

## Chapter

## 1

## p – Block Elements

## Day – 1

p – block elements

Group 13 to 18, contains metal, metalloids & non-metal general element configuration  $ns^2np^{1-6}$ .

1.1 Group – 13 Elements

The Boron family.

Element	Atomic Number	Electronic Configuration	
		Complete	With inert gas core
Boron (B)	5	$1s^2 2s^2 2p^1$	$[\text{He}] 2s^2 2p^1$
Aluminium (Al)	13	$1s^2 2s^2 2p^6 3s^2 3p^1$	$[\text{Ne}] 3s^2 3p^1$
Gallium (Ga)	31	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^1$	$[\text{Ar}] 3d^{10} 4s^2 4p^1$
Indium (In)	49	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^1$	$[\text{Kr}] 4d^{10} 5s^2 5p^1$
Thallium (Tl)	81	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10} 6s^2 6p^1$	$[\text{Xe}] 4f^{14} 5d^{10} 6s^2 6p^1$

1.2 Some Atomic and Physical Properties of Group 13 Elements

Property	Elements				
	B	Al	Ga	In	Tl
Atomic number	5	13	31	49	81
Atomic mass ( $\text{g mol}^{-1}$ )	10.81	26.98	69.72	114.82	204.38
Atomic radius/pm	85	143	135	167	170
Ionic radius $\text{M}^{3+}$ /pm	27	53.5	62.0	80.0	88.5
Ionic radius $\text{M}^{+}$ /pm	-	-	120	140	150
Ionisation enthalpy/ $\text{kJ mol}^{-1}$	801	577	579	558	589
$\Delta_i H_1$	2427	1816	1979	1820	1971
$\Delta_i H_2$	3659	2744	2962	2704	2877
$\Delta_i H_3$	25026	11578	6200	5200	-
$\Delta_i H_4$					
Electronegativity (Pauling scale)	2.0	1.5	1.6	1.7	1.8
Density/ $\text{g cm}^3$	2.35	2.70	5.90	7.31	11.85

Melting point/K	2453	933	303	430	576
Boiling point/K	3923	2740	2676	2353	1730
$E^0/V$ at 298 for $M^{3+}(aq) + 3e^- \rightarrow M(s)$	-	-1.66	-0.56	-0.34	+1.26
$E^0/V$ at 298 for $M^+(aq) + e^- \rightarrow M(s)$	-	+0.55	-0.79 (acid) -1.39 (alkali)	-0.18	-0.34

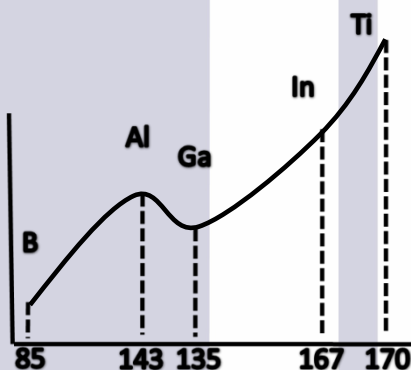
## Properties

### 1. Atomic radii / Ionic radii

Smaller than corresponding to group 2.

(i) The electrons in the same shell do not screen do not screen each other. Therefore, the effective nuclear charge increases and outer electron pulled more strongly towards nuclear.

(ii) **Atomic Radii of Ga (135 pm) < Al (143 pm)** – Due to the filling of electrons in d – orbitals in between Al(z = 13) & Ga(31) there are 10 elements of first transition series which have electrons in inner d – orbitals. The presence of additional 10 d – electrons offer only poor screening effect for the outer electron from the increased nuclear charge in Ga consequently the atomic radii of Ga (135 pm) < Al (143 pm).



### 2. Ionization Enthalpy

(i)  $IE_1$  of group 13 <  $IE_2$  of group 2.

(ii)  $IE_1$  of Ga >  $IE_1$  of Al (due to poor shielding effect)

$IE_2$  &  $IE_3$  of group 13 >  $IE_1$  of group 13.

### 3. Electronegativity

First decreases from B to Al then increases marginally due to discrepancy in atomic size.

### 4. Electropositive / metallic character

Less than group 1 & 2. Group 13 elements less electropositive than group 1 & group 2 elements.

## 5. Density

More in group 13 elements than group 2 elements due to smaller size.

## 6. Melting Point

Boron has high m.p. (2453 K) because its crystal structure consists of icosahedra (A solid with 20 faces & 12 corners) and bonded to five equidistant neighbours. Rests of the members are soft metals with low melting point and high electrical conductivity.

## Chemical Properties

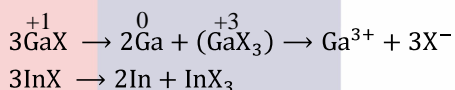
### Oxidation state and trends in chemical reactivity

Well known oxidation state is +3 but Ga, In & Tl due to inert pair effect show oxidation state of +1 & +3 both.

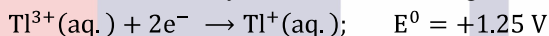
The order of stability of +1 oxidation state.



Since Ga & In are more stable in +3 oxidation state than +1 oxidation state. Therefore Ga & In both (in +1 oxidation state) undergo disproportionation reaction in aq. Solution



Tl<sup>+1</sup> compounds such as TlOH and TlClO<sub>4</sub> are more stable than their corresponding Tl<sup>3+</sup> compounds due lesser stability. Tl<sup>3+</sup> salt act as strong oxidising agent.



### Inert pair effect

As we more ↓ the group, the tendency of s-electron of the valence shell to participate in bond formation decreases. This reluctance of the s-electrons to participate in bond formation is called ***Inert pair effect.***

**This is due to poor of ineffective shielding of ns<sup>2</sup> electrons of the vol.**

Another reason for the inert pair effect is that as the size of atom increases from Al to Tl, the energy required to unpair ns<sup>2</sup> electron is not compensated by the energy released in forming the two additional bonds.

### Trends in chemical reactivity

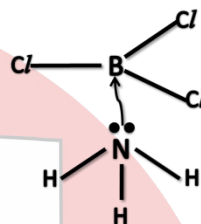
In +3 oxidation state, the elements of this group are expected to form covalent bonds because of the following three reasons

- (i) According to **Fajan's Rule**, the small size of ion and their high charge of +3 favours the formation of covalent bonds.
- (ii) The sum of three ionization energies is very high, which suggests that bonds will be largely covalent.

(iii) The Electronegativity values of group 13 > than group 1 & 2. When these elements react with other elements, the difference in electronegativity is small which favours the formation of covalent bond.

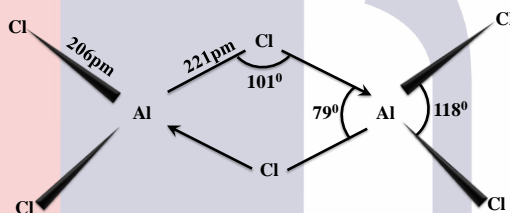
In +3 oxidation state, the no. of electron around the central atom in a molecule of the compound of these elements (e.g.  $\text{BF}_3$ ) will be only six. Such *electrons deficient* molecule have tendency to accept a pair of electron to achieve stable electronic configuration and thus behave as *Lewis acid*. This tendency decrease with increase in size.

$\text{BCl}_3$  easily accept lone pair of electrons

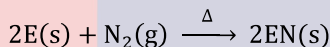
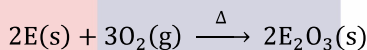


### $\text{AlCl}_3$ exist as dimer while $\text{BCl}_3$ not

Because B is so small that it cannot accommodate four large sized halogen atoms around it.



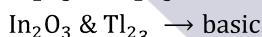
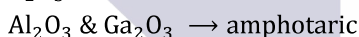
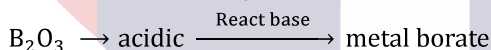
### Reactivity towards air



B is unreactive in crystalline form.

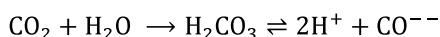
Al form a very thin oxide layer on the surface which protects the metal from further attack.

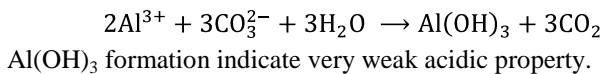
Amorphous B & Al form  $\text{Al}_2\text{O}_3$  &  $\text{AlN}$ .



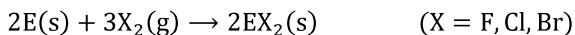
### Reactivity towards Acid & Alkalies

- B does not react with acid & alkalies.
- $2\text{Al}(\text{s}) + 6\text{HCl}(\text{aq.}) \rightarrow 2\text{Al}^{3+}(\text{aq.}) + 6\text{Cl}^{-}(\text{aq.}) + 3\text{H}_2(\text{g})$   
 $2\text{Al}(\text{s}) + 2\text{NaOH}(\text{aq.}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{Na}^+[\text{Al}(\text{OH})_4]^{-}(\text{aq.}) + 3\text{H}_2$   
 Sodium tetra hydroxoaluminate (III)
- Aluminates are important constituents of portland cement.
- $\text{Al}(\text{OH})_3$  : amphoteric and reacts principally as a base however,  $\text{Al}(\text{OH})_3$  shows some acidic property.

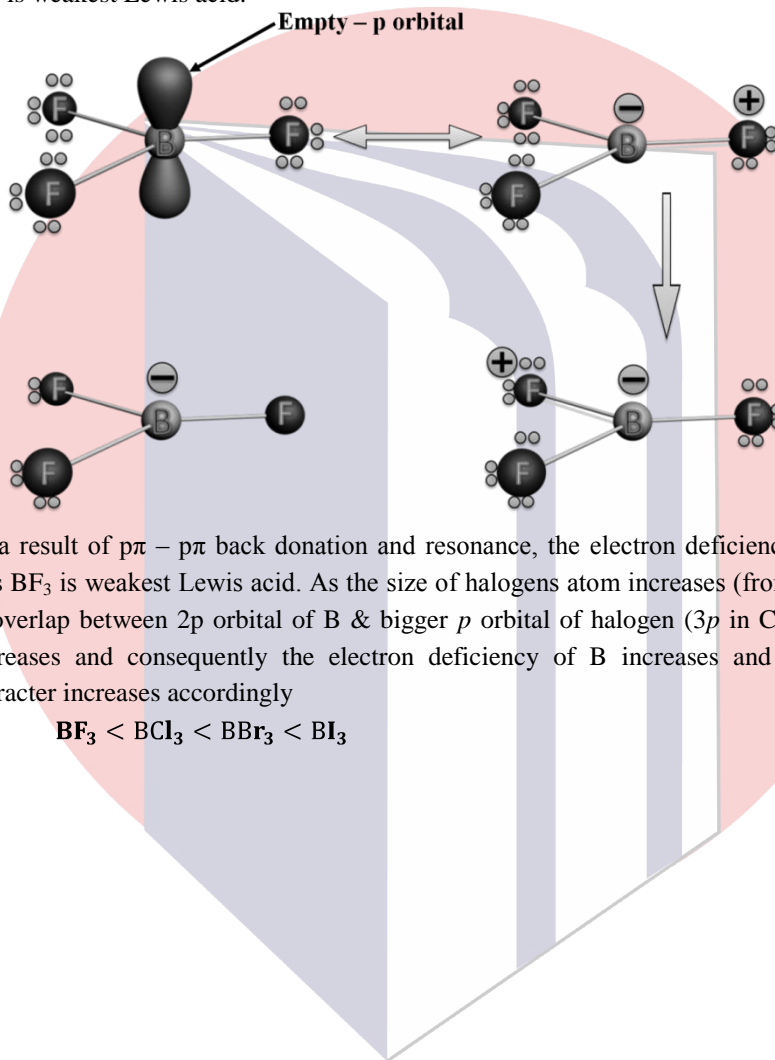




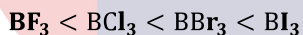
### Reactivity with Halogens



$\text{BF}_3$  is weakest Lewis acid.



As a result of  $\pi\pi - \pi\pi$  back donation and resonance, the electron deficiency of B decreases and thus  $\text{BF}_3$  is weakest Lewis acid. As the size of halogens atom increases (from Cl  $\rightarrow$  I). The extent of overlap between 2p orbital of B & bigger p orbital of halogen (3p in Cl, 4p in Br & 5p in I) decreases and consequently the electron deficiency of B increases and thus the Lewis acid character increases accordingly



**Chapter****2****d – Block Elements****Day – 1****d – Block Elements**

The element whose atom in ground state or ion in one of common oxidation state has in complete d – sub shell (partly filled) between 1 – 9

General electronic configuration  $(n - 1)d^{1-10} ns^{1-2}$

**Electronic Configurations of Transition Metals****1. First (3d) Transition Series (Sc – Zn)**

At. No.	21	22	23	24	25	26	27	28	29	30
Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
E.C	$3d^1 4s^1$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$	$3d^{10} 4s^1$

**2. Second (4d) Transition Series (Y – Cd)**

At. No.	39	40	41	42	43	44	45	46	47	48
Element	Y	Zr	Nb	Mo	Tc*	Ru	Rh	Pd	Ag	Cd
E.C	$4d^1 5s^1$	$4d^2 5s^2$	$4d^4 5s^2$	$4d^5 5s$	$4d^6 5s^2$	$4d^7 5s^1$	$4d^8 5s^1$	$4d^{10} 5s^0$	$4d^{10} 5s^1$	$4d^{10} 5s^2$

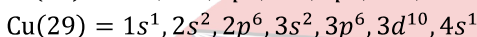
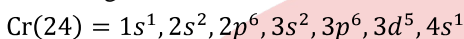
**3. Third (5d) Transition Series (La – Hg)**

At. No.	57	72	73	74	75	76	77	78	79	80
Element	La	Hr	Ta	W	Re	Os	Ir	Pt	Au	Hg
E.C	$5d^1 6s$	$5d^1 6s^2$	$5d^3 6s^2$	$5d^4 6s$	$5d^5 6s^2$	$5d^6 6s^2$	$5d^7 6s^2$	$5d^9 6s^1$	$5d^{10} 6s^1$	$5d^{10} 6s^2$

**4. Fourth (6d) Transition Series**

At. No.	89	104	105	106	107	108	109	110	111	112
Element	Ac	Ku	Ha	Sg (Unh)	Bh (Uns)	Hs (Uno)	Mt (Une)	Uun	Uuu	Uub
E.C	$6d^1 7s^1$	$6d^2 7s^2$	$6d^3 7s^2$	$6d^4 7s^1$	$6d^5 7s^2$	$6d^6 7s^2$	$6d^7 7s^2$	$6d^8 7s^2$	$6d^{10} 7s^1$	$6d^{10} 7s^1$

**Exceptional Configuration of Cr and Cu**



$3d^5, 3d^{10}$  have extra Stability (on the basis of exchange energy)

$Zn^{2+}, Cu^{2+}$  and  $Hg^{2+}$  excluded from transition element because the d-shell configuration of these atoms/ions are  $3d^{10}, 4d^{10}$  and  $5d^{10}$  respectively.

**Illustration**

Element  $[Xe]^{54} 4f^{14} 5d^1, 6s^2$  is a ?

**Solution**

d – block element.

**Trends in Properties**

These are greatest horizontal similarities in the properties.

**Atomic Radii**

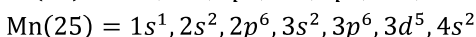
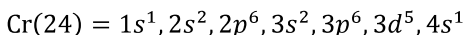
(1) The atomic radii lie in between s and p – block element.

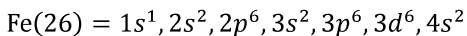
(2) From left to right size decrease but smaller decrease after midway.

**Atomic radii of d – block elements in pm**

Sc 162	Ti 147	V 134	Cr 127	Mn 126	Fe 126	Co 125	Ni 124	Cu 124	Zn 138
Y 180	Zr 160	Nb 146	Mo 139	Tc 136	Ru 134	Rh 134	Pd 137	Ag 144	Cd 154
La 187	*Hf 158	Ta 146	W 139	Re 137	Os 135	Ir 136	Pt 138	Au 144	Hg 157

↑  
Lanthanoid  
Contraction

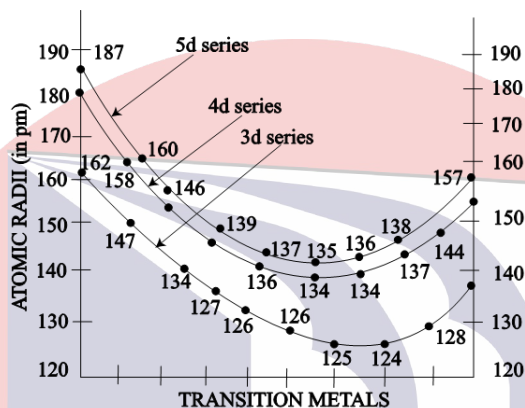




After mid way as the electron enter into d – block the added electrons shields (screens) 4s electrons hence increases in electron screening effect increases because of it atomic radii after Cr, are same.

(3) At the end the size increases (General).

(4) At Radii of 2<sup>nd</sup> and 3<sup>rd</sup> transition series are same



### Lanthanoid Contraction

When we move along the Lanthanoid series the nuclear charge increase by one unit. The new electron is added into same subshell..... As a result charge on the e<sup>-</sup> by nucleus increase and tends to decrease in size. Due to diffused shape of f - sub shell these is a imperfect shielding of one electron which is unable to counter balance the effect of increased nuclear size. Hence net result is a contraction in size through the decrease is very small. (11pm) which causes similarity in physical and chemical properties of Zr and Hf, Nb and Ta.

### Metallic Character

All the d- block elements display typical metallic character like

- High tensile strength
- Malleability
- Ductility
- High thermal and electrical conductivity
- Metallic luster

### Lattice Starch of Transition Metals

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
hcp	hcp	bcc	bcc	x	bcc	ccp	ccp	ccp	x
Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
hcp	hcp	bcc	bcc	hcp	hcp	ccp	ccp	ccp	x
La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
hcp	hcp	bcc	bcc	hcp	hcp	ccp	ccp	ccp	x

X = a typical metallic character

Enthalpy of atomisation = heat required to break the metal lattice to go free atoms.





**Self Efforts**

- The most abundant transition metal is :  
(a) Cr (b) Fe  
(c) W (d) Zn.
- A transition element X has a configuration  $[\text{Ar}]3d^4$  in +3 oxidation state. Its atomic number is  
(a) 25 (b) 26  
(c) 22 (d) 19.
- Which of the following ion contains 2 unpaired electrons  
(a)  $\text{Ni}^{2+}$  (b)  $\text{Sc}^{3+}$   
(c)  $\text{Cu}^+$  (d)  $\text{Tl}^{3+}$ .
- In general, the melting and boiling point of transition metals  
(a) increases gradually across the period from left to right  
(b) decreases gradually across the period from left to right  
(c) first increases till the middle of the period and then decreases towards the end  
(d) first decreases regularly till the middle of the period and then increases towards the end.
- Which metal has the highest melting point ?  
(a) Pt (b) W  
(c) Pd (d) Au.
- The transition metal present in vitamin  $\text{B}_{12}$  is  
(a) Fe (b) Co  
(c) Ni (d) Na.
- The trace metal present in insulin is  
(a) Fe (b) Co  
(c) Zn (d) Mn.
- Super conductors are derived from compounds of  
(a) p-Block elements (b) Lanthanides  
(c) Actinides (d) Transition elements  
(e) Scandium
- Zn and Ag can be separated from each other by  
(a) Distillation (b) Heating with conc. NaOH  
(c) Fractional distillation (d) Treating with dil.  $\text{HNO}_3$ .
- The transition metals which do not form amalgams are  
(a) Zn (b) Pt  
(c) Cd (d) Fe.

**Answers**

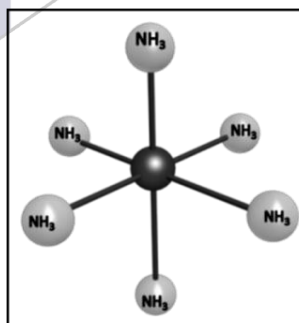
- |         |          |      |      |
|---------|----------|------|------|
| 1. b    | 2. a     | 3. a | 4. c |
| 5. b    | 6. b     | 7. c | 8. d |
| 9. a, b | 10. b, d |      |      |

**Chapter****3****Coordination Compounds****Day – 1****1. Co – ordination compounds**

Co – ordination compounds are those in which the central metal atom is linked to a number of ions/neutral molecules by co – ordinate bonds, i.e., donation of lone pairs of electron by these ion/neutral molecules to the central metal atom. The branch of inorganic chemistry dealing with the study of Co – Ordination compounds is known as **Coordination chemistry**.

**1.1 Difference between double salts and co – ordination compounds**

<b>Double Salts</b>	<b>Co – Ordination Compounds</b>
1. (i) Mohr's salt: $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (ii) Potash Alum : $\text{K}_2\text{SO}_4 \cdot \text{Al}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$	$\text{K}_4[\text{Fe}(\text{CN})_6]$ , $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$ .
2. Exist only in solid state, when dissolved in water, they dissociate completely into ions.	Exist in solid as well as in aqueous state because even in the solution the complex ion does not dissociate into ions.
3. Ionic compounds, and do not contain any coordinate bond.	May or may not be ionic but complex part always contain co – ordinate bond.
4. Properties of compounds are same as those of its constituent compounds.	The properties of compounds are entirely different from its constitute.
5. Metal ion show their normal valiancy	The metal ion satisfies its two type of valency (i) Primary Valency (ii) Secondary Valency
6. Double salt loses its identity in solution.	Complex compounds retain its identity in solution.

**1.2 Definition and Terminology****1. Central Metal Atom or Ion**

The metal atom or ion to which these ligands are attached is called. Central Metal Atom or Ion.

## 2. Ligands

The donor atoms, molecules or anion which donate a pair of electron to central metal atom/ion are called Ligands.

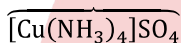
## 3. Co – ordination Number

The total number of ligands attached to a central ion is called the co - ordination number of that ion.  $[\text{Cu}(\text{NH}_3)_4]^{+2}$  C. NO. = 4.

[Most common co – ordination number exhibited by central metal/ion = 2,4,6 and some times 3,5,7,8,9 and 12 ]

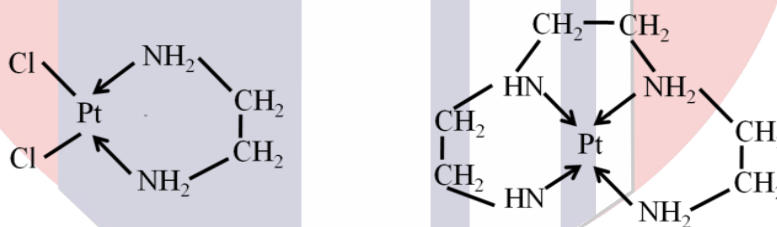
## 4. Co – ordination Sphere

The central atom and the ligands which are directly attached to it are enclosed in [ ] and are collectively termed as co – ordination sphere.



## 5. Denticity and Chelation

The number of co – ordinating or ligand groups presents in a ligand is called denticity of that ligand. They may contain two donor atoms (i.e., co – ordinating groups) positioned in such a way that 5 or 6 membered ring is formed with metal ion, than it is called bidentate/didentate chelating agent/ligands and ring is called chelate ring. The resulting complex is called metal chelate and this property is called chelation.



### 1.3 Importance of Chelates

1. In the softening of hard water.
2. In the separation of lanthanoides and actinoides.
3. In the detection of some metal ions in qualitative analysis ( $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ), and anion ( $\text{Cl}^-$ )

### 1.4 Types of ligands

#### (a) Unidentate ligands

Ligands which donate only one pair of electrons and can this is co – ordination to the central ion through only one atom.



**(b) Bi/Didentate ligands**

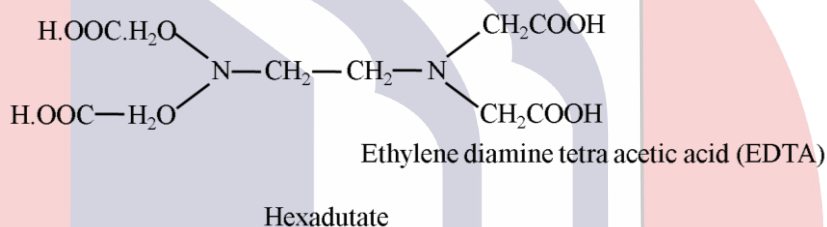
Ligands which have two donor atom and have the tendency to attach to the central atom/ion through two donor atoms are called Bi/didentate.

**(c) Ambidentate Ligands**

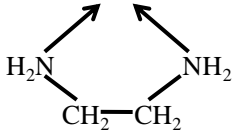
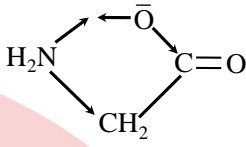
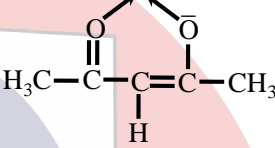
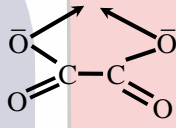
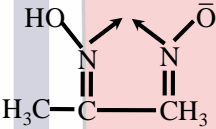
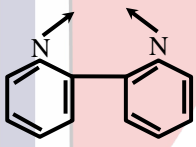
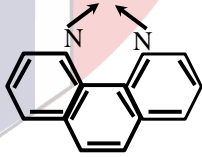
Unidentate ligand containing more than one co – ordination atoms are called ambidentate ligands.

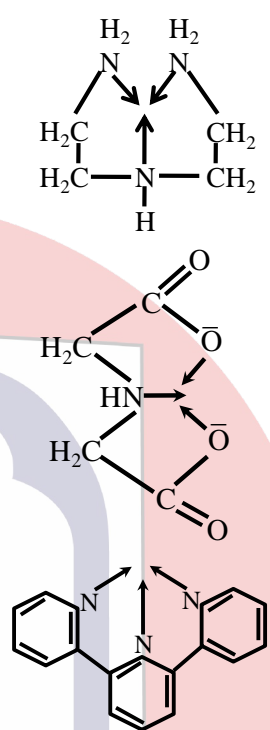
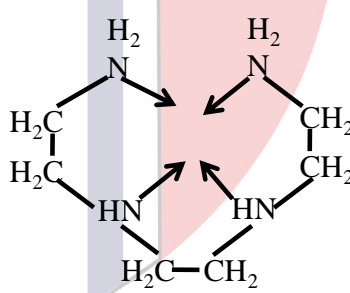
**(d) Polydentate ligands**

Ligands which co – ordinate with the central ion through more than two donor atoms present in the molecules are called polydentate ligand. They may be tridentate, tetradentate pentadentate or hexadentate ligands.

**1.5 Important Ligands Forming Complexes**

Type Of Ligand	Name Of Ligand	Symbol	Structure Showing Only Linkage Sites (By →) To Metal Ions
Unidentate	Water	aqua	
	Ammonia	ammine	
	Pyridine	Py	

<b>Bidentate</b>			
Ethylenedimine	en		
Glycinate anion	gly		
Acetylacetonate	acac		
Oxalate anion	ox		
Dimethylglyoximate anion	dMG		
2,2' Dipyridyl]	dipy		
1,10 Phenanthroline	phen		

<p><b>Tridentate</b></p>	<p>Diethylene triamine</p> <p>Iminodiacetate anion</p> <p>2,2',2'' Terpyridine</p>	<p>dien</p> <p>-</p> <p>Tery</p>	
<p><b>Tertridentate</b></p>	<p>Treithlene Tetraamine</p>	<p>trien</p>	
<p><b>Pentadentate</b></p>	<p>Ethylenediamine triacetate anion</p>	<p>-</p>	