

TRANS ELEMENTS & CO-ORDINATION COMPOUNDS

1. Transition Elements

1.1 Introduction

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.

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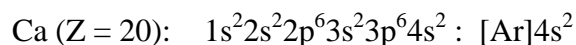
1.2 Metallic Character

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 lusture and are hard, strong and ductile. They also form alloys with other metals. Copper exceptionally is both soft and ductile and relatively noble.

1.3 Variable Oxidation States

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:



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: $3d^1$, $3d^2$, $3d^3 \dots 3d^{10}$. 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

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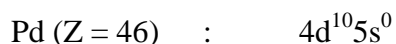
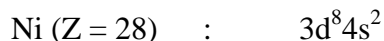
simple and straight forward. In the highest oxidation states of these first five elements, all of the s and d-electrons are being used for bonding. Thus, the properties depend only on the size and valency.

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.

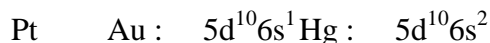
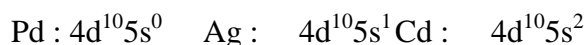
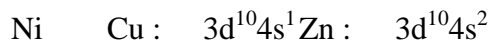
The oxidation number of all elements in the elemental state is zero. In addition, several of the elements have zero-valent and other low-valent states in complexes. Low oxidation states occur particularly with π -bonding ligands such as carbon monoxide and dipyrityl.

Important features about the oxidation states of transition elements

- (i) In group 8 (the iron group), the second and third row elements show a maximum oxidation state of (VIII) compared with (VI) for Fe.
- (ii) 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:



- (iii) 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.



- (iv) 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 coordination 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.

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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 ₂ O ₃	Mn ₂ O ₃	Fe ₂ O 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 ₂ O ₇	–

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1.4 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 $\text{Sc} \rightarrow \text{Y} \rightarrow \text{La}$. However, in the subsequent groups (4–12) there is an increase in radius of $0.1 \rightarrow 0.2 \text{ \AA}$ 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

1.5 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.

1.6 Melting and Boiling Points

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

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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. This is because the d–subshell is complete and d–electrons do not participate in metallic bonding.

1.7 Ionization Energy

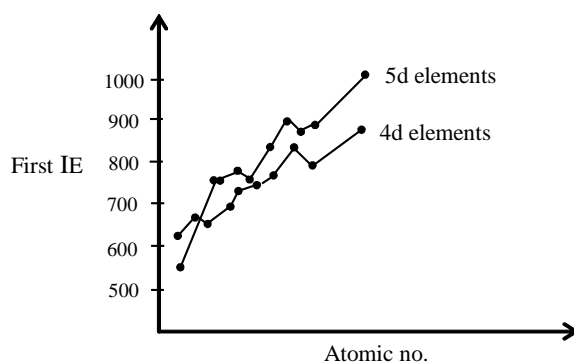
In a period, the first ionization energy gradually increases from left to right. This is mainly due to increase in nuclear charge. Generally, the ionization energies of transition elements are intermediate between those of s and p-block elements. The first ionization potential of the 5d-elements are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

From 3d → 4d series, general trend is observed but not from 4d → 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.

Ionisation energy values (in kJ/mole) of the transitions elements

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



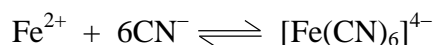
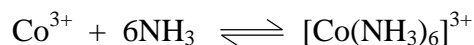
1.8 Reactivity of Metals

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.

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1.9 Formation of Complex Compounds

The transition elements have characteristic tendency to form co-ordination compounds with Lewis bases, i.e. 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.



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.

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)

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Common Coordination Numbers Shown By Transition Elements of First Row

(i) Scandium

Sc³⁺ forms complexes with coordination number of 6. Examples: [Sc(OH)₆]³⁻, [ScF₆]³⁻

(ii) Titanium

Ti⁴⁺ forms complexes with coordination number of 6. Examples: [TiCl₆]²⁻, [Ti(SO₄)₃]²⁻

(iii) Vanadium

V²⁺ forms mostly octahedral complexes (coordination number = 6). Examples: [V(H₂O)₆]²⁺, K₄[V(CN)₆].7H₂O. But K₄[V(CN)₇].2H₂O is also known with a pentagonal bipyramidal structure (coordination number = 7).

V³⁺ forms octahedral complexes such as [V(H₂O)₆]³⁺.

V⁴⁺ is known to form square pyramidal complexes with a coordination number of 5. Examples: [VOX₄]²⁻, [VO(OX)₂]²⁻, [VO(bipyridyl)₂Cl]⁺

(iv) Chromium

Cr²⁺ forms octahedral complexes, such as [Cr(H₂O)₆]²⁺ and [Cr(NH₃)₆]²⁺ with coordination number 6.

Cr³⁺ forms octahedral complexes, such as [Cr(H₂O)₆]³⁺ and [Cr(H₂O)₅Cl]²⁺ with coordination number 6.

(v) Manganese

Mn²⁺ forms octahedral complexes such as [MnCl₆]⁴⁻ and [Mn(en)₃]²⁺ with coordination number 6.

Mn³⁺ forms octahedral complexes such as K₃[Mn(CN)₆] with coordination number 6.

Mn⁴⁺ forms octahedral complexes such as K₂[MnF₆] and K₂[Mn(CN)₆] with coordination number 6.

(vi) Iron

Fe²⁺ forms mostly octahedral complexes like [Fe(H₂O)₆]²⁺ but few tetrahedral halides with coordination number 4 like [FeX₄]²⁻ are also known.

Fe³⁺ is known to form octahedral complexes such as [Fe(H₂O)₆]³⁺.

(vii) Cobalt

Co²⁺ is known to form both tetrahedral like [Co(H₂O)₄]²⁺ and octahedral such as [Co(H₂O)₆]²⁺ complexes.

Co³⁺ forms octahedral complexes. For example, [Co(NH₃)₆]³⁺ and [Co(CN)₆]³⁻.

(viii) Nickel group

Ni²⁺ commonly forms octahedral and square planar complexes. Few tetrahedral, trigonal bipyramidal and square based pyramidal structures are also formed.

Pd²⁺ and Pt²⁺ are all square planar.

Ni³⁺ forms octahedral compounds. For example, K₃[NiF₆] and [Ni(en)₂Cl₂]Cl.

Pd⁴⁺ forms a few octahedral complexes like [PdX₆]²⁻, where X = F, Cl or Br. These are generally reactive. Halide complexes are decomposed by hot water, giving [PdX₄]²⁻ and halogen. In contrast Pt⁴⁺ forms large number of very stable octahedral complexes like [PtCl₆]²⁻.

(ix) Copper, silver and gold

Cu⁺ forms tetrahedral complexes with Cl (for example, [Cu(Cl)₄]³⁻) and linear complexes like [CuX₂]⁻.

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Cu^{2+} forms complexes both of coordination number 4 (like $[\text{CuX}_4]^{2-}$) and of coordination number 6 {like $[\text{Cu(en)}_3]^{2+}$, $[\text{Cu}(\text{H}_2\text{O})_3(\text{NH}_3)_3]^{2+}$ }.

Ag^+ , Au^+ forms complexes with coordination number 2 like $[\text{M}(\text{CN})_2]^-$.

(x) Zinc and cadmium

Zn^{2+} and Cd^{2+} forms both tetrahedral and octahedral complexes. For example, $[\text{MCl}_4]^{2-}$, $[\text{M}(\text{NH}_3)_2\text{Cl}_2]$, $[\text{M}(\text{NH}_3)_4]^{2+}$, $[\text{M}(\text{H}_2\text{O})_6]^{2+}$ etc.

1.10 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 is 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 $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is blue, $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green and $[\text{Ni}(\text{NO}_2)_6]^{4-}$ 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 $f \rightarrow f$ 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

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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, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

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.

1.11 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; $\text{BM} = \frac{eh}{4\pi m_0 c}$ where e = magnitude of electronic charge,

m_0 = 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

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number of unpaired electrons in the complex/complex ion, which leads us to the bonding and structure elucidation of the complex/complex ion.

1.12 Catalytic Properties

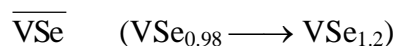
Transition metals and their compounds act as good catalysts for a variety of reactions. The presence of empty d-orbitals enables them to form various intermediates during a reaction, thus providing a reaction path with lower activation energy for the reaction. Many transition metals and their compounds 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 ₂ O ₅	Converts SO ₂ to SO ₃ in the contact process for making H ₂ SO 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 ₂ O 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 → SO ₃ in the contact process for making H ₂ SO 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) ₂ SiCl 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 ₂ O ₂).

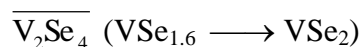
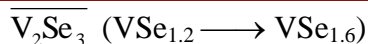
1.13 Non-Stoichiometric Compounds

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, $\overline{\text{FeO}}$ 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 VSe₂. These are given the formulae:



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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 .

2. 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*.

2.1 Electronic Configuration

Lanthanides

Ce (Z=58) to Lu (Z=71) – (6th 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: $[\text{Xe}] 4f^{1-14} 5d^{0-1} 6s^2$

Actinides

Th (Z = 90) to Lr (Z = 103) – (7th 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: $[\text{Rn}] 5f^{1-14} 6d^{0-1} 7s^2$

2.2 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.

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Electronic structures and oxidation states for lanthanide series

Element	Symbol	Outer electronic configuration	Oxidation states		
Lanthanum	La	$[\text{Xe}]5d^1 6s^2$		III	
Cerium	Ce	$[\text{Xe}]4f^1 5d^1 6s^2$		III	IV
Praseodymium	Pr	$[\text{Xe}]4f^3 6s^2$		III	(IV)
Neodymium	Nd	$[\text{Xe}]4f^4 6s^2$	(II)	III	
Promethium	Pm	$[\text{Xe}]4f^5 6s^2$	(II)	III	
Samarium	Sm	$[\text{Xe}]4f^6 6s^2$	(II)	III	
Europium	Eu	$[\text{Xe}]4f^7 6s^2$	II	III	
Gadolinium	Gd	$[\text{Xe}]4f^7 5d^1 6s^2$		III	
Terbium	Tb	$[\text{Xe}]4f^9 6s^2$		III	(IV)
Dysprosium	Dy	$[\text{Xe}]4f^{10} 6s^2$		III	(IV)
Holmium	Ho	$[\text{Xe}]4f^{11} 6s^2$		III	
Erbium	Er	$[\text{Xe}]4f^{12} 6s^2$		III	
Thulium	Tm	$[\text{Xe}]4f^{13} 6s^2$	(II)	III	
Ytterbium	Yb	$[\text{Xe}]4f^{14} 6s^2$	II	III	
Lutetium	Lu	$[\text{Xe}]4f^{14} 5d^1 6s^2$		III	

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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				
Mendelevium	Md	$5f^{13} 7s^2$	II	III				
Nobelium	No	$5f^{14} 7s^2$	II	III				
Lawrencium	Lr	$5f^{14} 6d^1 7s^2$						

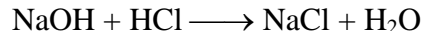
The most important oxidation states (generally the most abundant and stable) are shown in bold. Other well-characterized but less important states are shown in normal type. Oxidation states that are unstable or in doubt are given in parentheses.

3. Coordination Compounds / Complex Compounds

3.1 Some Basic Terms

Simple Salts

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



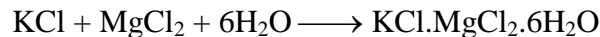
When dissolved in water, they produce ions in the solution. Depending on the extent of neutralisation of the acid or base, simple salts are further classified as normal, acid or basic salts.

Mixed Salts

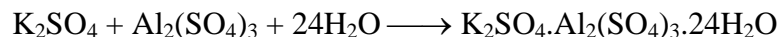
These salts contain more than one acidic or basic radicals. For example, NaKSO_4

Molecular or Addition Compounds

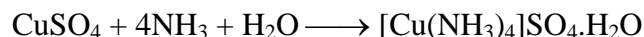
When solutions containing two or more simple stable salts in stoichiometric proportions are allowed to evaporate, addition compounds are formed. For example,



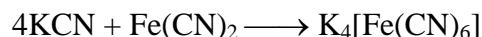
(Carnalite)



(Alum)



(Complex)

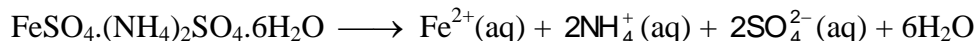


(Potassium ferrocyanide)

Addition compounds are of two types:

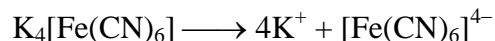
(a) Double salts (Lattice compounds):

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



(b) Coordination 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.



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 $\text{K}_4[\text{Fe}(\text{CN})_6]$, $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$, $[\text{Co}(\text{NH}_3)_6]$, $[\text{Cr}(\text{CN})_6]$ and $\text{Ni}(\text{CO})_4$ 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.

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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 ($M \rightleftharpoons CO$).

Coordination Number (Or Ligancy)

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

Coordination Sphere

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

EFFECTIVE ATOMIC NUMBER (EAN)

Sidgwick extended the Lewis theory to account for the bonding in the coordination compounds. He introduced the term coordinate 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	$2 \times 2 = 4$	$46 + 4 = 50$

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$K_4[Fe(CN)_6]$	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.

3.2 Classification of Ligands

There are two ways ligands can be classified:

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 ($M \xrightleftharpoons[\sigma]{\pi} L$).

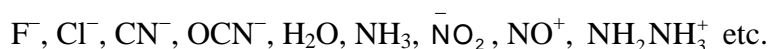
(b) Ligands, which have no vacant orbitals to get back donated electrons from the metal. e.g. H_2O , NH_3 , F^- etc.

(ii) Ligands having no lone pair of electrons but π -bonding electrons. e.g. C_2H_4 , C_6H_6 , $C_5H_5^+$ etc.

Classification based on the number of donor atoms present in the ligands

(i) Monodentate or unidentate ligands:

The ligands that can coordinate 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,

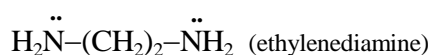


A monodentate ligand having more than one lone pair of electrons may simultaneously coordinate with two or more atoms and thus acts as a bridge between the metal ions. In such a case, it is called a bridging ligand and the complex thus formed is known as bridged complex. For example,



(ii) Bidentate ligand:

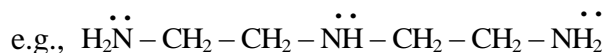
Ligands, which have two donor atoms and have the ability to coordinate with the central atom/ion at two different sites are called bidentate ligands. For example,



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(iii) Tridentate ligands:

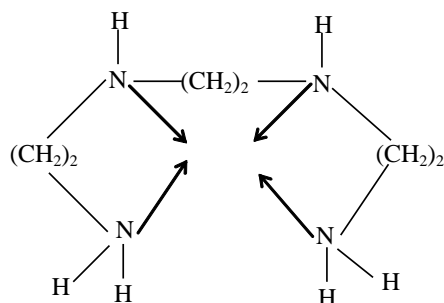
The ligands having three coordination sites are called tridentate ligands. For example,



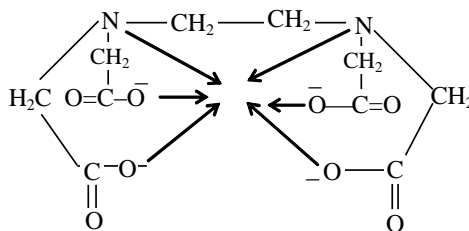
Diethylenetriamine

(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. Remember that the chelating ligands form more stable complexes than ordinary unidentate ligands.

3.3 Nomenclature of Complexes

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

- 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.
- Number of cations and anions are not mentioned while writing its name.
- 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.
- Within a complex ion, the ligands are named first in 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.
- 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.

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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^-	nitrate
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
$\text{C}_2\text{O}_4^{2-}$	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	$\text{S}_4\text{O}_6^{2-}$	tetrathionato
S^{2-}	sulphido	EDTA ($^- \text{O}_2\text{CCH}_2$) $_2\text{N}(\text{CH}_2)_2\text{N}$ (CH_2CO_2^-) $_2$	ethylenediaminetetraacetato
HSO_3^-	hydrogensulphito	$\text{NH}_2\text{CH}_2\text{CO}_2^-$	glycinato
$\text{S}_2\text{O}_3^{2-}$	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.

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Name of Neutral ligands:

Ligand	Name	Abbreviation	Ligand	Name	Abbreviation
H ₂ O	aqua/aquo	–	NH ₂ (CH ₂) ₂ NH ₂	ethylenediamine	(en)
NH ₃	ammine	–	CH ₃ NH ₂	methylamine	–
CO	carbonyl	–	C ₆ H ₆	benzene	–
NO	nitrosyl	–	N ₂	dinitrogen	–
CS	thiocarbonyl	–	O ₂	dioxygen	–
NS	thionitrosyl	–	Ph ₃ P	triphenylphosphine	–
C ₅ H ₅ N	pyridine	(py)	CH ₃ COCH ₃	acetone	–

Name of Positive ligands:

Ligand	Name
NO ⁺	nitrosonium
NO ₂ ⁺	nitronium
NH ₂ NH ₃ ⁺	hydrazinium

- (vi) 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.
- (vii) 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.
- (viii) 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 Latin names of metal.

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

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Lead

Plumbate

Coordination sphere is named in continuum.

- (ix) 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:

$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$	Hexaammineplatinum(IV) chloride
$[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}$	Tetraammineaquochlorocobalt(II) chloride
$[\text{Cu}(\text{en})_2]\text{SO}_4$	<i>Bis</i> (ethylenediamine)copper(II) sulphate
$[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]^+$	Tetraaquodichlorochromium(III) ion
$[\text{Fe}(\text{H}_2\text{O})_4(\text{C}_2\text{O}_4)]_2\text{SO}_4$	Tetraaquooxalatoiron(III) sulphate
$[\text{Cr}(\text{NH}_3)_4(\text{ONO})\text{Cl}]\text{NO}_3$	Tetraamminechloronitritochromium(III) nitrate
$[\text{Ag}(\text{NH}_3)_2]\text{Cl}$	Diamminesilver(I) chloride
$[\text{Co}(\text{NH}_3)_5(\text{NCS})]\text{Cl}_2$	Pentaammineisothiocyanatocobalt(III) chloride
$[(\text{C}_6\text{H}_5)_3\text{P}]_3\text{RhCl}$	Tris(triphenylphosphine)rhodium(I) chloride

Coordination compounds containing complex anionic ion:

$\text{K}_4[\text{Fe}(\text{CN})_6]$	Potassium hexacyanoferrate(II)
$\text{K}_3[\text{Fe}(\text{CN})_6]$	Potassium hexacyanoferrate(III)
$\text{K}_3[\text{Cr}(\text{C}_2\text{O}_4)_3]$	Potassium trioxalatochromate(III)
$\text{K}_3[\text{Co}(\text{C}_2\text{O}_4)_2\text{Cl}_2]$	Potassium dichlorodioxalatocobaltate(III)
K_2HgI_4	Potassium tetraiodomercurate(II)
$\text{K}_2[\text{PtCl}_6]$	Potassium hexachloroplatinate(IV)
$\text{Na}[\text{Ag}(\text{CN})_2]$	Sodium dicyanoargentate(I)
$[\text{Ni}(\text{CN})_4]^{2-}$	Tetracyanonickelate(II) ion
$\text{Na}_3[\text{Co}(\text{NO}_2)_6]$	Sodium hexanitrocobaltate(III)
$\text{K}_3[\text{Fe}(\text{CN})_5\text{NO}]$	Potassium pentacyanonitrosylferrate(II)

Coordination compounds containing complex cationic and anionic ions:

$[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$	Hexaamminechromium(III) hexacyanocobaltate(III)
$[\text{Pt}(\text{NH}_3)_4][\text{CuCl}_4]$	Tetraammineplatinum(II) tetrachlorocuprate(II)
$[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{C}_2\text{O}_4)_3]$	Hexaamminechromium(III) trioxalatocobaltate(III)
$[\text{Pt}(\text{py})_4][\text{PtCl}_4]$	Tetrapyridineplatinum(II) tetrachloroplatinate(II)

Non-ionic coordination compounds:

$\text{Fe}(\text{CO})_5$	Pentacarbonyliron(0)
$[\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]$	Triamminetrinitrocobalt(III)

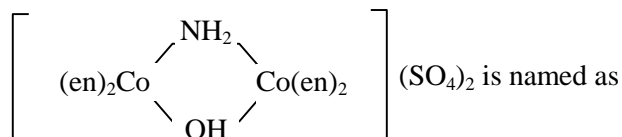
TRANS ELEMENTS & CO-ORDINATION COMPOUNDS

Cu(Gly)₂ Diglycinatocopper(II)

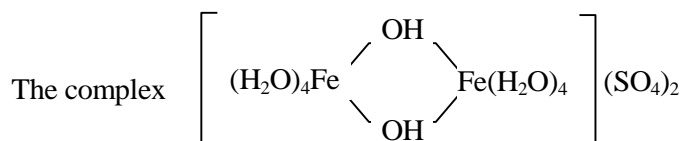
Ni(DMG)₂ Bis(dimethylglyoximate) nickel(II)

(x) 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 .



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



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

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3.4 Werner's Coordination 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.

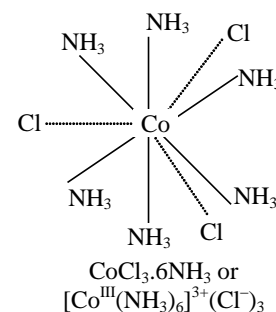
(ii) Every element tends to satisfy both its primary and secondary valencies. In order to meet this requirement a negative ion may often show a dual behaviour, i.e., it may satisfy both primary and secondary valencies (since in every case the fulfilment of coordination number of the central metal ion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

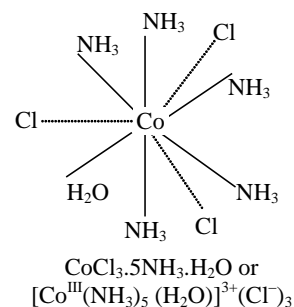
On the basis of postulates of his theory, Werner designated the ammines as given in figure and formulated them as described below

The molecule, $\text{CoCl}_3 \cdot 6\text{NH}_3$ which is formulated as $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}(\text{Cl}^-)_3$ 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. $[\text{Co}(\text{NH}_3)_6]^{3+}$ and 3Cl^- , which has been confirmed by conductivity measurements.

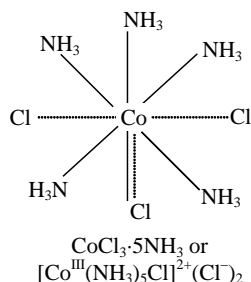


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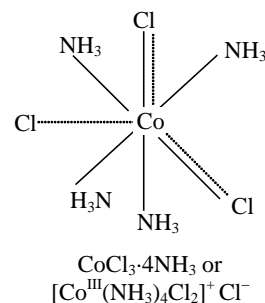
In the molecule, $\text{CoCl}_3 \cdot 5 \text{NH}_3 \cdot \text{H}_2\text{O}$ which is formulated as $[\text{Co}^{\text{III}}(\text{NH}_3)_5(\text{H}_2\text{O})]\text{Cl}_3$, five NH_3 molecules and one H_2O molecule satisfy the secondary valency (shown by thick lines in the designation). Primary valency is satisfied by three Cl^- ions. The solution of this compound also conducts current and gives in all four ions: one complex ion, $[\text{Co}^{\text{III}}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ and three simple ions, 3Cl^- .



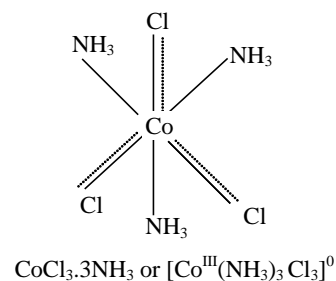
In the molecule $\text{CoCl}_3 \cdot 5\text{NH}_3$ which is formulated as $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}(\text{Cl}^-)_2$ on the basis of Werner's theory one Cl^- ion does the dual function, since it satisfies both primary and secondary valency. Werner, therefore, showed its attachment 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, $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}$ and two simple ions, 2Cl^- . Thus, $[\text{Co}^{\text{III}}(\text{NH}_3)_5\text{Cl}]^{2+}\text{Cl}_2$ satisfies both primary (+3) and secondary (Coordination number = 6) of Co^{3+} .



The formulation $[\text{Co}^{\text{III}}(\text{NH}_3)_4\text{Cl}_2]^+\text{Cl}^-$ of $\text{CoCl}_3 \cdot 4\text{NH}_3$ 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: $[\text{Co}^{\text{III}}(\text{NH}_3)_4\text{Cl}_2]^+$ and Cl^- .



The formulation $[\text{Co}^{\text{III}}(\text{NH}_3)_3\text{Cl}_3]^0$ of $\text{CoCl}_3 \cdot 3\text{NH}_3$ has no ionic Cl^- ions and hence it behaves as a non-electrolyte.



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3.4 Valence Body 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.

- (i) 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.
- (ii) The central metal ion makes available a number of empty s, p and d atomic orbitals equal to its coordination number.
- (iii) 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.
- (iv) The non-bonding metal electrons occupy 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.
- (v) The d-orbitals involved in the hybridisation may be either inner (n-1) d-orbitals or outer nd-orbitals.
- (vi) Each ligand (donor group) must contain a lone pair of electrons.
- (vii) 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.
- (viii) 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.
- (ix) 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.

Let us consider a few examples to explain the valence bond theory over the complexes.

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

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VBT-Octahedral Complexes

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

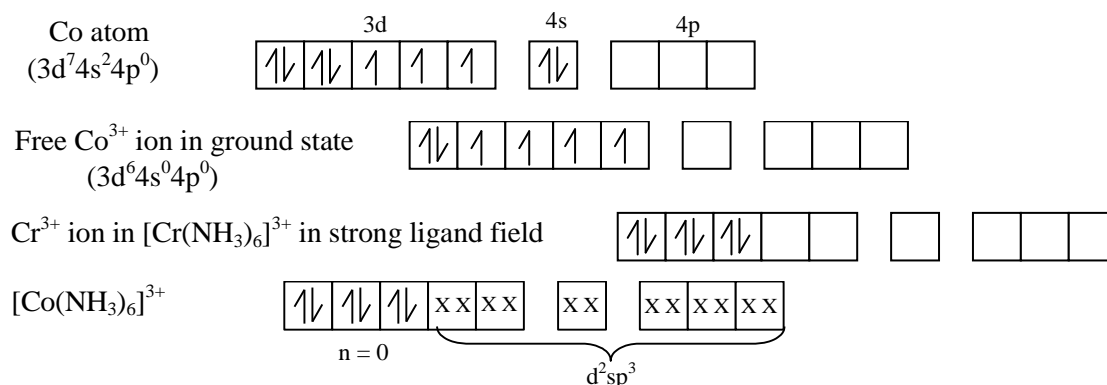
- Inner-orbital octahedral complexes, which result from d^2sp^3 hybridisation of the central metal atom/ion.
- Outer orbital octahedral complexes, which result from sp^3d^2 hybridisation.

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.

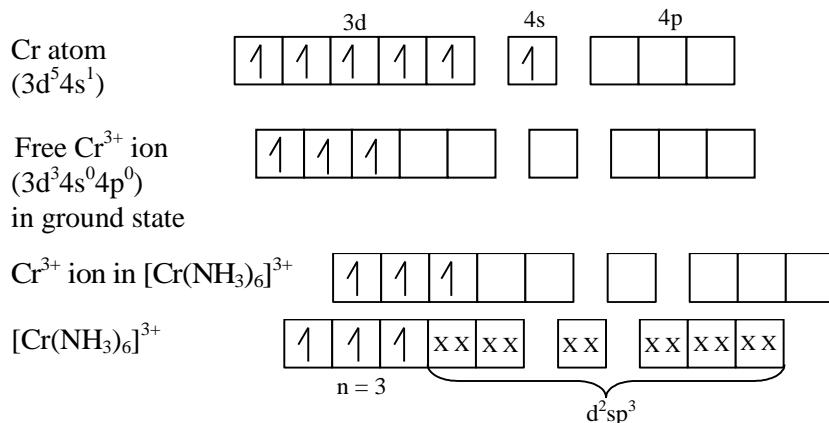
$[Co(NH_3)_6]^{3+}$:



TRANS ELEMENTS & CO-ORDINATION COMPOUNDS

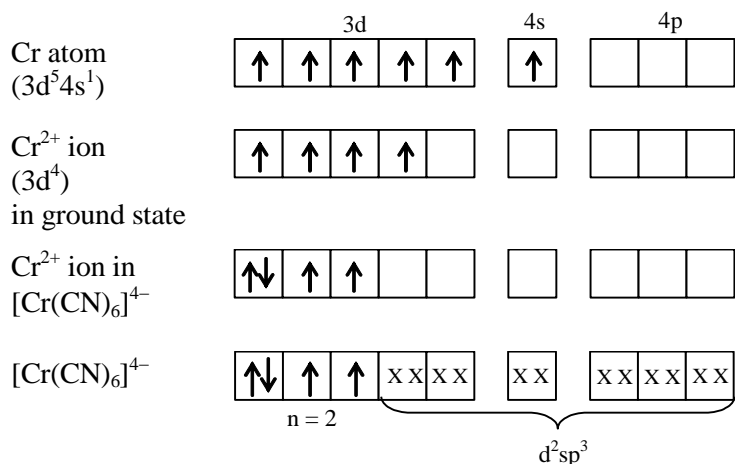
Here n represents the number of unpaired electrons and 'XX' represents an electron pair donated by each of free six NH_3 ligands. The two electrons of the electron pair have opposite spin. The above complex ion is diamagnetic as all the electrons are paired.

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.



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

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



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

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

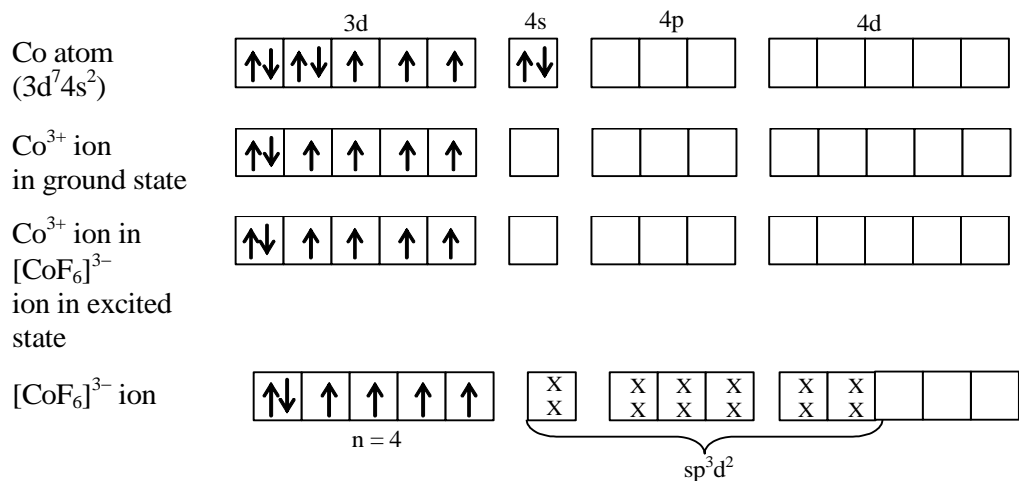
Other examples of inner orbital octahedral paramagnetic complexes are $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ ($n=1$), $[\text{Mn}(\text{CN})_6]^{4-}$ ($n = 1$), $[\text{Mn}(\text{CN})_6]^{3-}$ ($n = 2$), $[\text{Fe}(\text{CN})_6]^{3-}$ ($n = 1$), $[\text{Co}(\text{CN})_6]^{4-}$ ($n = 1$ in 5s orbital) while the examples of inner orbital octahedral diamagnetic complexes are: $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Co}(\text{CN})_6]^{3-}$, $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Co}(\text{NO}_2)_6]^{3-}$, $[\text{Pt}(\text{NH}_3)_6]^{4+}$ etc.

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

(b) Outer orbital octahedral complexes

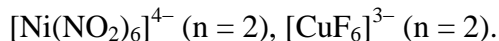
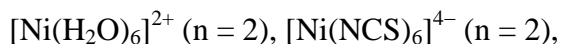
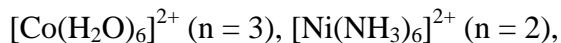
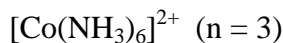
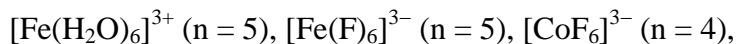
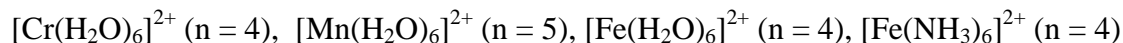
Octahedral complexes resulted from sp^3d^2 hybridisation, using outer d- and outer s and p orbitals are called outer-orbital octahedral complexes.



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:

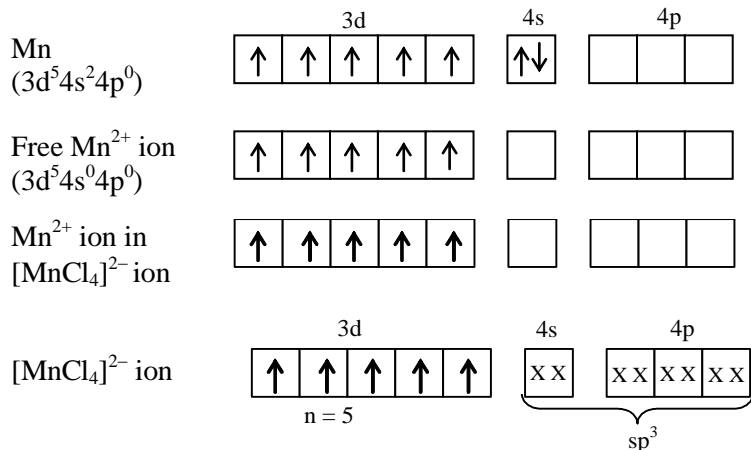


[Zn(NH₃)₆]²⁺ (n = 0) is an example of outer orbital octahedral diamagnetic complex.

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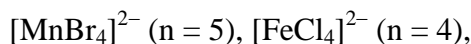
VBT-Tetrahedral Complexes (Coordination No. = 4, sp^3 Hybridisation)

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

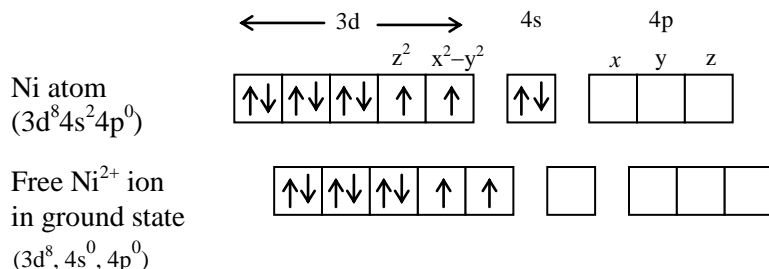


While the examples of some diamagnetic tetrahedral complexes are:

$[\text{Ni}(\text{CO})_4]$ ($n = 0$), $[\text{Cu}(\text{CN})_4]^{3-}$ ($n = 0$), $[\text{Zn}(\text{NH}_3)_4]^{2+}$ ($n = 0$), $[\text{ZnCl}_4]^{2-}$ ($n = 0$), $[\text{Cd}(\text{CN})_4]^{2-}$ ($n = 0$), etc. All these complexes result from sp^3 hybridisation of the central metal atom/ion.

VBT-Square Planar Complexes (Coordination 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 $[\text{Ni}(\text{CN})_4]^{2-}$. The measurement of magnetic moment value for $[\text{Ni}(\text{CN})_4]^{2-}$ ion has shown that $\mu = 0$ i.e. the complex ion has no unpaired electron and hence it is diamagnetic.

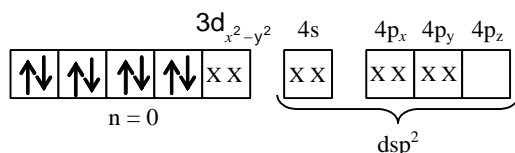


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Ni^{+2} ion in $\text{Ni}(\text{CN})_4^{2-}$
ion in excited state



$[\text{Ni}(\text{CN})_4]^{2-}$ ion



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: $[\text{Cu}(\text{CN})_4]^{2-}$ ($n = 1$), $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ($n = 1$), $[\text{CuCl}_4]^{2-}$ derived from $(\text{NH}_4)_2[\text{CuCl}_4]$ ($n = 1$) etc. While the examples of diamagnetic square planar complexes are: $[\text{Ni}(\text{CN})_4]^{2-}$ ($n = 0$), $[\text{PtCl}_4]^{2-}$ ($n = 0$), $[\text{Pt}(\text{NH}_3)_4]^{2+}$ ($n = 0$) etc.

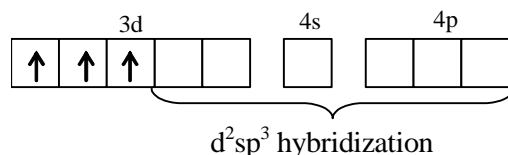
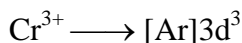
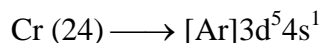
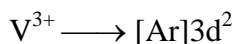
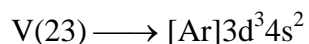
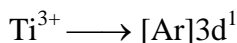
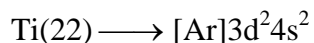
Limitations of VBT

- (i) 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.
- (ii) VBT cannot explain as to why $\text{Cu}(+2)$ forms only distorted octahedral complexes even when all the six ligands are identical.
- (iii) The valence bond theory does not provide any satisfactory explanation for the existence of inner orbital and outer orbital complexes.
- (iv) 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 $[\text{CuX}_4]^{2-}$).
- (v) The changes in the properties of the metal ion along with the ligands and the simple metal ions cannot 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.
- (vi) 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.
- (vii) The energy change of the metal orbitals on formation of complex is difficult to be calculated mathematically.
- (viii) VBT fails to explain the finer details of magnetic properties including the magnitude of the orbital contribution to the magnetic moments.
- (ix) The VBT does not explain why certain complexes are more labile than the others.
- (x) It does not give quantitative interpretation of thermodynamic or kinetic stabilities of coordination compounds.
- (xi) It does not make exact predictions regarding the tetrahedral and square planar structure of 4-coordinate complexes.
- (xii) It does not tell about the spectral properties of coordination compounds.

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

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



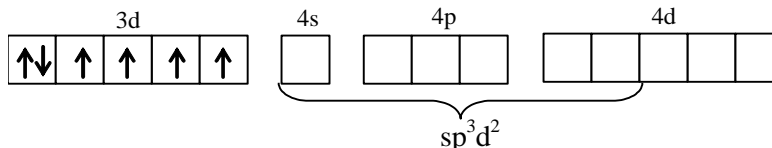
In all the three systems two vacant 3d orbitals ($n - 1$) d orbitals are available for d^2sp^3 hybridisation. Hence, these systems may accept six lone pairs from six ligands and thus they form octahedral complexes: $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, $[\text{V}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

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)

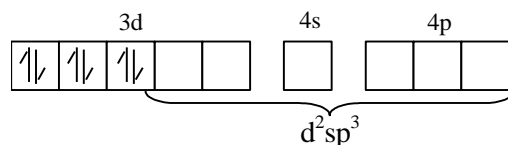


In d^4 , d^5 and d^6 systems, in ground state two 3d orbitals are not vacant to participate in d^2sp^3 hybridization forming octahedral complexes. Hence, two d-orbitals of outer shell are involved in hybridisation and the complexes are formed as outer orbital octahedral complexes. The energies of the 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:



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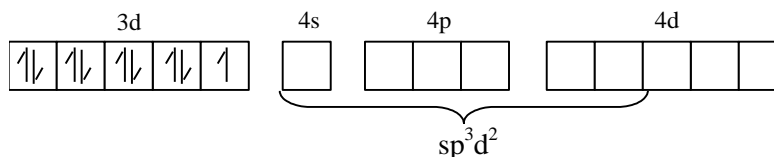
After maximum pairing of 3d electrons, two 3d orbitals may be made vacant for d^2sp^3 hybridisation forming octahedral complexes. As two d-orbitals of inner shell are involved in hybridisation, complexes are said to be inner orbital octahedral complexes.

$4s < 3d < 4p$; 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.

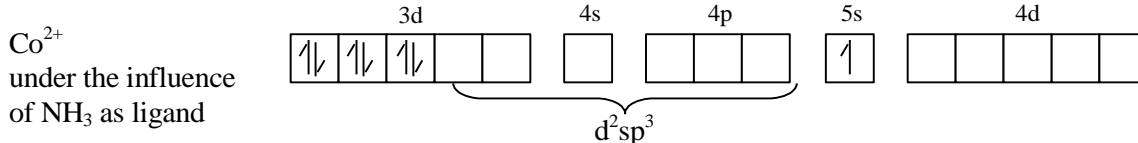
As the pairing of 3d electrons is forced in d^2sp^3 hybridisation in these systems (d^4 , d^5 and d^6), hence *the magnetic moment of the free metal ion undergoes change on complexation*.

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.



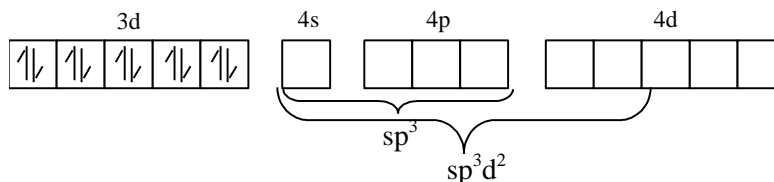
In d^7 system, after maximum pairing of the electrons in three of the d-orbitals and promoting one electron to 5s or 4d, two 3d orbitals may be made vacant for d^2sp^3 hybridisation and formation of inner orbital octahedral complex may take place with one unpaired electron.

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)



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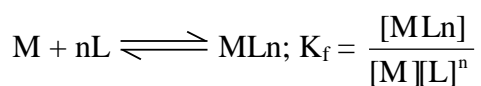
In d^{10} system, 3d orbitals are completely filled up. So, it may form tetrahedral complexes by sp^3 hybridization or outer orbital octahedral complexes by sp^3d^2 hybridisation.

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 pairing of 3d electrons and hence inner orbital octahedral complexes are formed by d^2sp^3 hybridization.

3.4 Factor Affecting Stability of Complexes

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



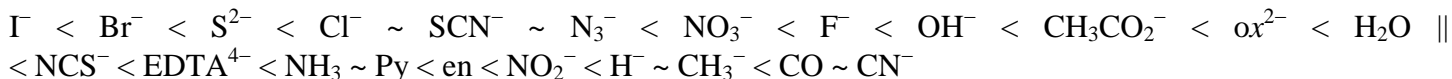
$\frac{1}{K_f}$ is called instability constant. Higher the value of K_f , more stable is the complex.

- (ii) 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 $[Fe(CN)_6]^{4-}$
- (iii) 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.
- (iv) Chelating ligands form more stable complexes than the monodentate ligands.

3.5 Crystal Field Theory (CFT)

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 a 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 field splitting are termed as **strong field ligands**. Ligands that cause only a small degree of crystal field 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**.



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:

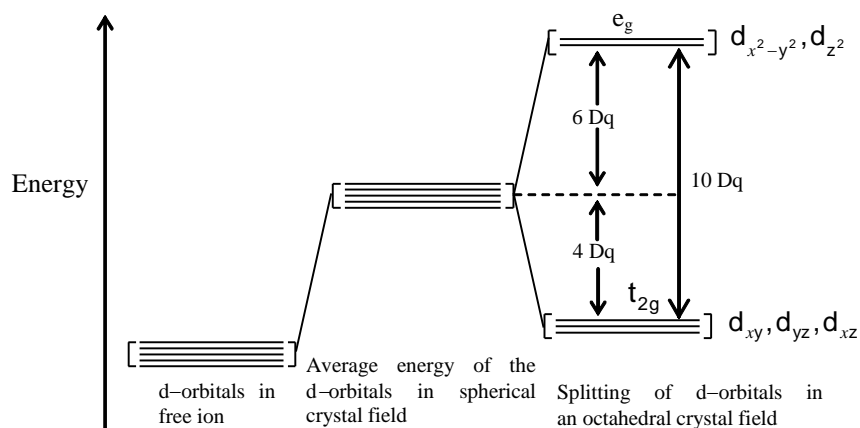
Halides donors < O donors < N donors < C donors

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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:



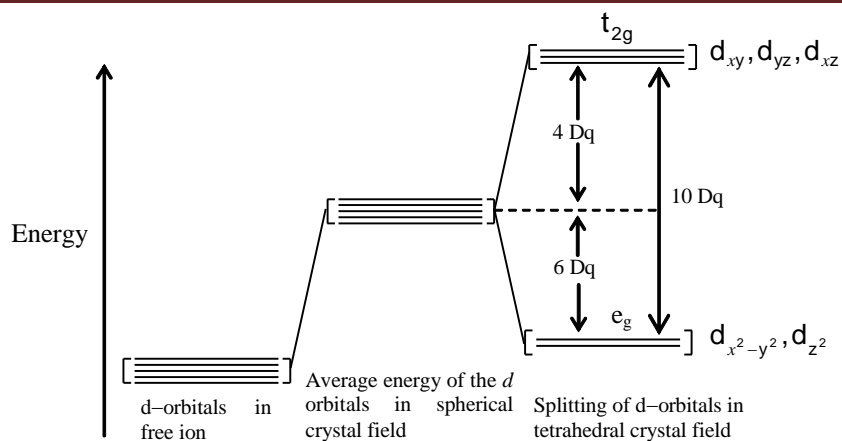
Significance of Δ_o :

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, $\Delta_o < P$ (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, $\Delta_o < P$ 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 $\Delta_o > P$) to give the configuration $t_{2g}^4 e_g^0$.

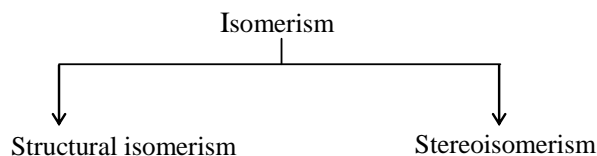
Crystal Field Effects in Tetrahedral Coordination Entities

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.



3.6 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 coordination complexes is of two types (Structural Isomerism and Stereoisomerism).



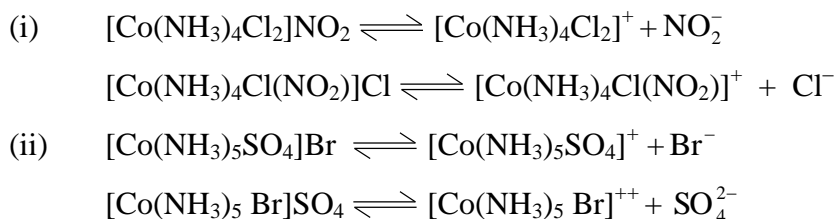
- | | |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------|
| <ul style="list-style-type: none"> (i) Ionisation Isomerism (ii) Hydrate isomerism (iii) Ligand isomerism (iv) Coordination isomerism (v) Linkage isomerism (vi) Coordination position isomerism (vii) Polymerisation isomerism | <ul style="list-style-type: none"> (i) Geometrical or cis-trans isomerism (ii) Optical isomerism |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------|

Structural Isomerism

Structural isomerism arises due to difference in structure of coordination compounds and is of following types.

(a) Ionisation isomerism:

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



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.

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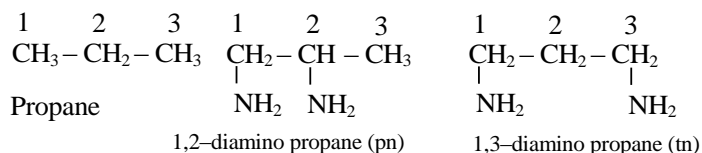
(b) Hydrate isomerism:

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

- (i) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (violet), does not lose water over H_2SO_4 and all Cl^- ions are immediately precipitated by (Ag^+) ions.
- (ii) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (green), loses H_2O over H_2SO_4 and two Cl^- ions are precipitated by (Ag^+) ions.
- (iii) $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (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 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. $[\text{Co}(\text{pn})_2\text{Cl}_2]^+$ and $[\text{Co}(\text{tn})_2\text{Cl}_2]^+$ 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) $[\text{Co}(\text{NH}_3)_6] [\text{Cr}(\text{CN})_6]$ and $[\text{Cr}(\text{NH}_3)_6] [\text{Co}(\text{CN})_6]$
- (ii) $[\text{Cu}(\text{NH}_3)_4] [\text{PtCl}_4]$ and $[\text{Pt}(\text{NH}_3)_4] [\text{CuCl}_4]$

(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.

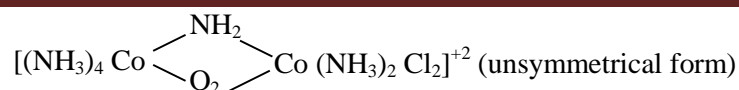
The best known ligands of this type are NO_2^- , SCN^- and $\text{S}_2\text{O}_3^{2-}$ ions. In complexes containing NO_2^- ion as ligand, NO_2^- ion may attach with the central ion either through O-atom or through N-atom.

- (i) $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)] \text{Cl}_2 \longrightarrow$ Pentaamminenitrocobalt(III) chloride.
- (ii) $[\text{Co}(\text{NH}_3)_5(\text{ONO})] \text{Cl}_2 \longrightarrow$ Pentaamminenitritocobalt(III) chloride.

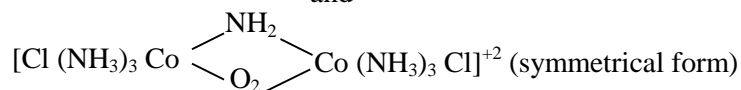
(f) Coordination position isomerism:

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,

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and



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, $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, $[\text{Pt}(\text{NH}_3)_4]$ $[\text{Pt}(\text{Cl}_4)]$, $[\text{Pt}(\text{NH}_3)_4]$ $[\text{Pt}(\text{NH}_3)\text{Cl}_3]_2$ and $[\text{Pt}(\text{NH}_3)_3\text{Cl}]_2$ $[\text{PtCl}_4]$ 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:

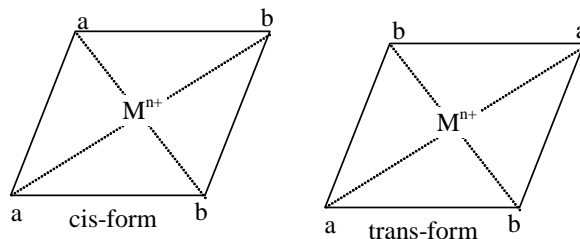
Geometrical isomerism is due to ligands occupying different positions around the central metal ion. The ligands occupy positions either adjacent to one another or opposite to one another. These are referred to as cis-form and trans-form respectively. This type of isomerism is, therefore, also referred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

(a) Geometrical isomerism in 4-coordinate complex

Complexes having central metal atom with coordination 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 cannot be expected in tetrahedral complexes.

Square planar complexes of $[\text{Ma}_4]$, $[\text{Ma}_3\text{b}]$ and $[\text{Mab}_3]$ type (a and b are monodentate ligands) do not show geometrical isomerism, since every conceivable spatial arrangement of the ligands around the metal ion is exactly equivalent.

(i) $[\text{Ma}_2\text{b}_2]$ type complexes



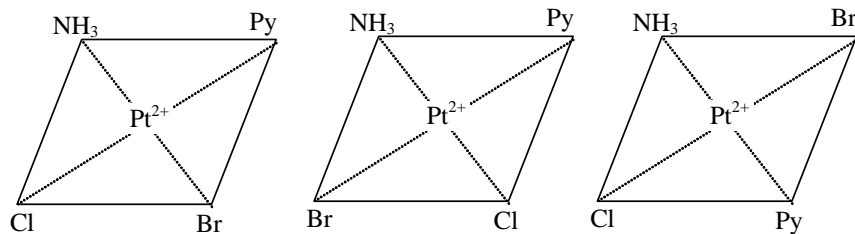
e.g. $[\text{Pt}^{+2} (\text{NH}_3)_2 \text{Cl}_2]$, $[\text{Pt}^{+2} (\text{NH}_3)_2 \text{Br}_2]$ and

$[\text{Pd}^{2+} (\text{NH}_3)_2 (\text{NO}_2)_2]$ are square planar complexes which exhibit cis-trans isomerism.

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(ii) [Mabcd] type complexes

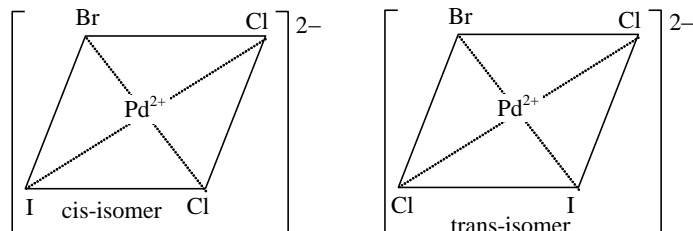
Square planar complexes of this type exist in three isomeric forms for example, $[\text{Pt}^{2+}(\text{NH}_3)(\text{Py})(\text{Cl})(\text{Br})]$ exist in the following structures.



$[\text{Pt}^{2+}(\text{NO}_2)(\text{Py})(\text{NH}_3)(\text{NH}_2\text{OH})]^+$ and $[\text{Pt}^{2+}(\text{C}_2\text{H}_4)(\text{NH}_3)(\text{Cl})(\text{Br})]$ are other examples of square planar complexes which exist in three isomeric forms.

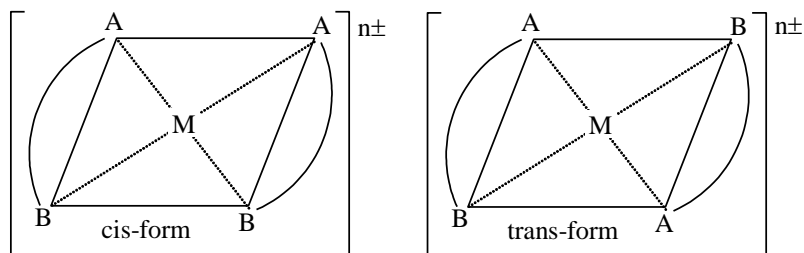
(iii) [Ma₂bc] type complexes

Square planar complexes of this type also show cis-trans isomerism. For example, $[\text{Pd}^{2+}\text{Cl}_2\text{BrI}]^{2-}$ exists in the following cis-trans

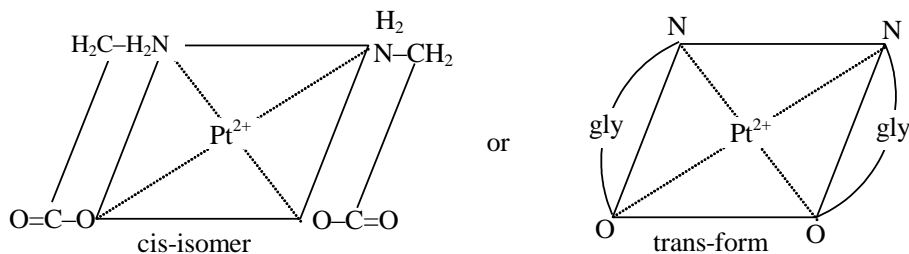


(iv) [M(AB)₂]^{n±} type complexes

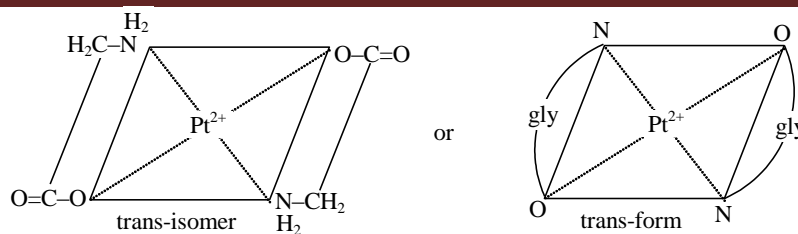
Here M is the central metal ion and (AB) represents an unsymmetrical bidentate ligand. (A) and (B) are the two ends (i.e., coordinating atoms) of the bidentate ligand. Such type of complexes also show cis and trans isomerism.



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

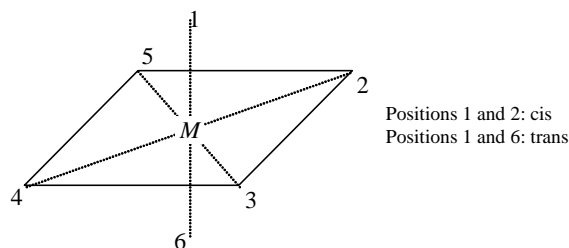


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(b) Geometrical isomerism in 6-coordinate complexes:

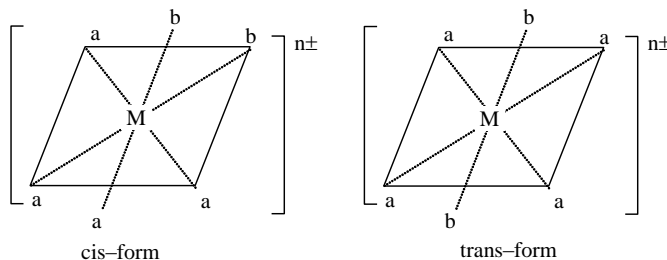
A complex compound having the central metal ion with coordination number equal to 6 has octahedral shape. The system used for numbering different positions of the ligands in an octahedral geometry has been shown below.



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

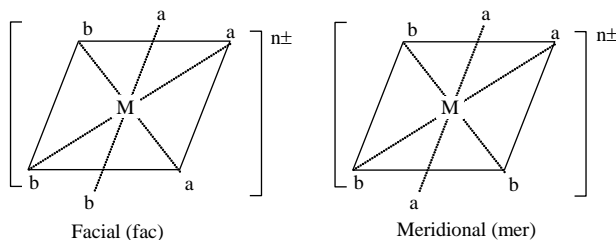
The following octahedral complexes give two or more geometrical isomers

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



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

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



(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.

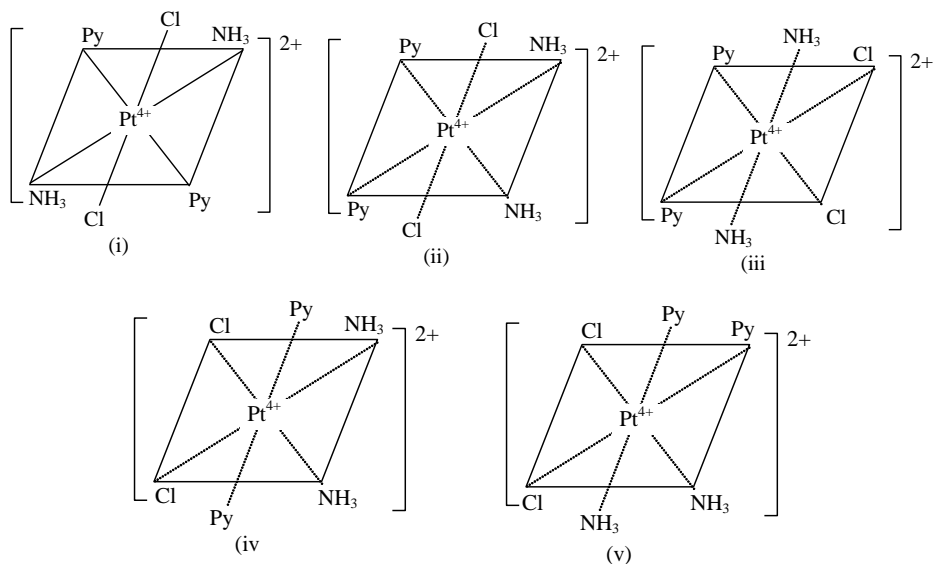
Complexes like $[Co^{3+}(NH_3)_3Cl_3]$, $[Cr^{3+}(H_2O)_3F_3]$, $[Pt^{3+}(Py)_3Cl_3]$, $[Cr^{3+}(NH_3)_3Cl_3]$, $[Ru^{3+}(H_2O)_3Cl_3]$, $[Pt^{4+}(NH_3)_3Br_3]^+$ etc exhibit such type of isomerism.

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(iii) $[Ma_2b_2c_2]$ type complexes

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

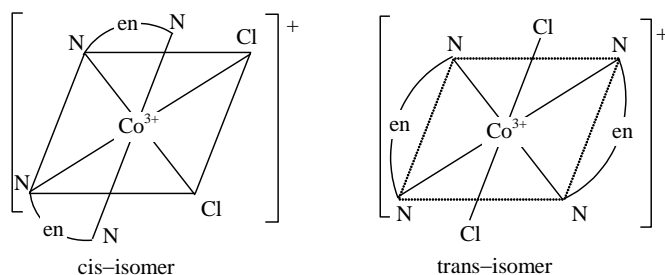
For example, consider $[Pt^{4+}(NH_3)_2(Py)_2Cl_2]^{2+}$ ion. It can theoretically exist in the following structures.



(iv) $[M(AA)_2a_2]$ 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).



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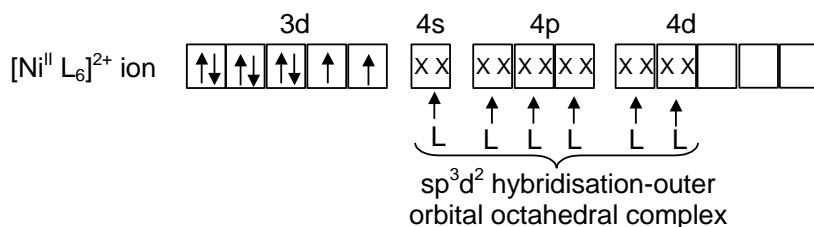
Solved Fundamental Examples

Example 1.

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.

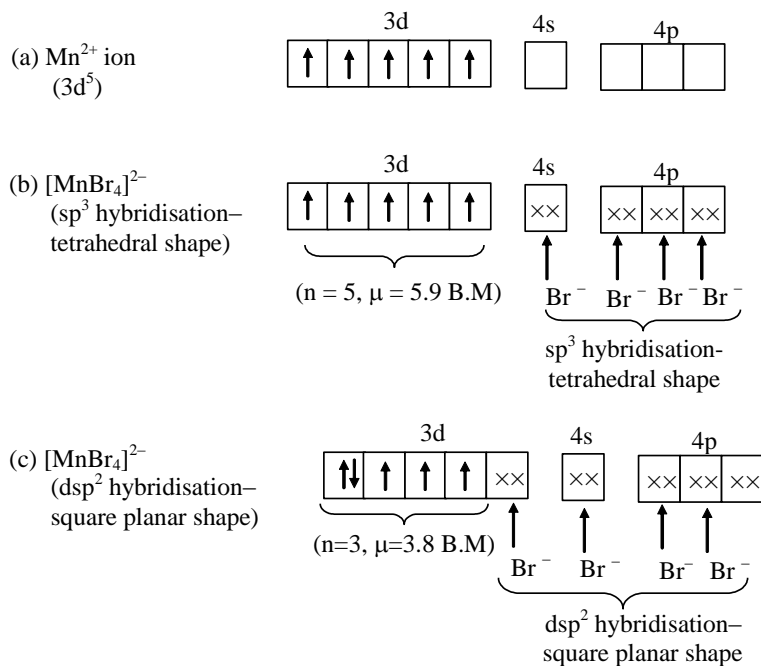


Example 2.

The magnetic moment of $[\text{MnBr}_4]^{2-}$ 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.



Example 3.

How would you account for the following?

(a) $[\text{Fe}(\text{CN})_6]^{3-}$ is weakly paramagnetic while $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic.

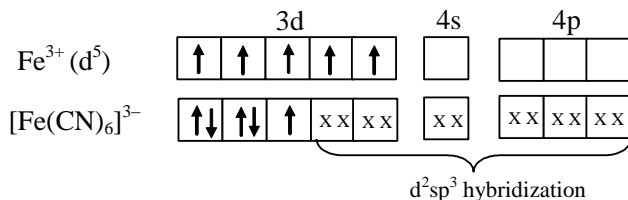
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(b) $\text{Ni}(\text{CO})_4$ possesses tetrahedral geometry while $[\text{Ni}(\text{CN})_4]^{2-}$ is square planar.

(c) $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic while $[\text{NiCl}_4]^{2-}$ is paramagnetic.

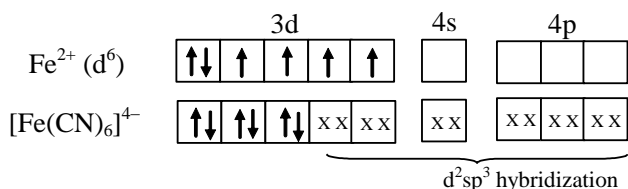
Solution:

(a) $[\text{Fe}(\text{CN})_6]^{3-}$ involves d^2sp^3 hybridization.



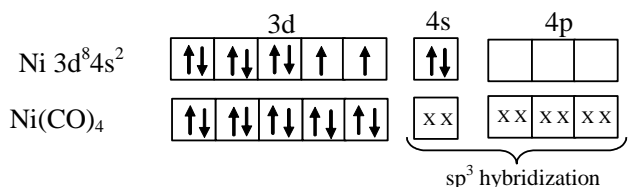
One d-orbital is singly occupied, hence it is weakly paramagnetic in nature.

$[\text{Fe}(\text{CN})_6]^{4-}$ involves also d^2sp^3 hybridization but it has Fe^{2+} ion as central ion.

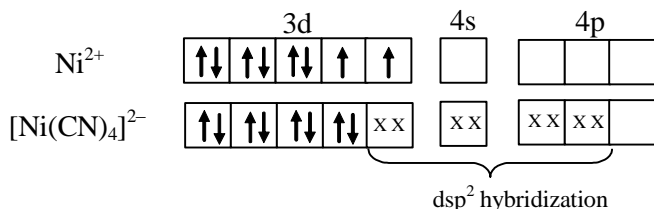


All orbitals are doubly occupied, hence it is diamagnetic in nature.

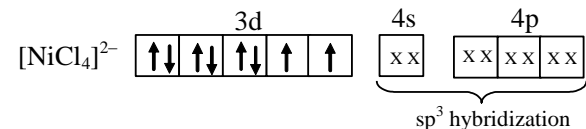
(b) In the formation of $\text{Ni}(\text{CO})_4$, nickel undergoes sp^3 hybridization, hence it is tetrahedral in shape.



(c) In $[\text{Ni}(\text{CN})_4]^{2-}$ ion, Ni^{2+} undergoes dsp^2 hybridization, hence it is square planar in shape.



In $[\text{Ni}(\text{CN})_4]^{2-}$, all orbitals are doubly occupied, hence it is diamagnetic ; while in $[\text{NiCl}_4]^{2-}$, 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.

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Example 4.

A metal complex having composition $\text{Cr}(\text{NH}_3)_4 \text{Cl}_2 \text{Br}$ 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 magnetic moments (spin-only value).

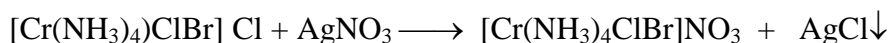
Solution:

Complex, $\text{Cr}(\text{NH}_3)_4 \text{Cl}_2 \text{Br}$, has two isomers. Since, coordination number of Cr is six, the two forms may be represented in the following way



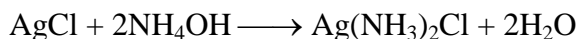
(A)

(B)

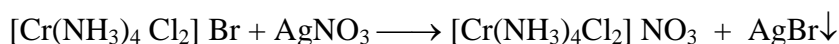


(A)

White ppt

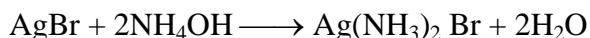


Soluble



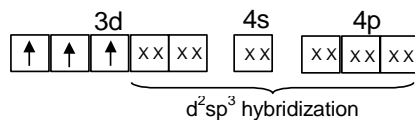
(B)

Pale yellow



Soluble

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 $= \sqrt{n(n+2)} \text{ B.M.} = \sqrt{3 \times 5} \text{ B.M.}$
 $= 3.87 \text{ B.M.}$

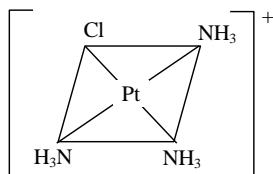
Example 5.

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) $[\text{Pt}(\text{NH}_3)_3 \text{Cl}]^+$ (b) $[\text{Pt}(\text{NH}_3) \text{Cl}_5]^-$
 (c) $[\text{Pt}(\text{NH}_3)_2 \text{ClNO}_2]$ (d) $[\text{Pt}(\text{NH}_3)_4 \text{ClBr}]^{2+}$

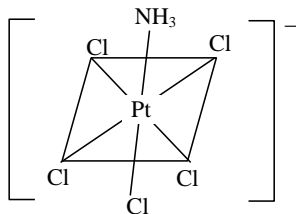
Solution:

(a) No isomers are possible for a square planar complex of the type MA_3B .

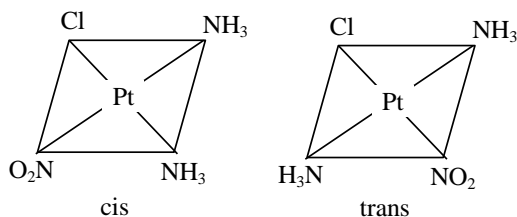


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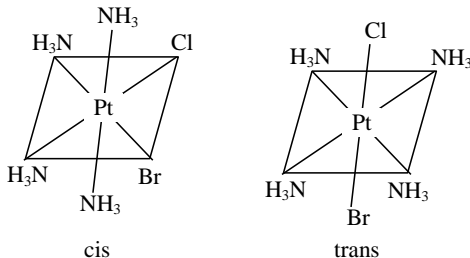
(b) No isomers are possible for an octahedral complex of the type MAB_5 .



(c) Cis and trans isomers are possible for a square planar complex of the type MA_2BC .

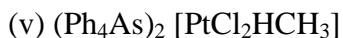
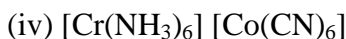
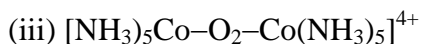
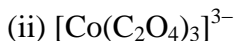
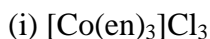


(d) Cis and trans isomers are possible for an octahedral complex of the type MA_4BC .



Example 6.

Write the IUPAC name of the following complexes:



Solution:

(i) Tris(ethylenediamine)cobalt(III) chloride

(ii) Trioxalatocobaltate(III) ion

(iii) Decaammine- μ -peroxodicobalt(III) ion

(iv) Hexaamminechromium(III) hexacyanocobaltate(III)

(v) Tetraphenylarsenium dichlorohydridomethylplatinate(II)

Example 7.

A solution containing 0.319 g of complex $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ 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 coordination sphere will be ionised to produce the acid, HCl.

Thus, milliequivalent of Cl^- ions outside = milliequivalent of HCl formed

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= milliequivalent of NaOH used

$$= 28.5 \times 0.125 = 3.56$$

$\frac{0.319}{266.5}$ 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 coordination sphere. Thus, the complex is $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$.

Example 8.

Give the structural formula of these complex compounds:

- (i) Ammonium aquapentafluoroferrate(III)
- (ii) Diaquabis(ethylenediamine)cobalt(III) sulphate
- (iii) Tetraisothiocyanatozincate(II) ion
- (iv) Sodium hexanitrocobaltate(III)
- (v) Tris(ethylenediamine)iron(II) tetracyanoferrate(II)

Solution:

- (i) $(\text{NH}_4)_2[\text{FeF}_5(\text{H}_2\text{O})]$
- (ii) $[\text{Co}(\text{H}_2\text{O})_2(\text{en})_2]_2(\text{SO}_4)_3$
- (iii) $[\text{Zn}(\text{NCS})_4]^{2-}$
- (iv) $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$
- (v) $[\text{Fe}(\text{en})_3][\text{Fe}(\text{CN})_4]$

Example 9.

(A), (B) and (C) are three complexes of chromium (III) with the empirical formula $\text{H}_{12}\text{O}_6\text{Cl}_3\text{Cr}$. 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) : $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ (Violet)
- (B) : $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (Green) Molecular weight = 266.5
- (C) : $[\text{Cr}(\text{H}_2\text{O})_4\text{Cl}_2]\text{Cl} \cdot 2\text{H}_2\text{O}$ (Dark green)

Compound (A) contains six water molecules as coordinated water and thus, does not lose H_2O on treatment with H_2SO_4 . Compound (B) contains five water molecules as coordinated 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 coordinated water molecules and two molecules of lattice water, which are taken out by H_2SO_4 to show a loss of 13.5%.

Example 10.

(a) Write down the IUPAC nomenclature of the given complex along with its hybridisation and structure



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(b) Draw the structures of $[\text{Co}(\text{NH}_3)_6]^{3+}$, $[\text{Ni}(\text{CN})_4]^{2-}$ and $[\text{Ni}(\text{CO})_4]$. Write the hybridisation of atomic orbitals of the transition metal in each case.

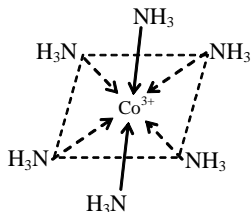
Solution:

(a) Potassium amminetetracyanonitrosoniumchromate(I)

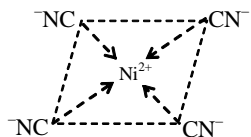
Cr is in +1 oxidation state and possess d^2sp^3 hybridisation with one unpaired electron.

$$\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM.}$$

(b) $[\text{Co}(\text{NH}_3)_6]^{3+}$: Co^{3+} is d^2sp^3 hybridised to show octahedral shape.



$[\text{Ni}(\text{CN})_4]^{2-}$: Ni^{2+} is dsp^2 hybridised to show square planar shape.



$[\text{Ni}(\text{CO})_4]$: Ni is sp^3 hybridised to show tetrahedral shape.

