

Classification of ligands

The ligands are lewis bases, metals are lewis acids and the complexes are lewis acid-base adducts.

Ligands can be classified on different basis:

- Organic and inorganic nature of the ligands;
- Hard soft character of the ligands;
- Nature of the donor electrons on the ligands;
- Number of binding sites (i.e. denticity) of the ligands;
- Mode of binding of the ligands to the metal centre;
- Charge bearing properties of the ligands;

(i) Depending on the organic and inorganic nature of the ligand, they may be classified as organic and inorganic ligands: Examples:

Organic ligands: oxalate (ox^{2-}), ethylene diamine (en), 2,2'-dipyridyl (dpy) etc.

Inorganic ligands: H_2O , OH^- , NH_3 , halides, carbonates, etc.

(ii) Depending on the hard soft character:

Hard ligands: NH_3 , H_2O , OH^- , F^-

Soft ligands: CO , CN^- , C_2H_4 , SCN^- , etc

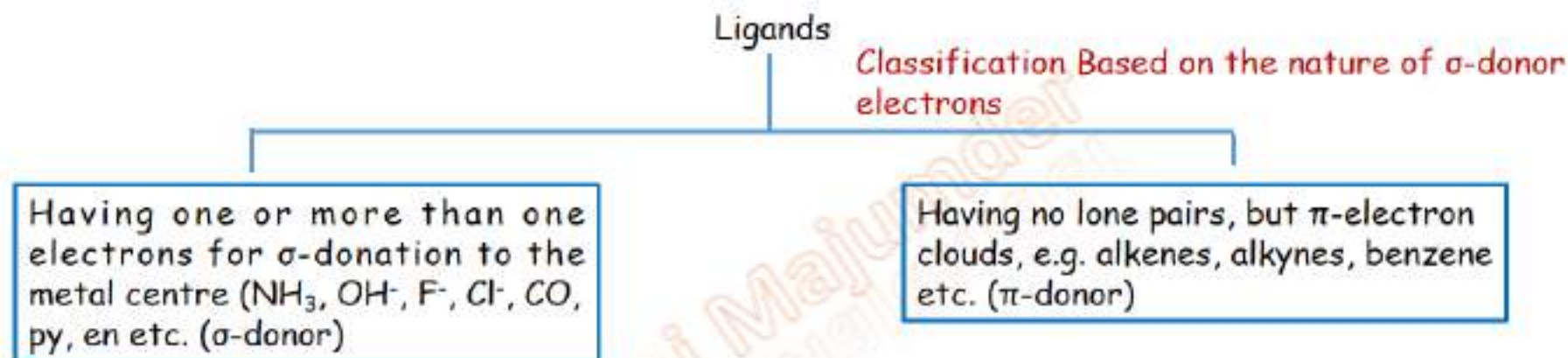
(iii) Depending on the charge:

Anionic ligands: Halides, OH^- , CO_3^{2-} , $\text{C}_2\text{O}_4^{2-}$ etc.

Neutral ligands: NH_3 , dpy, en, py, H_2O

Cationic ligands: NO^+ , $\text{NH}_2\text{-NH}_3^+$ (hydrazinium ion)

(iv) Depending on the nature of donor electrons:



Note:

- Some ligands possess no lone pair of electrons but π -electrons for donation to the metal centre for σ -bonding. This bond is known as μ -bond.
- Ligands having π -electron clouds for σ -bonding always carry vacant antibonding molecular orbitals that can receive electrons from the metal centres, called π -acids ligands.
- Similarly CO , CN^- are also called π -acid ligand.

Few important points:

- The π -acid ligands can stabilize the low oxidation state of the metal centres. The accumulated electrons on the metal centre from the ligand \rightarrow metal σ -donation, produces an unfavourable situation for the low oxidation state of the metal centre as the electropositive metal centre does not like the accumulation of much electron cloud. The π -acidic character (i.e. removal of electron cloud from the metal centre through the metal \rightarrow ligand π -back bonding) of the π -acid ligand can balance the unfavourable situation developed from the σ -donation of the ligands.
- For the π -acid ligands, both the ligand \rightarrow metal σ -donation and metal \rightarrow ligand π -back bonding go on simultaneously. These two bondings (ie. σ - and π -bonding) generally act in a synergistic fashion, i.e. if the σ -donation is favoured then the π -acceptance is also favoured.
- The π -acid ligands are generally the strong field ligands.
- Ligands having more than one lone pair may utilize the lone pair of lower energy (degeneracy of the lone pairs may be removed through splitting) for σ -donation. While the other lone pairs of relatively higher energy may participate in π -donation. Such π -donor ligands (OH^-) are called weak field ligands.
- The pure σ -donor ligands and the ligands with the π -donor properties can stabilize the higher oxidation state of the metal centres. Such ligands are generally weak field ligands.

Ligands

Based on the nature of metal ligand bond interaction

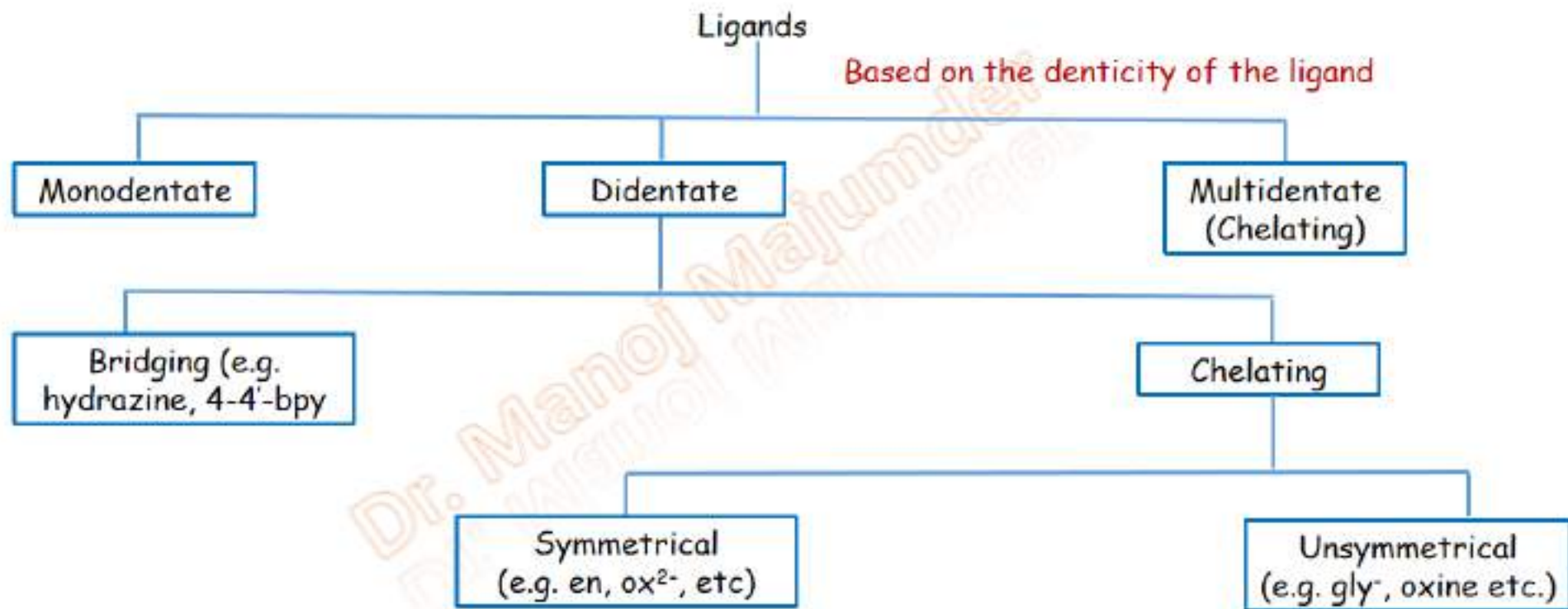
Only metal \rightarrow ligand σ -bonding σ -bonding (i.e. ligands having no suitable orbital for π -bonding with the metal centre), e.g. NH_3 , H_2O , en, edta^{4-} , trien etc.

Having no lone pairs, but π -electron clouds, e.g. alkenes, alkynes, benzene etc. (π -donor)

With suitable vacant orbitals to receive back the electrons from the metal centre (i.e. σ -donor and π -acceptor). These are called π -acid ligands, e.g. PR_3 , CN^- , CO , bpy, alkenes, benzene etc.

With suitable filled orbitals for π -donation to the metal centre (i.e. σ -donor and π -donor), These are called π -donor ligands. E.g. OH^- , F^- , I^- etc.

Ligands based on the number of donor sites and coordination behavior:



Examples:

Monodentate ligands:

<i>Formula (donor site bold)</i>	<i>Name of the ligand when present in complex</i>	<i>Formula (donor site bold)</i>	<i>Name of the ligand when present in complex</i>
Neutral molecules		Anions**	
H ₂ O	aqua	F ⁻	fluorido
NH ₃	ammine	Cl ⁻	chlorido
CH ₃ NH ₂	methylamine	Br ⁻	bromido
CO	carbonyl	I ⁻	iodido
NO	nitrosyl	OH ⁻	hydroxido
CS	thiocarbonyl	CN ⁻	cyanido-C
C ₅ H ₅ N	pyridine (py)	CN ⁻	cyanido-N (<i>i.e.</i> isocyanido)
PPh ₃	triphenyl phosphane	OCN ⁻	cyanato-O
AsR ₃	trialkyl arsane	OCN ⁻	cyanato-N (<i>i.e.</i> isocyanato)
(C ₂ H ₅) ₂ O	diethyl ether	SCN ⁻	thiocyanato-S

Examples:

Monodentate ligands:

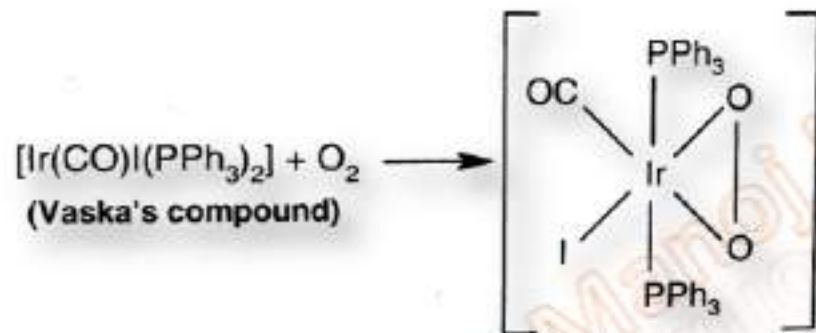
<i>Formula (donor site bold)</i>	<i>Name of the ligand when present in complex</i>	<i>Formula (donor site bold)</i>	<i>Name of the ligand when present in complex</i>
NF_3	nitrogen trifluoride	SCN^-	thiocyanato-N (<i>i.e.</i> isothiocyanato)
C_2H_4	ethene (ethylene)	NO_2^-	nitrito-N (nitro)
CH_3NC	methylisocyanide*	NO_2^-	nitrito-O
Cations		H^-	hydrido
NO^+	nitrosylium	N_3^-	azido
$\text{NH}_2\text{N}^+\text{H}_3$	hydrazinium	O^{2-}	oxido
		CH_3COO^-	acetato
		N^{3-}	nitrido
		NH_2^-	amido
		NO_3^-	nitrato
		NOS^-	nitrosylsulfido

Didentate ligands:

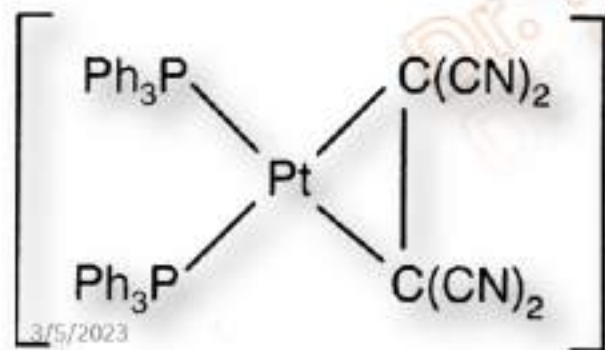
Didentate bridging ligands (e.g. hydrazine, pyrazine, peroxide, 4,4'-bipyridine)

Didentate chelating ligands (e.g. ethylene diamine, 2,2'-bipyridine)

Three membered chelate rings

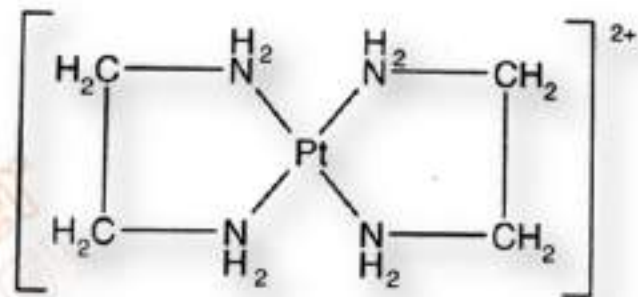


$\eta^2\text{-O}_2^{2-}$ (peroxo group) here acts as a didentate chelate ligand.



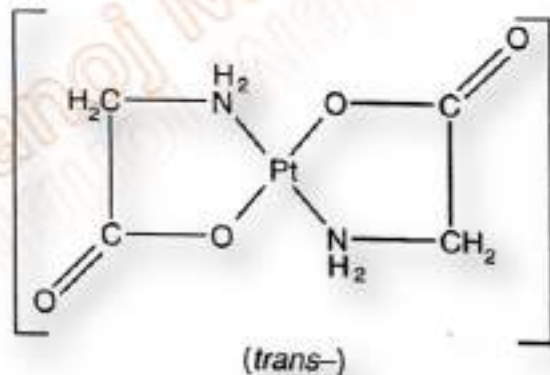
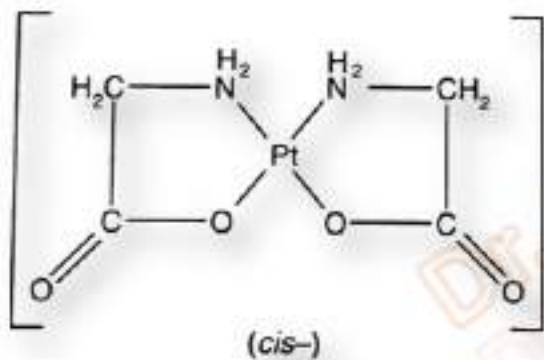
Here, $\eta^2\text{-C}_2(\text{CN})_4$ acts as a didentate chelate ligand.

Symmetrical didentate ligands (AA): en, acac, pn, diphos, glyme, bpy, phen, diars etc.



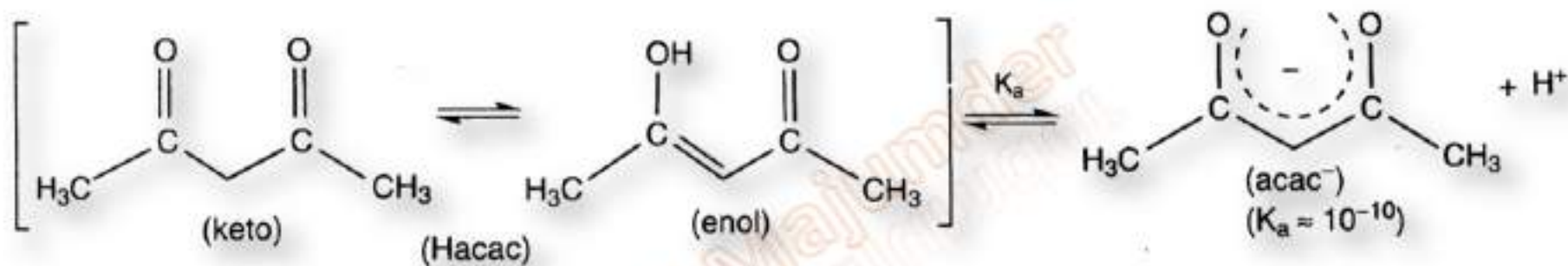
Unsymmetrical didentate ligands (AB): gly, oxine, pic etc.

No isomer



Lead to isomerism

Many ligands needs deprotonation for chelation:



Flexidentate ligands:

In some cases for the polydentate ligands (and even for the didentate ligands like oxyanions RCO_2^- , CO_3^{2-} , NO_3^- , SO_4^{2-} etc), all the available binding sites of a particular ligands may not participate in making the metal-ligand linkage. In such cases, the denticity of the ligands depends on the experimental conditions. This variable denticity character of the ligands is referred to as the flexidentate character of the ligands.

Examples of different types of ligands:

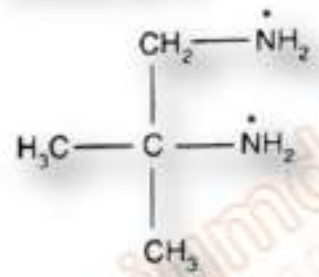
<i>Name of the ligand when present in complex</i>	<i>Abbreviation</i>	<i>Formula (donor sites denoted by *)</i>	<i>Donor Sites</i>
Carbonato	—		(O,O)
Nitrato	—		(O,O)
Sulfato	—		(O,O)
Carboxylato	—		(O,O)

<i>Name of the ligand when present in complex</i>	<i>Abbreviation</i>	<i>Formula (donor sites denoted by *)</i>	<i>Donor Sites</i>
Peroxido	—	$\begin{array}{c} \cdot\text{O}^- \\ \\ \cdot\text{O}^- \end{array}$	(O,O)
Ethylenediamine (en) or, 1,2-ethanediamine or, ethane-1,2-diamine	(en)	$\begin{array}{c} \text{H}_2\text{C} - \dot{\text{N}}\text{H}_2 \\ \\ \text{H}_2\text{C} - \dot{\text{N}}\text{H}_2 \end{array}$	(N,N)
Propylenediamine or, 1,2-propanediamine or, propane-1,2-diamine	(pn)	$\begin{array}{c} \text{H}_3\text{C} - \overset{2}{\text{C}}\text{H} - \dot{\text{N}}\text{H}_2 \\ \\ \overset{1}{\text{C}}\text{H}_2 - \dot{\text{N}}\text{H}_2 \end{array}$	(N,N)
Butylenediamine (may be <i>dl</i> and <i>meso</i>) or, butane-2,3-diamine	(bn)	$\begin{array}{c} \text{H}_3\text{C} - \text{C}\text{H} - \dot{\text{N}}\text{H}_2 \\ \\ \text{H}_3\text{C} - \text{C}\text{H} - \dot{\text{N}}\text{H}_2 \end{array}$	(N,N)

<i>Name of the ligand when present in complex</i>	<i>Abbreviation</i>	<i>Formula (donor sites denoted by *)</i>	<i>Donor Sites</i>
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Isobutylenediamine

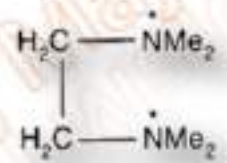
(i-bn)



(N,N)

N,N,N',N'-tetramethylethane-1,2-diamine

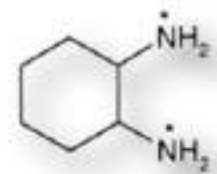
(tmen)



(N,N)

1,2-cyclohexanediamine
or, 1,2-diaminocyclohexane

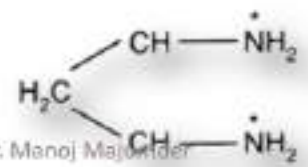
(chxn)



(N,N)

Trimethylenediamine
or, 1,3-diaminopropane
or, propane-1,3-diamine

(tn or tmd)



(N,N)

Name of the ligand
when present in
complex

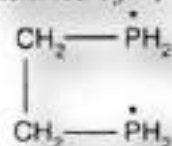
Abbreviation

Formula
(donor sites
denoted by *)

Donor Sites

Ethylenediphosphane
or, ethane-1,2-diylbis-
(phosphane)

(diphos)



(P,P)

Ethane-1,2-diylbis-
(dimethylphosphane)

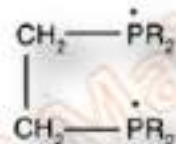
dmpe
(R = Me)

Ethane-1,2-diylbis-
(diethylphosphane)

depe
(R = Et)

Ethane-1,2-diylbis-
(diphenylphosphane)

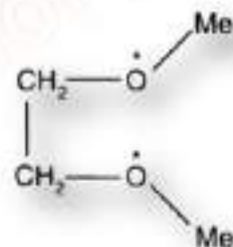
dppe
(R = Ph)



(P,P)

Dimethylglycol

(glyme)

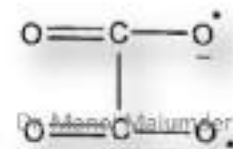


(O,O)

Oxalato

(ox)

(H₂ox)⁺

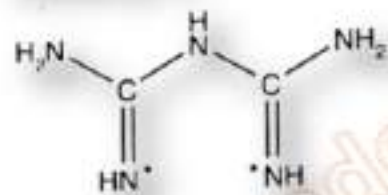


(O,O)

Name of the ligand when present in complex	Abbreviation	Formula (donor sites denoted by *)	Donor Sites
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Biguanide

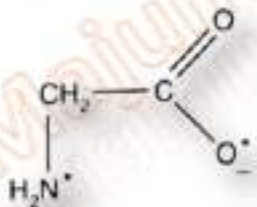
(Hbig)



(N,N)

Glycinato

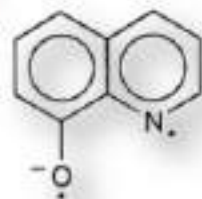
(gly)
(Hgly)*



(N,O)

8-Hydroxyquinolinato
or. oxinato
or. 8-quinolinolato

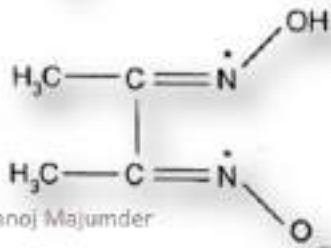
(oxinc)
(Hoxinc)*



(N,O)

Dimethylglyoximato

(Hdmg)
(H2dmg)*

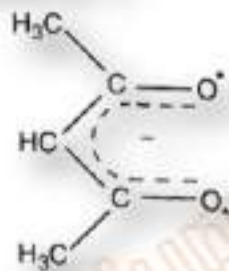


(N,N)

Name of the ligand when present in complex	Abbreviation	Formula (donor sites denoted by *)	Donor Sites
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Acetylacetonato
or, 2,4-pentanedionate

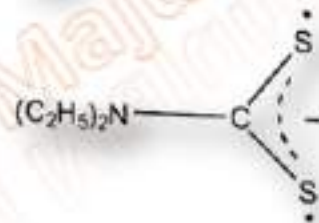
(acac)
(Hacac)*



(O,O)

N,N-diethyldithiocarbamate

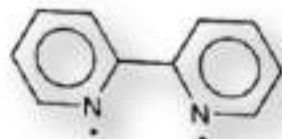
(dtc)
(Hdtc)*



(S,S)

2,2'-dipyridyl or
2,2'-bipyridyl (in old
literature, it is denoted
by bipy or dipy)

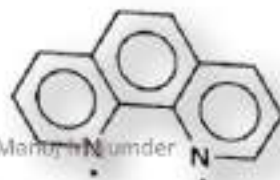
(dpy, bpy)



(N,N)

1,10-phenanthroline

(phen)



(N,N)