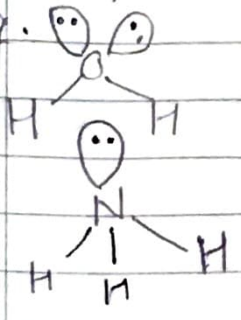
Classification of Ligands:

There are several ways to classify ligands.

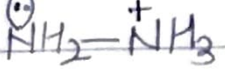
1. Based Upon Charges:

Neutral ligands

e.g. 

Positive Ligands

NO^+



Negative ligands

Cl^-, OH^-, NO_2^-

NO_3^-, CO_3^{2-}

SO_4^{2-}, CN^-

SCN^- etc

:CO Carbonyl

Pyridyl

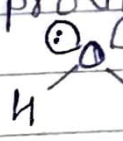
PH_3, PPh_3 etc

2. Based upon the Denticity of the Ligand:

Denticity: The number of donations provided by the ligand to the central metal (ion) is known as denticity of the ligand.

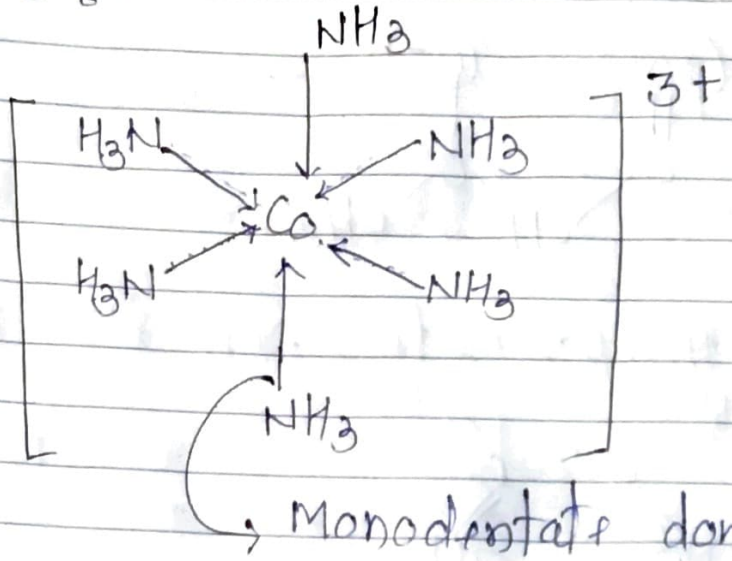
→ Ligands may be classified as follows based on their denticity.

(i) **Monodentate Ligands**: Only one donation is provided by the ligand.

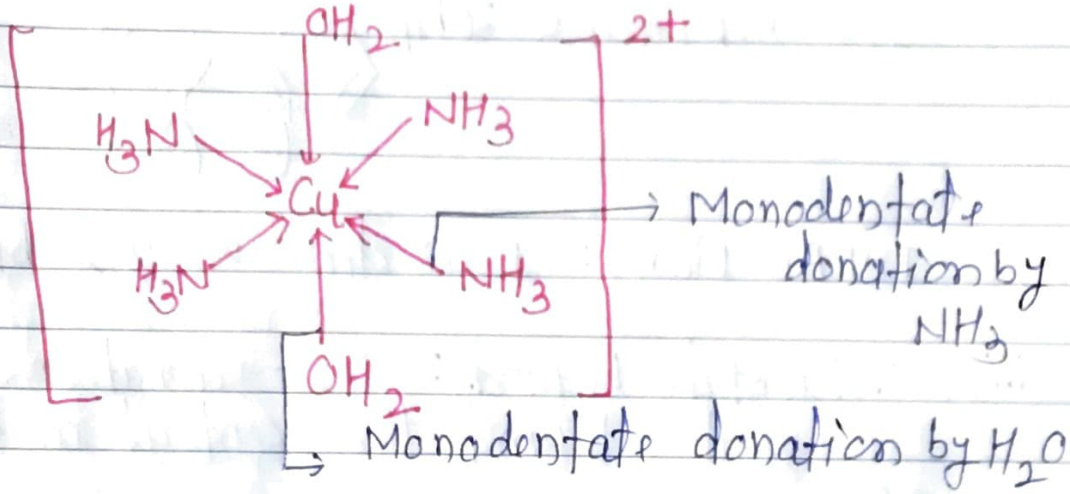
e.g.  ,  , $C\equiv O$, Cl^- , NH_2^-

etc.

$[Co(NH_3)_6]^{3+}$



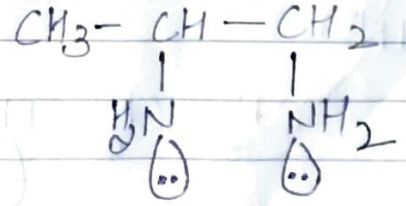
$[Cu(NH_3)_4(H_2O)_2]^{2+}$



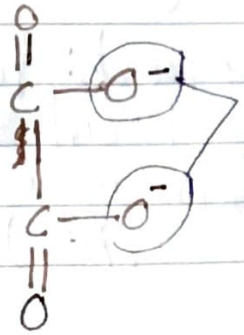
(ii) **Bidentate Ligands:** Two donations are provided by the ligand to the central metal (ion). e.g.

Ethylenediamine (en) $NH_2-CH_2-CH_2-NH_2$

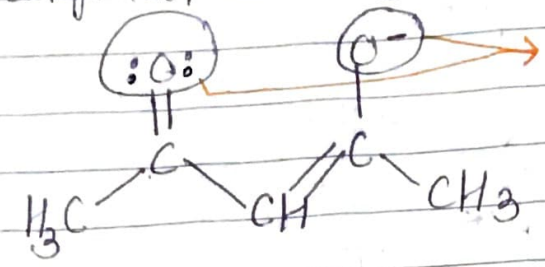
Propylenediamine (Pn)



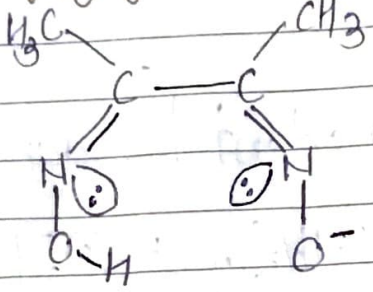
Oxalate (Ox^{2-})



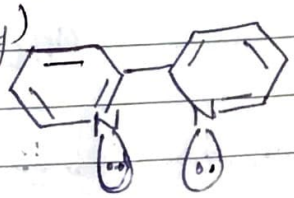
Acetylacetonate ($acac^-$)



Dimethylglyoximate (DMG):



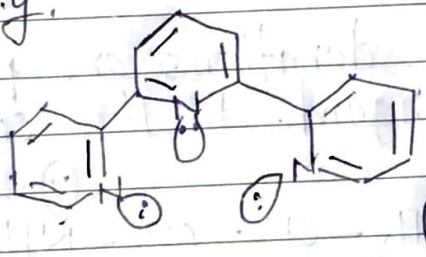
2,2'- bipyridine : (bipy)



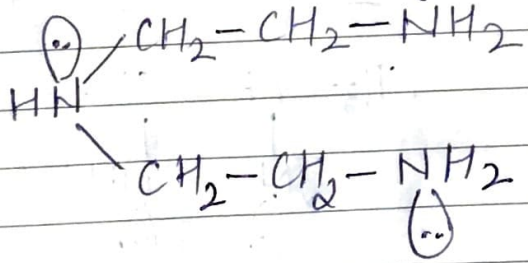
IUPAC Name: ~~1,10 diamine~~ 2,2'- bipyridyl

(iii) Tridentate Ligands: Three donations are provided by the ligand the central metal (ion).

e.g.



2,2',2''-terpyridyl (terpy)



diethylenetriamine (dien)

(iv) Tetradentate Ligands: four donations are provided by the ligand to the central metal (ion)
e.g. triethylenetetraamine (trien)
Nitrilotriacetate (NTA^{3-}).

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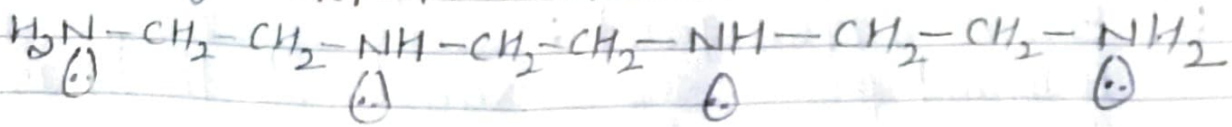
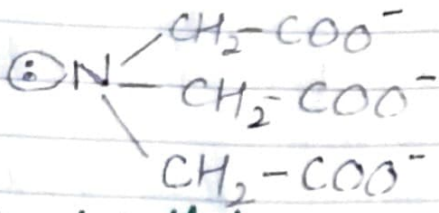
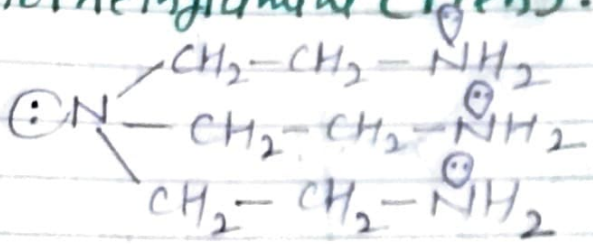
Triethylenetetraamine:



Nitrilotriacetate (NTA^{3-}):



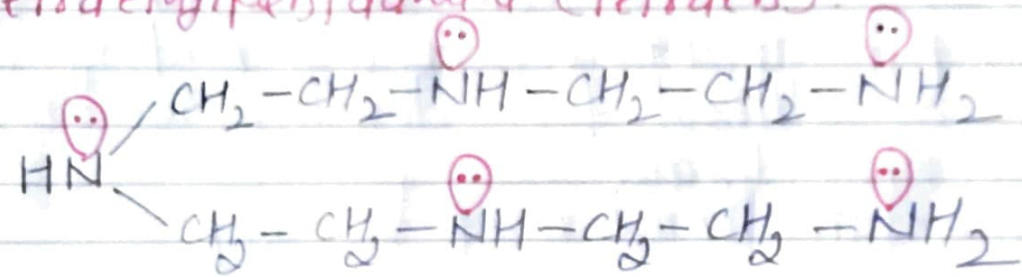
Triaminotriethylamine (tren):



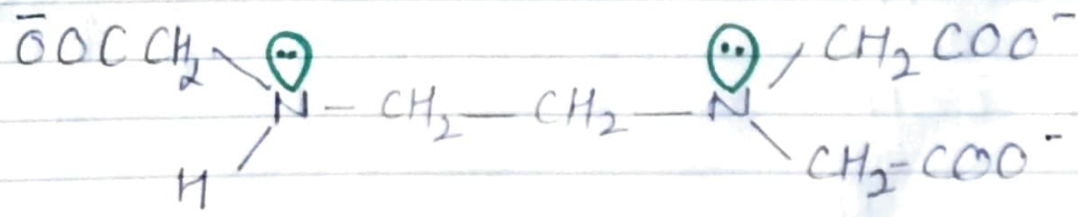
(v) Pentadentate Ligands: Five donations are provided by the ligand to the central metal (ion).

e.g.

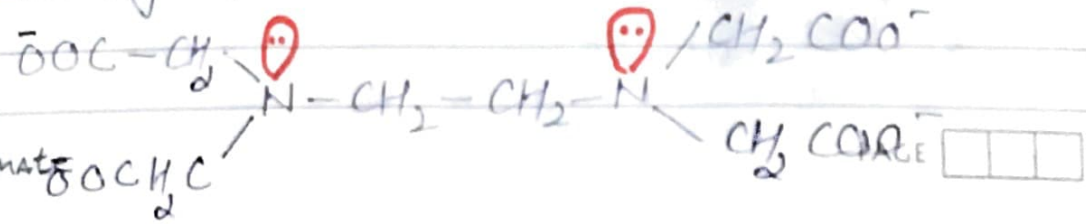
Tetraethylenepentaamine (tetraen):



Ethylenediaminetriacetato:



(vi) Hexadentate Ligands: Six donations are provided by the ligand to the central metal (ion).



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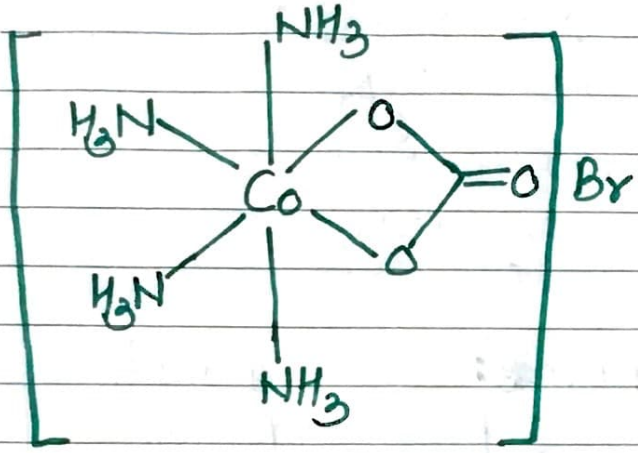
Note:

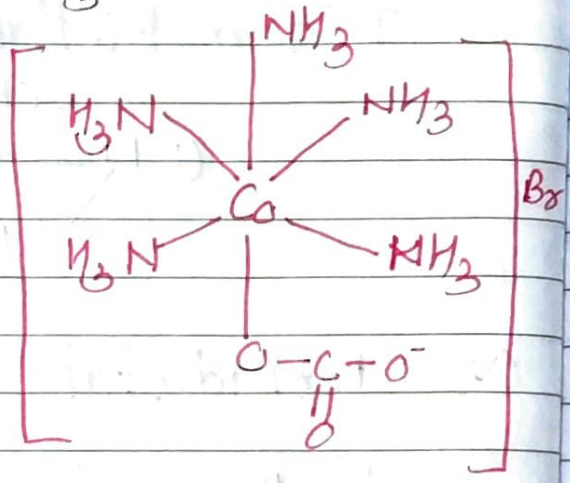
1. **Flexidentate Ligand:**
A ligand which shows variable denticity is called a flexidentate ligand.
e.g. CO_3^{2-}, SO_4^{2-} etc.

$[Co(NH_3)_4CO_3]Br$ and $[Co(NH_3)_5CO_3]Br$

CO_3^{2-} is bidentate



CO_3^{2-} is monodentate.

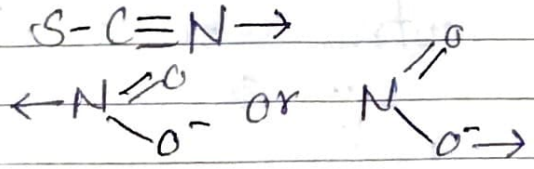


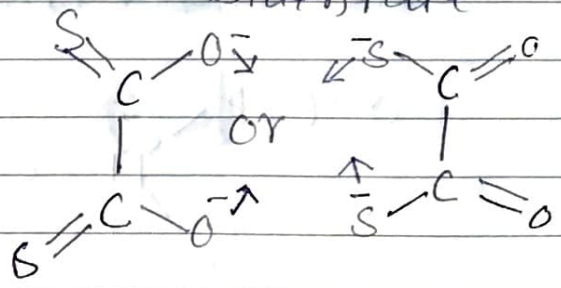
2. **Ambidentate Ligand:** A ligand that may have more than one kind of donor sites but at a time only one kind of donor site is utilized for donation is called as ambidentate ligand.
Ambidentate ligand is of two types.

- Monodentate
- Bidentate

e.g. $\leftarrow \bar{C}\equiv N$ or $\bar{C}\equiv N\rightarrow$

$\leftarrow S-C\equiv N$ or $S-C\equiv N\rightarrow$





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3. Based upon the Bonding Interaction between the Ligand and the Central Atom:

Two types

Classical or Simple donor ligand

→ These ligands only donate the lone pair of electrons to the central atom.

e.g. F^-, OH^-, NH_2^-, NH_3, N^{3-}, O^{2-} etc.

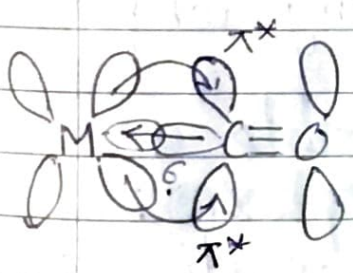
Non-classical or π-acid or π-acceptor ligand.

→ These ligands not only donate the lone pair of electrons to the central atom but also accept the electron cloud from the central atom in their low-lying vacant orbitals. This kind of back donation is known as 'synergic effect' or 'synergic bonding'. e.g. CO, CN^-, NO^+, PF_3, C_2H_4, PR_3 (R=H, Et, Ph) C_2H_2, CO_2 etc.

3 Cases

Case-I

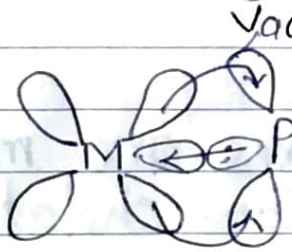
CO



Case-II

PR_3

Vacant 3d orbital accept the PR_3 back donation.

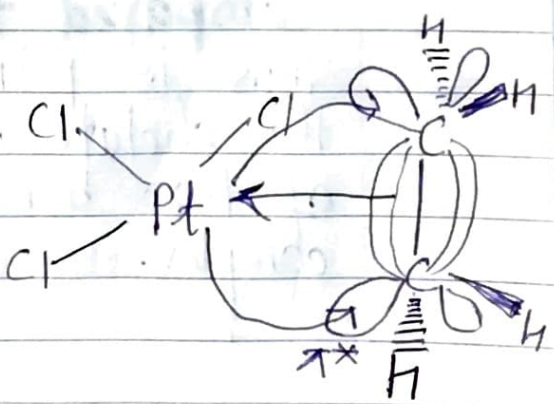


Case-III

C_2H_4

↓

Zeise salt



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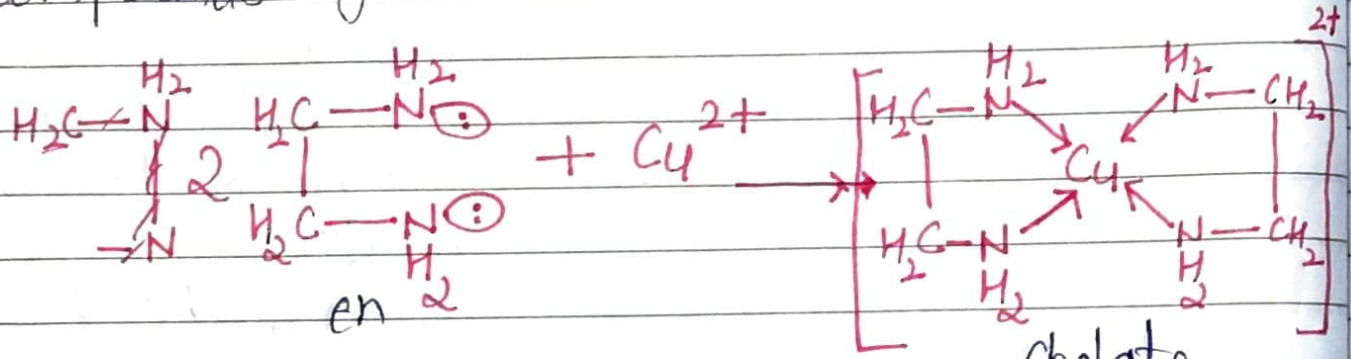
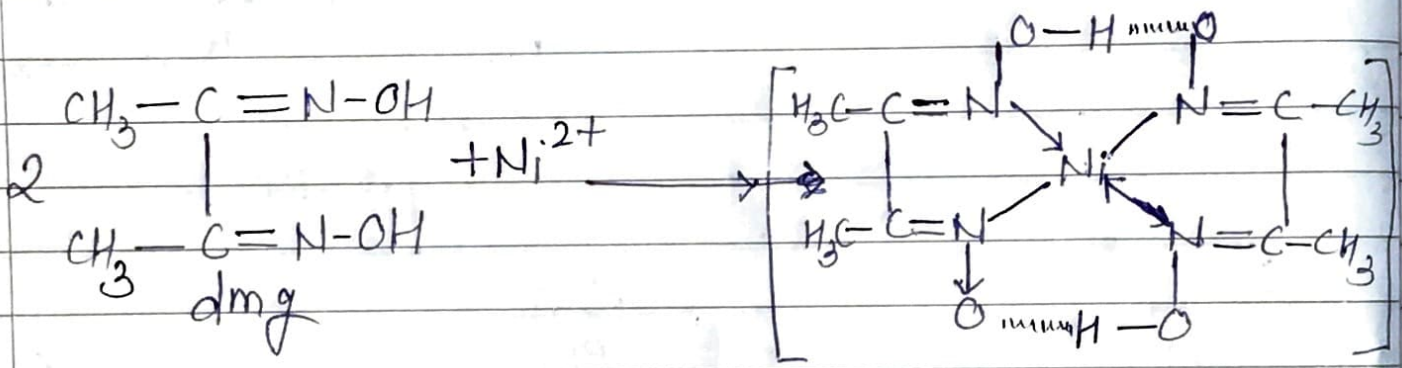
Chelates: Chelates are cyclic (or ring) compounds that are formed when a ligand binds to the central ~~atom~~ metal atom or ion through two or more donor atoms of a ligand. Such a ligand that binds the metal atom through two or more atoms is called a chelating ligand and the process is called chelation.

→ Chelating ligands are basically multidentate ligands which upon coordination with the central metal atom result in the formation of cyclic compounds. e.g.



Chelate



Ni-dmg complex

Chelated Complexes are more stable as compared to Non-chelated complexes:
This is primarily because the dissociation of the chelate which is cyclic involves the breaking of two bonds rather than one in non-chelated complex.

Factors Affecting Stability of Complexes

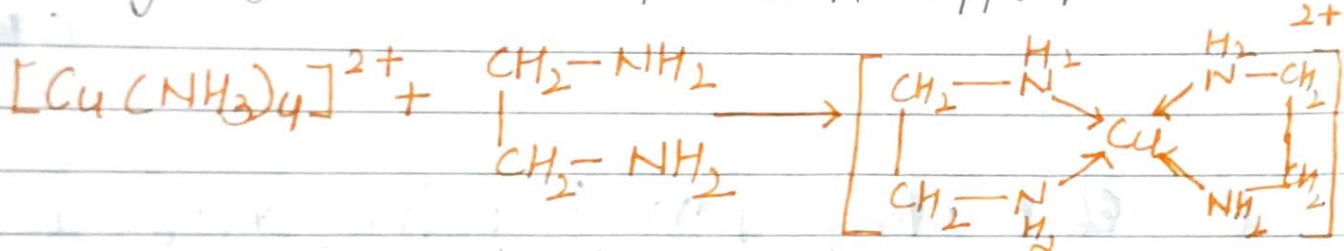
3 factors

- Chelate effect
- Number of chelate rings
- Size of the chelate ring

(i) Chelate Effect:

Chelated complexes formed by multidentate ligands such as EDTA, en, acac⁻ etc. have been found to be more stable than those formed by monodentate ligands such as H_2O, NH_3, Cl^-, Br^- etc.

→ This increased stability of the complexes containing chelating ligands is called chelate effect.



Less entropy → more entropy

- The stability of the chelated complex can be explained due to an increase in the entropy of the system.

(ii) Number of Chelate Rings:

→ Chelate in which more number of rings are formed is more stable.

1. $[Ni(NH_3)_2(H_2O)_4]^{2+}$
2. $[Ni(en)(H_2O)_4]^{2+}$
3. $[Ni(en)_2(H_2O)_2]^{2+}$
4. $[Ni(en)_3]^{2+}$

Stability Order:

4 > 3 > 2 > 1.

(iii) Size of the Chelate Ring:

→ 5-membered rings have been found to be more stable.

→ Rings of sizes greater than 6 are known but they are not very stable.

Reasons for Instability of Higher Membered Rings:

4-reasons

(a) Electrostatic force

(b) Decreased effective conc.

(c) Ring configuration

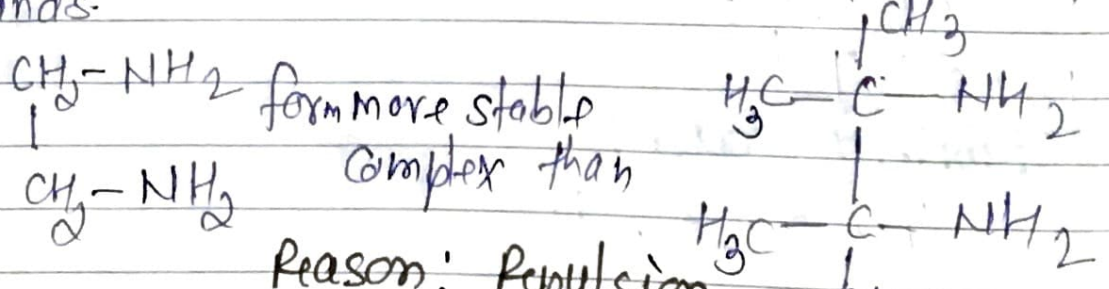
(d) Large bulkier ligands form less stable complexes.

(a) Electrostatic force: Extra energy is required to bring the coordinating atoms of the chelating ligand close to the metal ion for bonding against electrostatic forces.

(b) Decreased effective concentration of the other end of the ligand for large chelating molecule that form 7 or 8-membered rings.

(c) scarcity of finding sterically non-crowded ring configuration.

(d) Ligands Size: Large bulkier ligands form less stable complexes than the smaller ligands.



Reason: Repulsion