influence of NH_3 as ligand



In d^7 system, after maximum pairing of the electrons in three of the d–orbitals and promoting one electron to 5s or 4d, two 3d orbitals may be made vacant for d^2sp^3 hybridisation and formation of inner orbital octahedral complex may take place with one unpaired electron.

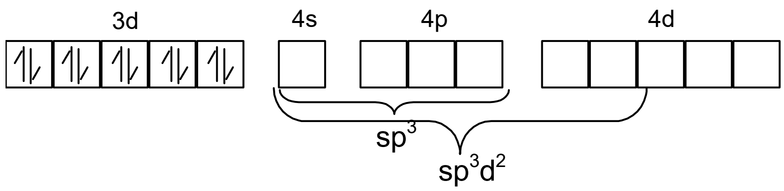
However, with the promotion of one 3d electron to 5s or 4d, it becomes loosely bonded to the nucleus and hence, it may easily be removed and so, Co(II) will easily be oxidised into Co(III). Virtually the oxidation of Co(II) has been found to be easy in the formation of inner orbital octahedral complexes by a d^7 system.

In d^7 and d^8 systems, after maximum pairing of 3d electrons, one 3d orbital may be vacated for dsp^2 hybridization and hence *d^7 and d^8 systems favour the formation of square planar complexes with changed magnetic nature.*

However, in the case of d^9, even after maximum pairing of electrons in 3d, one d orbital is not made available for dsp^2 hybridization. So, there is no question of the formation of square planar complexes by d^9 systems.

(iv) *d^{10} system*:

Zn(II), Cu(I)



In d^{10} system, 3d orbitals are completely filled up. So, it may form tetrahedral complexes by sp^3 hybridization or outer orbital octahedral complexes by sp^3d^2 hybridisation.

Magnetic properties of the free metal ion remains unchanged in tetrahedral or outer orbital octahedral complexes.

Note

If the ligand is very weak like F^-, H_2O, Cl^- etc. it does not force the pairing of 3d electrons and hence outer orbital octahedral complexes are formed by sp^3d^2 hybridisation. But if the ligand is strong like CN^-, $(COO)_2^{2-}$, ethylenediamine (en) etc., it forces the paring of 3d electrons and hence inner orbital octahedral complexes are formed by d^2sp^3 hybridization.

22 FACTORS AFFECTING THE STABILITY OF COMPLEXES

1. A coordination compound is formed in solution by the stepwise addition of ligands to a metal ion. The overall stability constant is given by

$$M + nL \rightleftharpoons MLn;\ K_f = \frac{[MLn]}{[M][L]^n}$$

$\frac{1}{K_f}$ is called instability constant. Higher the value of K_f, more stable is the complex.

2. Higher is the charge density on the central metal ion, greater is the stability of the complexes. For example, $[Fe(CN)_6]^{3-}$ is more stable than $[Fe(CN)_6]^{4-}$
3. More is the basic character of ligand, more stable is the complex.
   For example, the cyano and amino complexes are far more stable than the halo complexes.
4. Chelating ligands form more stable complexes than the monodentate ligands.

23 CRYSTAL FIELD THEORY

In crystal field theory, we assume the ligands to be the point charges and there is interaction between the electrons of the ligands and the electrons of the central metal atom or ion. The five d–orbitals in an isolated gaseous metal atom or ion are degenerate. This degeneracy is maintained if an spherically symmetrical negative field surrounds the metal atom/ion. However, when ligands approach the central metal atom/ion, the field created is not exactly spherically symmetrical and the degeneracy of the d–orbitals is lifted. It results in the splitting of d–orbitals and the pattern of splitting depends upon the nature of the crystal field. This splitting of d–orbitals energies and its effects, form the basis of the crystal field treatment of the coordination compounds.

Ligands that cause large degree of crystal filed splitting are termed as *strong field* ligands**.** Ligands that cause only a small degree of crystal filed splitting are termed as *weak field ligands*. The common ligands can be arranged in ascending order of crystal field splitting energy. The order remains practically constant for different metals and this series is called the *spectrochemical series.*

$I^- < Br^- < S^{2-} < Cl^- \sim SCN^- \sim N_3^- < NO_3^- < F^- < OH^- < CH_3CO_2^- < ox^{2-} < H_2O$ || $< NCS^- < EDTA^{4-} < NH_3 \sim Py < en < NO_2^- < H^- \sim CH_3^- < CO \sim CN^-$

The spectrochemical series is an experimentally determined series. It is difficult to explain the order as it incorporates both the effect of σ and π–bonding. The halides are in the order expected from electrostatic effects. In other cases, we must consider covalent bonding to explain the order. A pattern of increasing σ–donation is as follows:

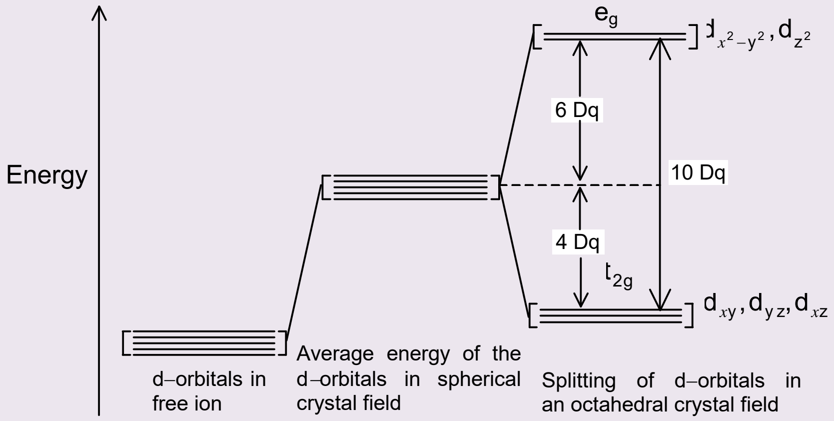
Halides donors < O donors < N donors < C donors

The crystal field stabilization produced by the strong CN^- is almost double that of halide ions. This is attributing π–bonding in which the metal donates electrons from a filled t_{2g} orbital into a vacant orbital on the ligand. In a similar way, many unsaturated N donors and C donors may also act as π–acceptors.

Crystal field effects in octahedral coordination entities

Let us assume that the six ligands are positioned symmetrically along the Cartesian axis with the metal atom or ion at the origin. As the ligands approach the central metal atom or ion, the energy of the d–orbitals of the central metal atom or ion increases. If the field created by the ligands is spherical, then the increase in the energies of all the d-orbitals is the same. However, under the influence of octahedral field, the energies of the d–orbitals lying along the axis (i.e. d_{z^2} and $d_{x^2-y^2}$) increases more than the d–orbitals lying between the axis (i.e. d_{xy}, d_{yz} and d_{xz}). Thus, the degenerate d–orbitals (with no field effect or spherical field effect) splits up into two sets of orbitals (i) the lower energy set,

t_{2g} (d_{xy}, d_{yz} and d_{xz}) and (ii) the higher energy set, e_g ($d_{x^2-y^2}$ and d_{z^2}). The energy separation is denoted by Δ_o or 10 Dq. (where $_o$ stands for octahedral field), as shown below:



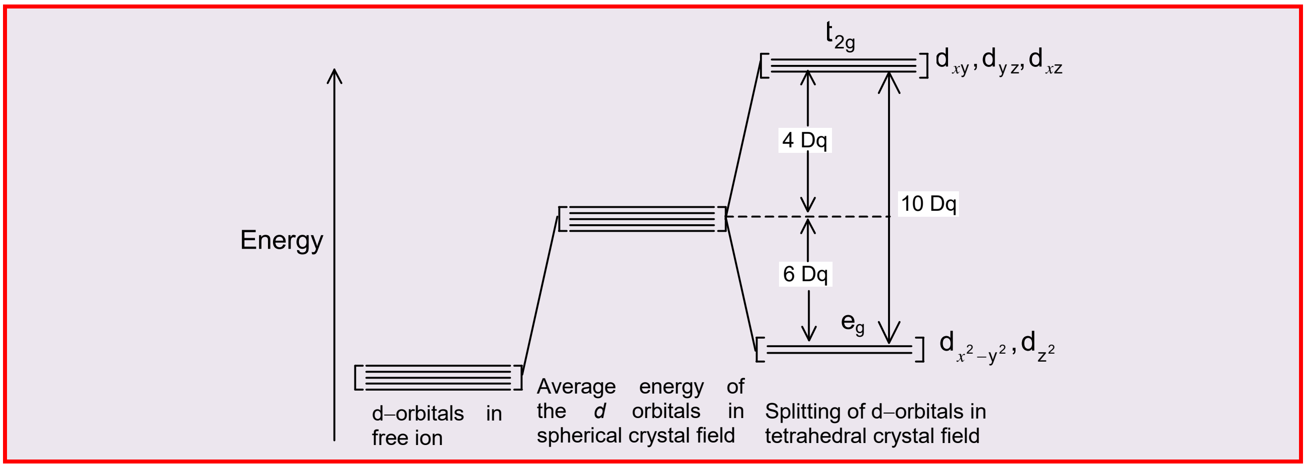
Significance of Δ_o

A strong field ligand approaches the central metal atom/ion strongly and thus the magnitude of Δ_o is high. Hence, in the case of strong field ligand, the magnitude of Δ_o is greater than the pairing energy (the energy required to pair up two negatively charged electrons having opposite spin in an orbital). However, under the influence of weak field ligand, Δ_o < P (where P represents the pairing energy).

Now, let us consider the d^4 configuration of the central metal atom/ion. The first three electrons will go into t_{2g} orbitals using Hund's rule of maximum multiplicity. The fourth electron will go in the e_g orbital when the ligands are weak as, Δ_o< P giving the configuration $t_{2g}^3 e_g^1$. But if the ligands are strong then the fourth electron will pair up with any of the singly occupied t_{2g} orbitals (as Δ_o > P) to give the configuration $t_{2g}^4 e_g^0$.

Crystal field effects in tetrahedral coordination entities

Under the influence of tetrahedral field, the d-orbital splitting is smaller as compared to the octahedral field splitting. For the same metal, the same ligands and metal-ligand distances, it can be shown that $\Delta_t = \frac{4}{9}\Delta_o$. Consequently the orbital splitting energies are not sufficiently large for forcing pairing and therefore low spin or spin paired configurations are rarely observed.



LIMITATIOIN OF CRYSTAL FIELD THEORY

Limitation

1. *The assumption that the interaction between metal- ligand is purely electrostatic cannot be said to be very realistic.*
2. *This theory takes only d-orbitals of a central atom into account. The s and p orbits are not considered for the study.*
3. *The theory fails to explain the behavior of certain metals which cause large splitting while others show small splitting. For example, the theory has no explanation as to why H2O is a stronger ligand as compared to OH–.*
4. *The theory rules out the possibility of having p bonding. This is a serious drawback because p bonding is found in many complexes.*
5. *The theory gives no significance to the orbits of the ligands. Therefore it cannot explain any properties related to ligand orbitals and their interaction with metal orbitals*

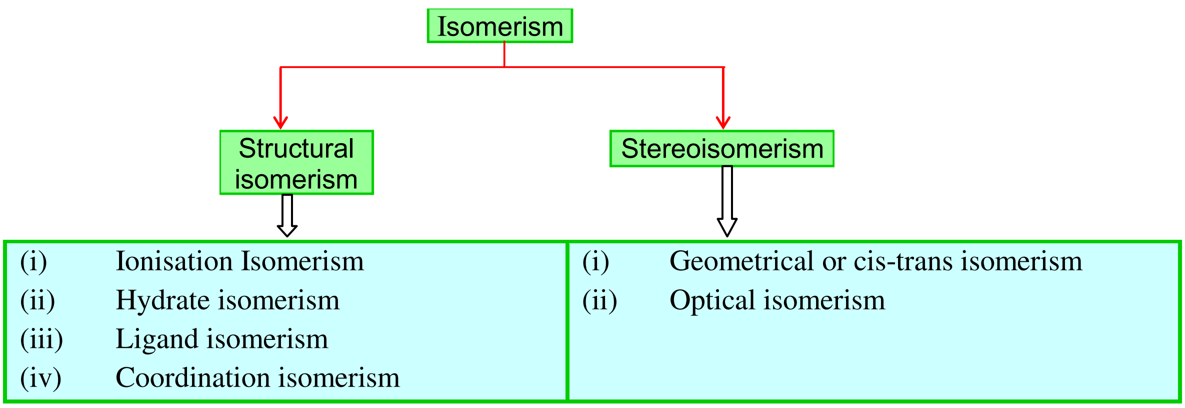
24 ISOMERISM

The compounds having same chemical formula but different structural arrangement of their atoms and hence different physical and chemical properties are called isomers and the phenomenon is called isomerism.

Isomerism in complexes are of two types:

(i) Structural Isomerism

(ii) Stereoisomerism



(v) Linkage isomerism
(vi) Coordination position isomerism
(vii) Polymerisation isomerism

STRUCTURAL ISOMERISM

This isomerism arises due to the difference in structures of coordination compounds and are of the following types.

(a) Ionisation Isomerism

Complexes that have the same empirical formula and are produced by the interchange of the position of the ligands inside the complex zone and outside the complex zone are called ionisation isomers. They give different ions e.g.

(i) $[Co(NH_3)_4Cl_2]NO_2 \rightleftharpoons [Co(NH_3)_4Cl_2]^+ + NO_2^-$

$[Co(NH_3)_4Cl(NO_2)]Cl \rightleftharpoons [Co(NH_3)_4Cl(NO_2)]^+ + Cl^-$

(ii) $[Co(NH_3)_5SO_4]Br \rightleftharpoons [Co(NH_3)_5SO_4]^+ + Br^-$

$[Co(NH_3)_5Br]SO_4 \rightleftharpoons [Co(NH_3)_5Br]^{++} + SO_4^{2-}$

The number of ions in a solution can be determined by conductivity measurement. More the number of ions in a solution more is the conductivity. Greater the charge on ions, greater is the conductivity of solution.

(b) Hydrate isomerism

This type of isomerism arises due to the different position of water molecules inside and outside the coordination sphere. For example,

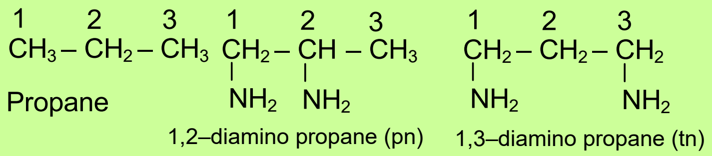
(i) $[Cr(H_2O)_6]Cl_3$ (violet), does not lose water over H_2SO_4 and all Cl^- ions are immediately precipitated by (Ag^+) ions.

(ii) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (green), loses H_2O over H_2SO_4 and two Cl^- ions are precipitated by (Ag+) ions.

(iii) $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (green), loses two water molecules over H_2SO_4 and only one Cl^- ion is precipitated by Ag^+ ions.

(c) Ligand Isomerism

Some ligands themselves are of capable of existing as isomers, for example diamino propane can exist both as 1, 2–diaminopropane (pn) and 1,3–diaminopropane, also called trimethylenediamine (tn)



When these ligands (for example, pn and tn) are associated to form complexes, the complexes are isomers of each other.
e.g. $[Co(pn)_2Cl_2]^+$ and $[Co(tn)_2Cl_2]^+$ ions.

(d) Coordination Isomerism

If both cation and anion of a complex compound are complex, there may be an exchange of ligands between the two coordination spheres, giving rise to isomers known as coordination isomers. e.g.

(i) $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

(ii) $[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

(e) Linkage Isomerism

Those complexes in which the ligands can coordinate with the central metal ion through either of the two atoms, give rise to the linkage isomerism.

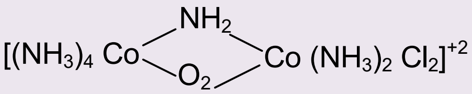
The best known ligands of this type are NO_2^-, SCN^- and $S_2O_3^{2-}$ ions. In complexes containing NO_2^- ion as ligand, NO_2^- ion may attach with the central ion either through O-atom or through N-atom.

(i) $[Co(NH_3)_5(NO_2)]Cl_2 \longrightarrow$ Pentaamminenitrocobalt(III) chloride.

$[Co(NH_3)_5(ONO)]Cl_2 \longrightarrow$ Pentaamminenitritocobalt(III) chloride.

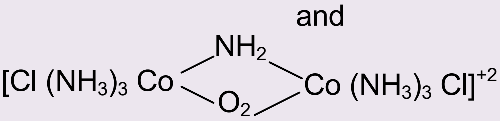
(f) Coordination Position Isomerism

In some poly-nuclear complexes, interchange of the ligands between the metal atoms which are present as a part of the complex is possible. This type of interchange of ligands between the metal atoms gives rise to coordination position isomerism for example,



(unsymmetrical form)

and



(symmetrical form)

are coordination position isomers.

(g) Polymerisation Isomerism

This is not the true isomerism because it occurs between compound having the same empirical formula, but different molecular weights. For example, $[Pt(NH_3)_2Cl_2]$, $[Pt(NH_3)_4]$ $[Pt(Cl_4)$, $[Pt(NH_3)_4]$ $[Pt(NH_3)Cl_3]_2$ and $[Pt(NH_3)_3Cl]_2$ $[PtCl_4]$ all have the same empirical formula.

STEREOISOMERISM OR SPACE ISOMERISM

When two compounds contain the same ligands coordinated to the same central ion, but the arrangement of ligands in the space is different, the two compounds are said to be stereoisomers and the type of isomerism is called stereoisomerism.

Stereoisomerism is of two types:-

(i) Geometrical or cis-trans isomerism

(ii) Optical or mirror image isomerism.

Geometrical isomerism

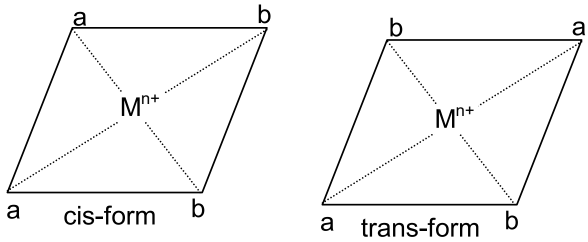
Geometrical isomerism is due to ligands occupying different positions around the central metal ion. The ligands occupy positions either adjacent to one another or opposite to one another. These are referred to as cis-form and trans-form respectively. This type of isomerism is, therefore, also referred to as cis-trans isomerism.

(a) Geometrical isomerism in 4–coordinate complex

Complexes having central metal atom with co–ordination number = 4 may be either tetrahedral or square planar. Geometrical isomerism cannot arise in tetrahedral complexes because this geometry contains all the ligands in the cis (i.e., adjacent) position with respect to each other, i.e., each ligand is equidistant from the other three ligands and all the bond angles are the same (109.5°). Hence geometrical isomerism can not be expected in tetrahedral complexes.

Square planar complexes of [Ma_4], [Ma_3b] and [Mab_3] type (a and b are monodentate ligands) do not show geometrical isomerism, since every conceivable spatial arrangement of the ligands a round the metal ion is exactly equivalent.

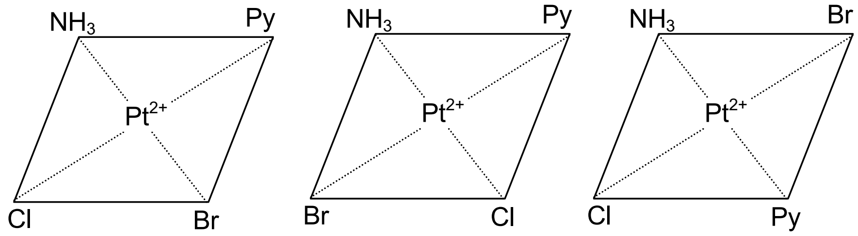
(1) [Ma_2b_2] type complexes



e.g. [Pt^{+2} $(NH_3)_2$ Cl_2], [$Pt^{2+}$$(NH_3)_2$ Br_2] and [Pd^{2+} $(NH_3)_2(NO_2)_2$] are square planar complexes which exhibit cis-trans isomerism.

(2) [Mabcd] type complexes

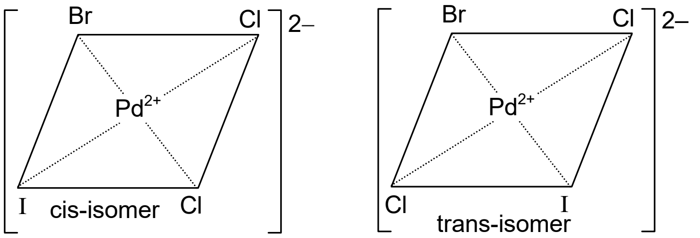
Square planar complexes of this type exist in three isomeric forms for example, [Pt^{2+} (NH_3) (Py) (Cl) (Br)] exist in the following structures.



[$Pt^{2+}$$(NO_2)$(Py) (NH_3) (NH_2OH)]$^+$ and [$Pt^{2+}$$(C_2H_4)$ (NH_3) (Cl) (Br)] are other examples of square planar complexes which exist in three isomeric forms.

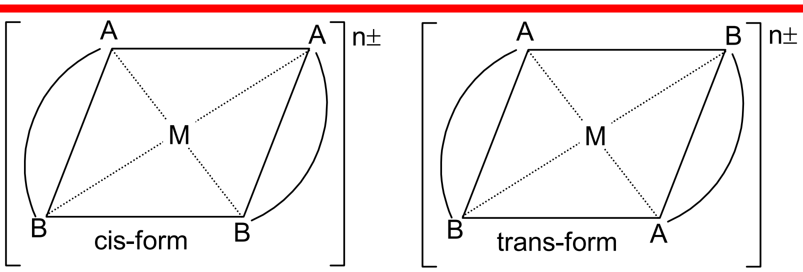
(3) [Ma_2bc] type complexes

Square planar complexes of this type also show cis-trans isomerism. For example, [$Pd^{2+}Cl_2BrI$]$^{2-}$ exists in the following cis–trans

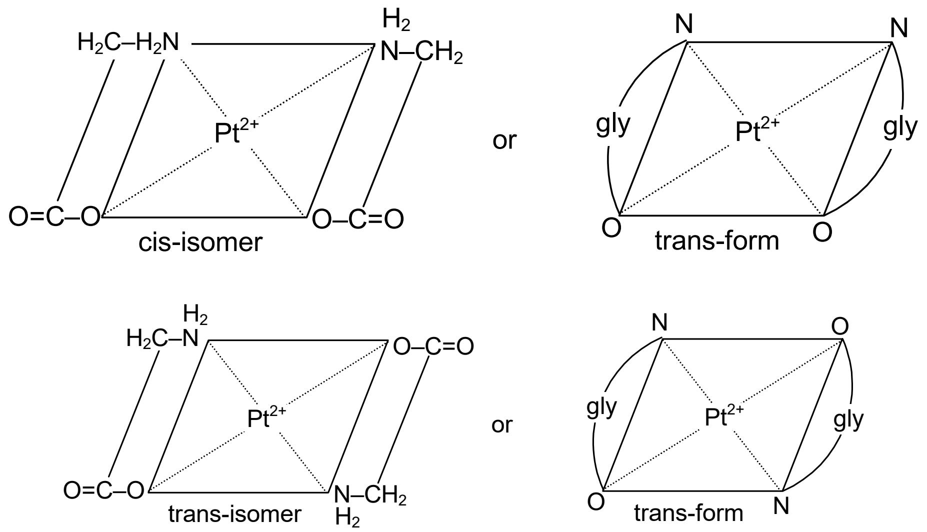


(4) [$M(AB)_2$]$^{n\pm}$ type complexes

Here *M* is the central metal ion and (AB) represents an unsymmetrical bidentate ligand. (A) and (B) are the two ends (i.e., coordinating atoms) of the bidentate ligand. Such type of complexes also show cis and trans isomerism.

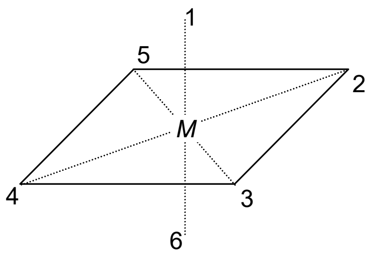


For example, [$Pt^{2+}(gly)_2$] ; Here gly represents the glycinato ligand, $NH_2CH_2COO^-$ which has N and O atoms as its donor atoms.



(b) Geometrical isomerism in 6–coordinate complexes

A complex compound having the central metal ion with coordination number equal to 6 has octahedral shape. The system used for numbering different positions of the ligands in an octahedral geometry has been shown below.

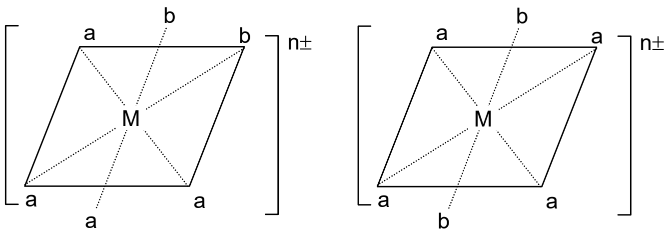


Positions 1 and 2: cis
Positions 1 and 6: trans

The octahedral complexes of the types $[Ma_6]$, $[M(AA)_3]$ and $[Ma_5b]$ do not show geometrical isomerism.

The following octahedral complexes give two or more geometrical isomers

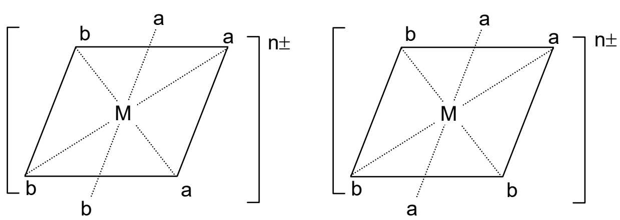
(1) $[Ma_4b_2]^{n\pm}$ type complexes:



cis–form   trans–form

Examples of such complexes are $[Co^{3+}(NH_3)_4Cl_2]^+$, $[Co^{3+}(NH_3)_4(NO_2)_2]^+$ etc.

(2) $[Ma_3b_3]^{n\pm}$ type complexes:



Facial (fac)   Meridional (mer)

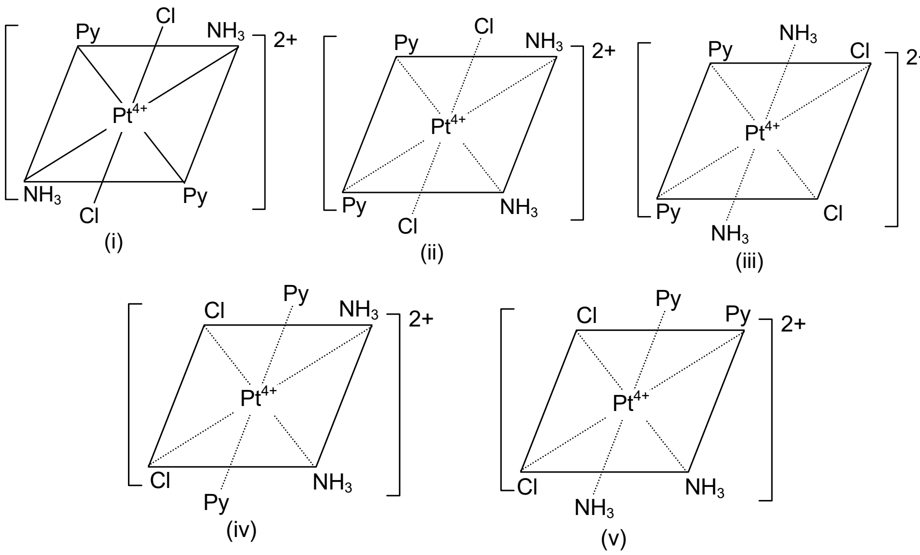
(When each trio of donor atoms (viz the ligands a, a and a) occupy adjacent positions at the corners of an octahedral face, we have facial (fac) isomer. When the positions are around the meridian of the octahedron, we get Meridional (mer) isomer.

Complexes like $[Co^{3+}(NH_3)_3Cl_3]$, $[Cr^{3+}(H_2O)_3F_3]$, $[Pt^{3+}(Py)_3Cl_3]$, $[Cr^{3+}(NH_3)_3Cl_3]$, $[Ru^{3+}(H_2O)_3Cl_3]$, $[Pt^{4+}(NH_3)_3Br_3]^+$ etc exhibit such type of isomerism.

(3) $[Ma_2b_2c_2]$ type complexes

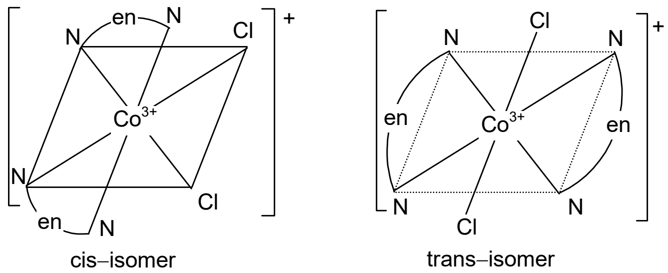
Octahedral complexes of this type can exist theoretically in five geometrical isomers. Out of these only three have been prepared.

For example, consider $[Pt^{4+}(NH_3)_2(Py)_2Cl_2]^{2+}$ ion. It can theoretically exist in the following structures.



(4) $[M(AA)_2a_2]$ type complexes: Here (AA) represents a symmetrical bidentate ligand in which *A* and *A* are two identical co-ordinating atoms.

Examples of such complexes are $[Co^{3+}(en)_2Cl_2]^+$, $[Co^{3+}(en)_2(NH_3)_2]^{3+}$, $[Co^{3+}(en)_2(NO_3)_2]^+$, $[Cr^{3+}(en)_2Cl_2]^+$, $[Cr^{3+}(C_2O_4)_2(H_2O)_2]^-$ (where en = ethylenediamine).



25 ZINC COMPOUNDS

Zinc Oxide (Zinc–white or Chinese white or Philosopher's wool) ; ZnO

Preparation:

$$2Zn + O_2 \xrightarrow{\Delta} 2ZnO$$

$$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2$$

$$2Zn(NO_3)_2 \xrightarrow{\Delta} 2ZnO + 4NO_2 + O_2$$

$$Zn(OH)_2 \xrightarrow{\Delta} ZnO + H_2O$$

Very pure zinc oxide is prepared by mixing a solution of zinc sulphate with sodium carbonate. The precipitated basic zinc carbonate on heating gives pure zinc oxide.

$$4ZnSO_4 + 4Na_2CO_3 + 3H_2O \longrightarrow \underset{\text{White ppt}}{ZnCO_3 \cdot 3Zn(OH)_2\downarrow} + 4Na_2SO_4 + 3CO_2$$

$$ZnCO_3 \cdot 3Zn(OH)_2\downarrow \xrightarrow{\text{Heat}} 4ZnO + 3H_2O + CO_2$$

Properties

(i) It is a white powder. It becomes yellow on heating and again turns white on cooling.

(ii) It is very light. It is insoluble in water. It sublimes at 400ºC.

(iii) It is an amphoteric oxide and dissolves readily in acids forming corresponding zinc salts and alkalies forming zincates.

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O$$

$$ZnO + 2HCl \longrightarrow ZnCl_2 + H_2O$$

$$ZnO + 2NaOH \longrightarrow \underset{\text{Sodium zincate}}{Na_2ZnO_2} + H_2O$$

(iv) When heated in hydrogen above 400ºC, it is reduced to metal.

$$ZnO + H_2 \longrightarrow Zn + H_2O$$

It is also reduced by carbon into zinc.

$$ZnO + C \longrightarrow Zn + CO$$

(v) When zinc oxide is heated with cobalt nitrate, a green mass is formed due to formation of cobalt zincate, which is known as **Rinmann's green.**

$$2Co(NO_3)_2 \longrightarrow 2CoO + 2NO_2 + O_2$$

$$ZnO + CoO \longrightarrow CoZnO_2 \text{ or } CoO \cdot ZnO$$

Zinc Chloride, $ZnCl_2 . 2H_2O$

Preparation :

$$ZnO + 2HCl \xrightarrow{\Delta} ZnCl_2 + H_2O$$

$$ZnCO_3 + 2HCl \xrightarrow{\Delta} ZnCl_2 + CO_2 + H_2O$$

$$Zn(OH)_2 + 2HCl \xrightarrow{\Delta} ZnCl_2 + 2H_2O$$

Anhydrous zinc chloride cannot be obtained by heating crystals of hydrated zinc chloride as hydrolysis occurs and basic chloride (zinc hydroxy chloride) is formed which on further heating gives zinc oxide.

$$ZnCl_2 \cdot 2H_2O \xrightarrow{\Delta} Zn(OH)Cl + HCl + H_2O$$

$$Zn(OH)Cl \xrightarrow{\Delta} ZnO + HCl$$

The anhydrous zinc chloride is obtained by heating zinc in the atmosphere of dry chlorine or dry HCl gas.

$$Zn + Cl_2 \longrightarrow ZnCl_2$$

$$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$$

This can also be formed by distilling zinc powder with mercuric chloride.

$$Zn + HgCl_2 \longrightarrow ZnCl_2 + Hg$$

Properties:

(i) Anhydrous zinc chloride is a white solid, deliquescent and soluble in water. It melts at 660ºC and boils at 730ºC.

(ii) Hydrated zinc chloride on heating forms zinc hydroxy chloride or zinc oxychloride.

$$ZnCl_2 \cdot 2H_2O \xrightarrow{\Delta} Zn(OH)Cl + HCl + H_2O$$

$$2ZnCl_2 \cdot 2H_2O \xrightarrow{\Delta} \underset{\text{Zinc oxychloride}}{Zn_2OCl_2} + 2HCl + 3H_2O$$

(iii) When H_2S is passed through the solution, a white precipitate of zinc sulphide is formed.

$$\underset{}{ZnCl_2} + H_2S \longrightarrow \underset{\text{White ppt}}{ZnS\downarrow} + 2HCl$$

(iv) When NaOH is added, a white precipitate of zinc hydroxide appears which dissolves in excess of sodium hydroxide forming sodium zincate.

$$ZnCl_2 + 2NaOH \longrightarrow \underset{\text{White ppt}}{Zn(OH)_2\downarrow} + 2NaCl$$

$$Zn(OH)_2\downarrow + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$$

(v) On adding NH_4OH solution, a white precipitate of zinc hydroxide appears which dissolves in excess of ammonia forming a complex salt.

$$ZnCl_2 + 2NH_4OH \longrightarrow \underset{\text{White ppt}}{Zn(OH)_2\downarrow} + 2NH_4Cl$$

$$Zn(OH)_2\downarrow + 2NH_4OH + 2NH_4Cl \longrightarrow \underset{\text{Tetramminezinc(II) chloride}}{[Zn(NH_3)_4]Cl_2} + 4H_2O$$

(vi) When the solution of zinc chloride is treated with a solution of sodium carbonate, a white precipitate of basic zinc carbonate is formed.

$$4ZnCl_2 + 4Na_2CO_3 + 3H_2O \longrightarrow \underset{\substack{\text{Basic zinc carbonate} \\ \text{White ppt}}}{ZnCO_3\cdot 3Zn(OH)_2\downarrow} + 8NaCl + 3CO_2$$

But when a solution of sodium bicarbonate is used, a white precipitate of normal zinc carbonate is formed.

$$ZnCl_2 + 2NaHCO_3 \longrightarrow \underset{\text{White ppt}}{ZnCO_3\downarrow} + 2NaCl + H_2O + CO_2$$

(vii) Anhydrous zinc chloride absorbs ammonia gas and forms an addition compound.

$$ZnCl_2 + 4NH_3 \longrightarrow ZnCl_2\cdot 4NH_3$$

(viii) Its syrupy solution dissolves cellulose. Its syrupy solution when mixed with zinc oxide (ZnO) sets to a hard mass forming an oxychloride, $ZnCl_2\cdot 3ZnO$.

Zinc Sulphate (White Vitriol) $ZnSO_4\cdot 7H_2O$

Preparation :

$$Zn + H_2SO_4\ (\text{dil.}) \longrightarrow ZnSO_4 + H_2$$

$$ZnO + H_2SO_4\ (\text{dil.}) \longrightarrow ZnSO_4 + H_2O$$

$$ZnCO_3 + H_2SO_4\ (\text{dil.}) \longrightarrow ZnSO_4 + H_2O + CO_2$$

Properties:

(i) It is a colourless, crystalline solid. It is an efflorescent substance. It is freely soluble in water.

(ii) On heating, the following changes occur.

$$ZnSO_4\cdot 7H_2O \xrightarrow[\substack{\text{Below 70°C} \\ -H_2O}]{\text{Above 39°C}} ZnSO_4\cdot 6H_2O \xrightarrow[-5H_2O]{\text{Above 70°C}} ZnSO_4\cdot H_2O \xrightarrow[-H_2O]{800°C} \underset{\text{(anhydrous)}}{ZnSO_4} \xrightarrow{\substack{\text{Above} \\ 800°C}} O_2 + SO_2 + ZnO$$

$$ZnSO_4 \xrightarrow{800°C} ZnO + SO_3$$

$$SO_3 \xrightarrow{\Delta} SO_2 + ½O_2$$

(iii) When sodium hydroxide is added to the solution of zinc sulphate, a white precipitate of zinc hydroxide appears which dissolves in excess of NaOH forming sodium zincate.

$$ZnSO_4 + 2NaOH \longrightarrow Zn(OH)_2\downarrow + Na_2SO_4$$

$$\underset{\text{White ppt}}{Zn(OH)_2\downarrow} + 2NaOH \longrightarrow Na_2ZnO_2 + 2H_2O$$

(iv) When sodium carbonate solution is added to the solution of zinc sulphate, a white precipitate of basic zinc carbonate is formed.

$$4ZnSO_4 + 4Na_2CO_3 + 3H_2O \longrightarrow \underset{\text{White ppt}}{ZnCO_3\cdot 3Zn(OH)_2\downarrow} + 4Na_2SO_4 + 3CO_2$$

However, when the solution of sodium bicarbonate is added, normal zinc carbonate is formed.

$$ZnSO_4 + 2NaHCO_3 \longrightarrow \underset{\text{White ppt}}{ZnCO_3\downarrow} + Na_2SO_4 + H_2O + CO_2$$

(v) With alkali metal sulphates and $(NH_4)_2SO_4$, it forms double sulphates such as $K_2SO_4\cdot ZnSO_4\cdot 6H_2O$.

26 SILVER COMPOUNDS

Silver Nitrate (Lunar caustic), $AgNO_3$

Preparation:

$$3Ag + \underset{\text{(Dilute)}}{4HNO_3} \xrightarrow{\text{Heat}} 3AgNO_3 + NO + 2H_2O$$

Properties:

(i) It is a colourless crystalline compound, soluble in water and alcohol. It melts at 212ºC.

(ii) In contact with organic substances, it blackens due to decomposition into metallic silver. Thus, it leaves black stain when comes in contact with skin and clothes.

It produces burning sensation like caustic and leaves a blackish–white stain (moon like colour) on skin and thus called as ***Lunar caustic***. It is decomposed by light also and therefore stored in coloured bottles.

(iii) On heating above its melting point, it decomposes to silver nitrite and oxygen.

$$2AgNO_3 \xrightarrow{\Delta} 2AgNO_2 + O_2$$

When heated in a red hot tube, it decomposes to metallic silver.

$$2AgNO_3 \xrightarrow{\Delta} 2\,Ag + 2NO_2 + O_2$$

(iv) Solutions of halides, phosphates, sulphides, chromates, thiocyanates, sulphates and thiosulphates, all give a precipitate of the corresponding silver salt with silver nitrate solution.

$$AgNO_3 + NaCl \longrightarrow \underset{\text{White ppt}}{AgCl\downarrow} + NaNO_3$$

$$AgNO_3 + NaBr \longrightarrow \underset{\text{Pale yellow ppt}}{AgBr\downarrow} + NaNO_3$$

$$AgNO_3 + NaI \longrightarrow \underset{\text{Yellow ppt}}{AgI\downarrow} + NaNO_3$$

$$3AgNO_3 + Na_3PO_4 \longrightarrow \underset{\text{Yellow ppt}}{Ag_3PO_4\downarrow} + 3NaNO_3$$

$$2AgNO_3 + K_2CrO_4 \longrightarrow \underset{\text{Brick red ppt}}{Ag_2CrO_4\downarrow} + 2KNO_3$$

$$AgNO_3 + NaCNS \longrightarrow \underset{\text{White ppt}}{AgCNS\downarrow} + NaNO_3$$

$$2AgNO_3 + Na_2SO_4 \longrightarrow \underset{\text{White ppt}}{Ag_2SO_4\downarrow} + 2NaNO_3$$

$$2AgNO_3 + Na_2S_2O_3 \longrightarrow \underset{\text{White ppt}}{Ag_2S_2O_3\downarrow} + 2NaNO_3$$

$$Ag_2S_2O_3 + H_2O \longrightarrow Ag_2S\downarrow + H_2SO_4$$

Black ppt

(v) Solid $AgNO_3$ absorbs ammonia gas with the formation of an addition compound, $AgNO_3 \cdot 3NH_3$.

(vi) When treated with a solution of NaOH, it forms precipitate of silver oxide. Originally, it has brown colour but turns black when dried.

$$2AgNO_3 + 2NaOH \longrightarrow \underset{\text{Brown ppt}}{Ag_2O\downarrow} + 2NaNO_3 + H_2O$$

(vii) When KCN is added to silver nitrate, a white precipitate of silver cyanide appears which dissolves in excess of KCN forming a complex salt, potassium argentocyanide.

$$AgNO_3 + KCN \longrightarrow \underset{\text{White ppt}}{AgCN\downarrow} + KNO_3$$

$$AgCN + KCN \longrightarrow \underset{\text{Potassium argentocyanide}}{K[Ag(CN)_2]}$$

(viii) When sodium thiosulphate is added to silver nitrate, a white precipitate of silver thiosulphate appears. This precipitate, however, dissolves in excess of sodium thiosulphate forming a complex salt.

$$2AgNO_3 + Na_2S_2O_3 \longrightarrow \underset{\text{White ppt}}{Ag_2S_2O_3\downarrow} + 2NaNO_3$$

$$Ag_2S_2O_3 + 3Na_2S_2O_3 \longrightarrow \underset{\text{Sodium argentothiosulphate}}{2Na_3[Ag(S_2O_3)_2]}$$

(ix) $AgNO_3$ reacts with iodine in two ways:

(a) $6AgNO_3\text{ (excess)} + 3I_2 + 3H_2O \longrightarrow AgIO_3 + \underset{\text{Yellow ppt}}{5AgI\downarrow} + 6HNO_3$

(b) $5AgNO_3 + 3I_2\text{ (excess)} + 3H_2O \longrightarrow HIO_3 + \underset{\text{Yellow ppt}}{5AgI\downarrow} + 5HNO_3$

(x) Silver is readily displaced from an aqueous silver nitrate solution by the base metals, particularly, if the solution is somewhat acidic.

$$2AgNO_3 + Cu \longrightarrow 2Ag\downarrow + Cu(NO_3)_2$$

$$2AgNO_3 + Zn \longrightarrow 2Ag\downarrow + Zn(NO_3)_2$$

(xi) Phosphine, arsine and stibine all precipitate silver from silver nitrate solution.

$$PH_3 + 6AgNO_3 + 3H_2O \longrightarrow 6Ag\downarrow + 6HNO_3 + H_3PO_3$$

$$AsH_3 + 6AgNO_3 + 3H_2O \longrightarrow 6Ag\downarrow + 6HNO_3 + H_3AsO_3$$

(xii) All halogen acids, except HF, precipitate silver halides from aqueous solution of $AgNO_3$.

$$AgNO_3 + HX \longrightarrow AgX\downarrow + HNO_3$$

Silver fluoride (AgF) is soluble in water.

(xiii) When NH_4OH is added to silver nitrate solution, a brown precipitate of silver oxide appears which dissolves in excess of ammonia forming a complex salt.

$$2AgNO_3 + 2NH_4OH \longrightarrow \underset{\text{Brown ppt}}{Ag_2O\downarrow} + 2NH_4NO_3 + H_2O$$

$$2Ag_2O + 2NH_4NO_3 + 2NH_4OH \longrightarrow 2[Ag(NH_3)_2]NO_3 + 3H_2O$$

The ammonical solution of $AgNO_3$ gives the following reaction:

(a) It reacts with acetylene to form white precipitate of silver acetylide.

$$2AgNO_3 + 2NH_4OH + C_2H_2 \longrightarrow \underset{\substack{\text{Silver acetylide} \\ \text{White ppt}}}{Ag_2C_2\downarrow} + 2NH_4NO_3 + 2H_2O$$

(b) It converts glucose to gluconic acid.

$$Ag_2O + C_6H_{12}O_6 \longrightarrow \underset{\text{Silver mirror}}{2Ag\downarrow} + C_6H_{12}O_7$$

(c) It oxidises formaldehyde to formic acid.

$$Ag_2O + HCHO \longrightarrow \underset{\text{Silver mirror}}{2Ag\downarrow} + HCOOH$$

Silver Oxide, (Ag_2O)

Preparation:

$$2AgNO_3 + 2NaOH \longrightarrow \underset{\text{Brown ppt}}{Ag_2O\downarrow} + 2NaNO_3 + H_2O$$

Properties:

It is brownish powder insoluble in water and thermally unstable. It decomposes to silver and oxygen.

$$2Ag_2O \longrightarrow 4Ag\downarrow + O_2$$

Ag_2O is soluble in aqueous ammonia.

Silver thiosulphate, $Ag_2S_2O_3$

Preparation:

Addition of more than the equivalent amount of sodium thiosulphate to a solution of silver acetate or fluoride, when a white precipitate of silver thiosulphate is formed.

$$2AgF + Na_2S_2O_3 \longrightarrow 2NaF + Ag_2S_2O_3\downarrow$$

Properties:

It forms needle–like crystals. It dissolves in excess of sodium thiosulphate solution producing a complex.

$$Ag_2S_2O_3 + 3Na_2S_2O_3 \longrightarrow 2Na_3[Ag(S_2O_3)_2]$$

Silver thiosulphate is decomposed by water giving **play of colour test**, changing from white to black through yellow and brown, when silver nitrate solution is mixed with dilute sodium thiosulphate solution.

$$Na_2S_2O_3 + 2AgNO_3 \longrightarrow 2NaNO_3 + Ag_2S_2O_3\downarrow$$

$$Ag_2S_2O_3\downarrow + H_2O \longrightarrow H_2SO_4 + Ag_2S\downarrow$$

Cupric Oxide, CuO (Black oxide of Copper)

Preparation

It is prepared by the following methods.

(i) By heating Cu_2O in air or by heating copper for a long time in air. The temperature should not exceed above 1100ºC.

$$Cu_2O + ½\, O_2 \xrightarrow[<1100\,^\circ C]{\Delta} 2CuO$$

$$2Cu + O_2 \xrightarrow[<1100\,^\circ C]{\Delta} 2CuO$$

(ii) By heating cupric hydroxide also, cupric oxide can be obtained.

$$Cu(OH)_2 \xrightarrow{\Delta} CuO + H_2O$$

(iii) By heating copper nitrate also, cupric oxide can be obtained.

$$2Cu(NO_3)_2 \xrightarrow{\Delta} 2CuO + 4NO_2 + O_2$$

(iv) On commercial scale, it is obtained by heating malachite, which is found in nature.

$$CuCO_3\cdot Cu(OH)_2 \xrightarrow{\Delta} 2CuO + CO_2 + H_2O$$

Properties:

(i) It is a black powdery substance and is stable towards moderate heating.

(ii) The oxide is insoluble in water but dissolves in acids forming corresponding salts.

$$CuO + 2HCl \longrightarrow CuCl_2 + H_2O$$

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$CuO + 2HNO_3 \longrightarrow Cu(NO_3)_2 + H_2O$$

(iii) When heated to 1100–1200ºC, it is converted into cuprous oxide with evolution of oxygen.

$$4CuO \longrightarrow 2Cu_2O + O_2$$

(iv) It is reduced to metallic copper by reducing agents such as hydrogen, carbon and carbon monoxide.

$$CuO + H_2 \longrightarrow Cu + H_2O$$
$$CuO + C \longrightarrow Cu + CO$$
$$CuO + CO \longrightarrow Cu + CO_2$$

Cupric Chloride ($CuCl_2 \cdot 2H_2O$)

Preparation: (i) The metal or cupric oxide or cupric hydroxide or copper carbonate is dissolved in concentrated HCl. The resulting solution on crystallization gives green crystals of hydrated cupric chloride.

$$2Cu + 4HCl + O_2 \longrightarrow 2CuCl_2 + 2H_2O$$
$$CuO + 2HCl \longrightarrow CuCl_2 + H_2O$$
$$CuCO_3.Cu(OH)_2 + 4HCl \longrightarrow 2CuCl_2 + 3H_2O + CO_2$$

(ii) Anhydrous cupric chloride is obtained as a dark brown mass when copper metal is heated in excess of chlorine gas or by heating hydrated cupric chloride in HCl gas at 150ºC.

$$Cu + Cl_2 \longrightarrow CuCl_2$$
$$CuCl_2 \cdot 2H_2O \xrightarrow[\text{HCl gas}]{150^{\circ}c} CuCl_2 + 2H_2O$$

Properties:

(i) It is a deliquescent compound and is readily soluble in water. The dilute solution is blue but the concentrated solution is green. It changes to yellow when concentrated HCl is added. The blue colour is due to complex cation $[Cu(H_2O)_4]^{2+}$ and yellow colour is due to the complex anion $[CuCl_4]^{2-}$ and green when both are present.

(ii) The aqueous solution is acidic due to hydrolysis of Cu^{2+}.

$$CuCl_2 + 2H_2O \rightleftharpoons Cu(OH)_2 + 2HCl$$

(iii) The anhydrous salt on heating forms Cu_2Cl_2 and Cl_2.

$$2CuCl_2 \longrightarrow Cu_2Cl_2 + Cl_2$$

While the hydrated salt on strong heating gives CuO, Cu_2Cl_2, HCl and Cl_2.

$$3CuCl_2 \cdot 2H_2O \longrightarrow CuO + Cu_2Cl_2 + 2HCl + Cl_2 + 5H_2O$$

(iv) It is readily reduced to Cu_2Cl_2 by copper turnings or SO_2 gas or hydrogen (nascent form obtained by the action of HCl on Zn) or $SnCl_2$.

$$CuCl_2 + Cu \longrightarrow Cu_2Cl_2$$
$$2CuCl_2 + SO_2 + 2H_2O \longrightarrow Cu_2Cl_2 + 2HCl + H_2SO_4$$
$$2CuCl_2 + 2[H] \longrightarrow Cu_2Cl_2 + 2HCl$$
$$2CuCl_2 + SnCl_2 \longrightarrow Cu_2Cl_2 + SnCl_4$$

(v) A pale blue precipitate of basic cupric chloride, $CuCl_2 \cdot 3Cu(OH)_2$ is obtained when NaOH is added.

$$CuCl_2 + 2NaOH \longrightarrow Cu(OH)_2 + 2NaCl$$
$$CuCl_2 + 3Cu(OH)_2 \longrightarrow \underset{\text{Blue ppt}}{CuCl_2 \cdot 3Cu(OH)_2\downarrow}$$

It dissolves in ammonium hydroxide forming a deep blue solution. On evaporating this solution, deep–blue crystals of tetramminecupric chloride are obtained.

$$CuCl_2 + 4NH_4OH \longrightarrow Cu(NH_3)_4Cl_2 \cdot H_2O + 3H_2O$$

Copper Sulphate (Blue Vitriol) $CuSO_4 \cdot 5H_2O$

Preparation:

(i) Copper sulphate is prepared in the laboratory by dissolving cupric oxide or hydroxide or carbonate in dilute sulphuric acid. The solution is evaporated and crystallized.

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$$

$$Cu(OH)_2 + H_2SO_4 \longrightarrow CuSO_4 + 2H_2O$$

$$CuCO_3.Cu(OH)_2 + 2H_2SO_4 \longrightarrow 2CuSO_4 + 3H_2O + CO_2$$

(ii) On a commercial scale, it is prepared from scrap copper. The scrap copper is placed in a perforated lead bucket, which is dipped into hot dilute sulphuric acid. Air is blown through the acid. Copper sulphate is crystallized from the solution.

$$Cu + H_2SO_4 + \tfrac{1}{2} O_2 \text{ (air)} \longrightarrow CuSO_4 + H_2O$$

Properties:

(i) It is a blue crystalline compound and is fairly soluble in water.

(ii) Heating effect

$CuSO_4 \cdot 5H_2O$ crystals effloresce on exposure to air and are converted into a pale blue powder, $CuSO_4 \cdot 3H_2O$. When heated to 100ºC, bluish white monohydrate $CuSO_4 \cdot H_2O$ is formed. The monohydrate loses the last molecule of water at 230ºC giving the anhydrous salt of $CuSO_4$, which is white.

$$\underset{\text{Blue}}{CuSO_4 \cdot 5H_2O} \underset{-2H_2O}{\overset{\text{Exposure}}{\rightleftharpoons}} \underset{\text{Pale Blue}}{CuSO_4 \cdot 3H_2O} \underset{-2H_2O}{\overset{100^\circ C}{\rightleftharpoons}} \underset{\text{Bluish white}}{CuSO_4 \cdot H_2O} \underset{-H_2O}{\overset{230^\circ C}{\rightleftharpoons}} \underset{\text{White}}{CuSO_4}$$

Anhydrous copper sulphate (white) regains its blue colour when moistened with a drop of water (test of water).

If the anhydrous salt is heated at 720ºC, it decomposes into cupric oxide and sulphur trioxide. $CuSO_4 \xrightarrow{720^\circ C} CuO + SO_3$

$$SO_3 \longrightarrow SO_2 + \tfrac{1}{2}O_2$$

(iii) Action of NH_4OH

With ammonia solution, it forms the soluble blue complex. First it forms a precipitate of $Cu(OH)_2$ which dissolves in excess of ammonia solution.

$$CuSO_4 + 2NH_4OH \longrightarrow \underset{\text{Blue ppt}}{Cu(OH)_2\downarrow} + (NH_4)_2SO_4$$

$$Cu(OH)_2\downarrow + 2NH_4OH + (NH_4)_2SO_4 \longrightarrow \underset{\text{Tetramminecupric sulphate}}{Cu(NH_3)_4SO_4} + 4H_2O$$

The complex is known as **Schweitzer's reagent**, which is used for dissolving cellulose in the manufacture of artificial silk.

(iv) Action of alkalies

With alkalies, $CuSO_4$ forms a pale blue precipitate of copper hydroxide.

$$CuSO_4 + 2NaOH \longrightarrow \underset{\text{Blue ppt}}{Cu(OH)_2\downarrow} + Na_2SO_4$$

(v) Action of potassium iodide

First cupric iodide is formed, which decomposes to give white cuprous iodide and iodine.

$$[CuSO_4 + 2KI \longrightarrow CuI_2 + K_2SO_4] \times 2$$

$$2CuI_2 \longrightarrow Cu_2I_2 + I_2$$

$$\overline{}$$

$$2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$$

(vi) Action of potassium cyanide

First cupric cyanide is formed which decomposes to give cuprous cyanide and cyanogen gas. Cuprous cyanide dissolves in excess of potassium cyanide to form a complex, potassium cuprocyanide $[K_3Cu(CN)_4]$.

$$[CuSO_4 + 2KCN \longrightarrow Cu(CN)_2 + K_2SO_4] \times 2$$
$$2Cu(CN)_2 \longrightarrow Cu_2(CN)_2 + (CN)_2$$
$$Cu_2(CN)_2 + 6KCN \longrightarrow 2K_3Cu(CN)_4$$
$$2CuSO_4 + 10KCN \longrightarrow 2K_3Cu(CN)_4 + 2K_2SO_4 + (CN)_2$$

27 IRON COMPOUNDS

Ferrous Sulphate (Green Vitriol), $FeSO_4 \cdot 7H_2O$

Preparation:

(i) By the oxidation of pyrites under the action of water and atmospheric air.

$$2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4$$

(ii) It is obtained by dissolving scrap iron in dilute sulphuric acid.

$$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$$

The solution is crystallized by the addition of alcohol as ferrous sulphate is sparingly soluble in it.

(iii) It can also be prepared in the laboratory from the Kipp's waste. Heating with a small quantity of iron fillings neutralizes the excess of sulphuric acid. The solution is then crystallised.

(iv) Commercially, ferrous sulphate is obtained by the slow oxidation of iron pyrites in the presence of air and moisture. The pyrites are exposed to air in big heaps.

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2FeSO_4 + 2H_2SO_4$$

The free sulphuric acid is removed by the addition of scrap iron. On crystallization, green crystals are obtained.

Properties:

(i) Hydrated ferrous sulphate ($FeSO_4 \cdot 7H_2O$) is a green crystalline compound. Due to atmospheric oxidation, the crystals acquire brownish–yellow colour due to formation of basic ferric sulphate.

$$4FeSO_4 + 2H_2O + O_2 \longrightarrow \underset{\text{Basic ferric sulphate}}{4Fe(OH)SO_4}$$

(ii) Action of heat

$$FeSO_4 \cdot 7H_2O \xrightarrow[-7H_2O]{300\,^\circ C} 2FeSO_4 \xrightarrow[\text{temp.}]{\text{High}} Fe_2O_3 + SO_2 + SO_3$$

Ferrous ammonium sulphate (Mohr's Salt)

$(NH_4)_2SO_4.FeSO_4.6H_2O$

Preparation:

The double salt is best prepared by making saturated solutions of pure ferrous sulphate and pure ammonium sulphate in air free distilled water at 40°C. Both the solutions are mixed and allowed to cool. Generally, few drops of sulphuric acid and a little iron wire are added before crystallisation so as to prevent oxidation of ferrous sulphate into ferric sulphate. The salt is obtained as pale green crystals.

Properties:

It is pale green crystalline compound, which does not effloresce like ferrous sulphate. It is less readily oxidised in the solid state. It is, therefore, a better volumetric reagent in preference of ferrous sulphate. Chemically, it is similar to ferrous sulphate. All the chemical reactions observed in the case of ferrous sulphate are given by ferrous ammonium sulphate.

Ferric chloride ($FeCl_3$)

This is the most important ferric salt. It is known in anhydrous and hydrated forms. The hydrated form consists of six water molecules, $FeCl_3.6H_2O$.

Preparation:

(i) Anhydrous ferric chloride is obtained by passing dry chlorine gas over heated iron fillings. The vapours are condensed in a bottle attached to the outlet of the tube.

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3$$

(ii) Hydrated ferric chloride is obtained by the action of hydrochloric acid on ferric carbonate, ferric hydroxide or ferric oxide.

$$Fe_2(CO_3)_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2O + 3CO_2$$

$$Fe(OH)_3 + 3HCl \longrightarrow FeCl_3 + 3H_2O$$

$$Fe_2O_3 + 6HCl \longrightarrow 2FeCl_3 + 3H_2O$$

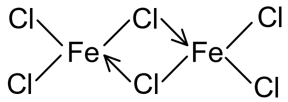
The solution on evaporation and cooling deposits yellow crystals of hydrated ferric chloride, $FeCl_3.6H_2O$.

Properties:

(i) Anhydrous ferric chloride is a dark red deliquescent solid. It is sublimed at about 300°C and its vapour density corresponds to dimeric formula, Fe_2Cl_6. The dimer dissociates at high temperature to $FeCl_3$. The dissociation into $FeCl_3$ is complete at 750°C. Above this temperature, it breaks into ferrous chloride and chlorine.

$$Fe_2Cl_6 \xrightleftharpoons{750°C} 2FeCl_3 \xrightleftharpoons{\text{Above } 750°C} 2FeCl_2 + Cl_2$$

(ii) Anhydrous ferric chloride behaves as a covalent compound as it is soluble in non–polar solvents like ether, alcohol, etc. It is represented by chlorine bridge structure.



(iii) It dissolves in water. The solution is acidic in nature due to its hydrolysis as shown below.

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$

The solution is stabilised by the addition of hydrochloric acid to prevent hydrolysis.

(iv) Anhydrous ferric chloride absorbs ammonia.

$$FeCl_3 + 6NH_3 \longrightarrow FeCl_3.6NH_3$$

(v) Ferric chloride acts as an oxidising agent.

(a) It oxidises stannous chloride to stannic chloride.

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$

(b) It oxidises SO_2 to H_2SO_4.

$$2FeCl_3 + SO_2 + 2H_2O \longrightarrow 2FeCl_2 + H_2SO_4 + 2HCl$$

(c) It oxidises H_2S to S

$$2FeCl_3 + H_2S \longrightarrow 2FeCl_2 + 2HCl + S$$

(d) It liberates iodine from KI.

$$2FeCl_3 + 2KI \longrightarrow 2FeCl_2 + 2KCl + I_2$$

(e) Nascent hydrogen reduces $FeCl_3$ into $FeCl_2$.

$$FeCl_3 + H \longrightarrow FeCl_2 + HCl$$

(vi) When ammonium hydroxide is added to the solution of ferric chloride, a reddish–brown precipitate of ferric hydroxide is formed.

$$FeCl_3 + 3NH_4OH \longrightarrow Fe(OH)_3 + 3NH_4Cl$$

(vii) When a solution of thiocyanate ions is added to ferric chloride solution, a deep red colouration is produced due to formation of a complex salt.

$$FeCl_3 + NH_4CNS \longrightarrow Fe(SCN)Cl_2 + NH_4Cl$$

or $$FeCl_3 + 3NH_4CNS \longrightarrow Fe(SCN)_3 + 3NH_4Cl$$

(viii) Ferric chloride forms a complex, prussian blue with potassium ferrocyanide.

$$4FeCl_3 + 3K_4Fe(CN)_6 \longrightarrow \underset{\substack{\text{Prussian blue} \\ \text{(Ferri ferrocyanide)}}}{Fe_4[Fe(CN)_6]_3} + 12KCl$$

(ix) On heating hydrated ferric chloride $FeCl_3.6H_2O$, anhydrous ferric chloride is not obtained. It is changed to Fe_2O_3 with evolution of H_2O and HCl.

$$2[FeCl_3.6H_2O] \xrightarrow{\text{Heat}} Fe_2O_3 + 6HCl + 9H_2O$$

Hydrated ferric chloride may be dehydrated by heating with thionyl chloride.

$$FeCl_3.6H_2O + 6SOCl_2 \longrightarrow FeCl_3 + 12HCl + 6SO_2$$

Ferrous oxide

Preparation:

Iron can burn in oxygen when heated, producing magnetic oxide of iron, Fe_3O_4 (an equimolar mixture of FeO and Fe_2O_3).

$$3Fe + 2O_2 \longrightarrow Fe_3O_4$$

Pure iron has no action with pure water but steam, reacts with red–hot iron liberating hydrogen and forming Fe_3O_4.

$$3Fe + 4H_2O \longrightarrow Fe_3O_4 + 4H_2\uparrow$$

Ferrous oxide (FeO) can be found wherever there is iron exposed to the oxygen in the atmosphere. The oxide is a black powder, formed by heating ferric oxide with hydrogen at 300°C or by heating ferrous oxalate in absence of air at 160°–170°C.

$$Fe_2O_3 + H_2 \xrightarrow{300°C} 2FeO + H_2O$$

$$FeC_2O_4 \xrightarrow{160–170°C} FeO + CO\uparrow + CO_2\uparrow$$

Properties:

(i) Iron oxide is naturally black in colour and it appears as a solid crystalline substance at room temperature.

(ii) Melting point of FeO is 1370°C and its density is 5.7 g/cm^3.

(iii) Iron oxide will decompose into its elements before boiling.

(iv) It is oxidized in air with incandescence (pyrophoric).

(v) It is sparingly soluble in water and as a basic oxide dissolves in dilute acids to give ferrous salts.

(vi) Iron oxide is commonly used as a pigment for colouring all sorts of materials like paints, plastics and rubber. It is also used for the dye in tattoos.

(vii) The iron and oxide ions in iron oxide are bonded with ionic bonds, making iron oxide a salt. There is a 1 : 1 ratio of iron ions to oxide ions and being a salt, iron oxide does not have individual molecules, but forms geometrical structure with all of the ions bonded by electrostatic forces.

Passivity of Iron

The inertness exhibited by metals under conditions when chemical activity is to be expected is called chemical passivity. The following are the common properties of iron.

(a) It evolves hydrogen gas, when made to react with dilute HCl or dilute H_2SO_4.

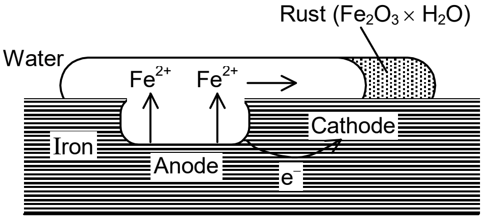
(b) It precipitates silver from silver nitrate solution and copper from copper sulphate solution.

But if a piece of iron is first dipped in concentrated nitric acid for sometime and then made to react with the above regents, neither hydrogen is evolved nor silver or copper are precipitated. Thus, iron by treatment with concentrated nitric acid has lost its usual properties or it has been rendered inert or passive. Such behaviour is not only shown by iron but also by many other metals like Cr, Co, Ni, Al etc. This phenomenon is known as passivity and the chemical substances, which bring passivity, are called passivators.

Other oxidising agents can render iron passive like chromic acid, $KMnO_4$, concentrated H_2SO_4 etc. The passivity of the iron is believed to be due to formation of an extremely thin film (invisible) of oxide on the surface of iron. Passive iron can be made active by scratching or heating in a reducing atmosphere of H_2 or CO, or heating in HNO_3 upto 75°C.

Corrosion of Iron

Corrosion is defined as the gradual transformation of a metal into its combined state because of the reaction with the environment. Metals are usually extracted from their ores. Nature tries to convert them again into the ore form. The process, by which the metals have the tendency to go back to their combined state, is termed ***corrosion***.



When iron is exposed to moist air, it is found to be covered with a reddish–brown coating, which can easily be detached. The reddish brown coating is called 'rust'. Thus, the corrosion of iron or formation of the rust is called ***rusting***. The composition of the rust is not certain but it mainly contains hydrated ferric oxide, $2Fe_2O_3.3H_2O$, together with a small quantity of ferrous carbonate. The rust is formed by the action of water on iron in the presence of dissolved oxygen and carbon dioxide. It has been observed that impure iron is more prone to rusting.

The following are the favourable conditions for the rusting or iron

(i) Presence of moisture

(ii) Presence of a weakly acidic atmosphere

(iii) Presence of impurity in the iron.

Various theories have been proposed to explain the phenomenon of rusting of iron but the most accepted theory is the modern electrochemical theory. When impure iron comes in contact with water containing dissolved carbon dioxide, a voltaic cell is set up. The iron and other impurities act as electrodes while water having dissolved oxygen and carbon dioxide acts as an electrolyte. Iron atoms pass into the solution as ferrous ions.

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

Iron, thus, acts as anode.

The impurities act as cathode. At the cathode, the electrons are used in forming hydroxyl ions.

$$H_2O + O + 2e^- \longrightarrow 2OH^-$$

In presence of dissolved oxygen, ferrous ions are oxidised to ferric ions, which combine with hydroxyl ions to form ferric hydroxide.

$$Fe^{3+} + 3OH^- \longrightarrow \underset{\text{Rust}}{Fe(OH)_3}$$

$$[2Fe^{2+} + H_2O + O \longrightarrow 2Fe^{3+} + 2OH^-]$$

Corrosion or rusting is a surface phenomenon and thus, the protection of the surface prevents the corrosion. Iron can be protected from the rusting by use of following methods:

(i) Applying paints, lacquers and enamels on the surface of iron.

(ii) By forming a firm and coherent protective coating of ferrosoferric oxide. This is done by passing steam over hot iron.

(iii) By coating a thin film of zinc, tin, nickel, chromium, aluminium, etc.

POTASSIUM PERMANGANET

Preparation

1. $$2MnO_2 + 4KOH + O_2 \xrightarrow{\text{Fuse}} 2K_2MnO_4 + 2H_2O$$
Pyrolusite — Potassium manganates (Green)

$$2MnO_2 + 2K_2CO_3 + O_2 \xrightarrow{\text{Fuse}} 2K_2MnO_4 + 2CO_2$$
Instead of oxygen any other oxidising agent such as KNO_3 may also be used.

2. The fused mass is extracted with water and current of Cl_2 or O_3 or CO_2 is passed so as to convert manganates into permanganate.
$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$
$$2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2$$
$$3K_2MnO_4 + 2CO_2 \longrightarrow 2KMnO_4 + MnO_2 + 2K_2CO_3$$

Manufacture

$$MnO_2 \xrightarrow[\text{oxidise with air or } KNO_3]{\text{Fuse with KOH}} MnO_4^{2-} \xrightarrow[\text{in alkaline solution}]{\text{electrolytic oxidation}} MnO_4^-$$
Permanganate

Properties

(i) $KMnO_4$ is a purple coloured crystalline compound. It is fairly soluble in water.

(ii) When heated alone or with an alkali, it decomposes evolving oxygen.
$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$
$$4KMnO_4 + 4KOH \longrightarrow 4K_2MnO_4 + 2H_2O + O_2$$

(iii) On treatment with concentrated H_2SO_4, it forms manganese heptaoxide which decomposes explosively on heating.
$$2KMnO_4 + 3H_2SO_4 \longrightarrow 2KHSO_4 + (MnO_3)_2SO_4 + 2H_2O$$
$$(MnO_3)_2SO_4 + H_2O \longrightarrow Mn_2O_7 + H_2SO_4$$
$$Mn_2O_7 \longrightarrow 2MnO_2 + \frac{3}{2}O_2$$

(iv) $KMnO_4$ acts as an oxidising agent in alkaline, neutral or acidic solutions.

(a) In alkaline solution

$KMnO_4$ is first reduced to manganate and then to insoluble manganese dioxide. Colour changes first from purple to green and finally becomes colourless. However, brownish precipitate is formed.
$$2KMnO_4 + 2KOH \longrightarrow 2K_2MnO_4 + H_2O + O$$
$$2K_2MnO_4 + 2H_2O \longrightarrow 2MnO_2 + 4KOH + 2O$$
$$\overline{2KMnO_4 + H_2O \xrightarrow{\text{Alkaline}} 2MnO_2 + 2KOH + 3[O]}$$
or $$2MnO_4^- + H_2O \longrightarrow 2MnO_2 + 2OH^- + 3[O]$$

(b) In neutral solution

Brownish precipitate of MnO_2 is formed.
$$2KMnO_4 + H_2O \longrightarrow 2MnO_2 + 2KOH + 3[O]$$
or $$2MnO_4^- + H_2O \longrightarrow 2MnO_2 + 2OH^- + 3[O]$$
or $$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$

(c) In acidic solution (in presence of dilute H_2SO_4)

Manganous sulphate is formed. The solution becomes colourless.
$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
or $$2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 3H_2O + 5[O]$$
or $$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

The important oxidation reactions are:

(i) Ferrous salts are oxidised to ferric salts.

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
$$[2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 5$$
$$2KMnO_4 + 10FeSO_4 + 8H_2SO_4 \longrightarrow 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$
or $2MnO_4^- + 10Fe^{2+} + 16H^+ \longrightarrow 10Fe^{3+} + 2Mn^{2+} + 8H_2O$

(ii) Iodide is evolved from potassium iodide.
$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$
$$[2KI + H_2SO_4 + [O] \longrightarrow K_2SO_4 + I_2 + H_2O] \times 5$$
$$2KMnO_4 + 10\,KI + 8H_2SO_4 \longrightarrow 6K_2SO_4 + 2MnSO_4 + 5I_2 + 8H_2O$$
or $2MnO_4^- + 10I^- + 16H^+ \longrightarrow 5I_2 + 2Mn^{2+} + 8H_2O$

(iii) $2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 5S + 8H_2O$

(iv) $2KMnO_4 + 5SO_2 + 2H_2O \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

(v) $2KMnO_4 + 5KNO_2 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5KNO_3 + 3H_2O$

(vi) $5\begin{array}{l}COOH\\ |\\ COOH\end{array} + 2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O$

In neutral medium

(i) H_2S is oxidised to sulphur
$$2KMnO_4 + H_2O \longrightarrow 2MnO_2 + 2KOH + 3[O]$$
$$[H_2S + [O] \longrightarrow H_2O + S] \times 3$$
$$2KMnO_4 + 3H_2S \longrightarrow 2KOH + MnO_2 + 2H_2O + 3S$$

(ii) Manganese sulphate is oxidised to MnO_2
$$2KMnO_4 + H_2O \longrightarrow 2MnO_2 + 2KOH + 3[O]$$
$$[MnSO_4 + H_2O + [O] \longrightarrow MnO_2 + H_2SO_4] \times 3$$
$$2KOH + H_2SO_4 \longrightarrow K_2SO_4 + 2H_2O$$
$$2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow K_2SO_4 + 5MnO_2 + 2H_2SO_4$$

(iii) Sodium thiosulphate is oxidised to sulphate and sulphur
$$2KMnO_4 + 3Na_2S_2O_3 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3Na_2SO_4 + 3S$$

In alkaline medium

(i) It oxidises ethylene to ethylene glycol.
$$\begin{array}{l}CH_2\\ \|\\ CH_2\end{array} + H_2O + [O] \longrightarrow \begin{array}{l}CH_2OH\\ |\\ CH_2OH\end{array}$$

In alkaline medium it is called Bayer's reagent.

29 POTASSIUM DICHROMATE

Manufacture

1. $4FeO.Cr_2O_3 + 8Na_2CO_3 + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$
   Chromite ore (from air)
2. Na_2CrO_4 is extracted with water, thereby leaving Fe_2O_3 (insoluble) behind and unconverted ore.
3. $2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$
4. This solution is concentrated, when Na_2SO_4 crystallizes out. On further concentration, $Na_2Cr_2O_7$ crystals are obtained.
5. The hot saturated solution of $Na_2Cr_2O_7$ is mixed with KCl. NaCl precipitates out from the hot solution, which is filtered off. On cooling the mother liquor, crystals of $K_2Cr_2O_7$ separates out.

Properties:

It is orange–red coloured crystalline compound. It is moderately soluble in cold water but freely soluble in hot water. It melts at 398°C. On heating strongly, it decomposes liberating oxygen.

$$2K_2Cr_2O_7 \longrightarrow 2K_2CrO_4 + Cr_2O_3 + 3/2O_2$$

On heating with alkalies, it is converted to chromate, i.e. the colour changes from orange to yellow. On acidifying, yellow colour again changes to orange.

$$K_2Cr_2O_7 + 2KOH \longrightarrow 2K_2CrO_4 + H_2O$$

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + 2OH^- \longrightarrow \underset{\text{Yellow}}{2CrO_4^{2-}} + H_2O$$

$$\underset{\text{Yellow}}{2CrO_4^{2-}} + 2H^+ \longrightarrow \underset{\text{Orange}}{Cr_2O_7^{2-}} + H_2O$$

In alkaline solution, chromate ions are present while in acidic solution, dichromate ions are present. Potassium dichromate reacts with hydrochloric acid and evolves chlorine.

$$K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$$

It acts as a powerful oxidising agent in acidic medium (dilute H_2SO_4).

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

The oxidation state of Cr changes from +6 to +3. Some typical oxidation reactions are given below:

(i) Iodine is liberated from potassium iodide.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$[2KI + H_2SO_4 + [O] \longrightarrow K_2SO_4 + I_2 + H_2O] \times 3$$

$$K_2Cr_2O_7 + 6KI + 7H_2SO_4 \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$$

The equation in terms of electron method may also be written as

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

$$6I^- \longrightarrow 3I_2 + 6e^-$$

$$Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O$$

(ii) Ferrous salts are oxidised to ferric salts.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$[2FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 3$$

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 7H_2O + K_2SO_4$$

or $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$

(iii) Sulphites are oxidised to sulphates

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$[Na_2SO_3 + [O] \longrightarrow Na_2SO_4] \times 3$$

$$K_2Cr_2O_7 + 3Na_2SO_3 + 4H_2SO_4 + 3Na_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O$$

or $Cr_2O_7^{2-} + 3SO_3^{2-} + 8H^+ \longrightarrow 3SO_4^{2-} + 2Cr^{3+} + 4H_2O$

(iv) H_2S is oxidised to sulphur

$$K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$$

or $Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 7H_2O + 3S$

(v) SO_2 is oxidised to H_2SO_4

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

$$[SO_2 + [O] + H_2O \longrightarrow H_2SO_4] \times 3$$

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

or $Cr_2O_7^{2-} + 3SO_2 + 2H^+ \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + H_2O$

When the solution is evaporated, chrome–alum is obtained.

(vi) It oxidises ethyl alcohol to acetaldehyde and acetaldehyde to acetic acid.

$$C_2H_5OH \xrightarrow{[O]} CH_3CHO \xrightarrow{[O]} CH_3COOH$$

Ethyl alcohol Acetaldehyde Acetic acid

It also oxidises nitrites to nitrates, arsenites to arsenates, thiosulphate to sulphate and sulphur ($S_2O_3^{2-} + O \longrightarrow SO_4^{2-} + S$), HBr to Br_2, HI to I_2, etc.

Chromyl chloride test

This is a test of chloride. When a mixture of a metal chloride and potassium dichromate is heated with concentration H_2SO_4, orange red vapours of chromyl chloride are evolved.

$$K_2Cr_2O_7 + 2H_2SO_4 \longrightarrow 2KHSO_4 + 2CrO_3 + H_2O$$

$$[NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl] \times 4$$

$$[CrO_3 + 2HCl \longrightarrow CrO_2Cl_2 + H_2O] \times 2$$

$$K_2Cr_2O_7 + 6H_2SO_4 + 4NaCl \longrightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

When chromyl chloride vapours are passed through NaOH solution, yellow coloured solution is obtained.

$$4NaOH + CrO_2Cl_2 \longrightarrow \underset{\text{Yellow solution}}{Na_2CrO_4} + 2NaCl + 2H_2O$$

29 OXIDES AND HALIDES OF TIN AND LEAD

CHLORIDES OF TIN

Stannous chloride, $SnCl_2$

Preparation:

Tin dissolved in hot concentrated hydrochloric acid yields $SnCl_2 \cdot 2H_2O$ on concentrating and crystallization.

$$Sn + 2HCl + 2H_2O \longrightarrow SnCl_2.2H_2O + H_2$$

Properties:

The hydrated salt on heating forms the oxychloride.

$$SnCl_2 \cdot 2H_2O \longrightarrow Sn(OH)Cl + HCl + H_2O$$

This hydrolysis can be prevented by the presence of excess HCl, with some pieces of tin added.

Aqueous and non–aqueous solutions of tin(II) salts are capable of acting as reducing agents, but they must be stored under an inert atmosphere because air oxidation is spontaneous and rapid.

$$Sn^{2+}(aq) + \tfrac{1}{2} O_2(g) + 2H^+(aq) \longrightarrow Sn^{4+}(aq) + H_2O(l) \quad ; \quad (E^\circ = 1.08 \text{ V})$$

Stannous chloride reacts with NaOH forming a white precipitate of tin(II) hydroxide which dissolves in excess of NaOH forming sodium stannite.

$$SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2\downarrow + 2NaCl$$

$$Sn(OH)_2\downarrow + 2NaOH \longrightarrow \underset{\text{Sodium stannite}}{Na_2SnO_2} + 2H_2O$$

Sodium stannite is oxidised by atmospheric oxygen to form sodium stannate, Na_2SnO_3. From a solution of stannous chloride, H_2S precipitates brown SnS, soluble in ammonium polysulphides.

$$SnCl_2 + H_2S \longrightarrow SnS\downarrow + 2HCl$$

$$SnS\downarrow + (NH_4)_2S_2 \longrightarrow (NH_4)_2SnS_3 \text{ (ammonium thiostannate)}$$

$SnCl_2$ is a powerful reducing agent, as the following reactions illustrate.

$$2FeCl_3 + SnCl_2 \longrightarrow 2FeCl_2 + SnCl_4$$

$$2HgCl_2 + SnCl_2 \longrightarrow SnCl_4 + Hg_2Cl_2 \text{ (white precipitate of mercurous chloride)}$$

$$Hg_2Cl_2 + SnCl_2 \longrightarrow \underset{\text{Grey}}{2Hg} + SnCl_4 \text{ (hot condition)}$$

$$2\,KMnO_4 + 16HCl + 5SnCl_2 \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5SnCl_4$$

$$K_2Cr_2O_7 + 14HCl + 3SnCl_2 \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3SnCl_4$$

$$2CuCl_2 + SnCl_2 \longrightarrow \underset{\text{White ppt}}{2CuCl\downarrow} + SnCl_4$$

$$HNO_3 + 6HCl + 3SnCl_2 \longrightarrow \underset{\text{Hydroxylamine}}{NH_2\text{–}OH} + 2H_2O + 3SnCl_4$$

Stannous chloride reduces nitro compounds to amino compounds and iodine to iodides.

$$C_6H_5\text{–}NO_2 + 6HCl + 3SnCl_2 \longrightarrow C_6H_5\text{–}NH_2 + 3SnCl_4 + 2H_2O$$

$$I_2 + 2HCl + SnCl_2 \longrightarrow SnCl_4 + 2HI$$

Anhydrous stannous chloride, a glassy substance is prepared by heating tin in a stream of HCl or with mercuric chloride.

$$Sn + 2HCl \longrightarrow SnCl_2 + H_2\uparrow$$

$$\underset{\text{Excess}}{Sn} + HgCl_2 \longrightarrow SnCl_2 + Hg$$

Anhydrous $SnCl_2$ forms a dimer (Sn_2Cl_4) in the vapour, dissolves in organic solvents and forms many addition compounds with NH_3. e.g. $SnCl_2{\cdot}2NH_3$.

In aqueous and non–aqueous solutions Sn(II) forms trihalo complexes, such as $[SnCl_3]^-$, where the pyramidal structure indicates the presence of a stereochemically active lone pair. The $[SnCl_3]^-$ ion can serve as a soft donor to d–metal ions. One unusual example of this ability is the red cluster compound $Pt_3Sn_8Cl_{20}$, which is trigonal bipyramidal.

Uses:

As a reducing agent in the laboratory, as a mordant in dyeing and in the preparation of purple of Cassius.

Stannic chloride, $SnCl_4$ (Butter of Tin)

Preparation:

Dry Cl_2 gas when passed over heated tin in a retort forms $SnCl_4$.

$$Sn + 2Cl_2 \longrightarrow SnCl_4$$

Liquid $SnCl_4$ is thus collected in a cooled receiver protected from moisture.

It is also made by heating Sn with excess of $HgCl_2$.

$$Sn + 2HgCl_2 \longrightarrow SnCl_4 + 2Hg$$

Another method of preparation is from heated SnO_2 by passing Cl_2 + S_2Cl_2 (sulphur monochloride) vapour over it.

$$2SnO_2 + 3Cl_2 + S_2Cl_2 \longrightarrow 2SnCl_4 + 2SO_2$$

It is also obtained by the removal of tin from (i.e., detinning of) scrap tin plates by chlorine.

Properties:

It is a colourless fuming liquid, soluble in organic solvents and volatile in nature. These properties indicate its covalent nature. It forms hydrates with a limited quantity of water but undergoes hydrolysis with excess of water.

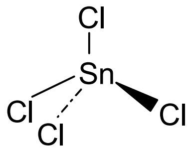
$$SnCl_4 \xrightarrow[\text{(limited quantity)}]{H_2O} SnCl_4{\cdot}3H_2O,\ SnCl_4{\cdot}5H_2O,\ SnCl_4{\cdot}6H_2O$$

$SnCl_4{\cdot}5H_2O$ is known as ***'butter of tin'*** or ***'oxymuriate of tin'***. It is used as a mordant and also for weighing silk.

$$SnCl_4 + H_2O \rightleftharpoons Sn(OH)Cl_3 + HCl$$

$$Sn(OH)Cl_3 + 3H_2O \rightleftharpoons Sn(OH)_4 + 3HCl$$

This hydrolytic reaction is slow, reversible and can be suppressed by HCl, with which the following reaction occurs: $SnCl_4 + 2Cl^- \longrightarrow [SnCl_6]^{2-}$. Salts with this ion e.g. $(NH_4)_2SnCl_6$ are known as chlorostannates. Other addition compounds are obtained with NH_3, PCl_5 etc., e.g. $SnCl_4{\cdot}4NH_3$. The structure of $SnCl_4$ is



The tetrachloride, bromide and iodide of tin are molecular compounds, but the tetrafluoride has a structure consistent with it being an ionic solid because the small F^- ion permits a six co–ordinate structure.

Uses:

Butter of tin is used as a mordant and for weighing silk.

OXIDES OF TIN

Tin(II) oxide, SnO

Preparation:

SnO is precipitated by boiling stannous chloride solution with sodium carbonate or by heating the hydroxide or oxalate in absence of air.

$$SnCl_2 + Na_2CO_3 \longrightarrow 2NaCl + SnO\downarrow + CO_2\uparrow$$

$$SnC_2O_4 \longrightarrow SnO\downarrow + CO\uparrow + CO_2\uparrow$$

When freshly precipitated, the oxide has the composition $2SnO.2H_2O$.

Properties:

It is usually an olive green powder, which gives greyish crystals in contact with water. When heated in air, it forms the dioxide. Both the oxide and hydrated oxide dissolve in acids forming stannous salts and in alkalies, forming stannites.

Uses:

SnO acts as strong reducing agent.

$$2SnO + 2NaOH \longrightarrow Na_2SnO_2 + Sn\downarrow + H_2O$$

Tin(IV) oxide, SnO_2

SnO_2 occurs in nature as tinstone or cassiterite.

Preparation:

It is easily obtained by the combustion of tin in air, by ignition of metastannic acid produced from the action of nitric acid on tin.

Cold and dilute nitric acid reacts with tin forming stannous nitrate, while concentrated nitric acid attacks tin with the formation of hydrated stannic oxide.

$$4Sn + 10HNO_3 \longrightarrow 4Sn(NO_3)_2 + 3H_2O + NH_4NO_3$$

$$Sn + 4HNO_3 \longrightarrow SnO_2.H_2O + 4NO_2\uparrow + H_2O$$

(hydrated stannic oxide–also known as meta stannic acid)

Properties:

It is a soft, white solid sparingly soluble in water and acids except concentrated sulphuric acid but readily soluble in fused alkalies to form stannate.

$$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$$

Uses:

Tin dioxide is used as a polishing powder and the name "putty powder" and for making milky glass and white glazes for tiles and enamels.

CHLORIDES OF LEAD

Lead chloride, $PbCl_2$

Preparation:

Prepared by slow direct combination or by the action of boiling concentrated HCl on lead (its oxide or carbonate).

$$Pb + Cl_2 \xrightarrow{\Delta} PbCl_2$$

$$Pb + 2HCl \longrightarrow PbCl_2 + H_2\uparrow$$

$$PbO + 2HCl \longrightarrow PbCl_2 + H_2O$$

The usual method of preparation is to precipitate $PbCl_2$ as a white crystalline precipitate by adding a soluble chloride to a lead salt solution.

$$Pb(NO_3)_2 + 2NaCl \longrightarrow PbCl_2 + 2NaNO_3.$$

Properties:

It is sparingly soluble in cold water but more soluble in hot water. In concentrated solutions of Cl^- ions, it dissolves forming complex ions, $[PbCl_3]^-$ and $[PbCl_4]^{2-}$.

Lead tetrachloride, $PbCl_4$

Preparation:

This is made by dissolving PbO_2 in ice-cold concentrated HCl. Concentrated H_2SO_4 decomposes ammonium chloroplumbate to yield $PbCl_4$.

$$PbO_2 + 4HCl \longrightarrow PbCl_2 + Cl_2\uparrow + 2H_2O$$

$$(NH_4)_2[PbCl_6] + H_2SO_4 \longrightarrow PbCl_4 + (NH_4)_2SO_4 + 2HCl$$

Properties:

$PbCl_4$ is a yellow oily liquid. It is heavy and dissolves in organic solvents. It is a covalent and unstable compound, readily decomposes on heating.

$$PbCl_4 \xrightarrow{\Delta} PbCl_2 + Cl_2\uparrow$$

It is easily hydrolysed by water and forms a double salt with NH_4Cl.

$$PbCl_4 + 2H_2O \longrightarrow PbO_2 + 4HCl$$

Lead tetrabromide and tetraiodide are unknown, so the dihalides dominate the halogen chemistry of lead.

OXIDES OF LEAD

Lead monoxide, PbO

It naturally occurs as lead ochre (an of various fine earths or days that contain ferric oxide, red, yellow or brown pigment. The colour of this oxide is yellow or red depending on the mode of preparation.

Preparation:

When lead is gently heated in air, yellow powder is formed as the monoxide, called massicot. When heating is continued it melts and on cooling gives the reddish–yellow scales of litharge. These differ only in crystalline structure. The transition temperature being 558°C. Lead monoxide can also be prepared by thermal decomposition of lead nitrate as well as lead carbonate..

$$2Pb(NO_3)_2 \xrightarrow{\Delta} 2PbO + 4NO_2\uparrow + O_2\uparrow$$

$$PbCO_3 \xrightarrow{\Delta} PbO + CO_2\uparrow$$

Dry air has no action on lead, but in moist air it tarnishes, forming a film of oxide first and finally basic carbonate, which protects it from further action. On heating in air or oxygen, it forms litharge, PbO. But prolonged heating gives red lead, Pb_3O_4.

$$2Pb + O_2 \longrightarrow 2PbO$$

$$6PbO + O_2 \longrightarrow 2Pb_3O_4$$

Properties:

(i) At room temperature, it is a yellow amorphous powder that is insoluble in water but dissolves in acids as well as alkalies.

$$PbO + 2HCl \longrightarrow PbCl_2 + H_2O$$

$$PbO + 2NaOH \longrightarrow Na_2PbO_2 + H_2O$$

Thus, it behaves as an amphoteric oxide. The acidic properties being rather feeble.

(ii) It is easily reduced to the metallic state by hydrogen, carbon or carbon monoxide.

(iii) In the red form of PbO, the Pb(II) ions are four co–ordinate but the O^{2-} ions around the Pb(II) lie in a square.

Uses:

Used in paints, in the vulcanisation of rubber and in the preparation of red lead and lead salts.

Lead dioxide, PbO_2

Preparation:

(i) Action of cold concentrated nitric acid on red lead gives lead nitrate in solution while lead dioxide is thrown as a chocolate powder.

$$Pb_3O_4 + 4HNO_3 \longrightarrow PbO_2\downarrow + 2Pb(NO_3)_2 + 2H_2O$$

(ii) Action of powerful oxidizing agents like chlorine, bromine or bleaching powder on alkaline lead salt solution.

$$Pb(OH)_2 + Cl_2 \longrightarrow PbO_2\downarrow + 2HCl$$

$$Pb(C_2H_3O_2)_2 + Ca(OCl)Cl \longrightarrow PbO_2\downarrow + 2CH_3COOH + CaCl_2$$

Properties:

(i) It is a chocolate coloured powder insoluble in water and dilute acids.

(ii) It liberates oxygen on gentle heating.

$$2PbO_2 \longrightarrow 2PbO + O_2\uparrow$$

(iii) At 440°C, it is converted into red lead, Pb_3O_4.

$$3PbO_2 \xrightarrow{440^\circ C} Pb_3O_4 + O_2\uparrow$$

(iv) PbO_2 is an amphoteric oxide.

$$PbO_2 + 4HCl \longrightarrow PbCl_2\downarrow + Cl_2\uparrow + 2H_2O$$

$$2PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4\downarrow + 2H_2O + O_2\uparrow$$

(v) It is a good oxidizing agent. It oxidizes manganous salts to pink permanganic acid when boiled in nitric acid solution.

$$2MnSO_4 + 5PbO_2 + 6HNO_3 \longrightarrow 2HMnO_4 + 2PbSO_4 + 3Pb(NO_3)_2 + 2H_2O$$

(vi) In alkaline medium, chromium hydroxide is oxidized to yellow chromate by PbO_2.

$$2Cr(OH)_3 + 10KOH + 3PbO_2 \longrightarrow 2K_2CrO_4 + 3K_2PbO_2 + 8H_2O$$

The maroon form of lead(IV) oxide, PbO_2, crystallizes in the rutile structure. This oxide is a component of the cathode of a lead–acid battery.

Uses:

In the laboratory, lead dioxide finds application as an oxidizing agent. It is also used as the cathode in lead storage battery.

Red lead, Pb_3O_4

Preparation:

Roasting of litharge in air at 450°C gives a bright red powder.

$$6PbO + O_2 \longrightarrow 2Pb_3O_4$$

It is also known as sindur.

Properties:

(i) Sparingly soluble in water but dissolves in dilute nitric acid.

$$Pb_3O_4 + 4HNO_3 \longrightarrow 2Pb(NO_3)_2 + PbO_2\downarrow + 2H_2O$$

The above reaction indicates that red lead may be considered as plumbous ortho plumbate, $2PbO.PbO_2$.

(ii) It turns dark when heated but restores the original colour on cooling. At about 550°C, it decomposes giving off oxygen.

$$Pb_3O_4 \xrightarrow{\Delta} 3PbO + \frac{1}{2} O_2$$

(iii) It reacts with concentrated HCl and sulphuric acid liberating chlorine and oxygen respectively.

$$Pb_3O_4 + 8HCl \longrightarrow 3PbCl_2 + 4H_2O + Cl_2\uparrow$$

$$2Pb_3O_4 + 6H_2SO_4 \longrightarrow 6PbSO_4 + 6H_2O + O_2\uparrow$$

Red lead, Pb_3O_4 contains Pb(IV) in an octahedral arrangement and Pb(II) in an irregular six co–ordinate environment. The assignment of different oxidation number to the lead in these two sites is based on the shorter Pb–O distance for the atom identified as Pb(IV).

Uses:

Red lead, mixed with linseed oil is extensively used as a red paint and also for plumbing work.

30 ORGANOMETALLIC COMPOUNDS

These compounds constitute a broad class of substances in which carbon atom is directly bonded to a metal. Thus organic compounds in which metal atom is directly linked to carbon atom are known as organometallic compounds.

For example, NaC≡CNa is an organometallic compound as sodium is directly linked to carbon whereas C_2H_5ONa, $Ti(OC_2H_5)_4$ are not organometallic compounds since the metal atom is linked to carbon through oxygen. Some representative organometallic compounds are

C_2H_5MgBr – Ethyl magnesium bromide
$(C_2H_5)_2Zn$ – Diethyl zinc
$(CH_3)_2Cd$ – Dimethyl cadmium
C_6H_5Li – Phenyl lithium
$(C_2H_5)_4Pb$ – Tetraethyl lead

Alkyl or aryl magnesium halides (RMgX or ArMgX) are also called as ***Grignard reagents***.

CLASSIFICATION OF ORGANOMETALLIC COMPOUNDS

(i) Ionic compounds of electropositive metals:

These compounds are mostly formed between the electropositive metals and the carbon compounds which are mostly acidic in nature. Thus organometallic compounds of alkali metals and alkaline earth metals consist of ions or ion pairs.

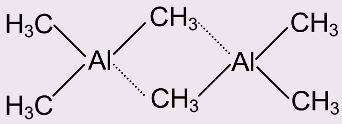
$\underset{\text{Alkyl sodium}}{R^- Na^+}$ $\quad$ $\underset{\text{Alkyl magnesium halide}}{R^- Mg^{2+} X^-}$

$\underset{\text{Sodium alkynide}}{R-C\equiv C^- Na^+}$ $\quad$ $\underset{\text{dialkylzinc}}{R^- Zn^{2+} R^-}$

These compounds are normally soluble in hydrocarbon solvent. They are very reactive towards air and water. The stability of these compounds depends upon the structure of the carbon containing part of the compound.

(ii) σ–bonded complexes:

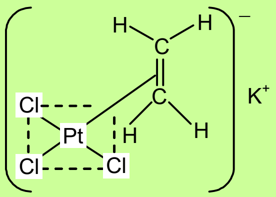
In a σ–bonded complex, a metal and a carbon atom of the ligand are joined together with a sigma bond. This means that the ligand contributes 1 electron and is therefore called one electron donor. Tetramethyl tin, $(CH_3)_4$ Sn and trimethyl aluminium, $(CH_3)_3Al$ are σ–bonded organometallic compounds. $(CH_3)_3Al$ exists as dimer and has structure analogous to diborane. Two methyl groups act as bridges between two aluminium atoms.



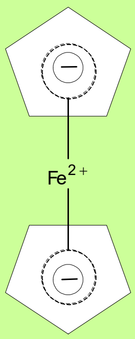
Trimethyl aluminium

(iii) π–complexes:

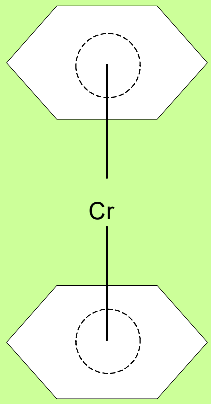
These are organometallic compounds which involve the use of π–bonds present in organic compounds. For example, Zeise's salt, ferrocene and dibenzene chromium are organometallic compounds of this type. In all these compounds the π–electrons of the organic compound interact with the metal ion and thus occupy one of the coordination sites. For example in ferrocene and dibenzene chromium, the iron and chromium atoms are sandwiched between two aromatic rings.



Zeise's salt K [Pt Cl_3 (η^2 –C_2H_4)]



Ferrocene Fe (η^5– C_5H_5)$_2$



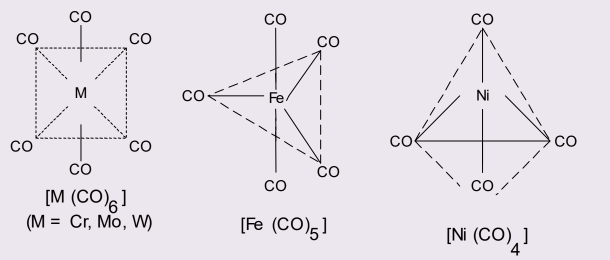
dibenzene chromium Cr(η^6 – C_6H_6)$_2$

[bis cyclopentadienyl iron]

The number of carbon atoms involved in the formation of π–complexes with metals is indicated by the power of η^x (eta). For example, ferrocene is represented as Fe[η^5(C_6H_6)$_7$] indicating that 5–carbon atoms or cyclo pentadienyl anion are involved in π–complexation with the metal. Similarly one can write dibenzene chromium as [Cr(η^6–C_6H_6)$_2$] indicating that all the six carbons of benzene are involved in π–complexation with chromium.

(iv) Metal Carbonyls:

These are the complexes where carbon of carbon monoxide donates a pair of electrons to the metal. Nickel carbonyl and iron carbonyl are the common examples.



In metal carbonyl the oxidation state of the metal is zero. These metal carbonyls may be monomeric bridged or polynuclear.

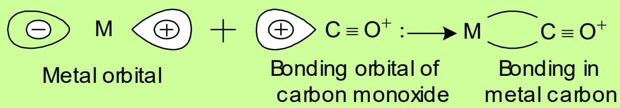
BONDING IN ORGANOMETALLIC COMPOUNDS

(a) Bonding in metal carbonyls:

The metal-carbon bond in metal carbonyls has σ as well as π character.

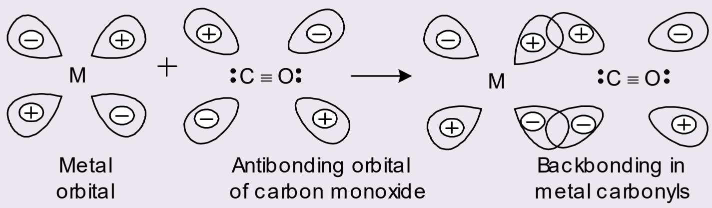
(i) σ–overlap :

In a sigma bonded complex, the lone pair of electrons is present on the bonding orbital of carbon monoxide. This bonding orbital containing lone pair interacts with the empty d-orbital of the metal to form a metal-carbon bond as shown below:



(ii) π–overlap :

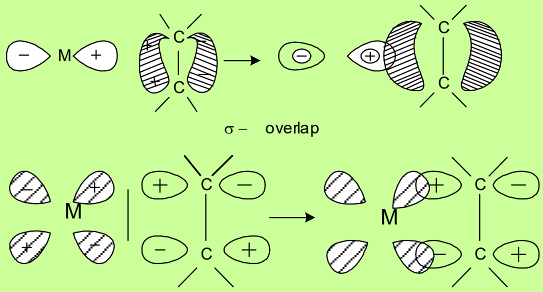
In addition to this, the antibonding orbitals of CO can also overlap with the filled d–orbitals of the metal resulting in back bonding as explained earlier. Thus metal carbonyls become much more stable compounds due to multiple bonding in them.



It is important to note here that the σ - bond is in the nodal plane of the σ-electrons whereas π-overlap is perpendicular to the nodal plane.

(b) Bonding of alkenes to a transition metal

The bonding of alkenes to a transition metal to form complexes has two components. First, the π–electron density of the alkene overlaps with a σ-type vacant orbital on the metal atom. Second is the back bonding formed by the flow of electron density from a filled d–orbital on the metal into the vacant π^x– antibonding molecular orbital on the carbon atom as shown.



SYNTHESIS OF ORGANOMETALLIC COMPOUNDS

1. By Direct Reaction of Metals :-

(a) Tetramethyl- and Tetraethyl-lead (which are used as anti-knock additives to petrol) are manufactured by the reaction between the alkyl chloride and a lead-sodium alloy.

$$4C_2H_5CL–CL + 4NA/PB \longrightarrow (C_2H_5)_4PB + 3PB + 4NACL$$

(b) Zinc alkyls are prepared by heating an alkyl iodide with zinc-copper couple.

$$2RI + 2Zn \longrightarrow 2RZnI \longrightarrow R_2Zn + ZnI_2$$

(c) Grignard reagent is generally prepared by reaction between magnesium and alkyl halide in dry, alcohol-free ether.

$$RX + MG \longrightarrow RMGX$$

(d) Alkyl-Lithium compounds are prepared by direct displacement.

$$NC_4H_9CL + 2LI \xrightarrow[\text{hexane}]{N_2} NC_4H_9LI + LICL$$

2. By Using an Alkylating agent

Grignard reagent and Alkyl lithium on reaction with most of the metal and non-metal halides in the presence of ether as solvent yield other organometallic compounds.

$$PCL_3 + 3C_6H_5MGCL \xrightarrow{\text{Ether}} P(C_6H_5)_3 + 3MGCL_2$$
Triphenyl Phosphine

$$SNCL_4 + 4N–C_4H_9LI \longrightarrow (N–C_4H_9)_4\,SN + 4LICL$$
Tetrabutyl Tin

$$PBCL_4 + 4C_2H_5MGBR \longrightarrow (C_2H_5)_4PB + 4MGBRCL$$
Tetraethyl Lead

$$CDCL_2 + 2RMGCL \longrightarrow R_2CD + 2MGBRCL_2$$
Dialkyl Cadmium

3. Preparation of π–complexes :-

(a) Preparation of Ferrocene

Ferrocene is prepared by the reaction of Iron Oxide with Cyclopentadiene at 523 K.

$$2C_5H_5 + FEO \xrightarrow{523\text{ K}} [(C_3H_5)_2FE] + H_2O$$
Ferrocene

It can also be prepared by treatment of Cyclopentadienyl Magnesium Bromide with Ferrous Chloride.

$$C_5H_5MGBR + FECL_2 \longrightarrow [(C_5H_5)_2FE] + 2MGBRCL$$

Cyclopenta Dienyl Ferrocene
Magnesium Bromide

(b) Preparation of Zeise's salt

It can be prepared by the action of Ethene with Tetrachloro Platinate (IV) anion.

$$\underset{\text{Ethene}}{C_2H_4} + \underset{\text{Tetrachloro Platinate (IV)}}{[PTCL_4]^{2-}} \longrightarrow \underset{\text{Zeise's Salt}}{[C_2H_4PTCL_3]^-} + CL^-$$

(c) Preparation of Dibenzene Chromium

Dibenzene Chromium is prepared by allowing the reaction between Benzene and Chromium vapours at high temperatures.

$$2C_6H_6 + CR(\text{Vapour}) \longrightarrow \underset{\text{Dibenzene Chromium}}{(C_6H_6)_2CR}$$

Dibenzene Chromium can also be prepared by reacting Chromium (iii) Chloride and Benzene in presence of Aluminium and Aluminium Chloride.

$$CRCL_3 + 2C_6H_6 + 3ALCL_3 \xrightarrow{Al} (\pi-C_6H_6)_2CR + 3AlCl_4^-$$

4. *Preparation of metal carbonyls :-*

(a) By Direct Synthesis

$$NI + 4CO \xrightarrow[\text{1 atm. Pr}]{\text{Room temp.}} NI(CO)_4$$

$$FE + 5CO \xrightarrow[\text{100 atm}]{200^\circ C} FE(CO)_5$$

(b) Reduction of Metal compounds in presence of CO

$$CRCL_3 + 6CO \xrightarrow[\text{in ether}]{(C_2H_5)_3Al} CR(CO)_6$$

(c) From $Fe(CO)_5$:- since CO Ligands in $Fe(CO)_5$ are labile, $Fe(CO)_5$ may be used to form certain carbonyls eg.,

$$MCL_6 + 3FE(CO)_5 \xrightarrow[\text{ether}]{100^\circ C} M(CO)_6 + 3FECL_2 + 9CO$$

(M = W, MO)

Applications of Organometallic Compounds

1. The soluble organometallic complexes of transition metals act as homogeneous catalyst. Some examples are:

(a) Selective hydrogenation of certain double bonds using Wilkinson's catalyst, $(Ph_3P)_3RhCl$.

(b) $(ET_3P)_2NICL_2$ acts as catalyst for the isomerization of alkenes.

2. Organometallic compounds can also act as heterogeneous catalyst. For example, Zeigler–Natta catalyst (a solution of $TiCl_4$, containing triethyl aluminium) for the polymerization of ethylene and the other alkenes.

3. Organometallic compounds of Magnesium (r–mg–x), Cadmium ($r_2$cd) and Lithium (r–li) are extensively used in organic synthesis.

4. Tetra ethyl lead is used as an antiknock compound.

5. A number of organometallics also find application in agriculture. For example, ethyl mercury chloride, C_2H_5HgCl is used as a fungicide for the protection of young plants and seeds against fungal infection.

6. Aryl arsenic compounds are used as chemotherapeutic agents.

7. Silicon rubbers, because of their high thermal stability, resistance to oxidation and chemical attack, are used in modern surgery for the purpose of production of artificial body parts.

8. Since $Ni(CO)_4$ is decomposed to metallic nickel, it is used in the production of nickel by Mond's process.

9. Ethyl Mercury Chloride is used to prevent the infection in young plants.

Practice Questions with Answers (For BOARD Aspirants)

Question 1: What is the ratio of uncomplexed to complexed Zn^{2+} ion in a solution that is 10 M in NH_3, if the stability constant of $[Zn(NH_3)_4]^{2+}$ is 3×10^9?

(A) 3.3×10^{-9} (B) 3.3×10^{-11}

(C) 3.3×10^{-14} (D) 3×10^{-13}

Solution:

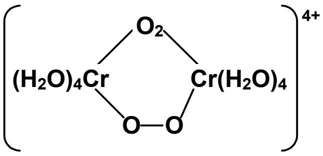
$$Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$$

$$K_f = \frac{[Zn(NH_3)_4]^{2+}}{[Zn^{2+}][NH_3]^4}$$

$$\frac{[Zn^{2+}]}{[Zn(NH_3)_4]^{2+}} = \frac{1}{K_f[NH_3]^4} = \frac{1}{3 \times 10^9 \times (10)^4} = 3.3 \times 10^{-14}$$

$\therefore$ **(c)**

Question 2: Oxidation state of Cr in the following complex is



(A) +3 (B) +6

(C) +4 (D) +5

Solution:

Among the bridging ligands, O_2 is a neutral ligand and $[O–O]^{2-}$ is a bidentate negative ligand. Since the net charge over the complex is 4+, each chromium atom has an oxidation state of +3.

$\therefore$ **(a)**

Question 3: A compound has an empirical formula $CoCl_3.5NH_3$. When an aqueous solution of this compound is mixed with excess of silver nitrate, 2 moles of AgCl precipitates per mole of the compound. On reaction with excess of HCl, no NH_4^+ is detected. Hence the compound is

(A) $[CO(NH_3)_5CL_2]CL$ (B) $[CO(NH_3)_5CL]CL_2$

(C) $[CO(NH_3)_5CL_3]$ (D) $[CO(NH_3)_4CL_2]CL.NH_3$

Solution:

As the moles of AgCl precipitated is 2 and no NH_4^+ is detected on reaction with excess of HCl, so the compound would be $[Co(NH_3)_5Cl]Cl_2$.

$\therefore$ **(B)**

Question 4: If excess of $AgNO_3$ solution is added to 100 ml of 0.024 M solution of dichlorobis(ethylene diamine)cobalt(III) chloride, how many moles of AgCl will be precipitated?

(A) *0.0012* *(B)* *0.0016*
(C) *0.0024* *(D)* *0.0048*

Solution:

The formula of the complex is $[CoCl_2(en)_2]Cl$.

$[CoCl_2(en)_2]Cl + AgNO_3 \longrightarrow AgCl\downarrow + [CoCl_2(en)_2]NO_3$

Moles of complex = Moles of AgCl = $100 \times 10^{-3} \times 0.024 = 0.0024$

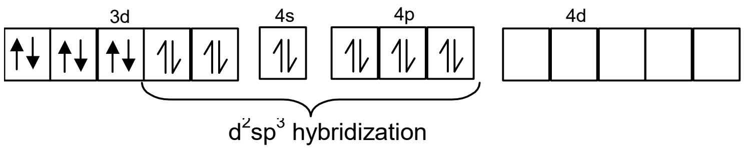
$\therefore$ **(c)**

Question 5: In nitroprusside ion, the iron and NO exist as Fe^{II} and NO^+ rather than Fe^{III} and NO. These forms can be distinguished by

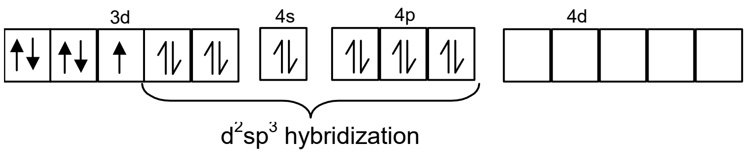
(a) *Estimating the concentration of iron*
(b) *Measuring the concentration of cn^-*
(c) *Measuring the solid state magnetic moment*
(d) *Thermally decomposing the compound*

Solution:

Nitroprusside ion is $[Fe(CN)_5NO]^{2-}$. If the central atom iron is present here in Fe^{2+} form, its effective atomic number will be 26–2 + (6×2) = 36 and the distribution of electrons in valence orbitals (hybridised and unhybridized) of the Fe^{2+} will be



It has no unpaired electron. So this anionic complex is diamagnetic. If the nitroprusside ion has Fe^{3+} and NO, the electronic distribution will be such that it will have one unpaired electron i.e. the complex will be paramagnetic.



Thus, magnetic moment measurement establishes that in nitroprusside ion, the Fe and NO exist as Fe^{II} and NO^+ rather then Fe^{III} and NO.

$\therefore$ **(c)**

Question 6: Which of the given statements is not true for the following reaction?

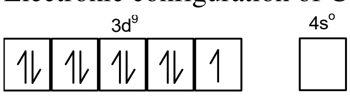
$$[Cu(H_2O)_4]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 4H_2O$$

(a) It is a ligand–substitution reaction.
(b) NH_3 is a relatively strong field ligand while H_2O is a weak field ligand.
(c) During the reaction, there is a change in colour from light blue to dark blue.
(d) $[Cu(NH_3)_4]^{2+}$ has a tetrahedral structure and is paramagnetic.

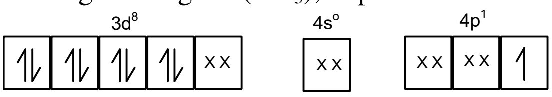
Solution:

For $_{29}Cu$, outermost shell has electronic configuration of $3d^{10}4s^1$.

Electronic configuration of $Cu^{2+} = 3d^9 4s^\circ$



But due to strong field ligand (NH_3), unpaired electron of $3d^9$ jumps to 4p. Hence,



$\therefore$ Hybridisation of Cu^{2+} in $[Cu(NH_3)_4]^{2+}$ is dsp^2 and it gives the square planar geometry.

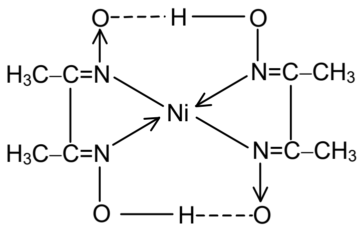
$\therefore$ **(d)**

Question 7: The IUPAC name of the complex $[Ni(C_4H_7O_2N_2)_2]$ formed from the reaction of Ni^{2+} with dimethyl glyoxime is

(a) Bis(methylgloxal)nickel(II) *(b) Bis(dimethyloxime)nickelate(IV)*

(c) Bis(2,3–butanedioldioximato)nickel(II) *(d) Bis(2,3–butanedionedioximato)nickel(II)*

Solution:



Bis(dimethylglyoximato)nickel(II) or Bis(2,3–butanedionedioximato)nickel(II)

∴ **(d)**

Question 8: The hybridization states of the central atoms in the complexes $[Fe(CN)_6]^{3-}$, $[Fe(CN)_6]^{4-}$ and $[Co(NO_2)_6]^{3-}$ are

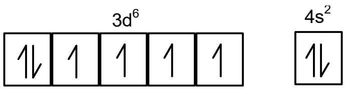
(a) d^2sp^3, sp^3 and d^4s^2 respectively *(b) d^2sp^3, sp^3d and sp^3d^2 respectively*

(c) d^2sp^3, sp^3d^2 and dsp^2 respectively *(d) all d^2sp^3*

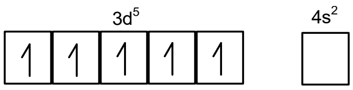
Solution:

$[Fe(CN)_6]^{3-}$ has Fe^{3+} ion.

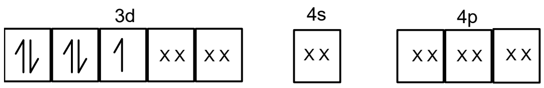
Outermost shell of Fe^{3+} (Z = 26) has the following configuration,



and outermost shell of Fe^{3+} has the configuration:



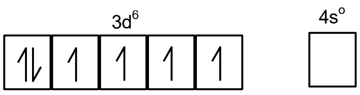
But due to strong field ligand (CN^-), the pairing of electrons takes place.



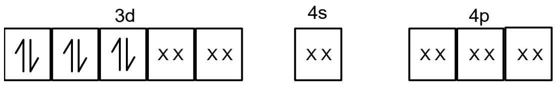
∴ Hybridisation is d^2sp^3.

$[Fe(CN)_6]^{4-}$ has Fe^{2+} ion.

Outermost shell of Fe^{2+} has the following configuration:



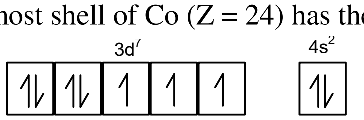
But due to strong field ligand (CN^-), the pairing of electrons takes place.



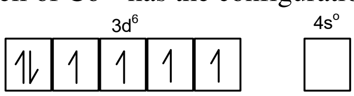
∴ Hybridisation is d^2sp^3.

$[Co(NO_2)_6]^{3-}$ has Co^{3+} ion.

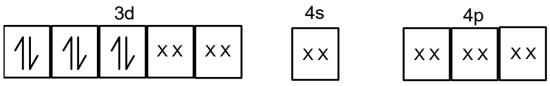
Outermost shell of Co (Z = 24) has the following configuration,



and outermost shell of Co^{3+} has the configuration:



But due to strong field ligand (NO_2^-), pairing of electrons occurs.



Hybridisation is d^2sp^3.

$\therefore$ **(d)**

Question 9: Which of the following statement is incorrect?

(a) Most four–coordinated complexes of Ni^{2+} ions are square planar rather than tetrahedral.

(b) The $[Fe(H_2O)_6]^{3+}$ ion is more paramagnetic than the $[Fe(CN)_6]^{3-}$ ion.

(c) Square planar complexes are more stable than octahedral complexes.

(d) The $[Fe(CN)_6]^{4-}$ ion is paramagnetic but $[Fe(CN)_6]^{3-}$ ion is diamagnetic.

Solution:

$[Fe(CN)_6]^{4-}$ has Fe^{2+} and have no unpaired electron, so it is diamagnetic and $[Fe(CN)_6]^{3-}$ has Fe^{3+} and having one unpaired electron, so it is paramagnetic.

$\therefore$ **(d)**

Question 10: Which of the following statement is correct?

(a) $[Co(NH_3)_6]^{2+}$ is oxidized to diamagnetic $[Co(NH_3)_6]^{3+}$ by the oxygen in air.

(b) $[Fe(CN)_6]^{3-}$ is stable but $[FeF_6]^{3-}$ is unstable.

(c) $[NiCl_4]^{2-}$ is unstable with respect to $[NiBr_4]^{2-}$.

(d) None of these.

Solution:

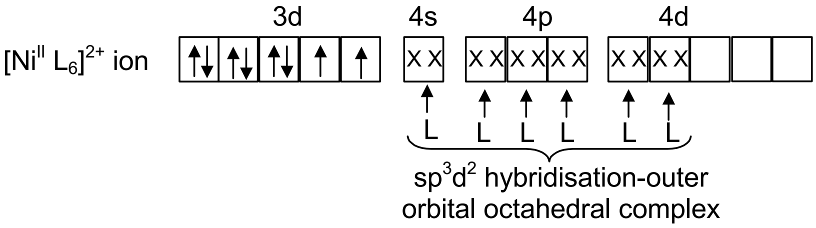
With the promotion of one 3d–electron to 5s or 4d, it becomes loosely bonded to the nucleus and hence, it may easily be removed and so, Co(II) will easily be oxidised into Co(III).

$\therefore$ **(a)**

Question 11:Show that all octahedral complexes of Ni^{2+} must be outer-orbital complexes.

Solution:

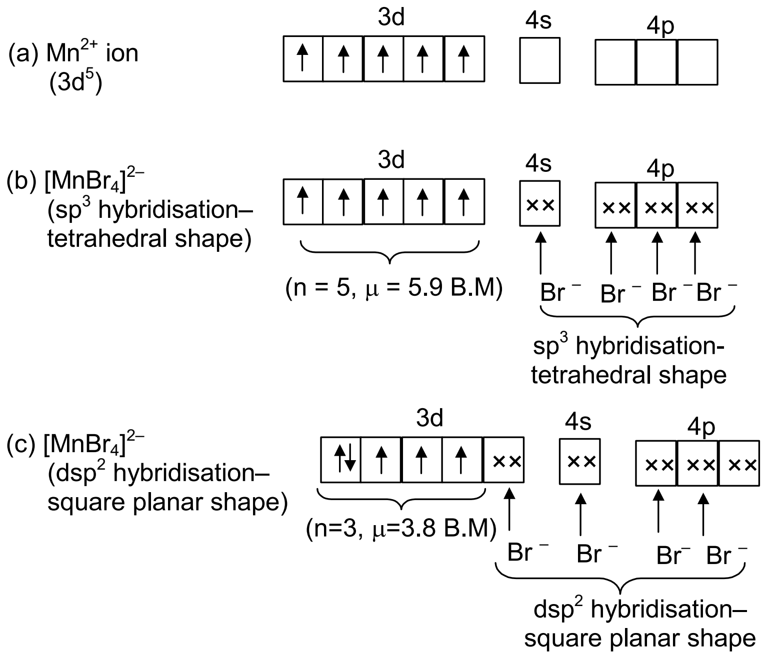
The electric configuration of Ni^{2+} ion ($3d^8$) indicates that two inner d-orbitals (3d-orbitals) cannot be made available to allow d^2sp^3 hybridisation. However, by using two 4d-orbitals, sp^3d^2 hybridisation may be possible.



Question 12:The magnetic moment of $[MnBr_4]^{2-}$ is 5.9 B.M. What is the geometry of this complex ion?

Solution:

Since the coordination number of Mn^{2+} ion in this complex ion is 4, it may be either tetrahedral (sp^3 hybridisation) or square planar (dsp^2 hybridisation) as shown below at (b) and (c). But the fact that the magnetic moment of the complex ion is 5.9 B.M. shows that it should be tetrahedral in shape rather than square-planar.



Question 13: How would you account for the following?

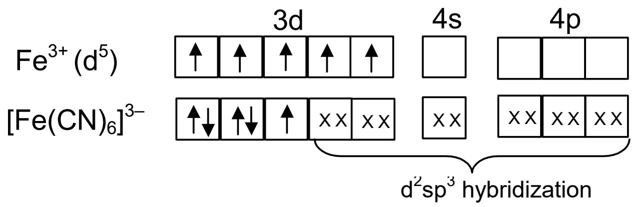
(a) $[Fe(CN)_6]^{3-}$ is weakly paramagnetic while $[Fe(CN)_6]^{4-}$ is diamagnetic.

(b) $Ni(CO)_4$ possesses tetrahedral geometry while $[Ni(CN)_4]^{2-}$ is square planar.

(c) $[Ni(CN)_4]^{2-}$ is diamagnetic while $[NiCl_4]^{2-}$ is paramagnetic.

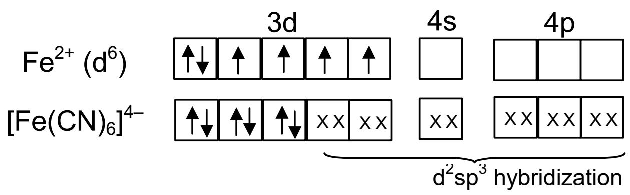
Solution:

(a) $[Fe(CN)_6]^{3-}$ involves d^2sp^3 hybridization.



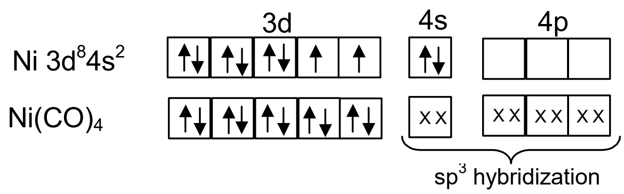
One d–orbital is singly occupied, hence it is weakly paramagnetic in nature.

$[Fe(CN)_6]^{4-}$ involves also d^2sp^3 hybridization but it has Fe^{2+} ion as central ion.

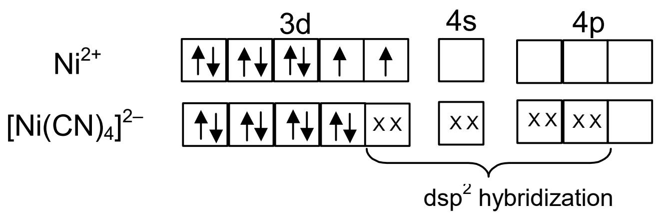


All orbitals are doubly occupied, hence it is diamagnetic in nature.

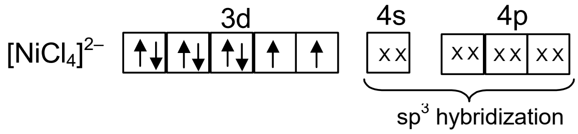
(b) In the formation of $Ni(CO)_4$, nickel undergoes sp^3 hybridization, hence it is tetrahedral in shape.



(c) In $[Ni(CN)_4]^{2-}$ ion, Ni^{2+} undergoes dsp^2 hybridization, hence it is square planar in shape.



In $[Ni(CN)_4]^{2-}$, all orbitals are doubly occupied, hence it is diamagnetic ; while in $[NiCl_4]^{2-}$, two orbitals are singly occupied, hence it is paramagnetic in nature.



Strong field ligands like CN^-, CO, en, NO_2^- have very strong electron donating tendency, hence electrons of central metal ion pair up against Hund's rule and low spin complexes are formed.

Question 14: A metal complex having composition $Cr(NH_3)_4\ Cl_2Br$ has been isolated in two forms (A) and (B). The form (A) reacts with $AgNO_3$ to give a white precipitate readily soluble in dilute aqueous ammonia, whereas (B) gives a pale yellow precipitate soluble in concentrated ammonia. Write the formula of (A) and (B) and state the hybridisation of chromium in each. Calculate the magnetic moments (spin-only value).

Solution:

Complex, $Cr(NH_3)_4Cl_2Br$, has two isomers. Since, coordination number of Cr is six, the two forms may be represented in the following way

$[Cr(NH_3)_4ClBr]Cl$ (A) $\qquad$ $[Cr(NH_3)_4Cl_2]Br$ (B)

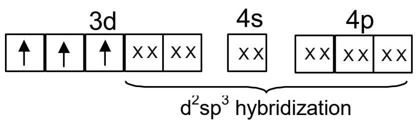
$$\underset{(A)}{[Cr(NH_3)_4)ClBr]\ Cl} + AgNO_3 \longrightarrow [Cr(NH_3)_4ClBr]NO_3 + \underset{\text{White ppt}}{AgCl\downarrow}$$

$$AgCl + 2NH_4OH \longrightarrow \underset{\text{Soluble}}{Ag(NH_3)_2Cl} + 2H_2O$$

$$\underset{(B)}{[Cr(NH_3)_4\ Cl_2]\ Br} + AgNO_3 \longrightarrow [Cr(NH_3)_4Cl_2]\ NO_3 + \underset{\text{Pale yellow}}{AgBr\downarrow}$$

$$AgBr + 2NH_4OH \longrightarrow \underset{\text{Soluble}}{Ag(NH_3)_2\ Br} + 2H_2O$$

The state of hybridisation of chromium in both the complexes is d^2sp^3. Chromium is in trivalent state (Cr^{3+}).



As three unpaired electrons are present, the magnetic moment $= \sqrt{n(n+2)}$ B.M. $= \sqrt{3\times5}$ B.M.

= 3.87 B.M.

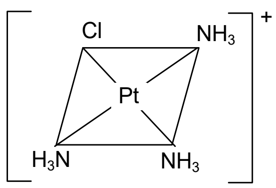
Question 15: Platinum (II) forms square planar complexes and platinum (IV) gives octahedral complexes. How many geometrical isomers are possible for each of the following complexes? Describe their structures.

(a) $[Pt\ (NH_3)_3\ Cl]^+$ $\qquad$ (b) $[Pt\ (NH_3)\ Cl_5]^-$

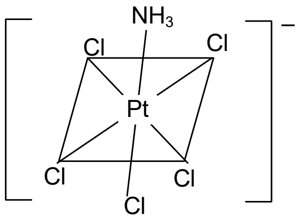
(c) $[Pt\ (NH_3)_2\ ClNO_2]$ $\qquad$ (d) $[Pt(NH_3)_4\ ClBr]^{2+}$

Solution:

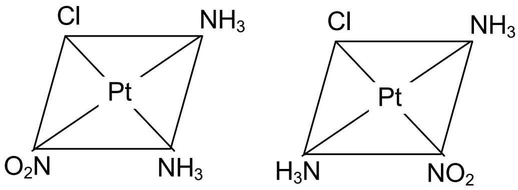
(a) No isomers are possible for a square planar complex of the type MA_3B.



(b) No isomers are possible for an octahedral complex of the type MAB_5.

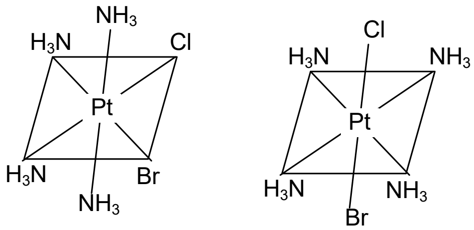


(c) Cis and trans isomers are possible for a square planar complex of the type MA_2BC.



cis trans

(d) Cis and trans isomers are possible for an octahedral complex of the type MA_4BC.



cis trans

Question 16: Write the IUPAC name of the following complexes:

(i) $[Co(en)_3]Cl_3$ *(ii) $[Co(C_2O_4)_3]^{3-}$*

(iii) $[NH_3)_5Co–O_2–Co(NH_3)_5]^{4+}$ *(iv) $[Cr(NH_3)_6]\ [Co(CN)_6]$*

(v) $(Ph_4As)_2\ [PtCl_2HCH_3]$

Solution:

(i) Tris(ethylediamine)cobalt(III) chloride

(ii) Trioxalatoccobaltate(III) ion

(iii) Decaammine–µ–peroxodicobalt(III) ion

(iv) Hexaamminechromium(III) hexacyanocobaltate(III)

(v) Tetraphenylarsenium dichlorohydridomethylplatinate(II)

Question 17: A solution containing 0.319 g of complex $CrCl_3.6H_2O$ was passed through cation exchanger and the solution given out was neutralised by 28.5 ml of 0.125 M NaOH. What is the correct formula of complex?

Solution:

The Cl atoms outside the co–ordination sphere will be ionised to produce the acid, HCl.

Thus, milliequivalent of Cl^- ions outside = milliequivalent of HCl formed

= milliequivalent of NaOH used

= 28.5×0.125

= 3.56

$\frac{0.319}{266.5}$ mole or 1.197 millimole of complex produce 3.56 milliequivalent or millimoles of Cl^-. Thus,

1 mole of complex will give 3 mole of Cl^-, i.e. all the three Cl atoms are outside the co–ordination sphere. Thus, the complex is **$[Cr(H_2O)_6]Cl_3$**.

Question 18: (A), (B) and (C) are three complexes of chromium (III) with the empirical formula $H_{12}O_6Cl_3Cr$. All the three complexes have water and chloride ions as ligands. Complex (A) does not react with concentrated H_2SO_4, whereas complexes (B) and (C) lose 6.75% and 13.5% of their original weight, respectively, on treatment with concentrated H_2SO_4. Identify the octahedral complexes (A), (B) and (C).

Solution:

(A) : $[Cr(H_2O)_6]Cl_3$ (Violet)
(B) : $[Cr(H_2O)_5Cl]Cl_2.H_2O$ (Green) Molecular weight = 266.5
(C) : $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ (Dark green)

Compound (A) contains six water molecules as co–ordinated water and thus, does not lost H_2O on treatment with H_2SO_4. Compound (B) contains five water molecules as co–ordinated water and one molecule as lattice water which is lost to H_2SO_4 showing a loss of 18 g out of 266.5 g, i.e., 6.75% loss. Similarly, compound (C) contains four co–ordinated water molecules and two molecules of lattice water, which are taken out by H_2SO_4 to show a loss of 13.5%.

Question 19: (a) Write down the IUPAC nomenclature of the given complex along with its hybridisation and structure

$K_2[Cr(NO)(NH_3)(CN)_4]$; μ = 1.73 B.M.

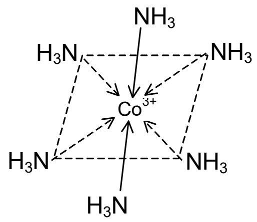
(b) Draw the structures of $[Co(NH_3)_6]^{3+}$, $[Ni(CN)_4]^{2-}$ and $[Ni(CO)_4]$. Write the hybridisation of atomic orbitals of the transition metal in each case.

Solution:

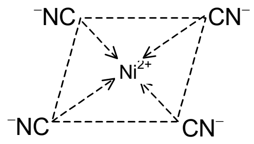
(a) Potassium amminetetracyanonitrosoniumchromate(I)
Cr is in +1 oxidation state and possess d^2sp^3 hybridisation with one unpaired electron.

$$\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = \mathbf{1.73\ BM}.$$

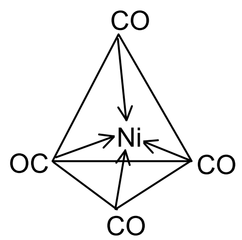
(b) **$[Co(NH_3)_6]^{3+}$:** Co^{3+} is d^2sp^3 hybridised to show octahedral shape.



$[Ni(CN)_4]^{2-}$: Ni^{2+} is dsp^2 hybridised to show square planar shape.



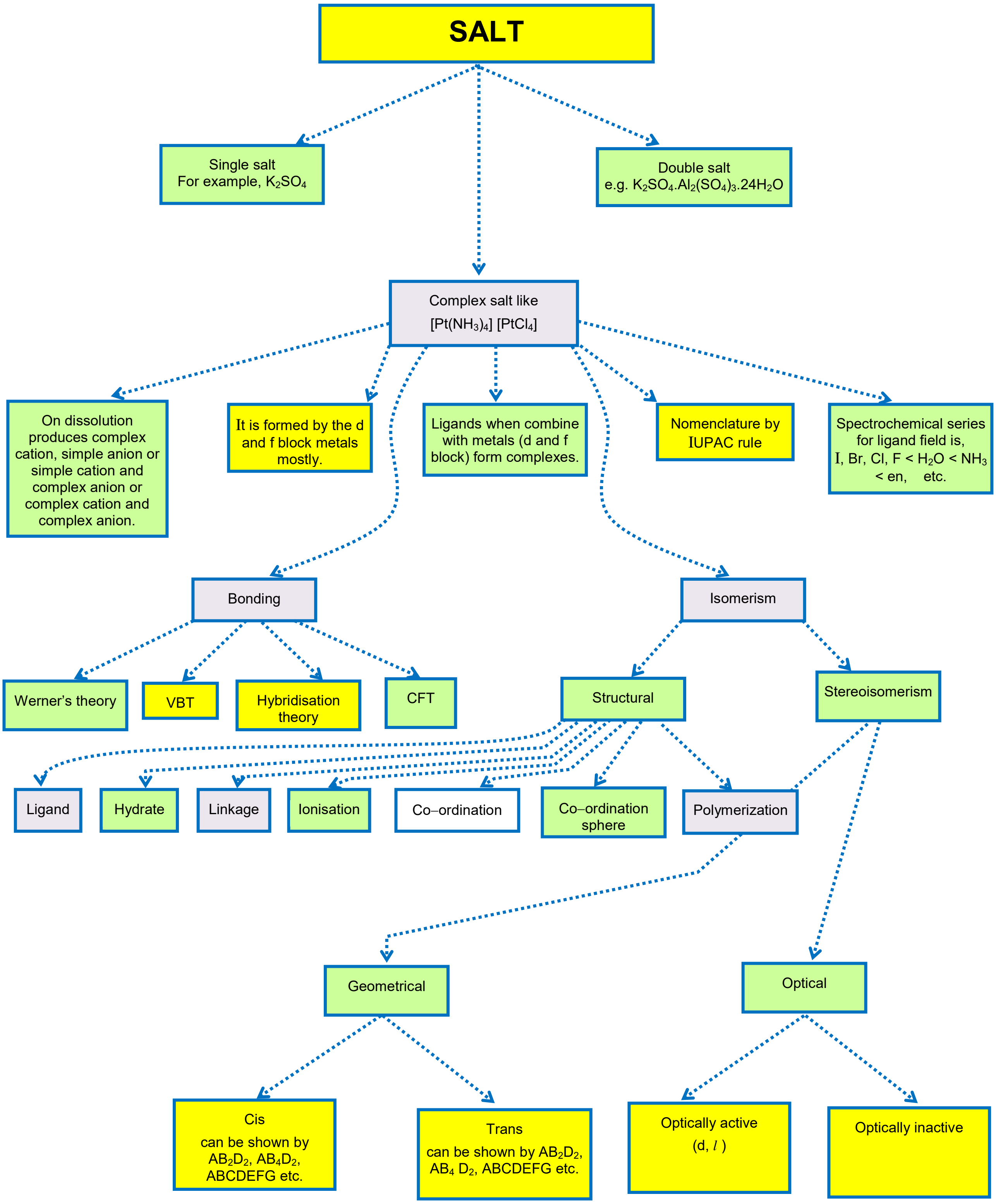
$[Ni(CO)_4]$: Ni is sp^3 hybridised to show tetrahedral shape.



DO YOU KNOW

An application of co-ordination compounds is there use as catalyst which serves to alter the rate of chemical reaction.
It play a key role in production of Polyethylene and Polypropylene.

MIND MAP


SALT
Single salt
For example, K_2SO_4
Double salt
e.g. $K_2SO_4.Al_2(SO_4)_3.24H_2O$
Complex salt like
$[Pt(NH_3)_4] [PtCl_4]$
On dissolution produces complex cation, simple anion or simple cation and complex anion or complex cation and complex anion.
It is formed by the d and f block metals mostly.
Ligands when combine with metals (d and f block) form complexes.
Nomenclature by IUPAC rule
Spectrochemical series for ligand field is,
I, Br, Cl, F < H_2O < NH_3 < en, etc.
Bonding
Isomerism
Werner's theory
VBT
Hybridisation theory
CFT
Structural
Stereoisomerism
Ligand
Hydrate
Linkage
Ionisation
Co–ordination
Co–ordination sphere
Polymerization
Geometrical
Optical
Cis
can be shown by AB_2D_2, AB_4D_2, ABCDEFG etc.
Trans
can be shown by AB_2D_2, AB_4 D_2, ABCDEFG etc.
Optically active
(d, *l*)
Optically inactive

Practice Questions with Answers (Important for IIT JEE & NEET Aspirants)

1. Fe^{3+} complexes are more stable than Fe^{2+} complexes. Why?

2. Write IUPAC name of linkage isomer of $[Cr(H_2O)_5SCN]^{2+}$.

3. What is the co–ordination number of Fe in [Fe(EDTA)]?

4. What is the hybridisation of Ni in $[Ni(CN)_4]^{2-}$ complex? Also predict the shape of the complex.

5. Explain the following:

(i) ferrocyanide ion is diamagnetic and ferricyanide ion is paramagnetic.

(ii) aqueous solution of potassium ferricyanide does not give test for ferric ions.

(iii) $Pt(NH_3)_2Cl_2$ has a square planar geometry but $Ni(CO)_4$ has tetrahedral geometry.

(iv) $[Sc(H_2O)_6]^{3+}$ is colurless while $[Ti(H_2O)_6]^{3+}$ is coloured.

6. What is meant by isomerism? Give examples of each of the following in relation to co–ordinate compounds:

(i) ionization isomerism

(ii) linkage isomerism

(iii) geometrical isomerism

(iv) optical isomerism

7. Give a chemical test to distinguish between $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$. What kind of isomerism do they exhibit?

8. What is polymerisation isomerism? Discuss with one example.

9. Complete the following statements for the coordination entity (complex ion) $[CrCl_2(OX)_2]^{3-}$

(a) OX is abbreviation for ____________

(b) The oxidation number of chromium is ____________

(c) The coordination number of chromium is ____________

(d) ____________ is a bidentate ligand.

10. Deduce the magnetic behaviour of each of the following:

(i) $[Cr(NH_3)_5Cl]^{2+}$ (ii) $Fe(CO)_5$

(Atomic numbers of Cr = 24, Fe = 26)

Multiple Choice Questions For IIT JEE (Part-1)

1. The IUPAC name for $[Pt(NH_3)_3(Br)(NO_2)(Cl)]Cl$ is

(a) triamminechlorobromonitroplatinum(IV) chloride
(b) triamminebromochloronitroplatinum(IV) chloride
(c) triaminenitrochlorobromoplatinum(IV) chloride
(d) triamminechloronitrobromoplatinum(IV) chloride

2. The IUPAC name of the complex $Ni[C_4H_7O_2N_2)_2]$, formed by the reaction between Ni^{2+} and dimethylglyoxime, is

(a) bis(methylglyoxal)nickel(II)
(b) bis(dimethylyoxime)nickel
(c) bis(2,3–butanediol dioximato)nickel(II)
(d) bis(2,3–butanedione dioximato)nickel(II)

3. Which of the following complex ions obeys Sidgwick's effective atomic number (EAN) rule?

(a) $[Fe(CN)_6]^{3-}$
(b) $[Fe(CN)_6]^{4-}$
(c) $[Cr(NH_3)_6]^{3+}$
(d) $[Ni(en)_3]^{2+}$

4. Which one of the following coordination compounds exhibits ionization isomerism?

(a) $[Cr(NH_3)_6]Cl_3$
(b) $[Cr(en)_3Cl_3]$
(c) $[Cr(en)_3]Cl_3$
(d) $[Co(NH_3)_5Br]SO_4$

5. The pair $[Co(NH_3)_5NO_3]SO_4$ and $[Co(NH_3)_5SO_4]NO_3$ will exhibit

(a) hydrate isomerism
(b) linkage isomerism
(c) ionization isomerism
(d) coordinate isomerism

6. Which of the following will have three stereoisomeric forms?

(i) $[Cr(NO_3)_3(NH_3)_3]$
(ii) $K_3[Co(C_2O_4)_3]$
(iii) $K_3[Co(C_2O_4)_2Cl_2]$
(iv) $[Co(en)_2ClBr]$

(where en = ethylene diamine)

(a) (iv) and (iii)
(b) (iv) and (i)
(c) (iii) and (ii)
(d) (i) and (ii)

7. A coordination compound of cobalt has the molecular formula containing five ammonia molecules, one nitro group and two chlorine atoms for one cobalt atom. One mole of this compound produces three moles of ions in an aqueous solution. The aqueous solution on treatment with an excess of $AgNO_3$ gives two moles of AgCl as a precipitate. The formula of this complex would be

(a) $[Co(NH_3)_4NO_2Cl]\,[NH_3Cl]$
(b) $[Co(NH_3)Cl][ClNO_2]$
(c) $[Co(NH_3)_5NO_2]Cl_2$
(d) $[Co(NH_3)_5][(NO_2)_2Cl_2]$

8. The hybridization states of the central atom in the complex ions $[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{3+}$ and $[Ni(NH_3)_6]^{2+}$ are

(a) sp^3d^2, dsp^2 and d^4s^2 respectively
(b) all $3d^24s4p^3$
(c) all $4s4p^34d^2$
(d) sp^3d^2, dsp^3 and p^4d^2 respectively

9. Among TiF_6^{2-}, CoF_6^{3-}, $CuCl_2$ and $NiCl_4^{2-}$ (atomic numbers of Ti = 22, Co = 27, Cu = 29, Ni = 28), the colourless species are

(a) CoF_6^{3-} and $NiCl_4^{2-}$ (b) TiF_6^{2-} and CoF_6^{3-}

(c) Cu_2Cl_2 and $NiCl_4^{2-}$ (d) TiF_6^{3-} and Cu_2Cl_2

10. Among $[Ni(CO)_4]$, $[Ni(CN)_4]^{2-}$ and $[NiCl_4]^{2-}$

(a) $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic.

(b) $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[Ni(CO)_4]$ is paramagnetic.

(c) $[Ni(CO)_4]$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $[NiCl_4]^{2-}$ is paramagnetic.

(d) $[Ni(CO)_4]$ is diamagnetic and $[NiCl_4]^{2-}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic.

11. Zeise salt, an organometallic compound, has the formula

(a) $(C_6H_6)_2Cr^+ AlCl_4^-$ (b) $(CH_3)_2AlF$

(c) $Ni(CO)_4$ (d) $K^+[PtC_2H_4Cl_3]^- H_2O$

12. Which of the following mixtures is known as Zeigler–Natta catalyst?

(a) $Al(OCH_3)_3 + TiCl_4$ (b) $(C_2H_5)_3Al + TiCl_4$

(c) $[(CH_3)_2CHO]_3Al + TiCl_4$ (d) $LiCH_3 + TiCl_4$

13. Which of the following is not an organometallic compound?

(a) Ferrocene (b) Ruthenocene

(c) Beryllium acetylacetonate (d) bis(benzene)chromium

14. Which is not a π–bonded complex?

(a) Zeise salt (b) Ferrocene

(c) bis(benzene) chromium (d) Tetraethyl lead

15. Which of the following is an organometallic compound?

(a) Lithium methoxide (b) Lithium acetate

(c) Lithium dimethylamide (d) Methyllithium

16. One mole of the complex compound $[Co(NH_3)_5Cl_3]$ gives 3 moles of ions on dissolution in water. One mole of the same complex reacts with two moles of $AgNO_3$ solution to yield two moles of AgCl(s). The structure of the complex is

(a) $[Co(NH_3)_4Cl]Cl_2.NH_3$ (b) $[Co(NH_3)_5Cl]Cl_2$

(c) $[Co(NH_3)_3Cl_3].2NH_3$ (d) $[Co(NH_3)_4Cl_2]Cl.NH_3$

17. Which of the following aquated metal ions has the highest paramagnetism?

(a) $[Cr(H_2O)_6]^{3+}$ (b) $[Fe(H_2O)_6]^{2+}$

(c) $[Cu(H_2O)_6]^{3+}$ (d) $[Zn(H_2O)_2]^{2+}$

18. Which of the following species is expected to be colourless?

(a) $[Ti(H_2O)_6]^{3+}$ (b) $[Ti(NO_3)_4]$

(c) $[Cr(NH_3)_2]^+$ (d) $[Fe(CN)_6]^{4-}$

19. Tollen's reagent contains

(a) $AgNO_3$ (b) AgOH

(c) $[Ag(NH_3)_2]^+$ (d) $[Ag(NO_3)_2]^+$

20. The ferric ion is detected by the formation of a Prussian blue precipitate on addition of potassium ferrocyanide solution. The formula of the Prussian blue precipitate is

(a) $Fe_4^{III}[Fe^{II}(CN)_6]_3$ (b) $Fe_3^{II}[Fe^{III}(CN)_6]_4$
(c) $KFe^{III}[Fe^{II}(CN)_6]$ (d) $KFe^{II}[Fe^{III}(CN)_6]$

21. When a solution of potassium ferricyanide is added to an aqueous solution of ferrous sulphate, a deep blue colour, known as Turnbull's blue, is produced. The formula of the compound responsible for this deep blue colour is

(a) $KFe^{III}[Fe^{II}(CN)_6]$ (b) $Fe_4^{III}[Fe^{II}(CN)_6]_3$
(c) $KFe^{II}[Fe^{III}(CN)_6]$ (d) $Fe_3^{III}[Fe^{III}(CN)_6]_3$

22. The coordination number of Ag in $[Ag(NH_3)_2]Cl$ is

(a) one (b) two
(c) three (d) zero

23. The formation of the complex ion $[Co(NH_3)_6]^{3+}$ involves sp^3d^2 hybridization of Co^{3+}. Hence, the complex ion should possess

(a) octahedral geometry (b) tetrahedral geometry
(c) square planar geometry (d) tetragonal geometry

24. The compounds $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2.H_2O$ and $[Cr(H_2O)_4Cl_2]Cl.2H_2O$ exhibit

(a) linkage isomerism (b) geometrical isomerism
(c) ionization isomerism (d) hydrate isomerism

25. Which of the following complex compounds exhibits cis–trans isomerism?

(a) $[PtCl_2(NH_3)_2]$ (b) $[PdCl_2BrI]$
(c) $[Pt(NH_3)(py)(Cl)(Br)]$ (d) All of these

1. Which of the following species has the electron configuration $[Ar]3d^4$?

(a) Ti (b) V^{2+}

(c) Cr^{2+} (d) Fe^{2+}

2. For transition elements, which of the following occurs as the effective nuclear charge increases?

(a) Both the atomic radius and density increases.

(b) Both the atomic radius and density decreases.

(c) The atomic radius increases and the density decreases.

(d) The atomic radius decreases and the density increases.

3. What is the name of the complex $[Ni(H_2O)_4(NH_2CH_2CH_2NH_2)]SO_4 \cdot 5H_2O$ as per IUPAC rules?

(a) Aquaethylenediaminenickel(II) sulfate 1–water

(b) Tetraaquaethylenediaminenickel(II) sulfate 5–water

(c) Tetraaquabis(ethylenediamine)nickel(II) sulfate 5–water

(d) Tetraaquabis(ethylenediamine)nickel(III) sulfate 5–water

4. How many unpaired electrons are present in the high spin form of the $[CoF_6]^{3-}$ complex and which metal orbitals are used in bonding?

(a) 0 unpaired electrons and 4s, 4p and 4d orbitals to give sp^3d^2 hybridization.

(b) 4 unpaired electrons and 4s, 4p and 4d orbitals to give sp^3d^2 hybridization.

(c) 0 unpaired electrons and 3d, 4s and 4p orbitals to give d^2sp^3 hybridization.

(d) 4 unpaired electrons and 3d, 4s and 4p orbitals to give d^2sp^3 hybridization.

5. The complex $[Ni(CN)_4]^{2-}$ is diamagnetic and the complex $[NiCl_4]^{2-}$ is paramagnetic. What can you conclude about their molecular geometries?

(a) Both complexes have square planar geometries.

(b) Both complexes have tetrahedral geometries.

(c) $[NiCl_4]^{2-}$ has a square planar geometry while $[Ni(CN)_4]^{2-}$ has a tetrahedral geometry.

(d) $[NiCl_4]^{2-}$ has a tetrahedral geometry while $[Ni(CN)_4]^{2-}$ has a square planar geometry.

6. What is the expected order for increasing octahedral (Δ_0) crystal field splitting for the ligands: I^-, F^-, H_2O, NH_3, en and CO?

(a) $I^- < F^- < H_2O < NH_3 <$ en $<$ CO (b) $F^- < I^- < NH_3 <$ en $<$ CO $< H_2O$

(c) $I^- < F^- < H_2O <$ CO $< NH_3 <$ en (d) CO $<$ en $< NH_3 < H_2O < F^- < I^-$

7. The hybridization states of the central atom in the complexes $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$ and $Co(NO_2)_6^{3-}$ are

(a) d^2sp^3, sp^3d^2 and dsp^2 respectively (b) d^2sp^3, sp^3d and sp^3d^2 respectively

(c) d^2sp^3, sp^3 and d^4s^2 respectively (d) all d^2sp^3

8. Tetrahedral complexes of the types of $[Ma_4]$ and $[Ma_3b]$ (where M = metal, a, b = achiral ligands) are not able to show optical isomerism because
(a) these molecules/ions possesses C_n axis of symmetry.
(b) these molecules ions possesses a plane of symmetry and hence are achiral.
(c) these molecules possesses a centre of symmetry.
(d) these molecules/ions have nonsuperimposable mirror images

9. Which of the following is an organometallic compound?
(a) Cyclobutadiene
(b) Thiotetraamminecopper(II)sulphate
(c) Potassium tetrafluorooxochromate(V)
(d) Bis(cyclopentadienyl)iron(II)

10. The magnetic moment of a complex ion is 2.83 BM. The complex ion is
(a) $[Cr(H_2O)_6]^{3+}$
(b) $[Cu(CN)_4]^{2-}$
(c) $[V(H_2O)_6]^{3+}$
(d) $[MnCl_4]^{2-}$

11. The E° values for some transition metals are as follows:
$Cr^{2+} | Cr = -0.9$ V, $Mn^{2+} | Mn = -1.2$ V, $Fe^{2+} | Fe = -0.4$ V,
$Cr^{3+} | Cr^{2+} = -0.4$ V, $Mn^{3+} | Mn^{2+} = +1.5$ V and $Fe^{3+} | Fe^{2+} = 0.8$ V
The correct statement is
(a) Fe^{3+} is more reducible than Cr^{3+} as well as Mn^{3+}.
(b) Cr is a better reducing agent than Mn but lesser than Fe.
(c) Fe^{3+} is more reducible than Cr^{3+} but less than Mn^{3+}.
(d) Fe^{2+} is a better oxidising agent than Mn^{2+} but lesser than Cr^{2+}.

12. What is the least reducing agent of the following set: $MnCl_2$, $Mn(OH)_3$, MnO_2 and $KMnO_4$?
(a) $MnCl_2$
(b) $Mn(OH)_3$
(c) MnO_2
(d) $KMnO_4$

13. Of the following, which ligand does not posses the name suggested by IUPAC when it acts as a ligand in complex?
(a) H_2O, aqua
(b) NH_3, ammonia
(c) CO, carbonyl
(d) F^-, fluoro

14. Which pair of isomers illustrates the concept of ionisation isomers?
(a) $[Cr(SCN)(NH_3)_5]^{2+}$ and $[Cr(NCS)(NH_3)_5]^{2+}$
(b) $[CoCl(NH_3)_5]SO_4$ and $[Co(SO_4)(NH_3)_5]Cl$
(c) cis–$[PtCl_2(NH_3)_2]$ and trans–$[PtCl_2(NH_3)_2]$
(d) (+)–$[Co(en)_3]^{3+}$ and (–)–$[Co(en)_3]^{3+}$

15. Which of the following complex ion is most likely to be colorless?
(a) $[Co(H_2O)_6]^{2+}$
(b) $[Mn(CN)_6]^{3-}$
(c) $[CrCl_3(H_2O)_3]$
(d) $[Ag(NH_3)_2]^+$

16. Which of the following complex has five unpaired electrons?
(a) $[Mn(H_2O)_6]^{2+}$
(b) $[Mn(CN)_6]^{3-}$
(c) $[CrCl_3(H_2O)_3]$
(d) $[Ag(NH_3)_2]^+$

17. Which ion would you expect to have the largest splitting of d–orbitals?
(a) $[Fe(CN)_6]^{4-}$ (b) $[Fe(CN)_6]^{3-}$
(c) $[Fe(H_2O)_6]^{2+}$ (d) $[Fe(H_2O)_6]^{3+}$

18. Which of the following co–ordination compound is incapable of showing geometrical isomerism?
(a) $[PtCl_2(NH_3)_2]$ (b) $[CoCl_2(NH_3)_4]^+$
(c) $[Co(NO_2)_3(NH_3)_3]$ (d) $[Co(en)_3]^{3+}$

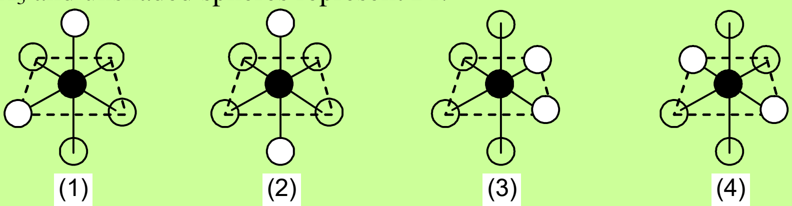
19. A six co–ordinate complex of formula $CrCl_3 \cdot 6H_2O$ has green colour. A 0.1 M solution of the complex when treated with excess of $AgNO_3$ gave 28.7 g of white precipitate. The formula of the complex would be
(a) $[Cr(H_2O)_6]Cl_3$ (b) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$
(c) $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (d) $[Cr(H_2O)_3Cl_3] \cdot 3H_2O$

20. Which of the following statements is incorrect?
(a) Most of the four–coordinated complexes of Ni^{2+} ions are square planar rather than tetrahedral.
(b) The $[Fe(H_2O)_6]^{3+}$ ion is more paramagnetic than the $[Fe(CN)_6]^{3-}$ ion.
(c) Square planar complexes are more stable than octahedral complexes.
(d) The $[Fe(CN)_6]^{4-}$ ion is paramagnetic but $[Fe(CN)_6]^{3-}$ is diamagnetic.

21. Which of the following is a high–spin (spin–free) complex?
(a) $[Co(NH_3)_6]^{3+}$ (b) $[Fe(CN)_6]^{4-}$
(c) $[CoF_6]^{3-}$ (d) $[Zn(NH_3)_6]^{2+}$

22. Which of the following ligands are bidentate or tridentate ligands, capable of forming chelate rings?
(i) $NH_2CH_2CH_2NH_2$ (ii) $CH_3CH_2CH_2NH_2$
(iii) $NH_2CH_2CH_2NHCH_2CO_2^-$ (iv) $NH_2CH_2CH_2\overset{\oplus}{N}H_3$
(a) (i) and (iii) (b) (ii) and (iv)
(c) (i), (ii) and (iii) (d) (i), (ii), (iii) and (iv)

Consider the following isomers of $[Co(NH_3)_4Br_2]^+$. The black sphere represents Co, gray spheres represent NH_3 and unshaded spheres represent Br.



Answer the following questions:

23. Which of the following are cis–isomers?
(a) isomers (1) and (2) (b) isomers (1) and (3)
(c) isomers (2) and (4) (d) isomers (3) and (4)

24. Which of the following are trans–isomers?
(a) isomers (1) and (2) (b) isomers (1) and (3)
(c) isomers (2) and (4) (d) isomers (3) and (4)

25. Whish structures are identical?
(a) None of the structures are identical
(b) Structure (1) = structure (2) and structure (3) = structure (4)
(c) Structure (1) = structure (3) and structure (2) = structure (4)
(d) Structure (1) = structure (4) and structure (2) = structure (3)

EXERCISE - I

ONE OR MORE THAN ONE CHOICE CORRECT

1. What is/are the co–ordination number(s) of Au in the complexes formed by Au?
(a) 6 (b) 4
(c) 5 (d) 2

2. If co–ordination number of cobalt in its complex is six then oxidation number of Co may be …… or …… .
(a) +2 (b) +3
(c) +4 (d) +6

3. $K_4[Fe(CN)_6]$ is
(a) Outer orbital octahedral complex (b) High spin complex
(c) Low spin complex (d) Inner orbital octahedral complex

4. The compounds which dissolve in NH_3 and form the soluble colourless complexes are
(a) $CuSO_4$ (b) AgCl
(c) $ZnSO_4$ (d) AgI

5. The oxides which dissolve in alkali and form the soluble complexes are
(a) ZnO (b) As_2O_3
(c) B_2O_3 (d) none

6. The sulphides which dissolve in yellow ammonium sulphide and give colourless soluble complexes are
(a) SnS (b) As_2S_3
(c) CuS (d) none of these

7. The d–orbitals involved in sp^3d^2 or d^2sp^3 hybridisation of the central metal ion are
(a) $d_{x^2-y^2}$ (b) d_{xy}
(c) d_{yz} (d) d_{z^2}

8. $[Cu(NH_3)_4]SO_4$ possesses
(a) dsp^2 hybridisation (b) tetrahedral geometry
(c) sp^3 hybridisation (d) square planar

9. The complex(es) which is/are blue in colour
(a) $Fe_4[Fe(CN)_6]_3$ (b) $Zn_2[Fe(CN)_6]$
(c) $Cu_2[Fe(CN)_6]$ (d) $Fe_3[Fe(CN)_6]_2$

10. Which of the following are co–ordination isomers of $[Co(NH_3)_6]\ [Cr(CN)_6]$?
(a) $[Cr(NH_3)_6]\ [Co(CN)_6]$ (b) $[Cr(NH_3)_2(CN)_4]\ [Co(CN)_4(NH_3)_2]$
(c) $[Cr(NH_3)_3(CN)_3]\ [Co(NH_3)_3(CN)_3]$ (d) none of these

11. Identify the complexes which are expected to be coloured.

(a) $Ti(NO_3)_4$
(b) $[Cu(CNCH_3)]^+BF_4^-$
(c) $[Cr(NH_3)_6]Cl_3$
(d) $Fe_4[Fe(CN)_6]_3$

12. Bidentate legends are

(a) $C_2O_4^{2-}$
(b) en
(c) DMG
(d) Gly

13. Which of the following can show co–ordination isomerism?

(a) $[Cu(NH_3)_4]\ [PtCl_4]$
(b) $[Fe(NH_3)_6]_2\ [Pt(CN)_6]_3$
(c) $[Co(NH_3)_6]\ [Cr(C_2O_4)_3]$
(d) $[Pt(en)_3]\ (SO_4)_2$

14. Which is/are correct statement(s)?

(a) $[Co(en)_3]\ [Cr(CN)_6]$ will display co–ordination isomerism.
(b) $[Mn(CO)_5(SCN)]$ will display linkage isomerism.
(c) $[Co(NH_3)_5(NO_3)]SO_4$ will display ionisation isomerism.
(d) None is correct.

15. Which of the following are paramagnetic?

(a) $[Ni(CN)_4]^{2-}$
(b) $[NiCl_4]^{2-}$
(c) $[CoF_6]^{3-}$
(d) $[Co(NH_3)_6]^{3+}$

EXERCISE – II

MATCH THE FOLLOWING

Note: Each statement in column I has one or more than one match in column II.

1.

Column I (Complex)	Column II (Hybridisation of central atom / ion)
I. $[Ni(H_2O)_6]^{2+}$	**(A)** sp^3
II. $[Ni(CN)_4]^{2-}$	**(B)** sp^3d^2
III. $[Ni(CO)_4]$	**(C)** d^2sp^3
IV. $[Cu(NH_3)_4]^{2+}$	**(D)** dsp^2

2.

Column I (Ligands)	Column II (Type of ligands)
I. (en)	**(A)** monodentate
II. EDTA	**(B)** bidentate
III. Trien	**(C)** tetradentate
IV. gly	**(D)** hexadentate

3.

Column I (Complex)	Column II (No. of unpaired electrons)
I. $[Fe(H_2O)_6]^{2+}$	**(A)** 0
II. $[Fe(H_2O)_6]^{3+}$	**(B)** 2
III. $[Fe(CN)_6]^{4-}$	**(C)** 5
IV. $[Ni(H_2O)_4]^{2+}$	**(D)** 4

REASONING TYPE

Directions: Read the following questions and choose

(A) **If both the statements are true and statement-2** is the correct explanation of **statement-1**.

(B) **If both the statements are true but statement-2** is not the correct explanation of **statement-1**.

(C) **If statement-1** is True and **statement-2** is False.

(D) **If statement-1** is False **and statement-2** is True.

1. **Statement-1:** Tetrahedral complexes with chiral structure exhibit optical isomerism.
Statement-2: They lack plane of symmetry.
(a) (A) (b) (B) (c) (C) (d) (D)

2. **Statement-1:** Oxidation state of Fe in $Fe(CO)_5$ is zero.
Statement-2: EAN of Fe in all its complexes is 36.
(a) (A) (b) (B) (c) (C) (d) (D)

3. **Statement-1:** Zeise's salt contains C_2H_4 molecule as one of the ligands.

Statement-2: Zeise's salt is an organometallic compound.

(a) (A) (b) (B) (c) (C) (d) (D)

4. **Statement-1:** $[Co(NH_3)_3Cl_3]$ does not give white precipitate with $AgNO_3$ solution.
Statement-2: Chlorine is not present in the ionisable part of the given complex.

(a) (A) (b) (B) (c) (C) (d) (D)

5. **Statement-1:** Transition metal ion forming octahedral complexes undergo sp^3d^2 or d^2sp^3 hybridisation.
Statement-2: Strong field ligands force the unpaired electrons of central metal ion to pair up causing d^2sp^3 hybridisation whereas weak field ligands cannot force the pairing and hence the metal ion undergoes sp^3d^2 hybridisation.

(a) (A) (b) (B) (c) (C) (d) (D)

LINKED COMPREHENSION TYPE

The IUPAC rules of writing names of mononuclear co–ordination compounds are as given below:

(a) If the compound is ionic, name of the cation is mentioned first followed by the name of the anion.
(b) For non–ionic compounds the name of the complex is written in one word.
(c) The sequence of naming co–ordination sphere is to write the names of ligands in the alphabetical order followed by the name of central metal atom / ion and then oxidation number of the metal in Roman numeral.
(d) For the ligands carrying a negative charge the name of the ligand has a characteristic ending in 'O'.
(e) For the ligands carrying a positive charge the name of the ligand has a characteristic ending of "ium".
(f) For organic ligands their names are used as such.
(g) In case of anionic complexes the suffix 'ate' is attached to the name of central atom/ion.
(h) Numerical prefixes are used to indicate number of ligands.

1. What is the name of the ligand NO^+?
(a) Nitronium (b) Hydrazinium
(c) Nitrosonium (d) Nitrosyl

2. The IUPAC name of $[Ag(NH_3)_2]Cl$ is
(a) Amine silver chloride (b) Diammine silver chloride
(c) Diammine silver (I) chloride (d) Chloroamine silver

3. Iron (III) hexacyanoferrate (II) is:
(a) $Fe_4[Fe(CN)_6]_3$ (b) $Fe_3[Fe(CN)_6]_2$
(c) $Fe(CN)_6$ (d) $Fe[Fe(CN)_6]$

4. The correct structural formula for Aquabromobis(ethylenediamine)chromium(III) chloride is
(a) $[CrBr_2(H_2O)_2(en)]Cl$ (b) $[CrBr_2(H_2O)_2(en)]Cl_2$
(c) $[CrBr(H_2O)(en)_2]Cl_2$ (d) $[CrBr(H_2O)(en)_2]Cl_2$

EXERCISE – III

SUBJECTIVE PROBLEMS

1. One pink solid has the formula $CoCl_3.5NH_3.H_2O$. A solution of this salt is also pink and rapidly gives 3 mol AgCl on titration with silver nitrate solution. When the pink solid is heated, it loses 1 mol H_2O to give a purple solid with the same ratio of NH_3:Cl:Co. The purple solid releases two of its chlorides rapidly; then, on dissolution and after titration with $AgNO_3$, releases one of its chlorides slowly. Deduce the structures of the two octahedral complexes and draw and name them.

2. The hydrated chromium chloride that is available commercially has the overall composition $CrCl_3.6H_2O$. On boiling a solution, it becomes violet and has a molar electrical conductivity similar to that of $[Co(NH_3)_6]Cl_3$. In contrast, $CrCl_3.5H_2O$ is green and has a lower molar conductivity in solution. If a dilute acidified solution of the green complex is allowed to stand for several hours, it turns violet. Interpret these observations with structural diagrams.

3. The complex first denoted β–$[PtCl_2(NH_3)_2]$ was identified as the trans isomer. (The cis isomer was denoted by α). It reacts slowly with solid Ag_2O to produce $[Pt(NH_3)_2(OH_2)_2]^{2+}$. This complex does not react with ethylenediamine to give a chelated complex. Name and draw the structure of the diaqua complex.

4. The 'third isomer' (neither α nor β) of composition $Pt_2Cl_4.4NH_3$, is an insoluble solid which, when grounded with $AgNO_3$, gives a solution containing $[Pt(NH_3)_4)$ $(NO_3)_2$ and a new solid phase of composition $Ag_2[PtCl_4]$. Give the structures and names of each of the three Pt(II) compounds.

5. A solution containing 2.665 g of $CrCl_3.6H_2O$ is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of $AgNO_3$ to give 2.87 g of AgCl. Deduce the structure of complex compound.

6. A rose–coloured compound (A) has the empirical formula $CoCl_3.5NH_3.H_2O$. Two moles of this compound reacts with concentrated sulphuric acid to form HCl(g) and 1 mole of a new compound (B) with empirical formula $Co_2(SO_4)_3.10NH_3.5H_2O$. When this new compound (B) is dried at room temperature, it loses three moles of water per mole of $Co_2(SO_4)_3.10NH_3.5H_2O$. Both complexes (A) and (B) have octahedral geometry. State the significance of each observation and deduce the formula of the complexes (A) and (B)

7. Studies of a complex gave a composition corresponding to the formula $CoBr(C_2O_4).4NH_3$. Conductance measurements indicate that there are two ions per formula unit. If calcium nitrate gives no immediate precipitate of calcium oxalate, then give the structural formula of the octahedral complex? Write the structural formula of an isomer of this complex.

8. Give the structural formula of these complexes.
(i) Tetraamminenickel(II) perchlorate
(ii) Hexaamminenickel(II) hexanitrocobalate(III)
(iii) Dicarbonyl–bis(triphenylphosphine)nickel(0)
(iv) Tetrakis(oxalato)–di–μ–hydroxodichromium(III)
(v) Chlorothiocyanato–S–bis(ethylenediamine)cobalt(II)

9. Write the IUPAC name of the following complexes.

(i) $[Co(en)_3]Cl_3$

(ii) $[(NH_3)_5Co–O_2–Co(NH_3)_5]^{4+}$

(iii) $[Cr(NH_3)_6]\ [Co(CN)_6]$

(iv) $[(NH_3)_5Co–NH_2–Co(NH_3)_4H_2O]Cl_5$

10. (i) In each of the following pair of complexes, choose the one that absorbs light at a longer wavelength.

(a) $[Co(NH_3)_6]^{2+}$, $[Co(H_2O)_6]^{2+}$

(b) $[FeF_6]^{3-}$, $[Fe(CN)_6]^{3-}$

(c) $[Cu(NH_3)_4]^{2+}$, $[CuCl_4]^{2-}$

(ii) Magnetic moments of four complexes are given. Predict the type of hybridization in each of these complexes.

Examples	Magnetic moment (in BM)
$[Cr(NH_3)_6]^{3+}$	3.57
$[Fe(C_2O_4)_3]^{3-}$	5.75
$[Ni(CN)_4]^{2-}$	0
$[MnCl_4]^{2-}$	5.90

ANSWERS

Practice Questions with Answers (Important for IIT JEE & NEET Aspirants)

1. Size of Fe^{3+} and Fe^{2+} are nearly same but the charge on Fe^{3+} is greater than the charge on Fe^{2+} hence more charge density, if the metal ion have more charge density the complex is more stable.

2. Linkage isomer of $[Cr(H_2O)_5SCN]^{2+}$ is $[Cr(H_2O)_5NCS]^{2+}$

The IUPAC name of its is Pentaavaaisothiocyanatochromium(III) ion

3. Co–ordination number is 6.

4. dsp^2. Square planar.

5. (i) In $K_4[Fe(CN)_6] \longrightarrow$ no unpaired electrons (Fe in d^2sp^3 hybridisation)

In $K_3[Fe(CN)_6] \longrightarrow$ one unpaired electron (Fe in d^2sp^3 hybridisation)

(ii) $K_3[Fe(CN)_6] \xrightleftharpoons{\text{aqueous}} 3K^+ + [Fe(CN)_6]^{3-}$

(iii) $Pt(NH_3)_2Cl_2 \longrightarrow dsp^2$ hybridisation

$Ni(CO)_4 \longrightarrow sp^3$ hybridisation

(iv) $[Sc(H_2O)_6]^{3+} \longrightarrow$ no unpaired electron

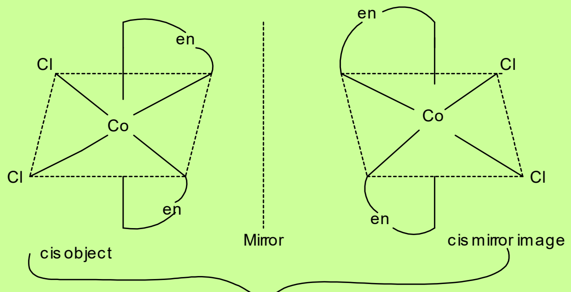
$[Ti(H_2O)_6]^{3+} \longrightarrow$ one unpaired electron.

6. (i) Ionization isomerism $[Co(NH_3)_5Br]SO_4$ and $[Co(NH_3)_5SO_4]Br$

(ii) Linkage isomerism $[Co(NH_3)_4SCN]^{2+}$

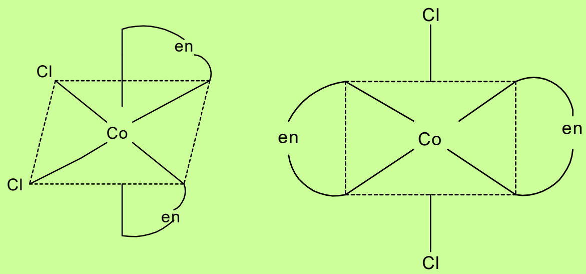
$[Co(NH_3)_4NCS]^{2+}$

(iii) Optical isomerism



optically active forms (non-superimposable)
Dichlorobis (ethylenediamine) cobalt (III) ion

(iv) Geometrical isomerism



trans

7. $[Co(NH_3)_5Br]SO_4 + 2AgNO_3 \longrightarrow Ag_2SO_4\downarrow$
White ppt.

$[Co(NH_3)_5SO_4]Br + AgNO_3 \longrightarrow AgBr\downarrow$

Ionisation isomerism yellow ppt.

8.	$[Pt(NH_3)_4]^{2+}$ $[PtCl_4]^{2-}$ and $[Pt(NH_3)_2Cl_2]$
9.	(a) oxalato (b) +3 (c) 6 (d) $C_2O_4^{2-}$
10.	Number of unpaired electron in Cr in the complex $[Cr(NH_3)_5Cl]^{2+}$ are 3. ∴ Paramagnetic behaviour. $r = \sqrt{n(n+2)} = \sqrt{3(3+2)} = \sqrt{15}$ B.M. Number of unpaired electrons in Fe in the complex $Fe(Co)_5$ are 0. ∴ Diamagnetic behaviour.

Multiple Choice Questions For IIT JEE (Part-1)

1. (b)	2. (d)	3. (b)	4. (d)	5. (c)
6. (b)	7. (c)	8. (c)	9. (d)	10. (c)
11. (d)	12. (b)	13. (c)	14. (d)	15. (d)
16. (b)	17. (b)	18. (b)	19. (c)	20. (c)
21. (c)	22. (b)	23. (a)	24. (d)	25. (d)

Multiple Choice Questions For IIT JEE (Part-2)

1. (c)	2. (d)	3. (b)	4. (b)	5. (d)
6. (a)	7. (d)	8. (b)	9. (d)	10. (c)
11. (c)	12. (d)	13. (b)	14. (b)	15. (d)
16. (a)	17. (b)	18. (d)	19. (b)	20. (d)
21. (c)	22. (a)	23. (b)	24. (c)	25. (c)

EXERCISE – I

ONE OR MORE THAN ONE CHOICE CORRECT

1. (b, d)	2. (a, b)	3. (c, d)	4. (b, c)	5. (a, b, c)
6. (a, b)	7. (a, d)	8. (a, d)	9. (a, d)	10. (a, b)
11. (c, d)	12. (a,b,c,d)	13. (a, b, c)	14. (a, b, c)	15. (b, c)

EXERCISE – II

MATCH THE FOLLOWING

1. I – (B) ; II – (D) ; III – (A) ; IV – (D)
2. I – (B) ; II – (D) ; III – (C) ; IV – (B)
3. I – (D) ; II – (C) ; III – (A) ; IV – (B)

REASONING TYPE

1. (a)	2. (c)	3. (b)	4. (a)	5. (a)

LINKED COMPREHENSION TYPE

1. (c)	2. (c)	3. (a)	4. (c)	

EXERCISE – III

SUBJECTIVE PROBLEMS

1. Pink: $[Co(NH_3)_5(H_2O)]Cl_3$; Petaammineaquacobalt(III) chloride
Purple: $[CoCl(NH_3)_5]Cl_2$; Pentaamminechlorocobalt(III) chloride

2. Violet: $[Cr(H_2O)_6]Cl_3$; Green: $[Cr(H_2O)_5Cl]Cl_2$
Both complexes are octahedral.

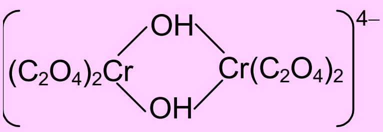
3. trans–Diamminediaquaplatinum(II) ; Square planar complex.

4. $[Pt(NH_3)_4]\ [PtCl_4]$; Tetraammineplatinum(II) tetrachloroplatinate(II)
$[Pt(NH_3)_4]\ (NO_3)_2$; Tetraammineplatinum(II) nitrate
$Ag_2[PtCl_4]$; Silver tetrachloroplatinate(II)

5. $[Cr(H_2O)_5Cl]Cl_2.H_2O$

6. (A): $[Co(NH_3)_5H_2O]Cl_3$.
(B): $[Co(NH_3)_5H_2O]_2(SO_4)_3.3H_2O$.

7. $[Co(C_2O_4)(NH_3)_4]Br$, $NH_4[Co(C_2O_4)(NH_2)(NH_3)_2Br]$

8. (i) $[Ni(NH_3)_4](ClO_4)_2$
(ii) $[Ni(NH_3)_6]_3[Co(NO_2)_6]_2$
(iii) $[Ni(CO)_2(PPh_3)_2]$
(iv) 

(v) $[CoCl(SCN)(en)_2]$

9. (i) Tris(ethylenediamine)cobalt(III) chloride
(ii) Decaammine–μ–peroxodicobalt(III) ion
(iii) Hexaamminechromium(III) hexacyanocobaltate(III)
(iv) Pentaamminecobalt(III)–μ–amidotetraammineaquacobalt(III) chloride

10. (i) (a) $[Co(H_2O)_6]^{2+}$, (b) $[FeF_6]^{3-}$ (c) $[CuCl_4]^{2-}$

(ii) d^2sp^3, sp^3d^2, dsp^2, sp^3