AR-7128

Model Answer of M Sc Second semester Exam 2013

Paper: CMT-202

(Inorganic Chemistry-II)

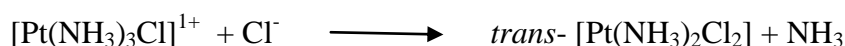Section A-   10x2= 20
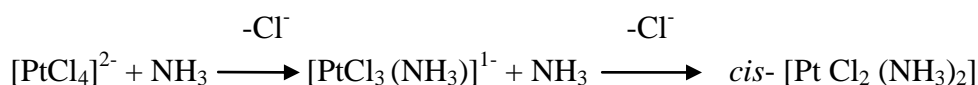
(**Short Answer Type Questions**)

1. **(i)** Ligand substitution in square planar metal Complexes extensively studied for square planar Ni2+, Pd2+ and Pt2+ (d^8) substitutions in water and non-polar solvents: e.g.

$[Pt(NH_3)_4]^{2+} + Cl^- \longrightarrow [Pt(NH_3)_3Cl]^{1+} + NH_3$

Or

$[Pt(NH_3)_3Cl]^{1+} + Cl^- \longrightarrow$ *trans*- $[Pt(NH_3)_2Cl_2] + NH_3$

Or

$[PtCl_4]^{2-} + NH_3 \xrightarrow{-Cl^-} [PtCl_3(NH_3)]^{1-} + NH_3 \xrightarrow{-Cl^-}$ *cis*- $[Pt Cl_2 (NH_3)_2]$

Since the Cl^- has stronger trans effect than NH_3

Or any other known or well studied examples.

(ii) Brief description of the following explanation:

Yes, cis effect is possible

🞣 In square planar complex the *cis* effect is very small compared to the *trans* effect. Relative *trans* and *cis* effect series based on rates of substitution of H_2O for Cl^- in $[PtCl_3L]^{n-}$ complexes*
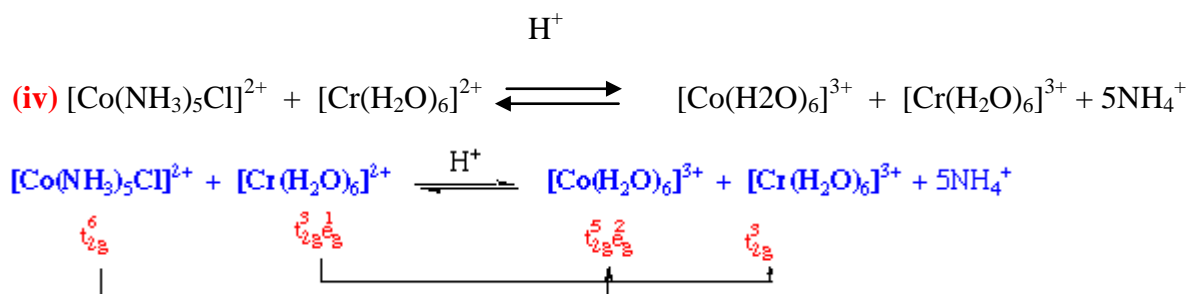
trans ligand	trans effect	cis ligand	cis effect
H_2O	1	H_2O	1
NH_3	200	NH_3	1
Cl^-	330	Cl^-	0.4
Br^-	3000	Br^-	0.3
DMSO	2x 106	DMSO	5
C_2H_4	1011	C_2H_4	0.05

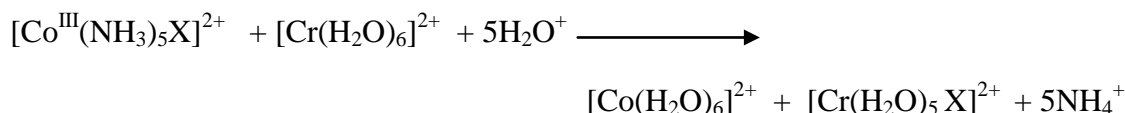*   L.I. Elding and O. Groning *Inorg. Chem.* **1978**, *17*, 1872-80.

- The *cis* effect is defined as the labilization (making unstable) of CO ligands that are cis to other ligands. CO is a well-known strong π-accepting ligand in organometallic chemistry that will labilize in the *cis* position when adjacent to ligands due to steric and electronic effects.
- The system most often studied for the *cis* effect is an octahedral complex $M(CO)_5X$ where X is the ligand that will labilize a CO ligand cis to it.
- Unlike trans effect, where this property is most often observed in 4-coordinate square planar complexes, the cis effect is observed in 6-coordinate octahedral transition metal complexes. It has been determined that ligands that are weak sigma donors and non- π acceptors seem to have the strongest *cis*-labilizing effects.
- Therefore, the *cis* effect has the opposite trend of the trans-effect, which effectively labilizes ligands that are trans to strong π accepting and sigma donating ligands.

(iii) The well studied $[Ru(bpy)_3]^{2+}$ complex is used as catalyst for the photochemical cleavage of water as reported by Creutz and Sutin[*]

*C. Creutz and N. Sutin *Proc. Natl. Acad Sci.* USA **1975**, *72*, 2858; N. Sutin and C. Creutz *Pure Appl. Chem.* **1980**, *52*, 2727.

$$H^+$$

(iv) $[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \rightleftharpoons [Co(H2O)_6]^{3+} + [Cr(H_2O)_6]^{3+} + 5NH_4^+$

Or

$[Co^{III}(NH_3)_5X]^{2+} + [Cr(H_2O)_6]^{2+} + 5H_2O^+ \longrightarrow$

$$[Co(H_2O)_6]^{2+} + [Cr(H_2O)_5 X]^{2+} + 5NH_4^+$$

X= F^-, Cl^-, Br^-, I^-, SO_4^{2-}, NCS^-, N^{3-}, PO_4^{4-}, $P_2O_7^{4-}$, CH_3COO^-

Or

$[Co^{II}(EDTA)]^{2-} + [Fe^{3+}(CN)_6]^{3-} \longrightarrow [Co^{III}(EDTA)]^- + [Fe^{2+}(CN)_6]^{4-}$

(v) The V-C bond lengths in $V(CO)_6^{-}$ and $V(CO)_6$ are 193 pm and 200 pm respectively. In the carbonyl complex $V(CO)_6$ there is certain amount of M $\rightarrow$C, π-back bonding interaction. But in case of $V(CO)_6^{-}$, due to the enhanced negative charge on the metal this M $\rightarrow$C, π-back bonding interaction gets increased, as a result V-C bond length decreased from 200 pm to 193 pm.

(vii) *Receptor and Substrate:*

Receptors are the species those can select one of many possible binding partners to form a complex those are stabilized by interactions such as hydrogen bonding or any other non-covalent interactions. The host component of a Supramolecular assemblies is called the receptor.

Crown ethers, Spherand, Cyclodextrin and calixarenes are the receptors.

The guest component of the Supramolecular assemblies is called the substrate. Normally

these possess divergent binding site.

Metal cations, alkyl ammonium cations and small organic molecules are the examples of receptors.

(viii) *Supramolecular Chemistry*:

The term "Supramolecular Chemistry" means "chemistry beyond the molecule. In the supramolecular system the molecular components (guests and hosts) are held together through the non-covalent intermolecular forces. Thus, Supramolecular Chemistry describes the chemistry of molecular assemblies held together through the noncovalent intermolecular forces. IN Supramolecular Chemistry the components match both sterically and electronically so that the component molecules can recognise each other. This leads to molecular recognition. This is the way the chemistry of molecular recognition is also kwon as guest-host Chemistry. C.J.Pederson, D.J. Cram and J.-M. Lehn received Nobel prize in Chemistry in 1987for their work in Supramolecular Chemistry

(ix) *Kerr effect:*

The Kerr effect, also called the quadratic electro-optic effect (QEO effect), is a change in the refractive index of a material in response to an applied electric field. The Kerr effect is distinct from the Pockels effect in that the induced index change is directly proportional to the *square* of the electric field instead of varying linearly with it. All materials show a Kerr effect, but certain liquids display it more strongly than others. The Kerr effect was discovered in 1875 by John Kerr, a Scottish physicist.

Two special cases of the Kerr effect are normally considered, these being the Kerr electro-optic effect, or DC Kerr effect, and the optical Kerr effect, or AC Kerr effect.

(x) *Optical rotatory power*:

The optical rotatory power of a pure substance mainly in the liquid state is the quantitative ability to rotate the polarised lught. It is usually expressed in terms of specific rotatory power.

It is given by the following mathematical expression,

$$[\alpha]^t = \alpha/dc$$

where **[α]** is the optical rotatory power,

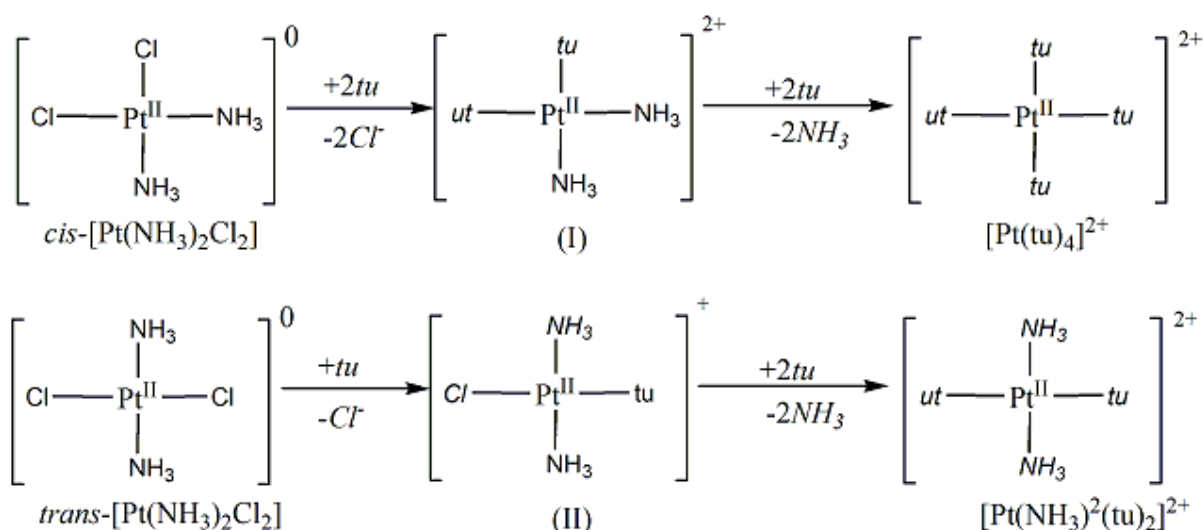**α** is the angle through which the plane polarised light rotated by a solution

c is the concentration (c gms of solute per ml of solution), **d** is the length of the sample cell and **t** is the temperature.

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Section B-   5x8= 40

(**Long Answer Type Questions**)

2. *To distinguish between cis- and trans- isomers of [PtA₂X₂]⁰ type complexes:*

- The *trans* effect has been used by Russian chemists (Kurnakov) to distinguish between the *cis* and *trans*- isomers of $[PtA_2X_2]^o$ type complexes (A= NH_3 or amine, X = a negative group), e.g. *cis*-$[Pt(NH_3)_2Cl_2]$ reacts with thiourea, NH_2CSNH_2 (*tu*) to give $[Pt(tu)_4]^{2+}$ whereas under the same conditions the trans -$[Pt(NH_3)_2Cl_2]$ gives $[Pt(tu)_2 (NH_3)_2]^{2+}$.
- Compound (I) in the first reaction reacts further with tu to give the completely substituted product, $[Pt(tu)_4]^{2+}$ because of the larger trans effect of tu than NH_3 . In compound (II) the trans effect of NH_3 being smaller than that of tu, the NH_3 molecule are not sufficiently reactive to be replaced by tu. Thus Cl^- ion trans to tu in (II) is replaced by further tu molecule to form $[Pt(NH_3)_2 (tu)_2]^{2+}$.
- The use of thiourea reaction to assign structures is known as Kurnakov's test.
- Similar results have been reported for reactions of thiosulphate ion ($S_2O_3^{2-}$) instead of thiourea, e.g. cis- and trans- -$[Pt(NH_3)_2Cl_2]$ reacts with excess of $S_2O_3^{2-}$ ion to form $[Pt(S_2O_3)_4]^{6-}$ and $[PtII(NH_3)_2(S_2O_3)_2]^{2-}$ respectively.

π-bonding theory of trans-effect

The Chatt (1955) and Orgel (1956) explained the high trans effect of the π-bonding ligands like PR_3, NO, CO, C_2H_4, CN^- and given π-bonding theory of trans effect.

According to this theory the vacant π and π* orbitals of the π-bonding ligands accept a pair of electrons from the filled d-orbitals of the metal (d_{xz} and d_{yz} orbital) to form metal-ligand π-bond ($d\pi$- $d\pi$ or $d\pi$- $p\pi$ bond).

In case of Pt(II) square-planar complexe, PtX_2L (L is the π- bonding ligand) the d_{yz} orbital of Pt(II) with a pair of electrons overlaps with the empty pz orbital of the π-bonding ligand, L to form the $d\pi$- $p\pi$ bond between Pt(II) and L. The formation of π- bond in the complex increases the electron density in the direction of L and diminishes it in the direction of the ligand, X *trans* to L. Thus Pt-X bond *trans* to L is weakened.
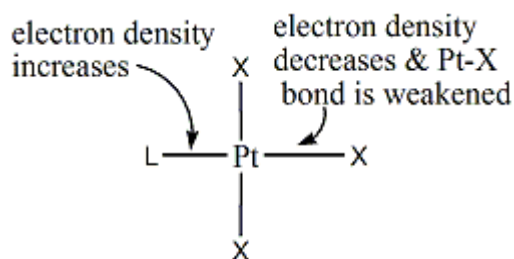

The weakening of Pt-X bond trans to L fascilitates the approach of the entering ligand, say Y: with its lone pair in the direction of diminished electron density to form the five-coordinated transition state complex, $PtLX_3Y$, which on losing X yields $PtLX_2Y$. In the formation of $PtLX_3Y$ the ligand trans to L is replaced by the incoming group, Y. The transition state complex has distorted *trigonal-bipyramidal (tbp)* structure in which tow X's
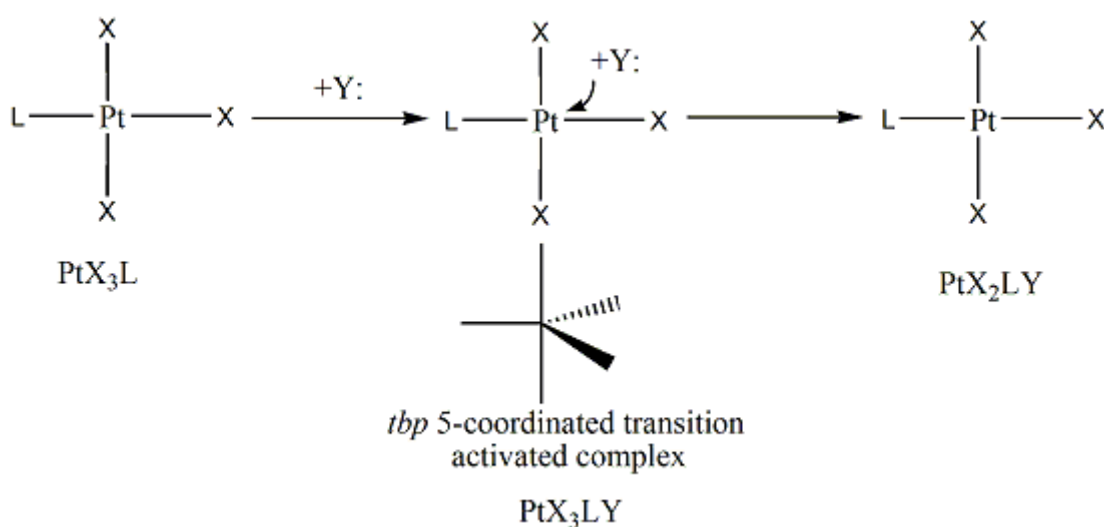

groups which are cis to L both in the initial and final states form the apexes.

The formation of $d\pi$-$p\pi$ bond between Pt(II) and π-bonding ligand, L in the 5-coordinated transition activated complex as in the below cited ***Figure 1*** Smaller d-orbital lobes adjacent to the group X which is to be replaced by Y may be marked in the figure.
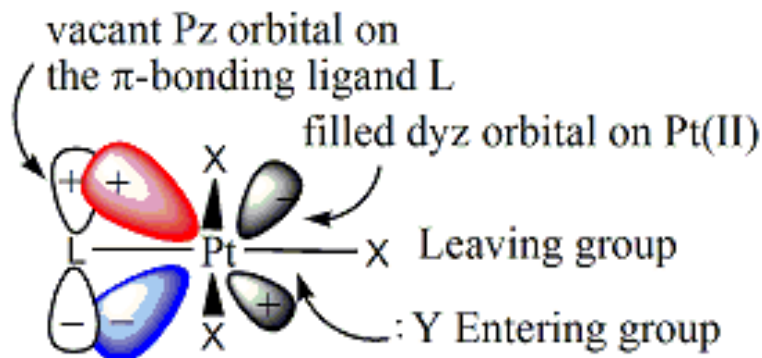
Figure 1: Formation of dπ- dπ bond in the 5-coordinated activated complex formed during the substitution reaction in Pt(II) square planar complex PtLX$_3$

$$PtLX_3 + Y \longrightarrow PtLX_2Y + X$$
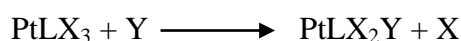
A Schematic representation of double bond in Pt-PR3 is shown in *Figure 2*. σ-bond is formed by the donation of a pair of electrons from the phosphorous to platinum and the π- bond by the overlap of filled d-orbital of platinum and a vacant d-orbital of phosphorous atom. If the ligand PR$_3$ and X are in the xy plane, the d-orbital shown in either d_{xz} or d_{yz}.
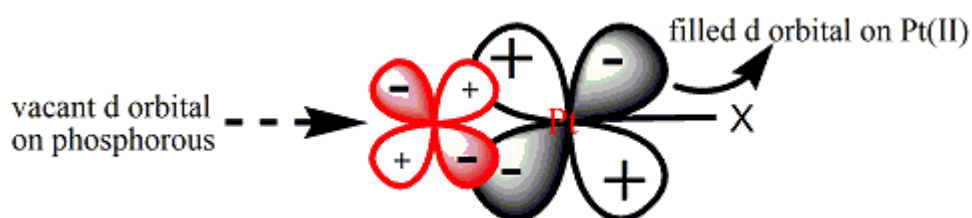
Figure 2: Schematic representation of *R$_3$P-Pt* double bond.

Chatt *et al* emphasises that the removal of charge from Pt(II) by π- bonding of L enhances the addition of the entering group, Y and favours a more rapid reaction. According to Orgel the formation of π- bond between Pt(II) and π- bonding ligand L enhances the stability of the 5-coordinated transition state complex, thus lowering the activation energy for its formation and speeding up the reaction.

The formation of π- bond weakens the metal-ligand bond trans to a π- bonding ligand is evident from the fact that in the square-planar complex anion, $[(C_2H_4)PtCl_3]$, the Pt-Cl bond trans to C_2H_4 is slightly larger than those cis to C_2H_4. Pt-trans-Cl stretching frequency is

lower than the average of the two Pt *cis*-Cl frequencies. Lower the frequency, the weaker (i.e. longer) the bond.
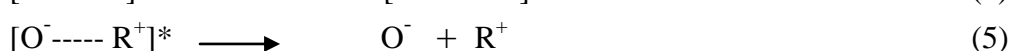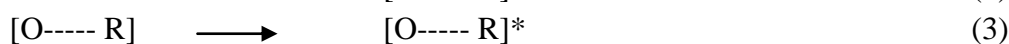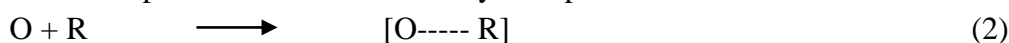
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3. $[Fe(CN)_6]^{4-} + [Mo(CN)_8]^{3-} \longrightarrow [Fe(CN)_6]^{3-} + [Mo(CN)_8]^{4-}$ (1)

Type: *Outer sphere mechanism (Electron transfer reaction)*

- Outer sphere refers to an electron transfer phenomena that occurs between metal complexes that remain separate intact before, during, and after the electron transfer. In contrast to inner sphere electron transfer in outer sphere electron transfer occurs between two non-connected species, the electron is forced to move through space from one redox center to the other.

- Such a reaction may be considered to approximate a simple collision model. The rate of reaction is faster than CN- exchange for either reactant so we consider the process to consist of electron transfer from one stable complex to another with no breaking of Fe-CN or Mo-CN bonds.

- An outer sphere electron transfer may be represented as follows:

    $O + R \longrightarrow [O----- R]$ (2)

    $[O----- R] \longrightarrow [O----- R]^*$ (3)

    $[O----- R]^* \longrightarrow [O^----- R^+]^*$ (4)

    $[O^----- R^+]^* \longrightarrow O^- + R^+$ (5)

- First the oxidant [O] and reductant [R] come together to form a precursor complex. Activation of the precursor complex which includes reorganization of solvent molecule and changes in a metal-ligand bond length must occur before electron transfer can take place. The final step is the dissociation of the ion-pair into product ions.

- A specific example further clarifies the activation and electron transfer steps. The exchange reaction between solvated Fe(III) and Fe(II) has been studied with radioactive isotopes (Fe*) of iron.[1]

    1. A. G. Sykes, *Kinetics of Inorganic Reactions*; Pergamon: Oxford, **1966**; *Chapter 2*

    $[Fe(H_2O)_6]^{3+} + [Fe^*(H_2O)_6]^{2+} \longrightarrow [Fe(H_2O)_6]^{2+} + [Fe^*(H_2O)_6]^{3+}$ (6)

The energy of activation $\Delta G^{\neq}$ for this reaction is 33 kJ mol^{-1} even if it seems to be zero as the reactants and products are the same except their oxidation states. In order for electron transfer to occur the energies of the participating electronic orbitals must be the same as required by the Frank-Condon principle. In this reaction an electron is transferred from a t_{2g} orbital of Fe(II) to t_{2g} orbital of Fe(III). The bond distances in Fe^{2+} and Fe^{3+} complexes are unequal, which signifies that the energies of the orbitals are not equivalent. If the electron transfer could take place without an input of energy we obtain as products the Fe(II) complex with bond lengths typical of Fe^{3+} and the Fe (III) complexes with bond lengths typical of Fe^{2+}; both could then relax with the release of energy. This would clearly violate the first law of thermodynamics. In fact there must be an input of energy in order the electron transfer to take place. The actual process occurs

with shortening of the bonds in Fe(II) complex and lengthening of the bond in Fe(III) complex until the participating orbitals are of the same energy (*Fig 1.*) Vibrational stretching and compression along the metal ligand bonds allow the required configuration to be achieved.
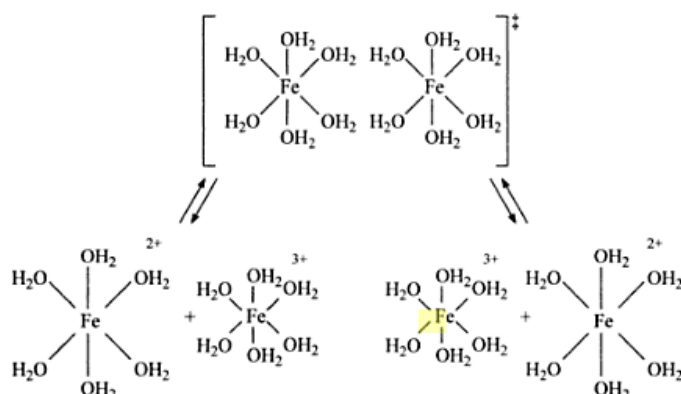
Fig. 1:   Extension and compression of the Fe-O bonds in $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{2+}$, respectively, to form an activated complex in which all metal-ligand distances are identical, a prerequisite for electron transfer between the two complexes.*

*N. A. Lewis *J. Chem. Educ.* **1980**, *57*, 478-483.

➕   The energy of the activation may be expressed as the sum of three terms:

$$\Delta G^{\neq}_t = \Delta G^{\neq}_t + \Delta G^{\neq}_i + \Delta G^{\neq}_o \qquad (7)$$

In which the $\Delta G^{\neq}_t$ is the energy required to bring the O and R into a configuration in which they are separated by required distance, $\Delta G^{\neq}_t$ is the energy required for the bond compression and stretching to achieve orbitals of equal energy and $\Delta G^{\neq}o$ is the energy needed for solvent reorganization outside of the first coordination sphere.

Potential energy diagrams further clarify the concentration between molecular motion and electron transfer. The potential energy of all reactant and associated solvent nuclei before electron transfer can be approximated as a harmonic potential well *Fig. 2a, R.* The potential energy of all products and solvent nuclei after electron transfer can be described similarly *Fig. 2a, P.*
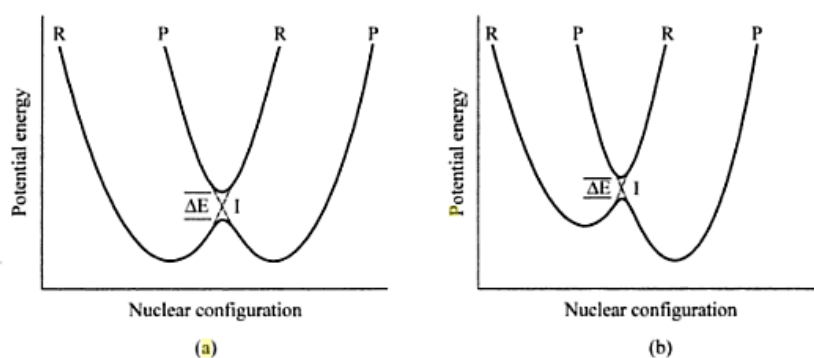
Fig 2: (a) Potential energy diagram for a homonuclear electron transfer reaction such as
$[Fe(H_2O)_6]^{3+}$ + $[Fe(H_2O)_6]^{2+}$ ⟶ $[Fe(H_2O)_6]^{2+}$ + $[Fe(H_2O)_6]^{3+}$
(b) Potential energy diagram for a hheteronuclear electron transfer reaction.

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- The reactants (R) and products (P) of **Eqn. 6** have the same energy as shown in Fig 2a.
  At the intersection of the potential energy surfaces I the requirement of equal orbital energies is met. For *electron transfer to occur at I, however, coupling of vibrational and electronic motion must take place*.
  The extent of this interaction is related to ΔE shown in figure. If the coupling interaction is strong, it is the condition when bond distortions are small, electron transfer is favourable.
  If the interaction is very weak, associated with large bond distortions, $\Delta G^{\neq}_i$ will be large and the reaction will be slow. These considerations are equally applicable to heteronuclear reactions as given in Fig *2b.*
- Marcus has derived a relationship from first principle that enables one to calculate rate constants for outer sphere reactions.*

$$k_{12} = (k_{11}\,k_{22}K_{12}f_{12})^{1/2} \qquad (8)$$

* R. A. Marcus *Annu. Rev. Phys. Chem.* **1964**, *15*, 155-196.

- To illustrate the application of the equation and the definitions of all its terms one can calculate the rate constant k_{12} for the reaction of *equ. 1,* called the cross reaction as compared to the self exchange reaction.
- For this reaction k_{11} is the rate constant for the self-exchange process involving the hexacyanoferrate complexes.

$$[Fe(CN)_6]^{4-} + [Fe*(CN)_6]^{3-} \longrightarrow [Fe(CN)_6]^{3-} + [Fe*(CN)_6]^{4-} \qquad (9)$$
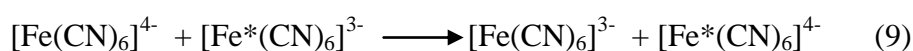
$$k_{11} = 7.4 \times 10^2\ M^{-1}\ s^{-1}$$

k_{22} is the rate constant for the singular reaction involving the octacyanomolybdenum complexes:

$$[Mo(CN)_8]^{3-} + [Mo(CN)_8]^{4-} \rightleftharpoons [Mo(CN)_8]^{4-} + [Mo*(CN)_8]^{3-}$$
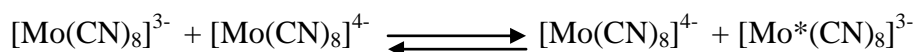
$$K_{22} = 3 \times 10^4\ M^{-1}\ s^{-1}$$

K_{12} is the equilibrium for the overall reaction *Equ 1*

And log $f_{12} = (\log K_{12})2/4 \log(k_{11}\,k_{22}/Z^2)$. This last term contains Z which is the collision frequency of two uncharged particles in solution and is taken as $10^{11}\ mol^{-1}\ s^{-1}$).

The factor f_{12} has been described as correction for the differences in the free energies of the two reactants and is often close to unity. In this example it is 0.85.

When all the appropriate value are substituted in the equation 8 k_{12} is calculated to be 4 X 10^4 mol^{-1} s^{-1} which compares quite well with the experimental value of 3.0 X 10^4 mol^{-1} s^{-1}.

The Marcus equation 8 is so well defined and established that if the calculated rate constant in Marcus equation is strong disagreement with experimental value it means other than outer sphere mechanism is operative. The Marcus equationconects thermodynamics and kinetics.

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4. (ii) Wade's rules:

British Chemist Kenneth Wade in the year 1970 proposed a set of rules for predicting the structures of cluster compounds based in the number of electrons in the framework counted in a particular way.

Wade's rules are used to rationalize the shape of borane clusters by calculating the total number of skeletal electron pairs (SEP) available for cluster bonding. In using Wade's rules it is key to understand structural relationship of various boranes.

The following general methodologies are followed in Wade's rules

1. Determination the total number of valence electrons from the chemical formula, i.e., 3 electrons per B, and 1 electron per H.

2. 2 electrons for each B-H unit (or C-H in a carborane) are subtracted.

3. The number of remaining electrons is divided by 2 to get the number of skeletal electron pairs (SEP).

4. A cluster with n vertices (i.e., n boron atoms) and $n+1$ SEP for bonding has a *closo* structure.

5. A cluster with n-1 vertices (i.e., n-1 boron atoms) and $n+1$ SEP for bonding has a *nido* structure.

6. A cluster with n-2 vertices (i.e., n-2 boron atoms) and $n+1$ SEP for bonding has an *arachno* structure.

7. A cluster with n-3 vertices (i.e., n-3 boron atoms) and $n+1$ SEP for bonding has an *hypho* structure.

8. If the number of boron atoms (i.e., n) is larger than $n+1$ SEP then the extra boron occupies a capping position on a triangular phase.

   Example: Structure determination of B_5H_{11}

1. Total number of valence electrons = (5 x B) + (11 x H) = (5 x 3) + (11 x 1) = 26

2. Number of electrons for each B-H unit = (5 x 2) = 10

3. Number of skeletal electrons = 26 – 10 = 16

4. Number SEP = 16/2 = 8

5. If $n+1 = 8$ and $n-2 = 5$ boron atoms, then $n = 7$

6. Structure of $n = 7$ is pentagonal bipyramd, therefore B_5H_{11} is an *arachno* based upon a pentagonal bipyramid with two apexes missing

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5.Circular birefringerence:

The wave length dependence of optical acivity , known as optical rotatory dispersion (ORD) is more useful source of information about asymmetric compounds than is the specific rotation at a single wave length. An ordinary beam of light can be resolved into two plane polarized beam and plane polarized radiation can be further resolved in into two beams which are circularly polarised in opposite directions. The refractive indices for left and right circularly polarized may not be the same and is designated as η_L and η_R respectively. For an isotropic medium $\eta_L = \eta_R$, for example, glass or water. The index is independent on the state of polarization. If $\eta_L \neq \eta_R$, a phase difference appears between the two components which is equal to saying that plane of polarization has been rotated that is angle $\alpha \neq 0$.

The angle of rotation is given by (as expressed in radians) if $\eta_L > \eta_R$, plane of emergent linearly polarized light is rotated to right $\alpha = \pi/\lambda(\eta_L - \eta_R)d$.

The quantity $\eta_L - \eta_R$ is called Circular birefringerence. Optical rotation is dependent on wavelength, especially in the region of an electronic absorption band of the atom or ion lying at the centre of dissymmetry. Moreover at a given wave lengththe value of $\eta_L - \eta_R$ for one enantiomorph are equal and opposite to those for the other enantiomorph.

A **polarimeter** is a scientific instrument used to measure the angle of rotation caused by passing polarized light through an optically activesubstance.

Some chemical substances are optically active, and polarized (unidirectional) light will rotate either to the left (counter-clockwise) or right (clockwise) when passed through these substances. The amount by which the light is rotated is known as the angle of rotation.

The polarimeter is made up of two Nicol prisms (the polarizer and analyzer). The polarizer is fixed and the analyzer can be rotated. The prisms may be compared to as slits S1 and S2. The light waves may be considered to correspond to waves in the string. The polarizer S1 allows only those light waves which move in a single plane. This causes the light to become plane polarized. When the analyzer is also placed in a similar position it allows the light waves coming from the polarizer to pass through it. When it is rotated through the right angle no waves can pass through the right angle and the field appears to be dark. If now a glass tube containing an optically active solution is placed between the polarizer and analyzer the light now rotates through the plane of polarization through a certain angle, the analyzer will have to be rotated in same angle.

Polarimeters measure this by passing monochromatic light through the first of two polarising plates, creating a polarized beam. This first plate is known as the polarizer. This beam is then rotated as it passes through the sample. The sample is usually prepared as a tube where the

optically active substance is dissolved in an optically inactive chemical such as <u>distilled water</u>,<u>ethanol</u>, <u>methanol</u>. Some polarimeters can be fitted with tubes that allow for sample to flow through continuously.

After passing through the sample, a second polarizer, known as the analyzer, rotates either via manual rotation or automatic detection of the angle. When the analyzer is rotated to the proper angle, the maximum amount of light will pass through and shine onto a detector.

(a)

Fig. 5.3 : Schematic Diagram of polarimeter.
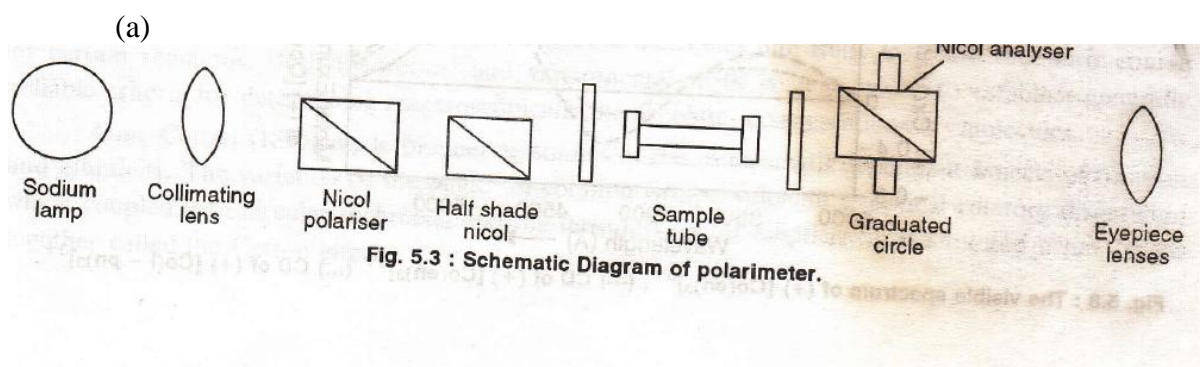
6. (a) (i) $B_6H_6^{2-}$

1. Total number of valence electrons = $(6 \times 3) + (6 \times 1) + 2 = 26$

2. Number of electrons for each B-H unit = $(6 \times 2) = 12$

3. Number of skeletal electrons = $26 - 12 = 14$

4. Number SEP = $14/2 = 7$

5. If $n+1 = 7$ and $n = 6$

6. Structure of $n = 6$ is octahedral, therefore $B_6H_6^{2-}$ is a *closo* structure based upon an octahedral structure with no apex missing.

(ii) B_5H_9

1. Total number of valence electrons = $(5 \times B) + (9 \times H) = (5 \times 3) + (9 \times 1) = 24$

2. Number of electrons for each B-H unit = $(5 \times 2) = 10$

3. Number of skeletal electrons = $24 - 10 = 14$

4. Number SEP = $14/2 = 7$

5. If $n+1 = 7$ and $n-1 = 5$ boron atoms, then $n = 6$

6. Structure of $n = 6$ is octahedral, therefore B_5H_9 is a *nido* structure based upon an octahedral structure with one apex missing.

(b) ***Capping rule:***

The Capping Rule

Many carbonyl-type clusters consist of a central polyhedron to which one or more additional metal atoms are appended by placement over a triangular face. These appended metal atoms are called capping atoms. The electron counting rules we have discussed can be extended to cover such structures by the rule that the addition of a capping atom does not change the skeletal electron requirement for the central cluster. Thus, the addition of a capping atom simply increases the total electron count by 12 electrons.

The $Os_7(CO)_{21}$ cluster provides a simple illustration. The TEC is given by $(7 \times 8) + (21 \times 2)$, namely, 98. Subtracting $7 \times 12 = 84$ and dividing by 2, we obtain $S = 7$, which implicates a six-vertex central polyhedron. This is consistent with there being a *closo* six-atom deltahedron (namely, an octahedron) capped on one face—which is, indeed, the actual structure of $Os_7(CO)_{21}$. Correct results are similarly obtained for $[Os_8(CO)_{22}]^{2-}$, which is a bicapped octahedron (16-XX) and $[Os_{10}C(CO)_{24}]^{2-}$, which is a tetracapped octahedron. For the latter, a capsule summary of the analysis is as follows:

$$\text{TEC:} \quad (10 \times 8) + 4 + (2 \times 24) + 2 = 134$$

$$S: \quad \tfrac{1}{2}[134 - (10 \times 12)] = 7$$
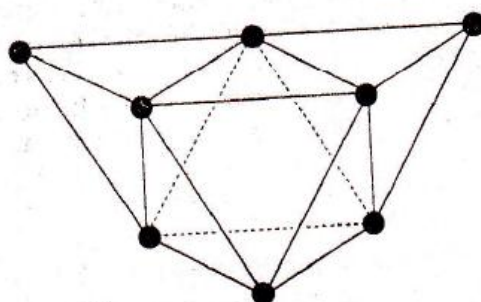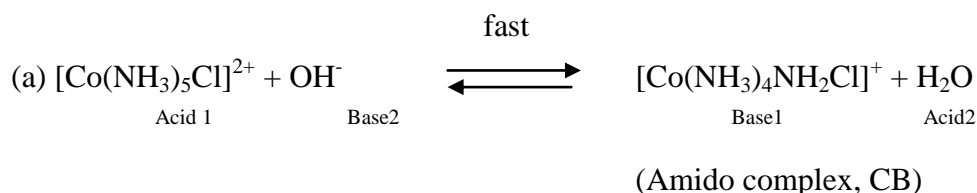

(16-XX)

7.

The ligand substitution reaction particularly the six coordinated Co (III) amine complexes the detailed kinetic studies have been performed. For amine complexes of Co(III) complexes containing N-H bonds it has been observed that the rate of base hydrolysis is often as much as 106 times faster than the corresponding rate of acidic ahydrolysis.

The nucleophilic substitution unimolecular conjugate base **S_N1CB (conjugate base) mechanism** which has been proposed by Garrick (1937), describes the pathway by which many metal amine complexes undergo substitution, that is ligand exchange. Typically, the reaction entails reaction of a polyamino metal halide with aqueous base to give the corresponding polyamine metal hydroxide:[1]

$$[Co(NH_3)_5Cl]^{2+} + OH^- \rightarrow [Co(NH_3)_5OH]^{2+} + Cl^-$$
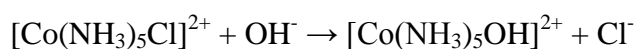
1. F.J. Garrick. *Nature*, Lond. **1937**, *139*, 507.

In this mechanism the complex which acts as a BrΦnsted acid is converted into its conjugate base (abbreviated as CB), $[Co(NH_3)_4 NH_2Cl]^+$ which is obtained by removing a proton (H^+) from the amino group (NH_3) present in the complex. CB is an amido complex (contains NH_2^-)
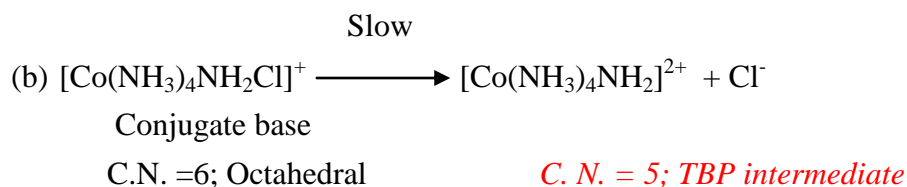
$$\text{(a)} \quad [Co(NH_3)_5Cl]^{2+} + OH^- \quad \underset{}{\overset{\text{fast}}{\rightleftharpoons}} \quad [Co(NH_3)_4NH_2Cl]^+ + H_2O$$

Acid 1   Base2   Base1   Acid2

(Amido complex, CB)

Fir this reaction the equilibrium constant K is

$$K = \frac{[CB] \; [H_2O]}{[Co(NH_3)_5Cl]^{2+} [OH^-]}$$

$$\text{Or} \quad CB = \frac{k_1K \; [Co(NH_3)_5Cl]^{2+} [OH^-]}{[H_2O]} \tag{i}$$

CB obtained as above is more labile than the original complex, $[Co(NH_3)_5Cl]^{2+}$ and hence undergoes SN$_1$ dissociation mechanism by a slow step to lose Cl$^-$ ion and gives 5-coordinated intermediate.

*S$_N$1 dissociation, rate determining and uni-molecular step*

$$\text{(b)} \quad [Co(NH_3)_4NH_2Cl]^+ \overset{\text{Slow}}{\longrightarrow} [Co(NH_3)_4NH_2]^{2+} + Cl^-$$

Conjugate base

C.N. =6; Octahedral   *C. N. = 5; TBP intermediate*

Thus the rate may be written as:

$$\text{Rate} = k_1[CB]$$

$$= \frac{k_1K \; [Co(NH_3)_5Cl]^{2+} [OH^-]}{[H_2O]} \quad\quad \text{[from equation (i)]}$$

$$= K_B \; [\text{Complex}] \; [\text{Base}]$$

Where K_B = rate constant used for the dissociation of the conjugate base as in (b) step and is equal to $k_1K/[H_2O]$

⬩ The intermediate formed as above reacts with the abundant solvent molecules (i.e. H_2O molecules) to produce the hydroxo complex, $[Co(NH_3)_5OH]^{2+}$. This process occurs in a relatively fast step.

$$\text{fast}$$
(c) $[Co(NH_3)_4NH_2]^{2+} + H_2O \xrightarrow{\hspace{2cm}} [Co(NH_3)_5OH]^{2+}$
Hydroxo complex
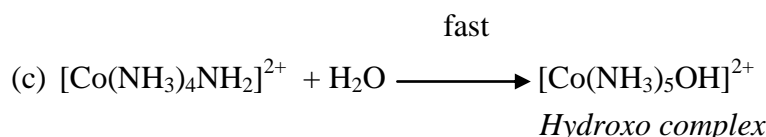
For $[Co(NH_3)_5Cl]^{2+}$, it was reported [2a] that the rate of base hydrolysis 'shows less than a first-order dependence on hydroxide ion concentration at high base concentrations. However, recent rate studies[2b] show no deviation from first-order dependence on [OH⁻] even at OH⁻ = 1.0M.

2. (a) S. C. Chan. *J. Chem. Soc. (A)* **1966**, 1124; (b) D. A. Buckingham, I. I. Olsen and A. M. Sargeson. *Inorg. Chem.* **1968**, *7*, 174.

Since the S_N1 dissociation step (b) which is the rate-determining step uses the conjugate base of the initial complex, the symbol ***S_N1CB has been used by Garrick*** in place of S_N1 symbol.

Evidences in favour of *SN₁CB*
➢ The proposed rapid acid base equilibrium (a) given above requires that the reacting complex should have at least one protonic hydrogen atom (H^+) on a non-leaving ligand so that H+ may transfer to OH to give its conjugate acid, H_2O and conjugate base , $[Co(NH_3)_4NH_2Cl]^+$ of $[Co(NH_3)_5Cl]^{2+}$ which acts as an acid. Thus aa complex having no proton (or no N-H hydrogen) should react with OH- much more slowly and the rate of reaction would be independent of concentration of [OH⁻]. In fact it has been reported that the complex like $[Co(CN)_5Br]^{3-}$ and *trans*-$[Co(py)_4Cl_2]^+$ which donot have N-H hydrogen undergo hydrolysis much more slowly in basic solution at a rate which is independent of [OH⁻] over a wide range of [OH⁻].
➢ In the both the mechanism (S_N2 or S_N1CB) of base hydrolysis of six coordinated Co (III) amine complexes give the same rate laws i.e. second order kinetics and the same hydroxo products in aqueous solution, because water is a good coordinating agent and proton shift is very fast. However in a non hydroxylic or non-protic solvent different products are predicted to be formed for both the mechanism under the condition that

an excess of some nucleophile reagent other than OH^- ion or H_2O (e.g. N_3^-, NO_2, SCN^-) is present.

➤ For the following reaction occurring in DMSO are readily explained by SN_1CB mechanism but can not explained with SN_2 mechanism.[3]

$$[Co(en)_2NO_2Cl]^+ + Y^- \xrightarrow{(CH_3)_2SO/OH^-} [Co(en)_2NO_2Y]^+ + Cl^-$$
$$(Y^- = N_3^-, NO_2, SCN^-)$$
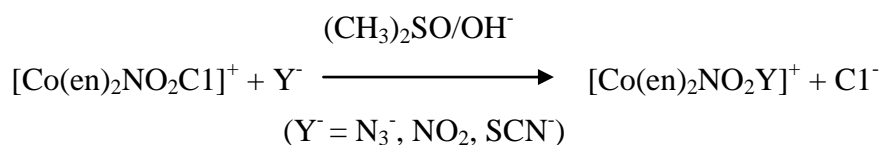
In the absence of base, the reaction is very slow, but it is extremely fast in the presence of added bases. Since $[Co(en)_2NO_2OH]^+$ does not react with Y, the role of OH^- is not one of direct attack on cobalt but rather one of producing some active intermediate. Presumably this is the five-coordinate conjugate base $[Co(en)(en-H) NO_2]^+$, which readily reacts with Y, picks up a proton to give the final product and regenerates the catalyst base. Identical results[4] were recently obtained for the base catalyzed reactions of *cis*-$[Rh(en)_2NO_2Cl]^+$ and of *trans*-$[Rh(en)_2NH_2CH_3Cl]^{2+}$.
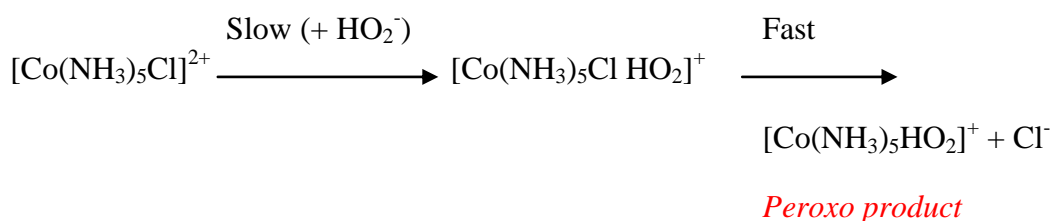
3. R.G. Pearson, H. H. Schmidtke and F. Basolo. *J. Am. Chem. Soc.* **1960**, *82*, 4434.
4. A. Panunzi and F. Basolo. Inorg. Chim. Acta **1967**, *1*, 223.

➤ Further interesting evidence in favour of SN_1CB mechanism comes from the study of the reaction of $[Co(NH_3)_5Cl]^{2+}$ and OH^- in aqueous solution at 25^oC in prersence of H_2O_2. When H_2O_2 is added to the reaction mixture of $[Co(NH_3)_5Cl]^{2+}$ and OH^- the following changes take place.

Since HO_2^- ion in H_2O_2 is a weaker base but a better nucleophile towards metal ions than OH^- the reaction of H_2O_2 with OH^- reduces the concentration of OH^- and increases that of water. Thus the reaction between OH^- and H_2O_2 occurs as

$$OH^- + H_2O_2 \longrightarrow H_2O + HO_2^-$$
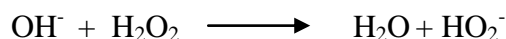
The tendency of O_2H^- ion to act as a better nucleophile than OH^- should, therefore, increase the rate of base hydrolysis reaction by it compare to OH^- , if it attacks the metal by SN_2 mechanism to form the peroxo product. As cited below:

$$[Co(NH_3)_5Cl]^{2+} \xrightarrow{\text{Slow} (+ HO_2^-)} [Co(NH_3)_5Cl\ HO_2]^+ \xrightarrow{\text{Fast}}$$

$$[Co(NH_3)_5HO_2]^+ + Cl^-$$

Peroxo product

- On the other hand if the reaction occurs by an SN_1CB mechanism the addition of H_2O_2 to the reaction mixture should reduce the rate of base hydrolysis reaction compared to OH^- because of the reduction in the concentration of OH^- ions as as is evident from the equilibrium represented by equation (i) given above.
- The rate of an SN_1CB reaction is directly proportional to the concentration of OH^-. Experimentally it has been verified that when 0.018 M H_2O_2 is added to the rearction mixture consisting of 0.0029 M $[Co(NH_3)_5Cl]^{2+}$ and 0.0029 M OH^- in aqueous solution at 25oC, there is a decrease in the value of rate constant by a factor of 3.6 i.e. if k_{Abs} = rate constant in the absence of H_2O_2 and k_{pres} = rate constant in the presence of H_2O_2 then $k_{Abs}/ k_{pres} = 3.6$.
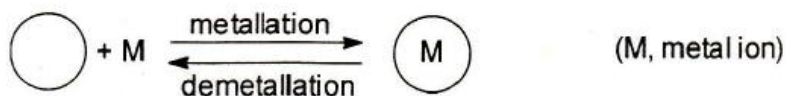
These are the various experimental data which supports *SN₁CB* mechanism of base hydrolysis of six coordinated Co (III) amine complexes.
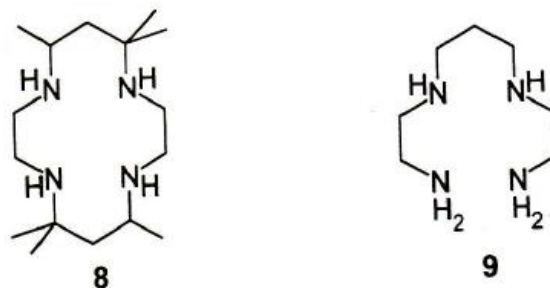
8. (i) Macrocyclic Effect

I.2. Macrocyclic Effect

Since 1969 it has been realised that a macrocycle imparts more stability against demetallation compared to the corresponding acyclic analogue.

For example, the stability constant for the copper(II) complex of **8**, the reduced form of **5**, is almost 10^4 times higher than the copper(II) complex of the open chain tetraamine

N,N'-bis(2-aminoethyl)propane-1,3-diamine (2.3.2 tet; **9**); this difference is much more than that expected on the basis of the increase in the number of chelate rings in going from the complex of **9** to that of **8** (chelate effect). This additional stability has been termed as

"macrocyclic effect" by Cabbiness and Margerum.[7] Thermodynamically, this effect originates mainly from the entropy factor; associated enthalpy factor may favour it.[8] This effect is reflected in the kinetics of demetallation also.[8] For example, $[Cu(\mathbf{8})]^{2+}$ has a dissociation half life of 22 days in 6.1 M HCl at room temperature which is 10^7 times slower than that of $[Cu(\mathbf{9})]^{2+}$ in similar conditions.[9]

Among the various factors controlling the stability of a macrocyclic complex, the following two have been identified as the most important ones in the closely related macrocyclic ligands:

(i) matching between the macrocycle hole size and the metal ion radius [just to give an idea, it is mentioned here that the hole size of 14-ane-N_4 (i.e., **2**) is 2.07 Å, that of 12-ane-N_4 1.83 Å and that of 16-ane-N_4 2.38 Å[10] (cf. hole size of porphyrin,[11] 2.03 Å); the strain free metal-N bond lengths for Zn(II), Cu(II) and low-spin Ni(II) are calculated[10] as 2.15, 2.03 and 1.91 Å respectively]

(ii) number of six membered chelate rings afforded by the macrocycle.

However, these two factors are often counteracting. While assessing their effects on the stability of the tetraaza macrocyclic complexes of mainly Cu(II), Zn(II), Cd(II), Pb(II) and low-spin Ni(II), Hancock[10] has proposed a rule in 1990 which says that "increase of chelate ring size from five memebered to six membered in a complex will increase the stability of complexes of smaller relative to larger metal ions." Interestingly, this rule applies to complexes of non-macrocyclic ligands as well.

8.(ii)   H-Bond directed Supramolecules:

18

H-Bond Directed Molecular Assembly

directional property of H-bond is very much important for the molecular assembly. DNA is a **supramolecule** where the specific H-bonding interaction is the key factor. *Cyanuric acid (CA)* *and melamine (M) are possessing the complementary H-bonding sites.* Cyanuric acid provides three **hydrogen bonding** sites *donor-acceptor-donor (DAD)* while melamine provides the *complementary* **ADA** which electronically and sterically fit with the *DAD* sites of *CA*. In aqueous solution, they **will complex** to produce a crystalline solid that can withstand high temperature upto 450°C. The **supramolecular** structure looks *rosette-like* (Fig. 13.5.15.1).
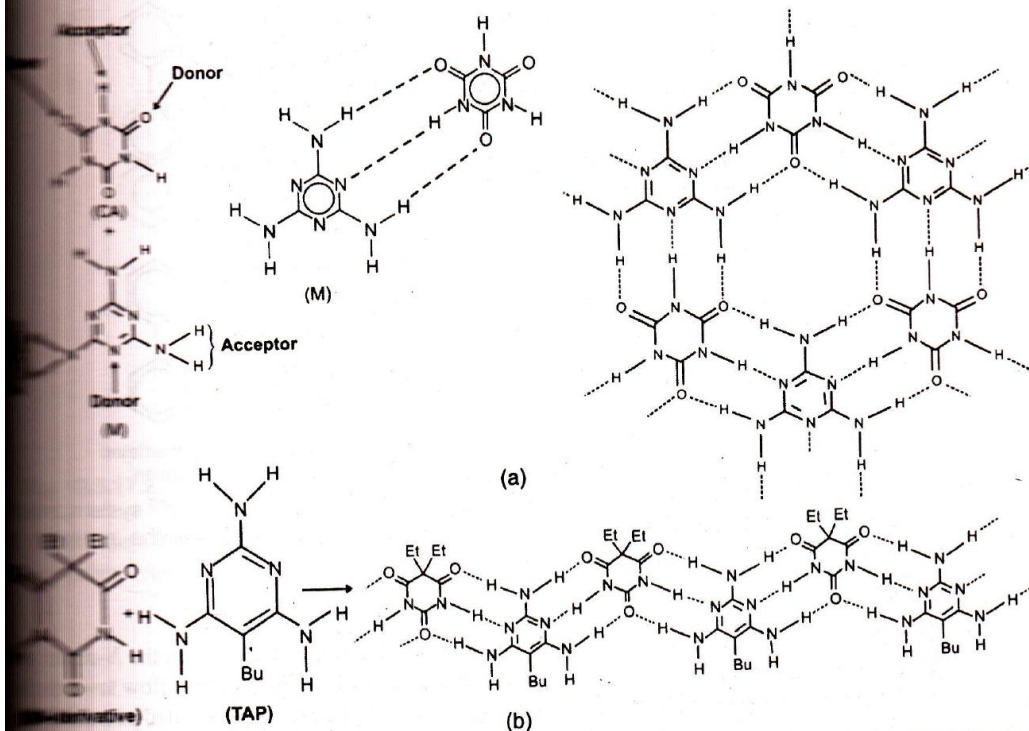

Fig. 13.5.15.1. H-bond directed molecular assembly (i.e. supramolecular polymer) (a) cyanuric acid-melamine polymer; CA exists as keto-enol tautomers; M is cyanuric amide. (b) formation of a **molecular ribbon** through H-bonding between barbituric acid (BA) derivative and triaminopyrimidine TAP.

Barbituric acid (BA) derivative possesses a structure similar to that of cyanuric acid while 2,4,6–**triaminopyrimidine** (TAP) is similar to melamine. They can form 1:1 cocrystal looking like a *molecular ribbon* **which** may be considered as a *supramolecular polymer*.