COORDINATION COMPOUNDS

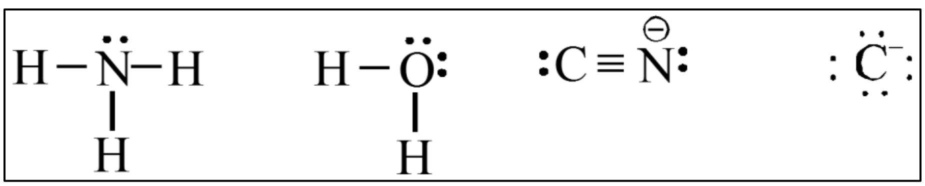
DEFINITIONS OF SOME IMPORTANT TERMS PERTAINING TO COORDINATION COMPOUNDS

❖ **CENTRAL METAL ATOM / ION**

Central ion acts as an acceptor (Lewis's acid) and has to accommodate electron pairs donated by the donor atom of the ligand, it must have empty orbitals. This explains why the transition metals having empty d-orbitals form co-ordination compounds readily. Thus, in complexes $[Ni(NH_3)_6]^{2+}$ and $[Fe(CN)_6]^{3-}$, Ni^{2+} and Fe^{3+} respectively are the central metal ions.

LIGANDS

Species which are directly linked with the central metal atom/ ion in a complex ion are called ligands. The ligands are attached to the central metal atom /ion through co-ordinate or dative bond free ligands have at least one lone pair.

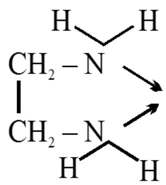


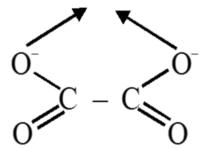
The ligands are thus Lewis bases and the central metal ions / atoms are Lewis acids.

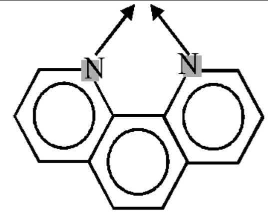
Ligands can be of following types depending on the number of donor atoms present in them :

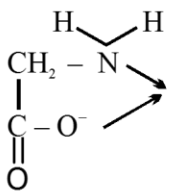
(i) **Mono / Unidentate Ligands** They have one donor atom, i.e., they can donate only one electron pair to the central metal atom /ion eg., F^-, Cl^-, Br^-, H_2O, NH_3, CN^-,NO_2^-, OH^-, CO etc.

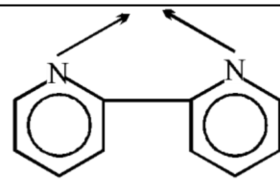
(ii) **Bidentate Ligands** Ligands which have two donor atoms and have the ability to link with the central metal atom /ion at two position are called bidentate ligands e.g.

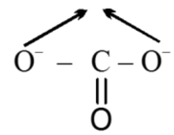

ethylenediamine (en)


oxalate (ox)

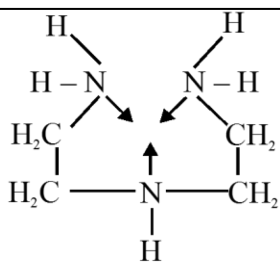

1,10-phenanthroline (phen)

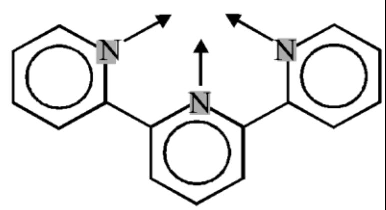

glycinate (Gly)


2,2-dipyridine (dipy)

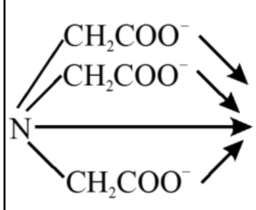

carbonate

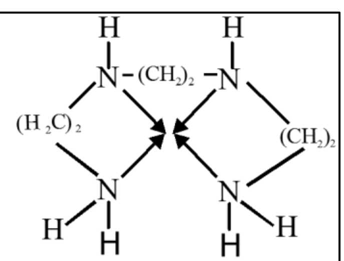
(iii) Tridentate Ligands Ligands having three donor atoms are called tridentate ligands. Examples are


diethylene triamine (dien)

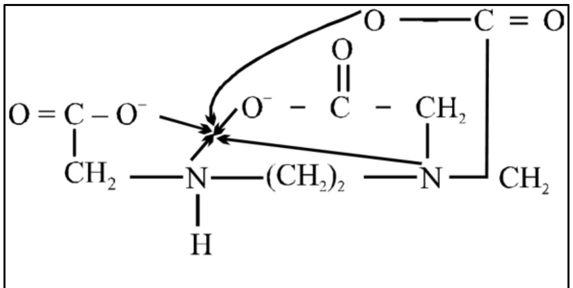

2,2'2"-terpyridine (terpy)

(iv) Tetradentate Ligands These ligands possess four donor atoms. Examples are


Nitriloacetate

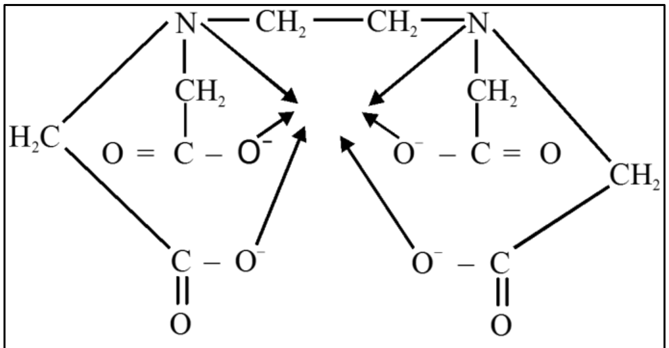

Triethylene tetramine (trien)

(v) Pentadentate Ligands They have five donor atoms. For example, ethylenediamine triacetate ion.



ethylendiamine triacetate ion

(vi) **Hexadentate Ligands** They have six donor atoms. The most important example is ethylenediamine tetraacetate ion.



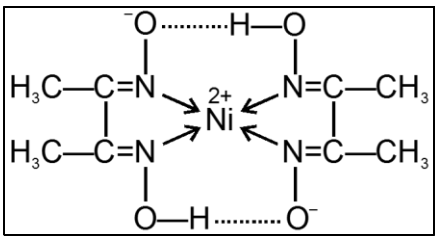
ethylenediamine tetraacetate (EDTA)

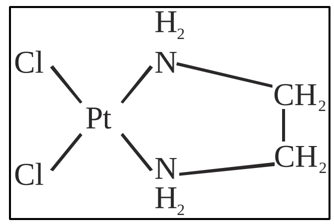
(vii) **Ambidentate ligands:** There are certain ligands which have two or more donor atoms but in forming complexes, only one donor atom is attached to the metal / ion. Such ligands are called ambidentate ligands. Some examples of such ligands are

M	$\longleftarrow NO_2^-$	M	$\longleftarrow ONO^-$
	nitrite – N		nitrite –O
M	$\longleftarrow CN^-$	M	$\longleftarrow NC^-$
	cyanide		isocyanide
M	$\longleftarrow SCN^-$	M	$\longleftarrow NCS^-$
	thiocyanide		isothiocyanide

(viii) Ligands having more than two donor atoms are called polydentate or multidentate ligands. Multidentate ligands are known as a chelating ligand, it results in the formation of a stable cyclic ring thus, the complexes formed are also called chelates. Chelating ligands are usually organic compounds.

(ix) Chelate ligand: Chelate ligand is a di or polydentate ligand which uses its two or more donor atoms to bind a single metal ion producing a ring. The complex formed is referred to as a chelate complex and the process of chelate formation is called chelation. The number of such ligating groups is called the denticity of the ligand. Chelate rings may have any number of atoms; the most common contain five or six atoms, including the metal ion. Smaller rings have smaller angles and distances that lead to strain; larger rings frequently result in crowding both within the ring and between adjoining ligands. Some ligands can form more than one ring; ethylene diamine tetraacetate (EDTA) can form five by using the four carboxylate groups and the two amine nitrogens as given in the structures.





The chelate complexes are more stable than similar complexes containing unidentate ligands. The greater stability of the chelate complex in comparison to normal complex is called chelate effect. For example,

$$Ni^{2+}(aq) + 6\,NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq) \quad K_{formation} = 10^8$$

$$Ni^{2+}(aq) + 3\,NH_2CH_2CH_2NH_2(aq) \rightleftharpoons [Ni(en)_3]^{2+}(aq) K_{formation} = 10^{18}$$

The five and six membered rings are more stable.

Denticity and Chelation:

Common Monodentate Ligands

Common Name	IUPAC Name	Formula
methyl isocyanide	methylisocyanide	CH_3 NC
triphenyl phosphine	triphenyl phosphine/triphenyl phosphane	PPh_3
pyridine	pyridine	C_5H_5N(PY)
ammonia	ammine	NH_3
methyl amine	methylamine	$MeNH_2$
water	aqua or aquo	H_2O
carbonyl	carbonyl	CO
thiocarbonyl	thiocarbonyl	CS

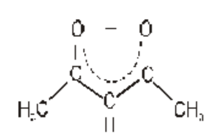
nitrosyl	nitrosyl	NO
fluoro	fluoro or fluorido*	F^-
Chloro	chloro or chlorido*	Cl^-
bromo	bromo or bromido*	Br^-
iodo	iodo or iodido*	I^-
cyano	cyanido or cyanido-C* (C-bonded)	Cn^-
Isocyano	isocyanido or cyanido-N* (N-bonded)	NC^-
thiocyano	thiocyanato-S(S-bonded)	SCN^-
isothiocyano	thiocyanato-N(N-bonded)	NCS^-
cyanato (cyanate)	cyanato-O (O-bonded)	OCN^-
isocyanato (isocyanate)	cyanato-N (N-bonded)	NCO^-
hydroxo	hydroxo or hydroxido*	OH^-
nitro	nitrito–N (N–bonded)	NO_2^-
nitrito	nitrito–O (O–bonded)	ONO^-
nitrate	nitrato	NO_3^-
amido	amido	NH_2^-
imido	imido	NH^{2-}
nitride	nitrido	N^{3-}
azido	azido	NO_3^-
hydride	hydrido	H^-
oxide	oxido	O^{2-}
peroxide	peroxido	O_2^{2-}
superoxide	superoxido	O_2^-
acetate	acetato	CH_3COO^-
sulphate	sulphato	SO_4^{2-}
thiosulphate	thiosulphato	$S_2O_3^{2-}$
sulphite	sulphito	SO_3^{2-}
hydrogen sulphite	hydrogensulphito	HSO_3^-
sulphide	sulphido or thio	S^{2-}
hydrogen sulphide	hydrogensulphido or mercapto	HS^-
thionitrito	thionitrito	$(NOS)^-$
nitrosylium	nitrosylium or nitrosonium	NO^+
nitronium	nitronium	SNO_2^+

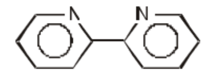
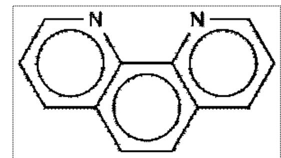
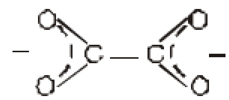
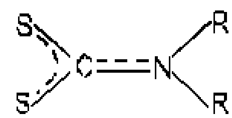
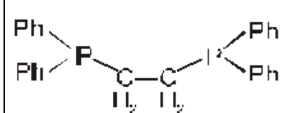
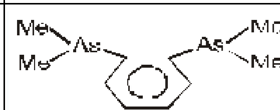
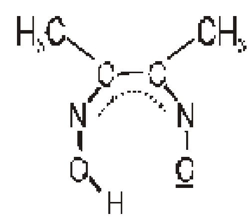
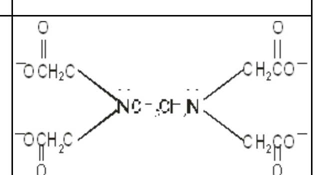
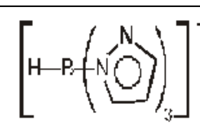
*The 2004 IUPAC draft recommends that anionic ligands will end with-ido.

Common Chelating Amines

Chelating Points	Common Name	IUPAC Name	Abbre-viation	Formula
bidentate	propane diamine	1,2-propane-diamine	pn	$NH_2{-}CH{-}CH_2{-}NH_2$ (with CH_3 on CH)
Tri-dentate	Diethylene-triamine	[N-(2-aminoethyl)-1 2-ethane-diamine or diethylene-triamine	dien	$NH_2CH_2CH_2NHCH_2CH_2NH_2$
Tetra-dentate	Triethylene-tetramine	[N, N'-bis-(2-aminoethyl)-1, 2-ethane-diamine or triethylene-tetraamine	trien	$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
	Triamino-triethylamine	-tris(2-aminoe-thyl) amine.	tren	$NH_2CH_2CH_2NCH_2CH_2NH_2$ (with $CH_2CH_2NH_2$ on N)
Penta-dentate	tetraethyl-lenepen-taamine	1,4,7,10 pentaaza-tridecane or tetraethyl-lenepentaamine		$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$
Hexa-dentate	Ethy-lenediamine-tetraacetate	1,2–ethanediol (dinitrilo) tetraacetate or ethylenediamine-tetraacetate	EDTA	$^-OOCH_2C$ CH_2COO^- \ / NCH_2CH_2N / \ $^-OOCH_2C$ CH_2COO^-

Common Multidentate (Chelating) Ligands

Common Name	IUPAC Name	Abbreviation	Formula	Structure
Acetylace-tonato	2,4-pentanediono or acetylaceto-nato	acac	$CH_3COCHCOCH_3^-$	

2,2'-bipyridine	2,2'-bipyridyl	bipy	$C_{10}H_8N_2$	
1,10-phenanthroline/ phenanthroline	1,10-diaminophenanthrene	phen, o-phen	$C_{12}H_8N_2$	
oxalato	Oxalato	OX	$C2O_4^{2-}$	
dialkyldithiocarbamato	dialkylcarbamodithioato	dtc	$S2CNR_2^-$	
1,2-bis(diphenylphophine)ethane	1,2-ethanediylbis (dipheylphosphene)	dppe	$Ph_2PC_2H_4PPh_2$	
o-phenylenebis (dimethylarsine)	1,2-phenylenebis (dimethyl-larsene)	Diars	$C_6H_4(AS(CH_3)_2)_2$	
dimethylglyoximato	butanedienedioxime or dimethylgly-oximato	DMG	$HONC(CH_3)C(CH_3)NO-$	
ethylenediaminetetraacetato	1,2-ethanediyl (dinitrilo)tetraacetato or ethylenediaminetetraacetato	EDTA	$(^-OOCCH_2)_2$ NCH_2 $CH_2N(CH_2COO-)_2$	
Pyrazoly-lborato	hydrotris-(pyrazo-1-yl) borato			

(x) Flexidentate Ligand:

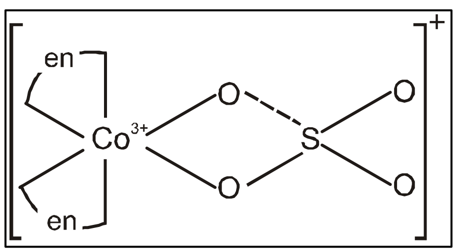
It is not necessary that all the donor items present in the polydentate ligands should form coordinate bonds with the central metal atom or ion i.e., a polydentate ligand which is found to have different denticity in different coordination compounds is called a flex dentate ligand. Note that in a particular complex denticity of a particular ligand is fixed, it cannot be flexible in the same compound.

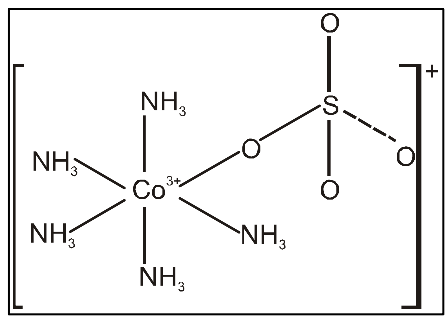
EDTA can act as hexa, penta as well as tetra dentate ligand.

For example;

EDTA usually acts as hexadentate ligand but in $[Cr(III)(OH)(EDTA)]^{2-}$ and $[Co(III)Br(EDTA)]^{2-}$ as pentadentate and in $[Pd(II)H_2(EDTA)]^0$ as a tetradentate ligand.

Sulphate ion, SO_4^{2-} can also be mono or bi dentate ligand. For example;





Effective atomic number -EAN (Sidgwick Theory and EAN Rule) : Total no. of electrons present on central metal atom /ion. after accepting electron pairs from donar atom of ligands through coordinate bond is called E.A.N. of central metal atom /ion.

$$\text{E.A.N} = \text{Z} - \text{O.S.} + 2 \times \text{C.N.}$$

Sidgwick also suggested that the metal ion will continue accepting electron pairs till the total number of electrons in the metal ion and those donated by ligands is equal to that of nearest noble gas. This total number of electrons is called effective atomic number (EAN) of the metal /ion. This will become clear by taking the example of hexamminecobalt (III) ion $[Co(NH_3)_6]^{3+}$

Atomic number of cobalt = 27

In the present complex, cobalt is present in the oxidation state of +3.

$\therefore$ E.A.N. of $Co^{3+} = Z - O.S. + 2 \times C.N.$

$$= 27 - 3 + 2 \times 6 = 36$$

In the above example since the number 36 corresponds to the atomic number of krypton, according to Sidgwick, the complex will be stable. Though EAN rule (which states that those complexes are stable whose EAN is the same as the atomic number of the next noble gas) is applicable in many metal carbonyl complexes, however there are several examples in which EAN rule is not obeyed.