Ligand : Electron rich species which can donate one or more than one electron pairs to the vacant orbital of central metal atom/ion is called ligands.

Classification of Ligands

(I) On the basis of charges
- Negative ligands
- Neutral ligands
- Positive ligands

(II) On the basis of Denticity
- Monodentate ligands
- Bidentate ligands
- Polydentate ligands
- Ambidentate ligands

(III) On the basis of e⁻ pair donating & accepting tendency
- Classical (normal) lignads ($M \xleftarrow{\sigma} L$)
- Non classical (π-acid) ligands ($M \overset{\sigma/\pi}{\rightleftharpoons} L$)

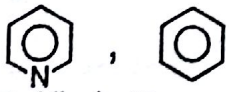
(I) On the Basis of charges

Negative Ligands : Carry negative charge

H^-	Hydride	SCN^-	Thiocyanate	CH_3COO^-	Acetate
F^-	Flouride	NCS^-	Isothiocyanate	$C_2O_4^{2-}$	Oxalate
Cl^-	Chloride	SO_4^{2-}	Sulphate	CO_3^{2-}	Carbonate
Br^-	Bromide	SO_3^{2-}	Sulphite	CH_3^-	Methyl
I^-	Iodide	$S_2O_3^{2-}$	Thiosulphate	$CH_3CH_2^-$	Ethyl
O_2^{2-}	peroxide	N_3^-	Azide	$C_6H_5^-$	Phenyl
O_2^-	Superoxide	N^{3-}	Nitride	$SnCl_3^-$	Trichlorostannite
O^{2-}	Oxide	NH_2^-	Amide	$C_5H_5^-$	Cyclopentadienyl
OH^-	Hydroxide	NH^{2-}	Imide	$CH_2=CH-CH_2^-$	Allyl
CH_3O^-	Methoxide	NO_2^-	Nitrite		
OCN^-	Cyanate	NO_3^-	Nitrate		
NCO^-	Isocyanate	CN^-	Cyanide		

Neutral ligands : Carry no charge

e.g. NH_3 (Ammine), H_2O(Aqua), CO (Carbonyl), NO(Nitrosyl), O_2(Dioxygen), N_2(Dinitrogen), PH_3(Phosphene), PMe_3(Trimethyl phosphene), PPh_3(Triphenyl phosphene), N_2H_4(Hydrazine), $MeNH_2$(Methyl amine), $EtNH_2$(Ethyl amine), R_2O(Normal ether), R_2S (Thio ether),


(Pyridine) (Benzene)

Positive ligands : Carry positive charge

e.g. $N_2H_5^+$: Hydrazinium.
NO^+ : Nitrosylium or Nitrosonium

Denticity : Denticity of a ligand represents number of co-ordinate bonds that it can form simultaneously to same central metal atom/ion.

(II) On the Basis of Denticity

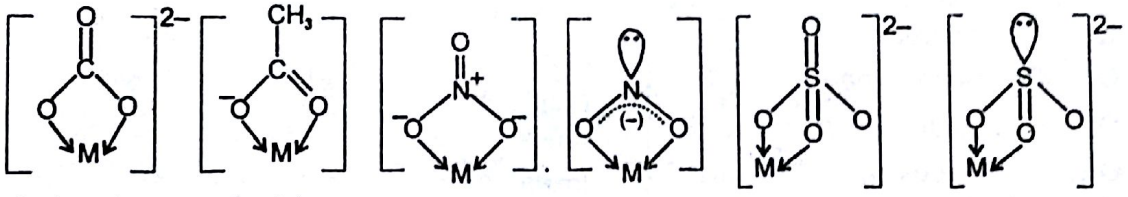
→ **Monodentate ligands : (with their IUPAC names)**

$\underline{H}^-$	: Hydrido	$\underline{CH_3O}^-$	: Methoxo / Methoxido	$\underline{N}^{3-}$	: Nitrido
$\underline{F}^-$	: Flouro/Flourido	$\underline{Me_2O}$	: Dimethyl ether	$\underline{NH_3}$	: Ammine
$\underline{Cl}^-$	: Chloro/Chlorido	$\underline{Me_2S}$	: Dimethyl thioether	$\underline{NH_2}^-$	: Amido
$\underline{Br}^-$	: Bromo/Bromido	$\underline{O}CN^-$	: Cyanato	$\underline{NH}^{2-}$	: Imido
$\underline{I}^-$	: Iodo/Iodido	$\underline{N}CO^-$	: Isocyanato	$H_2\underline{N}-\underline{NH_2}$	: Hydrazine
$\underline{O}^{2-}$	: Oxo/Oxido	$\underline{S}CN^-$	: Thiocyanato/Thiocyanato - S	$\underline{NO_2}^-$	: Nitro/Nitrito-N
$\underline{O_2}^{2-}$	: Peroxo/peroxido	$\underline{N}CS^-$	: Isothiocyanato/Thiocyanato-N	$\underline{O}NO^-$	: Nitrito/Nitrito-O
$\underline{O_2}^-$	: Superoxo/Superoxido	$\underline{SO_4}^{2-}$	: Sulphato	$\underline{NO_3}^-$	: Nitrato
$\underline{O}H^-$	: Hydroxo/Hydroxido	$\underline{SO_3}^{2-}$	: Sulphito	$\underline{C_5H_5N}$	: Pyridine
$\underline{O_2}$	: Dioxygen	$\underline{S_2O_3}^{2-}$	: Thiosulphato	$CH_3\underline{COO}^-$	: Acetato
$\underline{H_2O}$	: Aqua	$\underline{N_3}^-$	: Azido	$\underline{CO_3}^{2-}$	: Carbonato
$\underline{C}O$	: Carbonyl	$\underline{N}O$	: Nitrosyl	$\underline{SnCl_3}^-$	: Trichlorostannito
		$\underline{C}N^-$	: Cyano / Cyanido		
		$\underline{N}C^-$	: Isocynido		

(Underlined Atoms are donar site of ligands.)

Note : In IUPAC naming, negative ligand has Suffix '–o' and positive ligand has Suffix '–ium' and neutral ligand has no Suffix, but negative organic lignads having 'yl' suffix of hydrocarbon origin are not replaced by '–o'

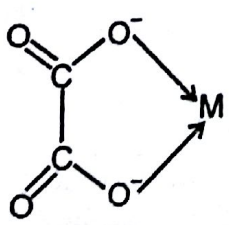
Among these monodentate ligands, some ligands like SO_3^{2-}, SO_4^{2-}, $S_2O_3^{2-}$, NO_2^-, NO_3^-, CH_3COO^-, CO_3^{2-} can also act as bidentate ligands, therefore these ligands are also called **flexidentate ligands** because of their variable denticity. Such monodentate ligands form unstable four membered ring when they act as bidentate ligands however their preferred denticity is one.



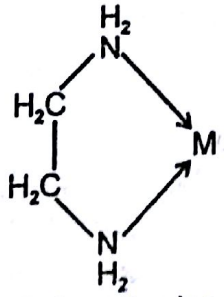
Carbonate Acetate Nitrate Nitrite Sulphate Sulphite

→ **Polydentate ligands :** Such ligands are capable of donating two or more lone pair e⁻s to same central metal atom/ion through co-ordinate bonds. While doing so they form 5/6 membered stable ring. Hence such ligands are also called chelating ligands.

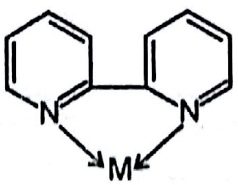
(a) Bidentate Ligands : Having two donor atoms/coordination sites.



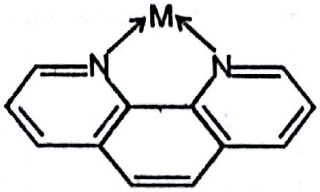
Oxalate (ox)
(Symmetrical ligand)



Ethylenediamine (en)
(symmetrical ligand)

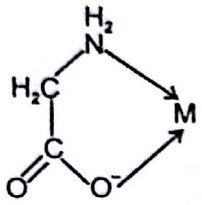


Dipyridine (dipy)
(symmetrical ligand)

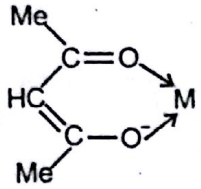


Phenanthrolene (phen)
(Symmetrical ligand)

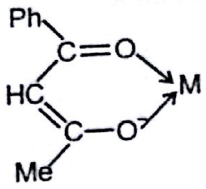
to



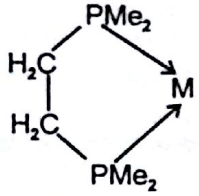
Glycinate (gly)
(unsymmetrical ligand)



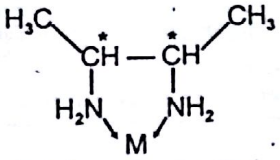
Acetylacetonate (acac)
(symmetrical ligand)



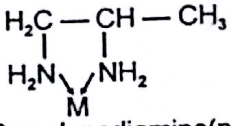
Benzoylacetonate (bcac)
(unsymmetrical ligand)



1, 2 bis (dimethylphosphino)
ethane. (dmpe)
(symmetrical ligand)

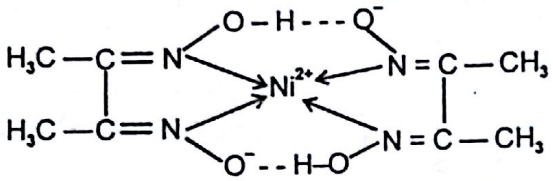


Butylenediamine(bn)
(symmetrical ligand)



Propylenediamine(pn)
(unsymmetrical ligand)

$NiCl_2 + 2DMG \rightarrow [Ni(DMG)_2]\downarrow$(Rosy Red ppt.)



bis (dimethylglyoximato)nickel(II)
Number of formed rings = 4
2 rings : 5 membered
2 rings : 6 membered

In DMG donor sites are both N-atoms rather than one O and one N-atom because in this case formed complex get extra stability due to formation of additional stable rings through H-bonds.

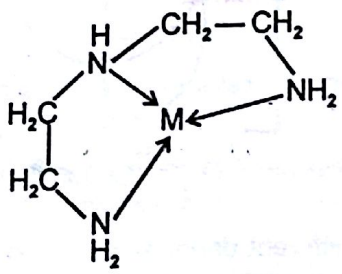
Symmetrical ligands : Ligands having plane of symmetry (P.O.S.) w.r.t. donor sites and passing through central metal atom/ion are called symmetrical ligands. e.g. ox , en , dipy , phen , acac.

Unsymmetrical ligands : Ligands having no plane of symmetry (P.O.S.) w.r.t. donor sites and passing through central metal atom/ion are called unsymmetrical ligands. e.g. DMG , gly , bcac , pn.

Note : No. of rings formed by a polydentate ligand = (denticity) – 1

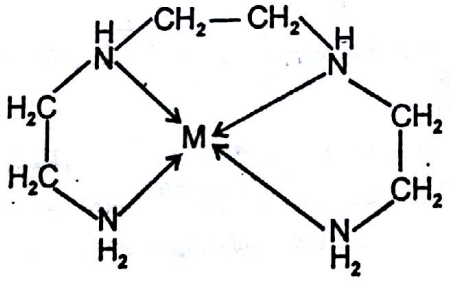
TYPES OF POLYDENTATE LIGANDS

(b) Tridentate Ligand : Having three donor atoms/coordination sites.



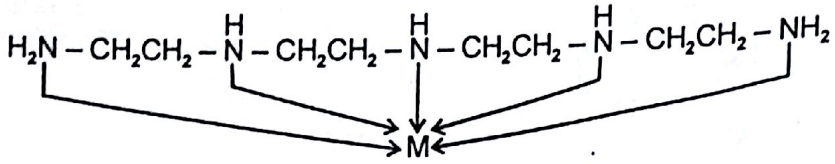
Diethylenetriamine (dien)

(c) Tetradentate Ligands : Having four donor atoms/coordination sites.



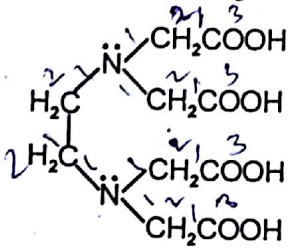
Triethylenetetraamine (trien)

(d) Pentadentate ligand :



tetraethylenepentaamine (teten)

(e) Hexadentate Ligand :



(H_4EDTA)

$H_4EDTA \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} EDTA^{4-}$

(H_4EDTA) (water insoluble) Ethylenediaminetetraacetic acid

$EDTA^{4-}$ (water soluble) Ethylenediaminetetraacetate

Flexidentate character of $EDTA^{4-}$

Ligands		Denticity
H_4EDTA		2
H_3EDTA^-	[ethylenediamineacetate]	3
H_2EDTA^{2-}	[ethylenediaminediacetate]	4
$HEDTA^{3-}$	[ethylenediaminetriacetate]	5
$EDTA^{4-}$	[ethylenediaminetetraacetate]	6

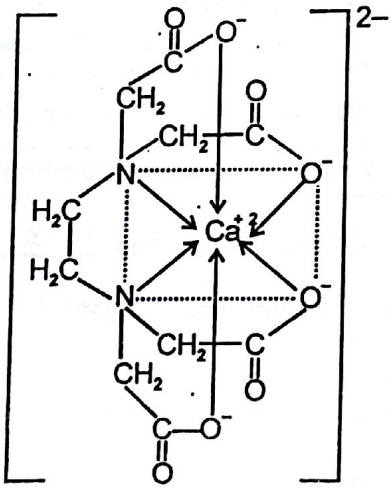
As pH of solution decreases denticity of $EDTA^{4-}$ also decreases

* $EDTA^{4-}$ always gives octahedron geometry due to six coordinaion sites.

No. of N – Ca – N Bond angles = 1

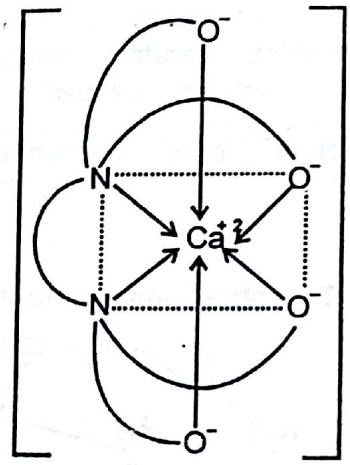
No. of O – Ca – O Bond angles = 6

No. of N – Ca – O Bond angles = 8



$[Ca(EDTA)]^{2-}$

OR



$[Ca(EDTA)]^{2-}$

(III) Ambidentate Ligands : When negative ligands have at least two different donor sites, but at a time of coordination one donor site is used are called ambidentate ligands with monodentate behaviour. However Ambidentate ligands having sp^2 or sp^3 hybridized central atom, can also act as flexidentate ligands.

M ← $\underline{S}CN^-$: Thiocyanate - S
M ← $\underline{N}CS^-$: Thiocyanate - N
M ← $\underline{O}CN^-$: Cyanate
M ← $\underline{N}CO^-$: Isocyanate
M ← $\underline{C}N^-$: Cyanide
M ← $\underline{N}C^-$: Isocyanide

These ambidentate Ligands show monodentate behaviour.

$M \leftarrow NO_2^-$: Nitrite - N
$M \leftarrow ONO^-$: Nitrite - O
$M \leftarrow S_2O_3^{2-}$: Thiosulphate -S
$M \leftarrow OS_2O_2^{2-}$: Thiosulphate - O
$M \leftarrow SO_3^{2-}$: Sulphite - S
$M \leftarrow OSO_2^{2-}$: Sulphite - O
$M \leftarrow NOS^-$: Thionitrite - N
$M \leftarrow ONS^-$: Thionitrite - O
$M \leftarrow SNO^-$: Thionitrite - S

These ambidentate Ligands can also show flexidentate behaviour as they are Non-linear.

(III) Classical (Normal) and Nonclassical (π-Acid) ligands.

Ligands

Classical Ligands ($M \xleftarrow{\sigma} L$)
(Normal ligands)

When ligands can only donate their electron pair to the vacant orbital of the central metal atom/ion through coordinate bond are called classical (normal) ligands.

eg. H^-, OH^-, NH_3, H_2O, NH_2^-, NH^{2-}, F^-, CH_3^-, $C_2H_5^-$, $MeNH_2$

Types of Complexes :

On the basis of M – L interaction complex compounds are of three types

(i) σ-Bonded complex compound :

(Having (M) $\xleftarrow[\text{donation}]{\sigma}$ (L) interaction)

eg. $[FeF_6]^{3-}$, $[Ag(NH_3)_2]^+$, $[Fe(H_2O)_6]^{3+}$

$R-Mg-X$, $Zn(C_2H_5)_2$, $Pb(C_2H_5)_4$(TEL)

σ-Bonded OMC

(ii) σ and π-bonded complex compound

(Having (M) $\underset{\pi\text{-acceprance}}{\overset{\sigma\text{-donation}}{\rightleftharpoons}}$ (L) interaction)

eg. $\underbrace{M(CO)_x}_{OMC}$, $[Fe(CN)_6]^{4-}$, $[Ag(CN)_2]^-$

(iii) π-bond complex compound

(Having (M) $\underset{\pi\text{-acceprance}}{\overset{\pi\text{-donation}}{\rightleftharpoons}}$ (L) interaction)

eg. $Cr(C_6H_6)_2$, $Fe(\eta^6\text{-}C_5H_5)_2$ (ferrocene), $K[PtCl_3(\eta^2 - C_2H_4)]$ (Zise's salt)

π-Bonded OMC

Non classical Ligands ($M \underset{\pi}{\overset{\sigma/\pi}{\rightleftharpoons}} L$)

(π - acid / π - acceptor ligand)

When ligands donate their electron pair to the vacant orbital of central metal atom/ion and simultaneously accept electron pair from filled d-atomic orbital of central metal atom/ion through back bond either into vacant atomic orbital of donor atom or into π* MO of ligand are called non-classical (π-acid) ligands.

$M \underset{\pi}{\overset{\sigma}{\rightleftharpoons}} L$

Ligands of such category are :
CO, NO, NO^+, N_2,
PPh_3, PF_3, CN^-
σ-allyl, σ-cyclopentadienyl

$M \underset{\pi}{\overset{\pi}{\rightleftharpoons}} L$

Ligands of such category are :
η^2 - $CH_2 = CH_2$ (π-ethene)
η^6 - C_6H_6 (π-benzene)
η^5 - $C_5H_5^-$ (π-cyclopentadienyl)
η^3 - $CH_2 = CH - CH_2^-$ (π-allyl)
η^4 - $CH_2 = CH - CH = CH_2$ (π-butadiene)

Organometallic Compound : OMC are type of complex compunds with metal carbon linkage M ← C linkage (where M : mostly metal / may be non-metal or metalloid with less EN value than carbon and C atom is of alkyl/aryl group including CO)

NOTE : All OMC are complex compound but all complex compounds are not OMC.

Co-ordination number (C.N.) of metal cation

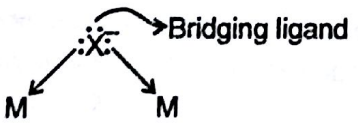
Total number of e^- pairs accepted by central metal atom /ion from donor atom of surrounding ligands is called C.N. of central metal atom/ion. It is also called secondary valency of central metal atom / ion.

Table for Coordination Number of metal cation in a particular oxid^n state (Stable oxid^n state)

Monovint Cation	C.N.	Divalent Cation	C.N.	Trivalent Cation	C.N.	Tetravalent Cation	C.N.	Other Cation	C.N.
Cu^+	2, 4	Ti^{2+}	4, 6	Sc^{3+}	6	Ni^{4+}	6	Cr^{6+}	6
Ag^+	2, 4	V^{2+}	4, 6	Ti^{3+}	6	Pd^{4+}	6	Os^{8+}	6
Au^+	2, 4(rare)	Cr^{2+}	4, 6	V^{3+}	6	Pt^{4+}	6	Os^{6+}	6
Cr^+	6(rare)	Mn^{2+}	4, 5, 6	Cr^{3+}	6	Pb^{4+}	6		
		Fe^{2+}	4, 6	Mn^{3+}	6	Sn^{4+}	6		
		Co^{2+}	4, 6	Fe^{3+}	6	Mo^{4+}	6		
		Ni^{2+}	4, 5, 6	Co^{3+}	6				
		Cu^{2+}	4, 5, 6(rare)	Rh^{3+}	6				
		Zn^{2+}	4(Alwys Td)	Ir^{3+}	6				
		Cd^{2+}	4, 6	Ru^{3+}	6				
		Hg^{2+}	2, 4	Os^{3+}	6				
		Pd^{2+}	4(Alwys Sq.pl.)	Ag^{3+}	4(Alwys Sq.pl.)				
		Pt^{2+}	4(Alwys Sq.pl.)	Au^{3+}	4(Alwys Sq.pl.)				
		Pb^{2+}	4	Al^{3+}	4, 6				
		Sn^{2+}	4	Bi^{3+}	4, 6				
		Ca^{2+}	4, 6						
		Mg^{2+}	4, 6						
		Be^{2+}	4(Alwys Td)						

Note :

1. NH_4^+ cation never act as ligand.
2. Metal cation with more than +2 oxidation state usually have their stable C.N. = 6
3. Monodentate ligands having more than one lone pair on donor site can act as bridging ligands except CO.



4. Neutral ligands in which two different atoms are having lone pairs, then preferential donor site is less electronegative atom eg. CO, NO.
5. N_2H_4 never act as bidentate ligand because it will form unstable three membered ring with central metal atom/ion eg. $H_2N-\times-NH_2$ (M)
6. Ligands containing carbon and nitrogen atom as donor sites are called strong field ligands (SFL) and rest of them are considered as weak field ligands (WFL) in spectrochemical series.
7. $Cr^{3+} \longrightarrow$ Coordination Number (C.N.) = 6
   $[Cr(NH_3)_5(SO_4)]^+$: SO_4^{2-} act as monodentate ligand.
   $[Cr(NH_3)_4(SO_4)]^+$: SO_4^{2-} act as bidentate ligand.