

Class - P.G. Sem. I

Subject - Chemistry

Paper - CC-I

Unit - III

Dr. Kumud Kumari
H.D. Jain college, Ara.

METAL LIGAND EQUILIBRIUM IN SOLUTION-II

Factors affecting the stability of metal complexes -

Properties of the ligand -

1. Size and charge of ligand - if a ligand is smaller, it can approach the metal ion more closely forming a stable bond. similarly highly charged ligand would also form a strong bond with metal. thus the high charge and small size of a ligand also form a strong bond with metal.

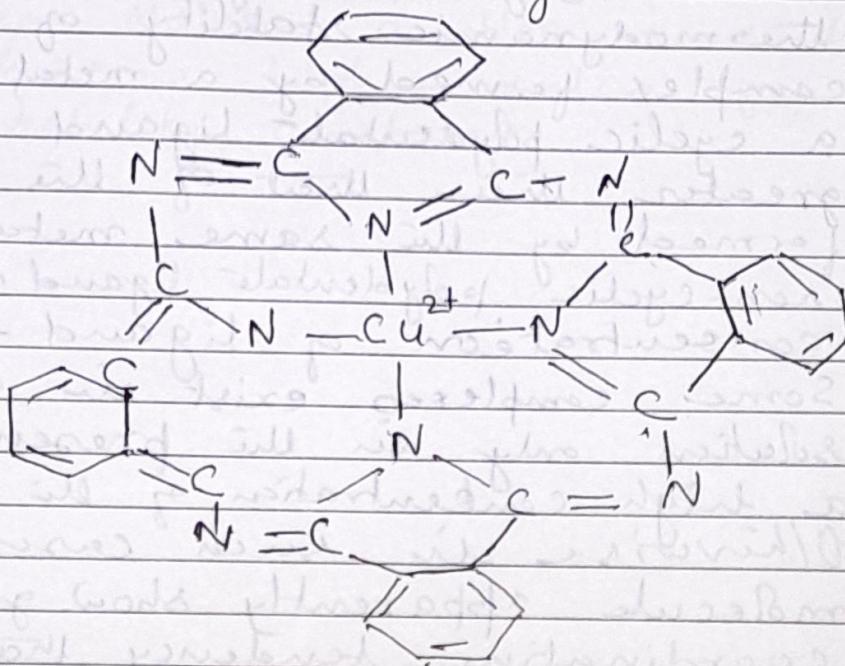
2. Dipole moment of the ligand - For the neutral ligands, the larger the magnitude of permanent dipole moment, the greater is the stability of the complexes for example - $\text{NH}_3 > \text{ethylamine} > \text{diethylamine} > \text{triethylamine}$.

(2) Basic character of ligands —
Basic ligands can donate ~~poles~~
~~more~~ ~~only~~ electron pairs to
the central metal ion more easily.
One ligand that bind H⁺ firmly
from poor stable complexes. Thus F⁻
should form a stable complexes than
Cl⁻, Br⁻ or I⁻. N H₃ is better ligand
than H₂O.

(4) π -bonding capacity of ligand —
The ligands like CN⁻, CO, PR₃,
As R₃, Sb give more stable
complexes.

(5) Steric hindrance due to bulky
ligands — When a bulky group
is either attached to or is
present near a donor atom of
a ligand, repulsion between the
donor atom of the ligand and
the bulky group is produced and
this mutual repulsion weakens
the metal-ligand bonding and
decreases the stability of the
complexes. The effect of the presence
of bulky group on the stability of
a complex is commonly known
as steric hindrance.

(6) Forced configuration of ligands —
 Ligands like porphyrin and phthalocyanine which have completely fused planar ring system, form extraordinary stable complexes with metal ion for example Cu^{2+} complex with phthalocyanine, Fe^{2+} with porphyrin (because are very stable).



Copper(II) phthalocyanine complex

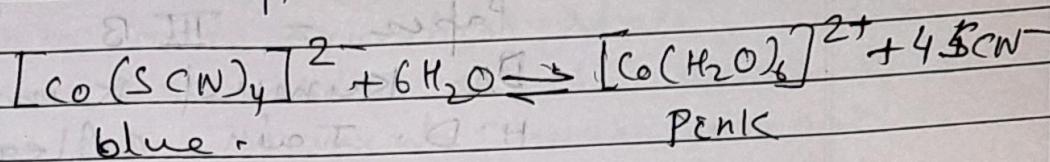
F. Macrocyclic ligands and macrocyclic effect — A macrocyclic ligand is a nine or more membered cyclic molecule having 3 or more potential donor atoms.

which can bind a metal atom inside the cavity of the macrocycle. Many synthetic macrocyclic ligands have only N-donor atoms, some are mixed (N, O), (N, S), (N, O), (N, O, S), (N, O, P) etc. Some macrocyclic ligands have conjugated π system. The thermodynamic stability of a complex formed by a metal with a cyclic polydental ligand is greater than that of the complex formed by the same metal with non-cyclic polydental ligand.

8. Concentration of Ligand —

Some complexes exist in aqueous solution only in the presence of a high concentration of the ligand. Otherwise in such cases, water molecule apparently show greater coordinating tendency than the groups in which are originally present. For example Co^{2+} in presence of a high concentration thiocyanate (SCN^-) forms stable blue complex ion, $[Co(SCN)_6]^{2-}$. But on dilution, the blue solution gets destroyed and is replaced by a pink hydrated complex $[Co(H_2O)]^{2+}$. On further addition of SCN^- in,

disappears and the original blue colour reappears.



- (9) chelate effect → A chelated complex dissociates less than a non-chelated complex and hence has a higher value for its stability constant.