* Ligands :- An ion/molecule with a F.Gr (functional group) that bonds the central atom to form coordination complex

- Lewis acid :- e^- pair acceptor [CMA → Central Metal Atom]
- Lewis base :- e^- pair donor [Ligands]

$M \leftarrow :L$ → coordinate/dative bond

acceptor donor

* Primary v/s Secondary Valency

Primary valency :- Oxidation no. of C.M.A
Secondary valency :- No. of σ-bonds formed by ligands with C.M.A
(π bonds if formed are NOT COUNTED)

Eg :- $[Co(en)_3]^{3+}$

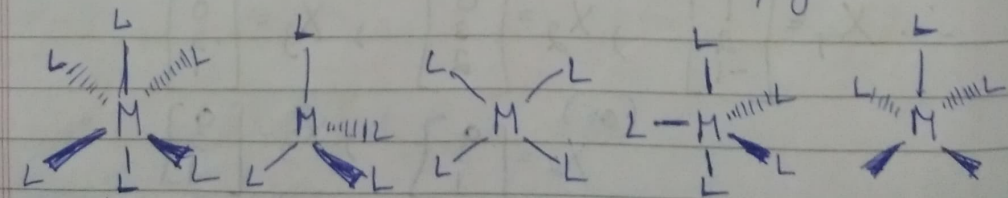
Here, en → can make 2 coordinate bonds [bidentate ligand]
∴ $(en)_3$ → can make $2 \times 3 = 6$ coordinate bonds

∴ C.N (Secondary valency of Co) = 6

* Counter ions :- Ionisable groups are written outside the square bracket (coordination sphere)

Eg :- In $K_4[Fe(CN)_6]$:- K^+ is the counter ion

* Coordination Polyhedron :- The spacial arrangements of ligands around central metal atom (CMA) is called coordination polyhedron



Octahedral (CN = 6) | Tetrahedral (CN = 4) | Square planner (CN = 4) | Trigonal bipyramidal (CN = 5) | Square pyramidal (CN = 5)

Q. Find Primary Valency of following :- (in CMA)

* do not consider counter ion into calculation of primary/secondary valency

(i) $[\underset{x}{Fe}(\underset{0}{CO})_5]$ ⇒ $x + 0 \times 5 = 0$
⇒ $x = 0$

(ii) $K_2[\underset{x}{Ni}\underset{(-1)}{Cl_4}] \rightarrow 2K^+ + [NiCl_4]^{2-}$ ⇒ $x + (-1) \times 4 = -2$
⇒ $x = +2$

(iii) $[\underset{x}{Fe}\underset{-1}{F_6}]^{3-}$ ⇒ $x + (-1)6 = -3$
⇒ $x = +3$

(iv) $[\underset{x}{Co}(\underset{0}{NH_3})_4\underset{-1}{(Cl)_2}]^+$ ⇒ $x + 0 \times 4 + (-1)2 = +1$
⇒ $x = +3$

* Types of Complexes :-

1. Homoleptic → one type of ligand Eg :- $[Co(NH_3)_6]^{3+}$
2. Heteroleptic → more than one type of ligand Eg :- $[Co(NH_3)_4(Cl)_2]^+$

* Classification of ligands :-

1. On basis of charge on ligands :-

(i) Anionic ligands :- -ve charged • Eg :- F^-, Cl^-, S^{2-}, SO_4^{2-} etc

(ii) Neutral ligands :- uncharged & e^- donor Eg :- CO, $\ddot{N}H_3$, $H_2\ddot{O}$ (en)

(iii) Cationic ligands :- +ve charged Eg :- $\ddot{N}O^+$, $\ddot{N}H_2-\overset{+}{N}H_3$

* Here,

Neutral ligands :- $\ddot{N}H_3$ > $H_2\ddot{O}$ > $H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2$ (en)

Cationic ligands :- $\ddot{N}O^+$ > $\ddot{N}H_2-NH_3^+$

Eg :- $\ddot{N}O^+$ → 5, 6 valence e^- [Due to '+' sign remove 1 e^- from Total valence e^- no.]

$\therefore 5 + 6 - 1 = 10$ valence e^-

$\therefore :O \equiv N$

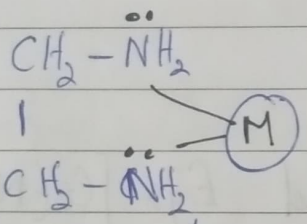
2. On the basis of denticity :-

Denticity :- no. of coordinate bonds formed by one ligand

(i) Monodentate :- Ligands with single donor atom
Eg :- Cl^-, $H_2\ddot{O}$, $\ddot{N}H_3$, $\ddot{N}H_2-NH_3^+$ [Denticity = 1]

(ii) Bidentate :- Ligands with 2 donor atom
Eg :-

① Ethylene diamine (en) → $H_2N-CH_2CH_2-NH_2$ (Neutral ligand)



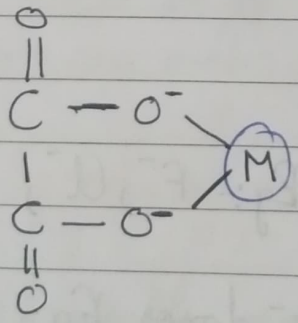
Here both ligands form bond with C.M.A by donating their lone pair e⁻

∴ Denticity = 2

* Here, en is making a closed ring with CMA

∴ Ligands that form closed ring with C.M.A → Chelate ligands

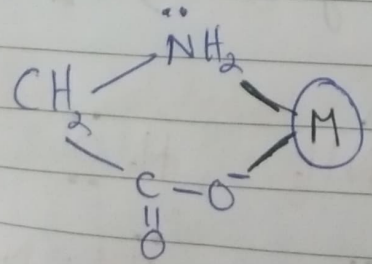
② oxalato (ox) → $C_2O_4^{2-}$ (Anionic ligand)



$C_2O_4^{2-}$ (ox) → chelate ligand

∴ Denticity = 2

③ glycinato (gly) → $C_2H_4NO_2^-$ (Anionic ligand)

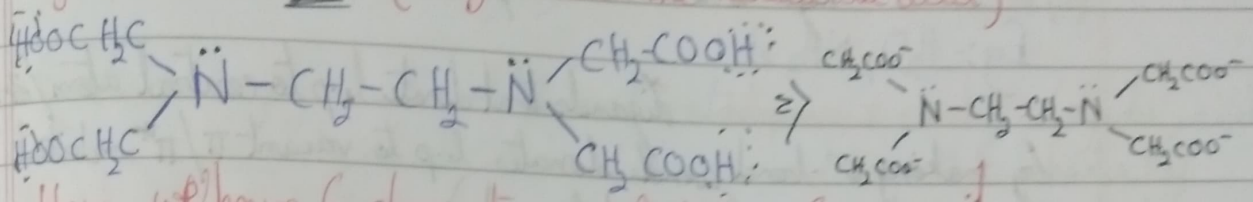


It is chelate ligand

∴ Denticity = 2

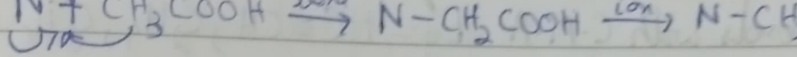
(iii) Polydentate :- Ligands with several donor atoms

Eg:- $EDTA^{4-}$ ion (Ethylene diamine tetraacetic acid)



Here, we have 6 donar atoms ∴ Denticity = 6 ⟶ (hexadentate ligand)
(4 O^- & 2 N)

Note,



(iv) Ambidentate :- Ligands can bind through 2 donar atoms (but only one of the combo can be used at a time) to form coordinate bond.

Eg:- ① CN^- / NC^- [cyano / isocyano] ($C \equiv N^-$)
If bond formed bet^n C & M ⇒ M ← CN^- (cyano)
" " " N & M ⇒ M ← NC^- (isocyano)

② NO_2^- / ONO [nitrito N / nitrito O] ($N^{-}(=O)_2$)
If bond formed bet^n N & M ⇒ M ← NO_2 (nitrito N)
" " " O & M ⇒ M ← ONO (nitrito O)
(O − N = O)

③ SCN^- / NCS [thiocyanato / iso thiocyanato]
If bond formed bet^n S & M ⇒ M ← SCN (thiocyanato)
" " " N & M ⇒ M ← NCS (iso thiocyanato)

3. On the bases of type of donation of lone pair :-

(i) σ-donar :- ligands that donate l.p (lone pair) and make σ-bond with C.M.A
Eg :- H_2O, NH_3 etc

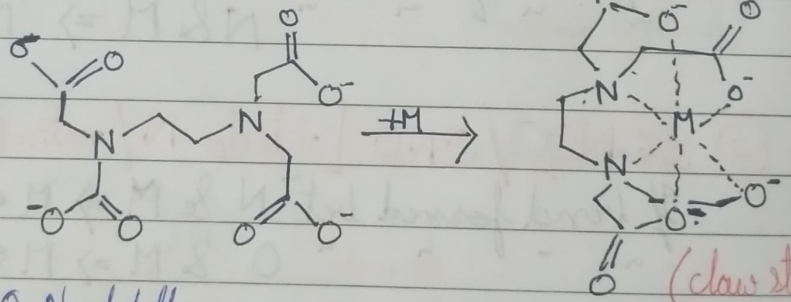
(ii) σ-donar π-acceptor :- ligands that donate l.p to central atom/ion by making σ-bond and donates l.p to vacant π/π* orbital
Eg :- CO, NO (π acid ligands)

(iii) π-donor π-acceptor :- ligands that donate & ~~accept~~ accept π e⁻ through π-bonds with C.M.A Eg :- $HC \equiv CH$, C_2H_4, C_6H_6 etc

Types of complexes :- Complex cation, anion & neutral complex

Q1. What are chelating ligands?
↳ ligands that bind with C.M.A & form closed ring like structures
Eg :- $[Cu(en)_2]^{2+}$, $[Fe(C_2O_4)_3]^{3-}$

* for EDTA,



(claw structure)

Q2. Find C.N & O.N of following-

(i) $[Co(\underset{0}{NH_3})_4(\underset{0}{H_2O})\underset{-1}{Br}]\overset{0}{[}(NO_3)]_2$ ∴ ON ⇒ $x-1=0 \Rightarrow x=1$
CN = 6

(ii) $K_3[Fe(\underset{-2}{C_2O_4})_3] \rightarrow 3K^+ + [Fe(\underset{-2}{C_2O_4})_3]^{3-}$ ∴ ON ⇒ $x-(-2)3=-3 \Rightarrow x=+3$
CN = 3×2 = 6 [∵ bidentate]

(iii) $[Co(en)_3]Cl_3 \rightarrow [Co(\underset{0}{en})_3]^{3+} + 3Cl^-$ ∴ ON ⇒ $x+(0)3=+3 \Rightarrow x=+3$
CN = 3×2 = 6 [bidentate]

(iv) $K_4[Fe(CN)_6] \rightarrow 4K^+ + [Fe(\underset{-1}{CN})_6]^{4-}$ ∴ ON ⇒ $x+(-1)6=-4 \Rightarrow x=+2$
CN = 6

(v) $[Ni(\underset{0}{CO})_4]^0$ ∴ ON ⇒ $x=0$
CN = 4