CBSGS QP Code 03712.

M.Sc - Sem I. Exam - 12-4-17.

Paper - II : Inorganic chemistry -

Q1 (a). (i) Define rate of reaction:- It is defined as the time required for the total concentration of the reactant complexes to be transformed into product complexes. [1M]

[1½] Methods: (1) Photometric method. (2) conductometric method explanation of both methods wring examples. [1½]

(ii) Ligand substitution reaction in octahedral complexes without breaking of metal - ligand bond.

There are reactions in which ligand exchange takes place without breaking the metal - ligand bond. Preparation of an aquo complex from it's carbonato complex is an example of this type of reaction. ie conversion of $[Co^{+3}(NH_3)_5CO_3]^+$ to $[Co^{+3}(NH_3)_5(H_2O)]^{3+}$. when this reaction is carried out in the presence of $(H_3O^{18})^+$, none of O^{18} is found in the resulting aquo complex and CO_2. Hence CO_2 is produced by the cleavage of C-O bond which keeps Co-O bond intact during the aquation reaction.

[2M] $\left[(NH_3)_5Co^{3+}-O+CO_2\right]^+ + 3(H_3O^{18})^+ \longrightarrow \left[Co^{3+}(NH_3)_5(H_2O)\right]^{3+} +$ carbonato complex. $+ 2H_2O^{18} + CO_2$ → Aquo complex.

Mechanism:

The most likely path for this reaction is believed to involve proton attack on the oxygen atom bonded to Co followed by the expulsion of CO_2 and H_2O & then protonation of the hydroxo complex.

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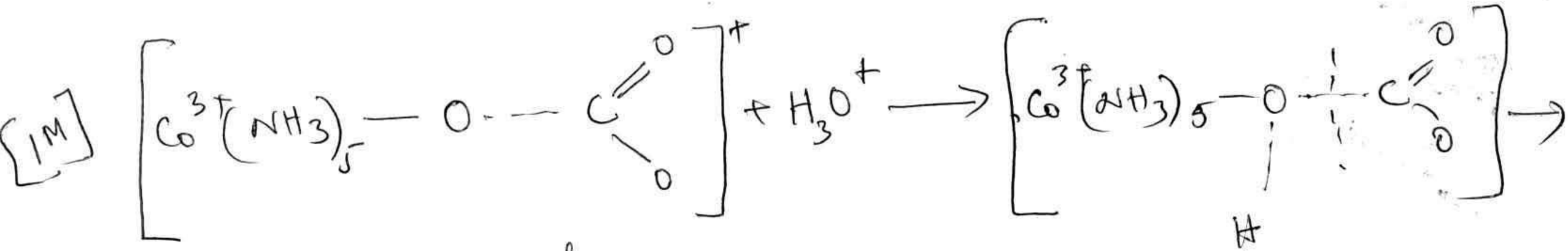
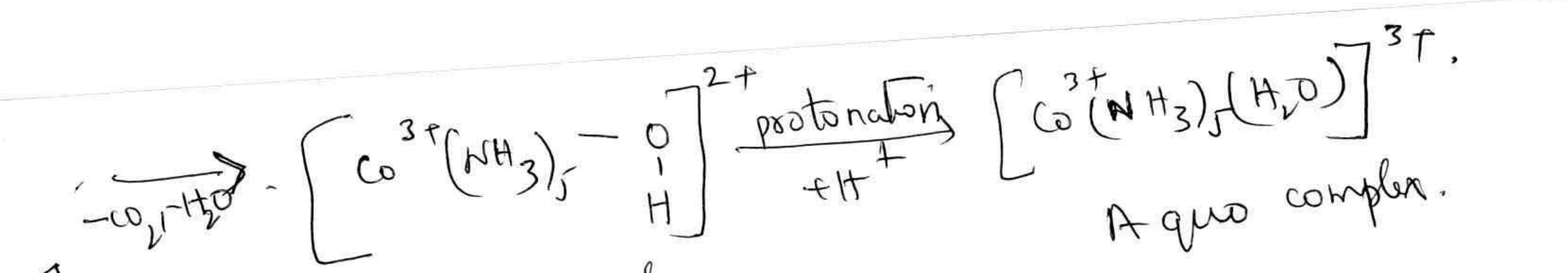
[IM] 

carbonato complex



Hydroxo complex.

Aquo complex.

[IM]

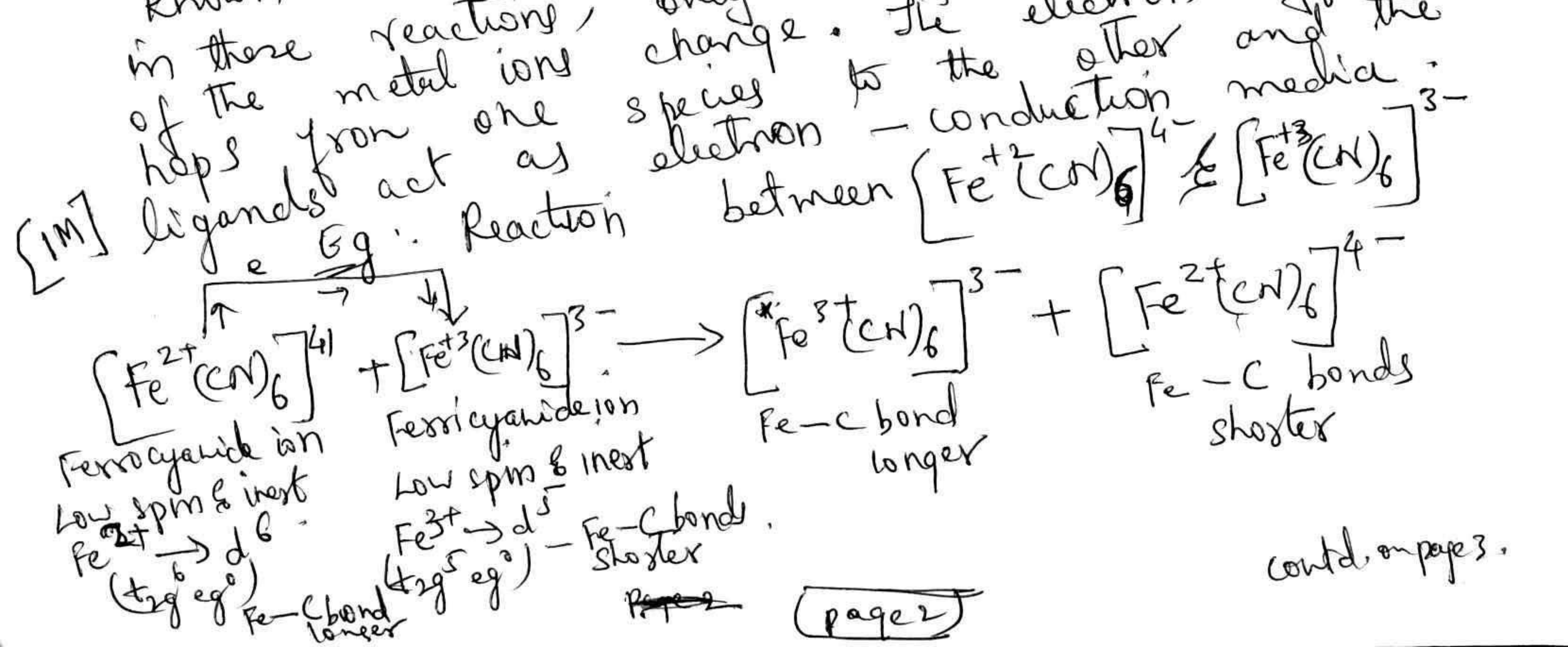
(iii) What are electron transfer reactions? Describe the mechanism of outer sphere electron transfer reaction.

Electron transfer reactions: The reactions in which the transfer of an electron from one atom to the other takes place are known as electron transfer reactions.

[IM] Mechanism of outer sphere electron transfer Reactions.

Outer sphere electron transfer reactions are also known as 'direct electron transfer reactions' because, in these reactions, only the formal valence states of the metal ions change. The electron hops from one species to the other and the ligands act as electron - conduction media.

[IM] e.g.: Reaction between $[Fe^{+2}(CN)_6]^{4-}$ & $[Fe^{+3}(CN)_6]^{3-}$



Ferrocyanide ion
Low spin & inert
$Fe^{2+} \rightarrow d^6$
$(t_{2g}^6 e_g^0)$
Fe–C bond longer

Ferricyanide ion
Low spin & inert
$Fe^{3+} \rightarrow d^5$
$(t_{2g}^5 e_g^0)$ – Fe–C bonds shorter

Fe–C bond longer

Fe–C bonds shorter

contd. on page 3.

The above reaction is fast with 2nd order constant ~ 10^5 at 25°C. There is no heat change in the reaction.

Both the anions are inert. $[Fe(CN)_6]^{4-}$ is a low spin d^6 ($t_{2g}^6 e_g^0$) system and $[Fe(CN)_6]^{3-}$ is a low spin d^5 ($t_{2g}^5 e_g^0$) system. Thus the loss of exchange of CN^- or any substitution [IM] reaction is very fast. The possibility of an electron transfer through a bridged activated complex is eliminated.

When both the reactants are inert as in the present case, the close approach of the metal atoms is impossible & hence electron - transfer takes place by a tunnelling or outer - sphere mechanism.

[IM] In this mechanism, each complex retains it's full co-ordination shell in the activated complex so that there is no ligand common to each central metal atom and an electron is believed to pass through both the coordination shells.

(iv) Mechanism of racemization reaction in octahedral complexes.

Racemization Reaction:- There are reactions, in which one optical form of an optically active metal complex forms it's other form and gets racemised.

[IM] For eg. when (+) $[Cr(C_2O_4)_3]^{3-}$ is placed in water, it racemises to it's optically inactive form.

$$(+)\,[Cr(C_2O_4)_3]^{3-} \longrightarrow (-)\,[Cr(C_2O_4)_3]^{3-} \xrightarrow{(+)\text{-form}}$$

Racemic mixture.

Mechanism: There are two mechanisms by which optically active octahedral complexes racemise. There are ① Intermolecular mechanism and ② Intramolecular mechanism.

contd. on page 4.

① <u>Intermolecular Mechanism</u>:- According to this mechanism, racemisation involves a ligand inter-change process as represented by the equilibria.

[1½M]

$$D - M(AA)_3 \underset{+AA}{\overset{-AA}{\rightleftharpoons}} M(AA)_2 \underset{-AA}{\overset{+AA}{\rightleftharpoons}} L - M(AA)_3.$$

Eg:- The acid hydrolysis of $cis\left[Co(en)_2Cl_2\right]^+$ gives a mixture of cis and trans $\left[Co(en)_2(H_2O)Cl\right]^{2+}$

The mechanism is

$(+)\ cis\left[Co(en)_2Cl_2\right]^+ \xrightarrow{k} (+)\ cis\text{-}\left[Co(en)_2(H_2O)Cl\right]^{2+}$.

$(+)\ cis\left[Co(en)_2Cl_2\right]^+ \xrightarrow{k'} trans\left[Co(en)_2(H_2O)Cl\right]^{2+}$.

Kinetic studies on the racemisation of $(+)\ cis\left[Co(en)_2Cl_2\right]^+$ reveal that the loss of optical rotation does not result from the formation of a symmetrical 5-coordinated intermediate but due to trans isomerisation.

② <u>Intramolecular Mechanism</u>:-

Intramolecular mechanism has been observed in $\left[Fe(phen)_3\right]^{2+}$ to $\left[Fe(bipy)_3\right]^{2+}$ ions. The rate of racemisation is greater than rate of dissociation. The intramolecular racemisation of Fe(II) complex results from an process of expansion which allows loss of activity. Thus, an increase in the inter-atomic distances occurs between donor atom and metal due to the excitation of the low-spin to a high spin state, which then rearrange before returning to the original state. The racemisation may be represented by the equilibria

[1½M]

$$\left[Fe(AA)_3\right]^{2+} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \left[Fe\cdots(AA)_3\right]^{2+} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \left[Fe\cdots(AA)_2\right]^{2+} + AA.$$

from the above equilibria following points are noted

ⓐ if $k_2 > k_3$, then racemisation takes place by intramolecular process

ⓑ if $k_2 < k_3$, " " " intermolecular "

ⓒ if $k_2 \approx k_3$, both mechanisms may contribute to the observed rate of isomerisation.

contd on pg 5

Q1 (a)

(iv). Racemisation Reaction :-

(1M) for octhedl complexes which racemize at an observable rate, mainly two mechanisms are involved,

(a) Intermolecular

(b) Intramolecular

This mechanism is observed in a no. of tris chelate complexes.

(1M) $d-[Ni(phen)_3]^{2+} \rightleftharpoons dl-[Ni(phen)_2(H_2O)_2]^{2+} + phen.$

$dl-[Ni(phen)_2(H_2O)_2]^{2+} + phen \rightleftharpoons l-[Ni(phen)_3]^{2+}$

$[M(C_2O_4)_3]^{-3}$, $[M(acac)_3]$

wher M = Co^{+3}, Cr^{+3}

$[Co(EDTA)]^{-}$, $[Co(bigH)_3]^{3+}$

$[Fe(phen)_3]^{2+}$.

These complexes racemise faster than they exchange ligands.

bigH = biguanide.

↓

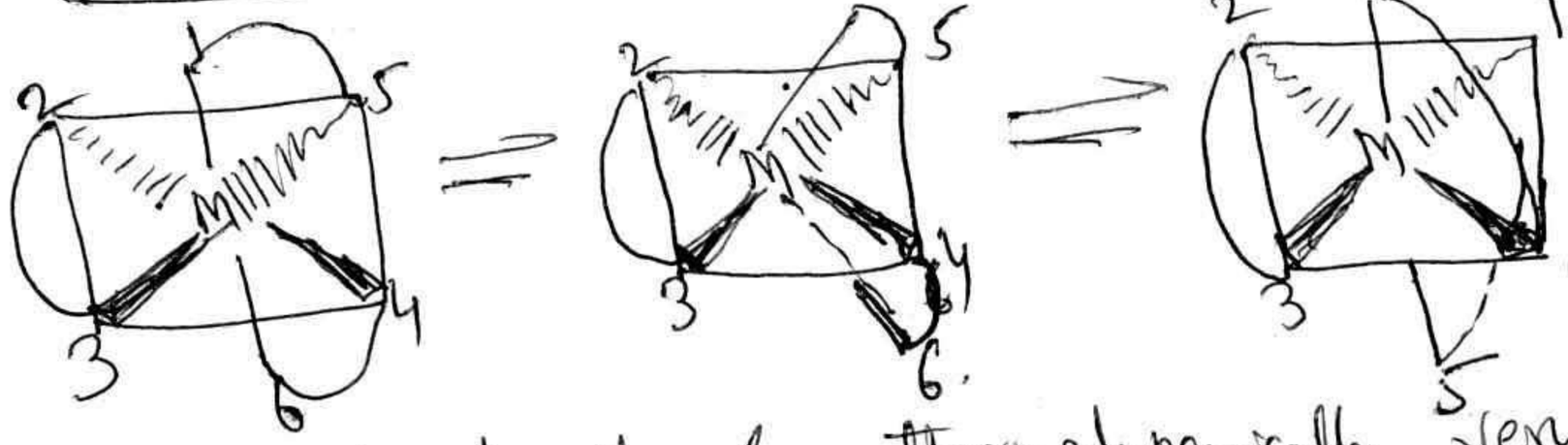
(i) Ray-Dutt twist &.

(ii) Bailer twist.

{Racemisation of $[Co(bigH)_3]^{3+}$

(i). Ray-Dutt twist :-

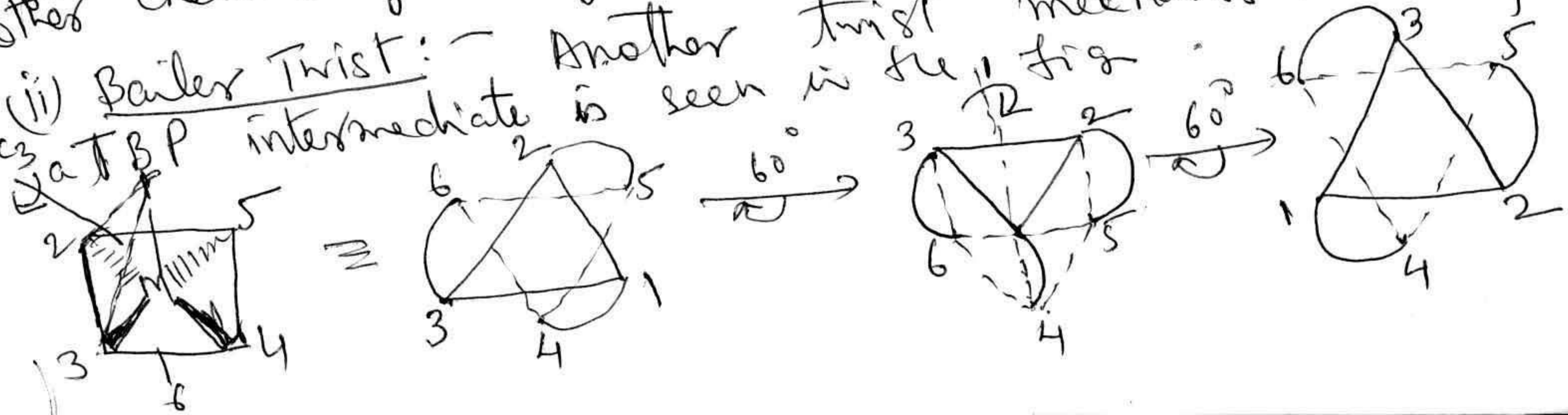
(2M)



It is both kinetically & thermodynamically very stable.

Instead of detachment of one end of a chelate ring, a distortion of the structure occurs by one chelate ring moving up & the other chelate ring moving down.

(ii) Bailer Twist :- Another twist mechanism involving TBP intermediate is seen in fig.



Adolescence

Early adolescence begins with the onset of puberty and ends with the graduation from high school (or roughly at age 18).This stage is characterized by rapid physical changes, significant cognitive and emotional maturation, newly energized sexual interest and a heightened sensitivity to peer relations . This stage is characterized by group identity vs alienation.

PHYSICAL MATURATION:

Early adolescence is marked by rapid physic changes , including height spurt, maturation of reproductive system, appearance of secondary sexual characteristics, increased muscle strength and the redistribution of body weight . At the same time , the brain continues to develop with the changes that increase emotionally, modify memory and gradually improve connections among areas of the brain that regulate emotion , impulse control and judgement (Brownlee, 1999;Spear2000).The time from the appearance of breast buds too full maturity may range from 1 to 6 yrs-girls, the male genitalia may take 2-5 yrs to adult size. These individual differences in maturation suggest that during early adolescence, chronological peer group is biologically far more diverse than it was during early and middle childhoods.

PUBERTY :

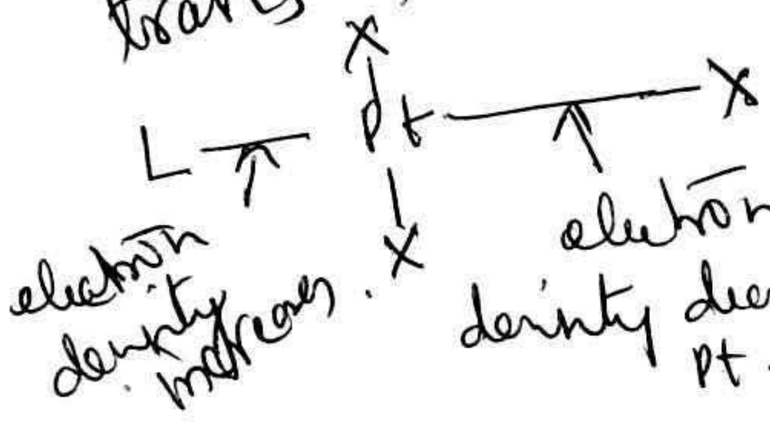
Puberty encompasses a group of inter related neurological and endocrinological changes that influences brain development , changes in sexual maturation, cycles and levels of hormone production and physical growth .Puberty starts when the hypothalamus begins releasing a hormone called gonadotropin releasing hormone (GnRH) GnRH then signals the pituitary gland to release two more hormones (FSH)-to start sexual development. This system – the Hypothalamus, pituitary gland and the gonads often referred to as the HPA axis is responsible for the production and regulation of the sex hormones that result in the growth and the maturation of the reproductive organs (NICHD, 2007). The hypothalamus and pituitary glands are also linked to the

q1 (b) (i) Trans-effect? Explain π-bonding theory of trans-effect.

[1M]

Trans-effect: It defined as the effect of a coordinated group on the rate of the replacement of a group lying trans to it in a metal complex. Chatt et al have proposed that the trans-effect of a group coordinated to a metal ion is the tendency of that group to direct an incoming group to occupy the position trans to that group.

π-bonding theory:- The electrostatic polarisation theory could not explain the high trans-effect of the π bonding ligands like PR_3, NO, CO, C_2H_4 etc which lie at the high end of the series. According to this theory, the vacant π or π* orbitals of the π-bonding ligands accept a pair of electrons from the filled d-orbitals of the metal (d_{xz} or d_{yz} orbital) to form π bond ($d\pi - d\pi$ or $d\pi - p\pi$ bond). In case of [1M] Pt(II) square-planar complex, PtX_3L (L is the π-bonding ligand), the d_{yz} orbital of Pt(II) with a pair of electrons overlaps with the empty p_z orbital of the ligand L to form $d\pi - p\pi$ bond between Pt(II) and L. The formation of the π-bond in the complex increases the electron density in the direction of the ligand, X trans to L and diminishes it in the direction of the trans to L is weakened. The weakening of Pt—X bond trans to L facilitates 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 $PtLX_3Y$



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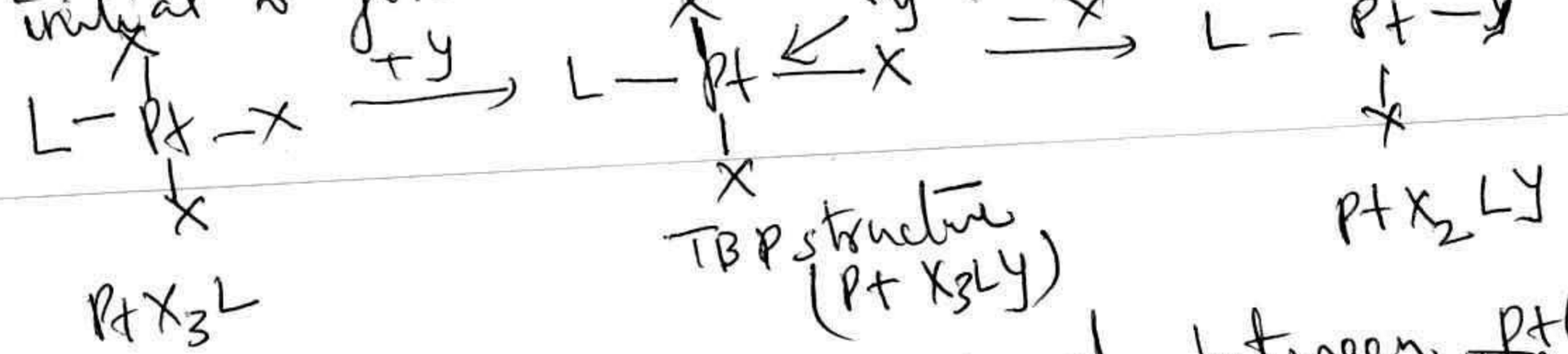
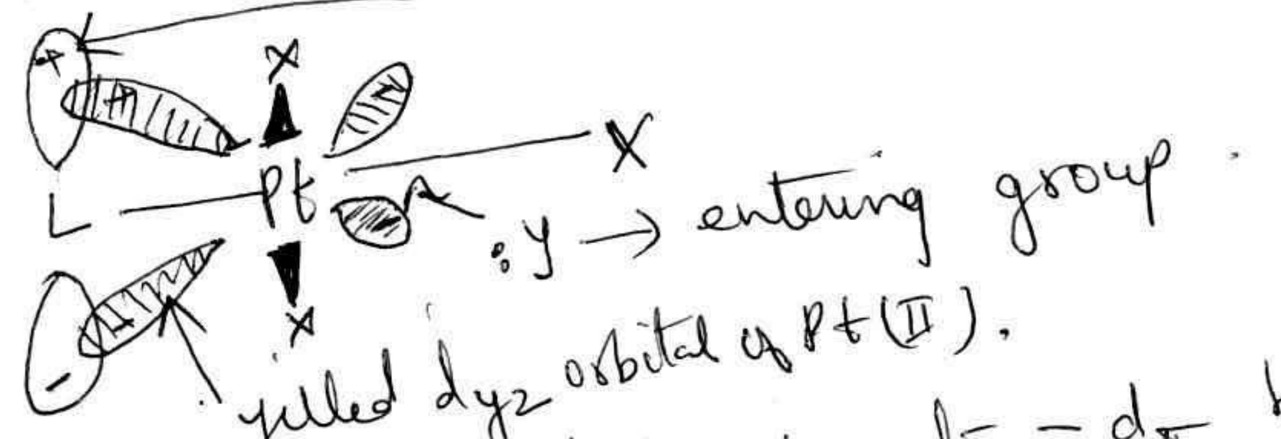
contd. π-bonding theory of trans-effect:

which on losing X, yields $PtLX_3Y$. In the formation of $PtLX_3Y$ the ligand X trans to L is replaced by the incoming group Y. The transition state complex has distorted trigonal-bipyramidal (TBP) structure in which two X's groups which are cis to L both in the initial & final states form the apexes.



The formation of $d_\pi - p\pi$ bond between Pt(II) & the π-bonding ligand, L in the 5-co-ordinated transition activated complex is shown below



[IM] Fig. A :- formation of 5-coordinated activated complex in S_N2 substitution reaction in Pt(II) square-planar complex $PtLX_3$.

A schematic representation of double bond in $Pt=PR_3$ is shown in fig B. A σ-bond is formed by the donation of a pair of electrons from Phosphorus to Platinum and the π-bond by the overlap of a filled d-orbital of Platinum by the vacant d-orbital of P atom of the ligand PR_3 & X are in the xy plane, the d-orbital shown is either d_{xz} or d_{yz}. The removal

[IM] of charge from Pt(II) by π-bonding of L enhances the addition of the entering group Y and favours a more rapid reaction.

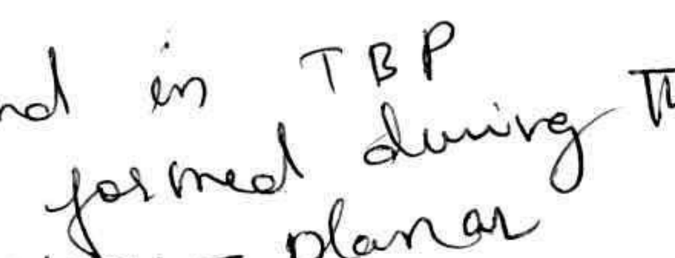


Fig B schematic representation of R_3P-Pt double bond.

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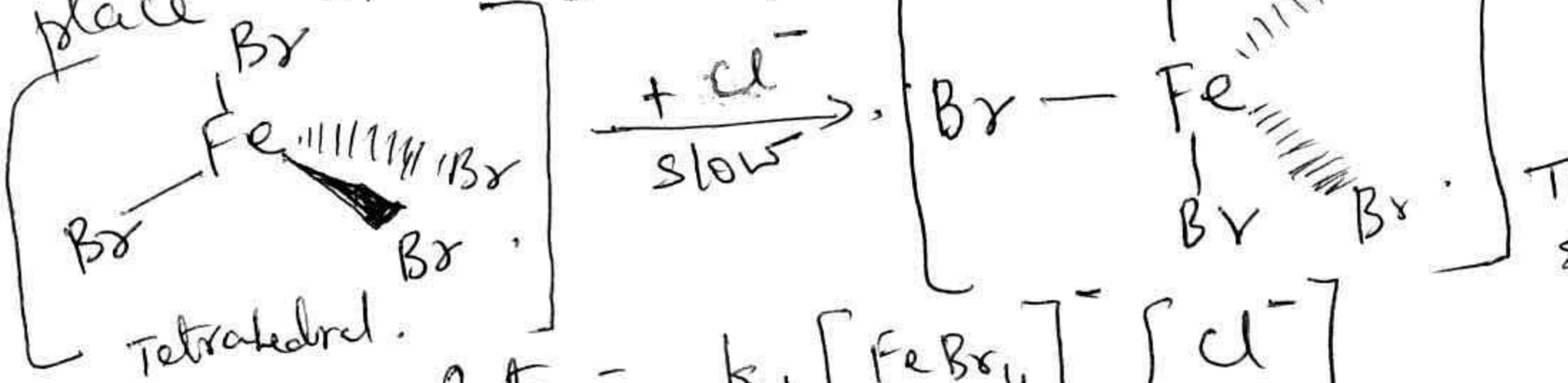
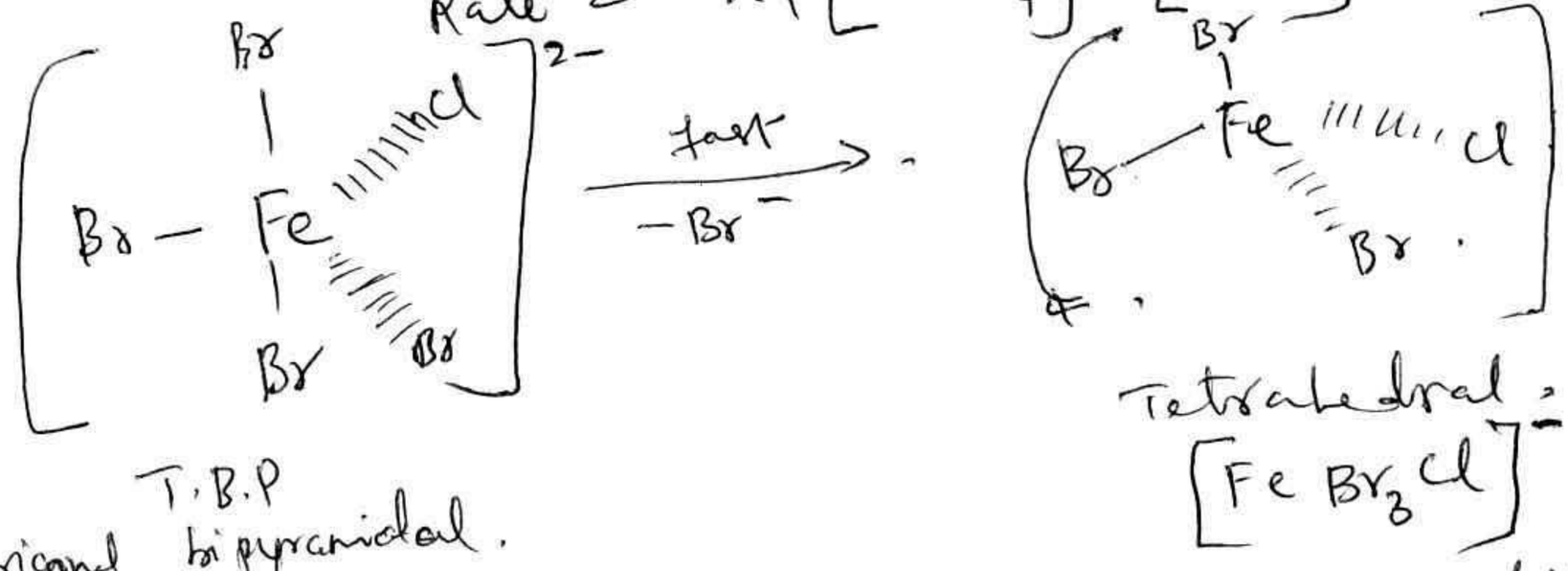
Q | b (ii) Discuss the mechanism of ligand substitution in $[FeBr_4]^-$ by Cl^-

The ligand substitution reactions in complexes, wherein the total no. of electrons in the valency of the central metal atom / ion will be different as compared to the complexes wherein the no. of electrons in the valence shell is 18.

[1M] for eg. in $[FeBr_4]^-$, the no. of electrons in $Fe^{3+} = 3d^5 = 5$ electrons. The total number of electrons in Fe^{3+} in the complex $[FeBr_4]^-$ will be $5 + 4\times2 = 5 + 8 = 13$ electrons. Hence $[FeBr_4]^-$ is a 13 electron species. This complex [1M] will undergo a ligand exchange in which the rate of the reaction depends on the concentration of the complex as well as on the concentration of the ligand Cl^-. The reaction takes place in 2 steps.

step (i) 

$$\text{Rate} = k_1[FeBr_4]^-[Cl^-]$$

[1M] step (ii) 

[1M] From step (i) we can conclude that the substitution reaction is of S_N2 type as the rate of the reaction is dependent on the concentration of the starting complex as well as on the Cl^- in coming ligand Cl^-.

Q2 a) Attempt any two of the following

i) Give any one method of preparation and any two characteristics reactions of transition metal alkyl complexes.

Transition metal alkyl Complexes can be prepared by various methods. The important methods are

1. Halide carbanion exchange reaction (Metathesis)

$$MR + EX \longrightarrow MX + ER$$

$$4\,LiMe + TiCl_4 \xrightarrow[-80^\circ C]{ether} 4LiCl + TiMe_4$$

2. Transmetallation reaction. [1M]

$$M + M'R \longrightarrow MR + M' \quad (M \text{ is more electro positive than } M')$$

$$TiCl_4 + PbR_4 \longrightarrow TiCl_3R + PbClR_3.$$

3. Insertion reaction:

$$trans\,[PtHCl(PEt_3)_2] + C_2H_4 \longrightarrow trans\,[PtCl(C_2H_5)(PEt_3)_2]$$

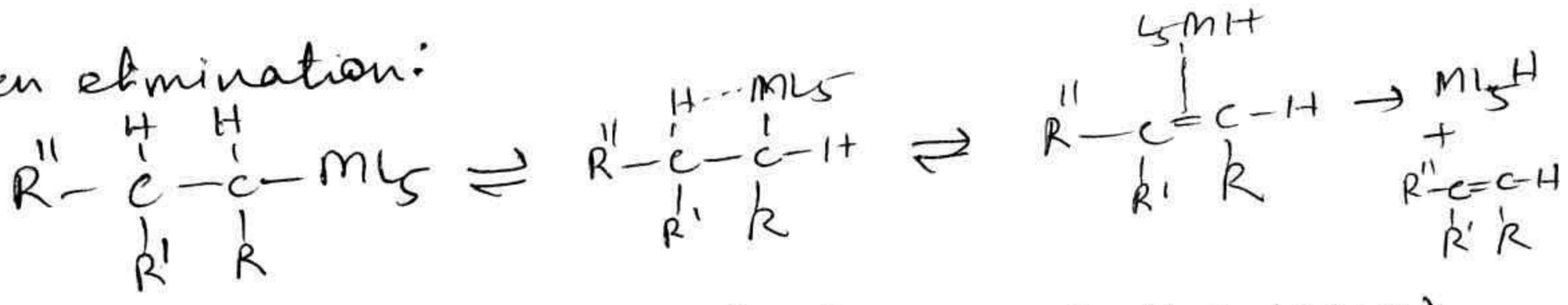
4. Oxidative addition reaction.

$$[IrCl(CO)(PPh_3)_2] + CH_3I \longrightarrow [Ir(CH_3)(Cl)(I)(CO)(PPh_3)_2]$$

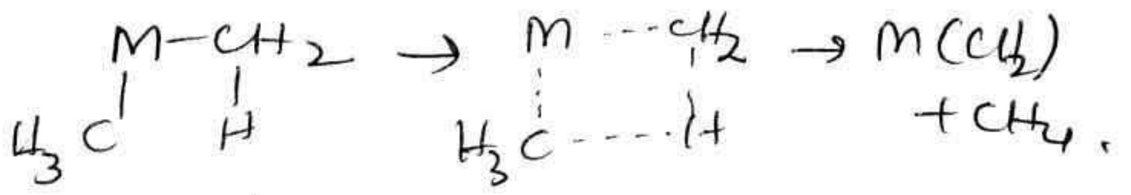
General characteristics reaction

Transition metal alkyls are less stable Compared to main group analogues. The instability is due to presence of empty 'd' orbitals which facilitates their decomposition via routes in which transition increase their coordination number.

1) β-hydrogen elimination: [3M]



ii) α-elimination reaction : $W(Me)_6 \longrightarrow 3CH_4 + W(CH_2)_3$.



3) Intermolecular reductive elimination.

$$4\,MXY \longrightarrow 4\,M + X-Y$$

$$[Pt(CH)(R)(PPh_3)_2] \longrightarrow Pt(PPh_3)_2 + RH.$$

4) Insertion reaction: insertion of CO, SO_2

$$Mn(CH_3)(CO)_5 + CO \longrightarrow (CO)_5Mn-CO-CH_3$$

2 a ii) With reference to Fischer Carbene Complexes, give
1) any two characteristics 2) any one method of
preparation 3) any two chemical reactions.

[1M] 1) Characteristics of Fischer carbenes : $(M=C\begin{smallmatrix}X\\Y\end{smallmatrix})$

1) metal in low oxidation state
2) $:C\begin{smallmatrix}X\\Y\end{smallmatrix}$ ligand has atleast one electronegative hetero atom attached.
a) π accepting auxillary ligands (CO)
b) Substituents on carbene carbon capable of donating π e⁻ density eg: alkoxy, alkylated amines
3) Carbene carbon behaves as an electrophile
4) acts as 2e⁻ donor.

[1M] 2) Preparation ① From metal carbonyl

$$W(CO)_6 + PhLi \rightarrow \left[(CO)_5W-C(O^-Li^+)Ph\right] \xrightarrow[\text{oxonium salts}]{OMe_3^+} \left[(CO)_5W=C(OMe)Ph\right]$$

② From Coordinated thiocarbonyls.

$$[(CO)_5WCS] + HNR_2 \longrightarrow \left[(CO)_5W=C(SH)NR_2\right]$$

③ Nucleophilic attack on coordinated unsatmated ligand followed by proton transfer.

$$trans\left[Cl(PEt_3)_2Pt(C\equiv NR)\right]^+ + HY \rightarrow trans\left[Cl(PEt_3)_2Pt=C(NHR)Y\right]$$

3) any two chemical reaction.

[2M] 1) The carbene carbon is electrophilic in nature.

$$(CO)_5Cr=C(OMe)Me \xrightarrow{NH_3} (CO)_5Cr-C(OMe)(Me)(NH_3) \rightarrow (CO)_5Cr=C(NH_2)Me + MeOH.$$

2) Ligand substitution reaction

$$(CO)_5Cr=C(OMe)Me \xrightarrow{PR_3} (CO)_4(PR_3)Cr=C(OMe)Me + CO.$$

$$(CO)_5Cr=C(OMe)Me \xrightarrow{Me_2NH} (CO)_5Cr=C(NMe_2)Me + MeOH$$

2a iv) State 16e⁻ rule. With the help of suitable examples show which of the following complexes obey the rule.

Organometallic complexes (usually square planar d8 metals obey 16e⁻ rule.

[1M] "Central metal atom keeps on accepting ligands till it possesses 16 valence electrons."

[1M] 1) $[Rh(CH_3)(Br)(CO)_3]$

Rh =
CH_3 =
Br =
3CO = 3

does not obey the rule.

[1M] 2) $[Ir(PPh_3)_3Cl]$

Ir =
$3PPh_3 = 3x$
1Cl =

obeys the rule.

[1M] 3) $[Pt(\eta^2C_2H_4)(PPh_3)_3]$

Pt
$\eta^2C_2H_4$
$3PPh_3$ =

does not obey the rule.

2a iii) Give any one method of preparation of dibenzene chromium(0). Explain its structure and bonding on the basis of valence bond theory.

[1M] Preparation: 1) Generation of a highly unsaturated metal by reducing a higher oxidation state in presence of arene.

$3CrCl_3 + AlCl_3 + 6C_6H_6 + 2Al \longrightarrow 3[Cr(\eta^6C_6H_6)_2]^+[AlCl_4]^-$

$\downarrow Na_2S_2O_4$

$[Cr(\eta^6C_6H_6)_2] + NaAlCl_4 + SO_2$

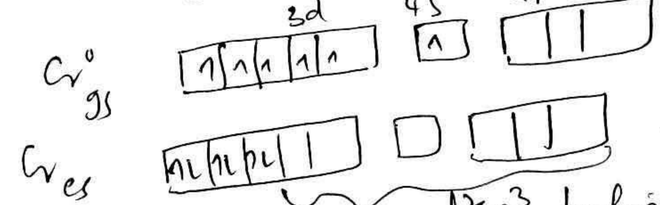
2) Metal vapour synthesis:

$Cr(s) + C_6H_6 \xrightarrow[\text{warm}]{\text{Co-condense}} [Cr(C_6H_6)_2]$

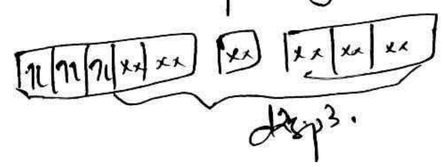
[1M] Structure:

Complex is diamagnetic. obey 18e⁻ rule.

VBT: Cr^0 [Ar] $3d^4 4s^2$ / $3d^5 4s^1$



$Cr \equiv [Cr(\eta^6C_6H_6)_2]$



xx : e⁻ donated by $\eta^6C_6H_6$.

$\eta^6C_6H_6$ acts as 6e⁻ donor. Two $\eta^6C_6H_6$ donate 12e⁻

[2M]

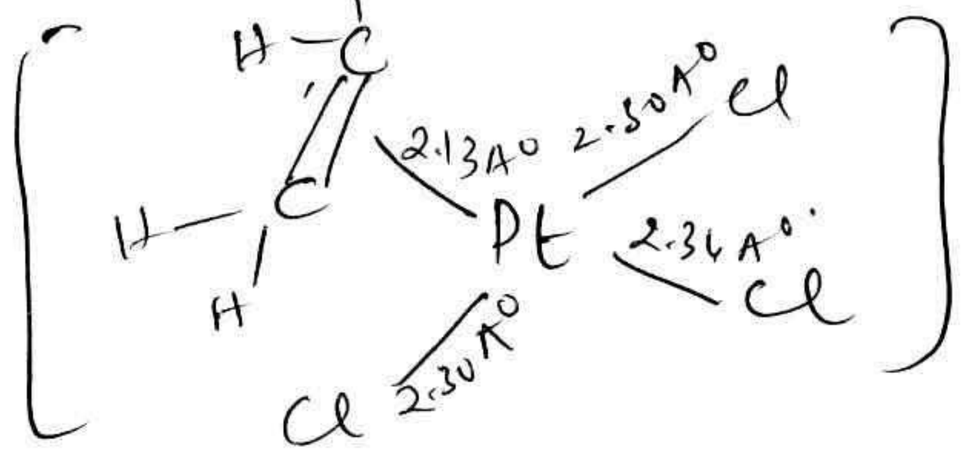
Attempt any one of the following: (13)

2b i) Give any one method of preparation of Zeise's salt. Draw its structure and explain the bonding.

Preparation: Synthensed by passing ethylene through an Aqueous solution Potassium chloroplatinate (II)

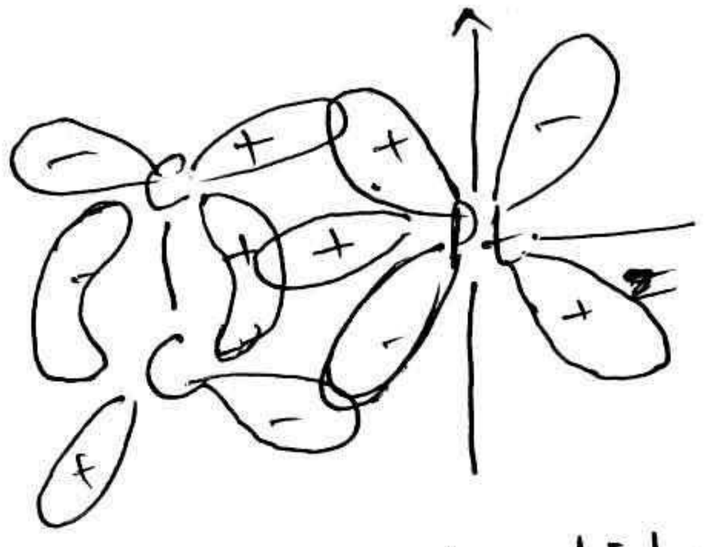
[1M] $[PtCl_4]^{-2} + CH_2=CH_2 \longrightarrow [Pt(C_2H_4)Cl_3]^- + Cl^-$

[1M]



Ethylene occupies fourth site of the square planar Complex with C–C axis to the plane. Both the Carbons atoms are equidistant from platinum but the C–C bond length is increased from 133.7pm in ethylene to 137.1pm in the complex.

[2M]



1) dsp^2 hybrid orbital of platinum overlaps with filled π BMO of ethylene. (σ bond)

2) Back bonding takes place by overlap of [filled dxz orbital & empty π^* orbital of ethylene.

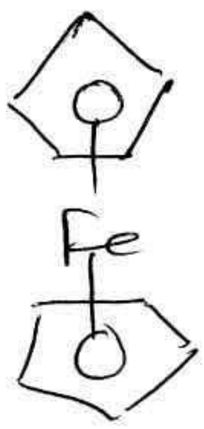
2 b ii) How is ferrocene prepared by using cyclopentadienyl Grignard reagent? Give any three chemical reactions of ferrocene.

Preparation:

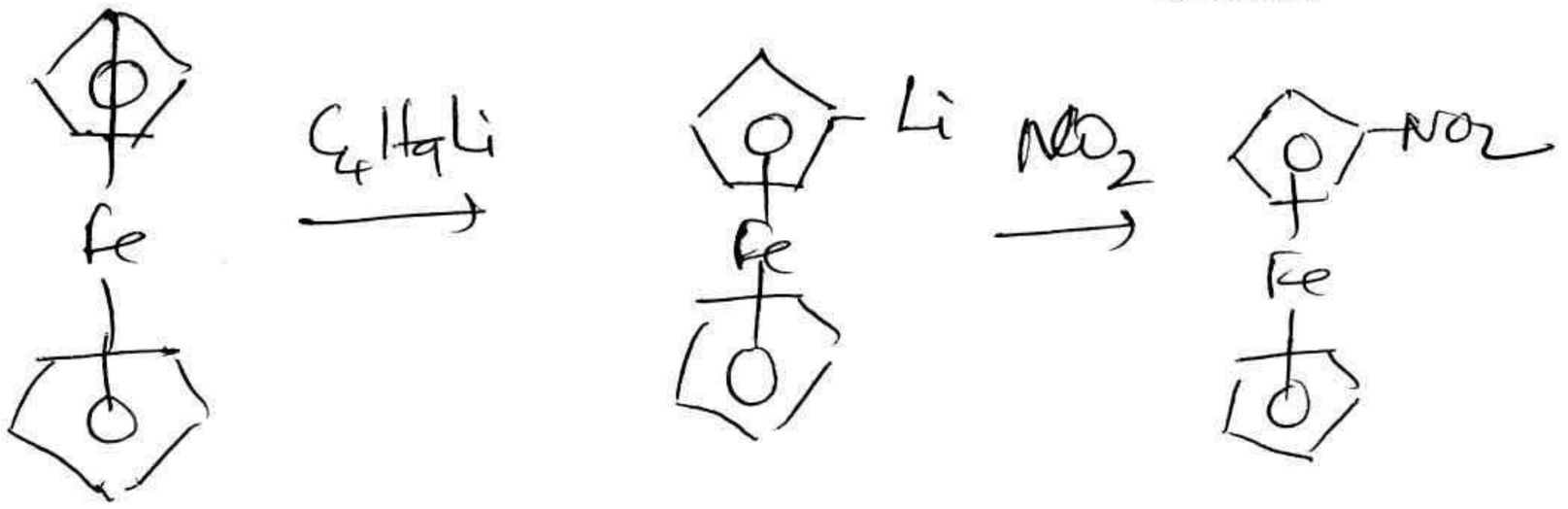
$$2\,FeCl_3 + 2\,C_5H_5MgBr \longrightarrow 2\,FeCl_2 + C_5H_5{-}C_5H_5 + MgBr_2 + MgCl_2$$

$$2\,C_5H_5MgBr + FeCl_2 \longrightarrow (C_5H_5)_2Fe + MgCl_2 + MgBr_2$$

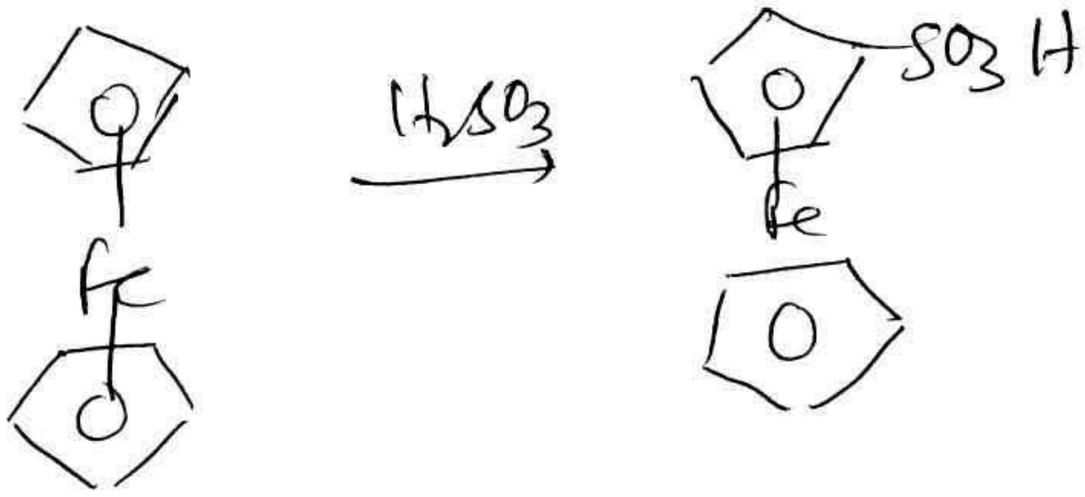
[1M]

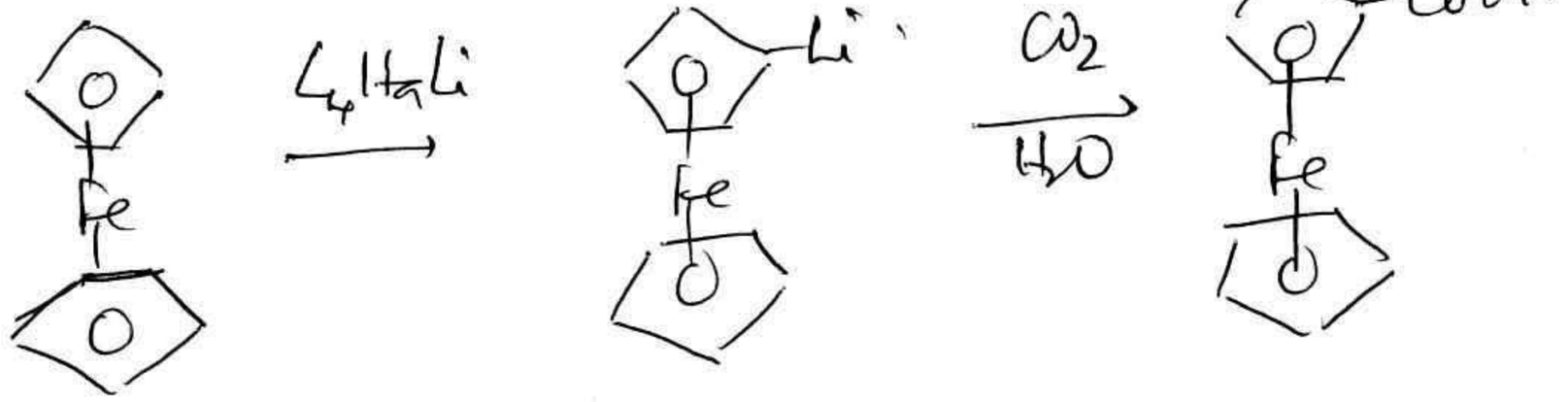
1) 

monoacetyl deriv

2) 

[3M for 3 reactions]

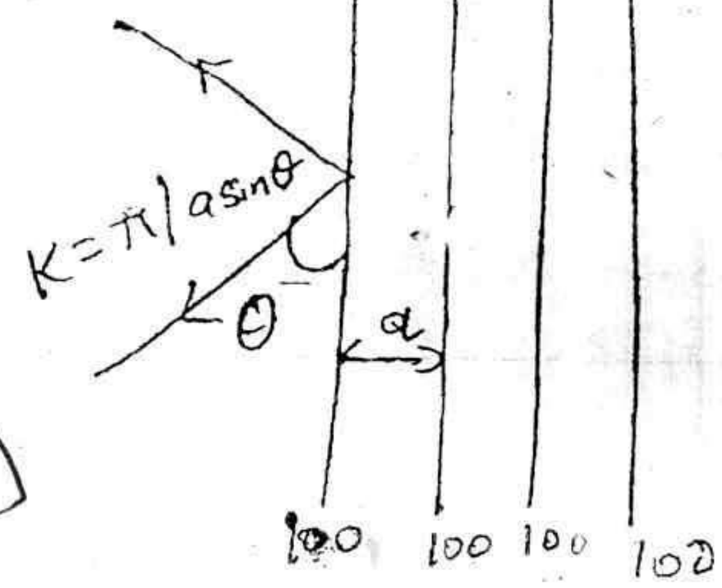
3) 

4) 

Q2 a;) Explain the origin of 1st Brillouin zone boundary in K space and diffraction of e⁻ in 100 plane.

The 1st Brillouin zone is defined as a set [1M] of points in K space that can be reached from origin without crossing Braggs plane.

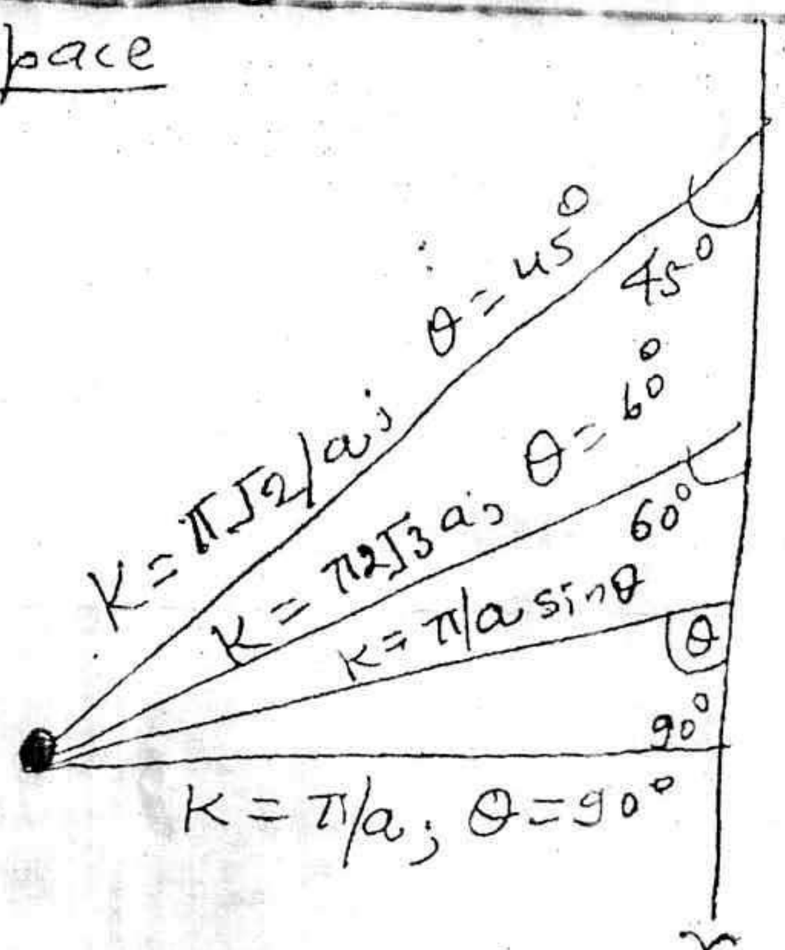
(a) Real Space



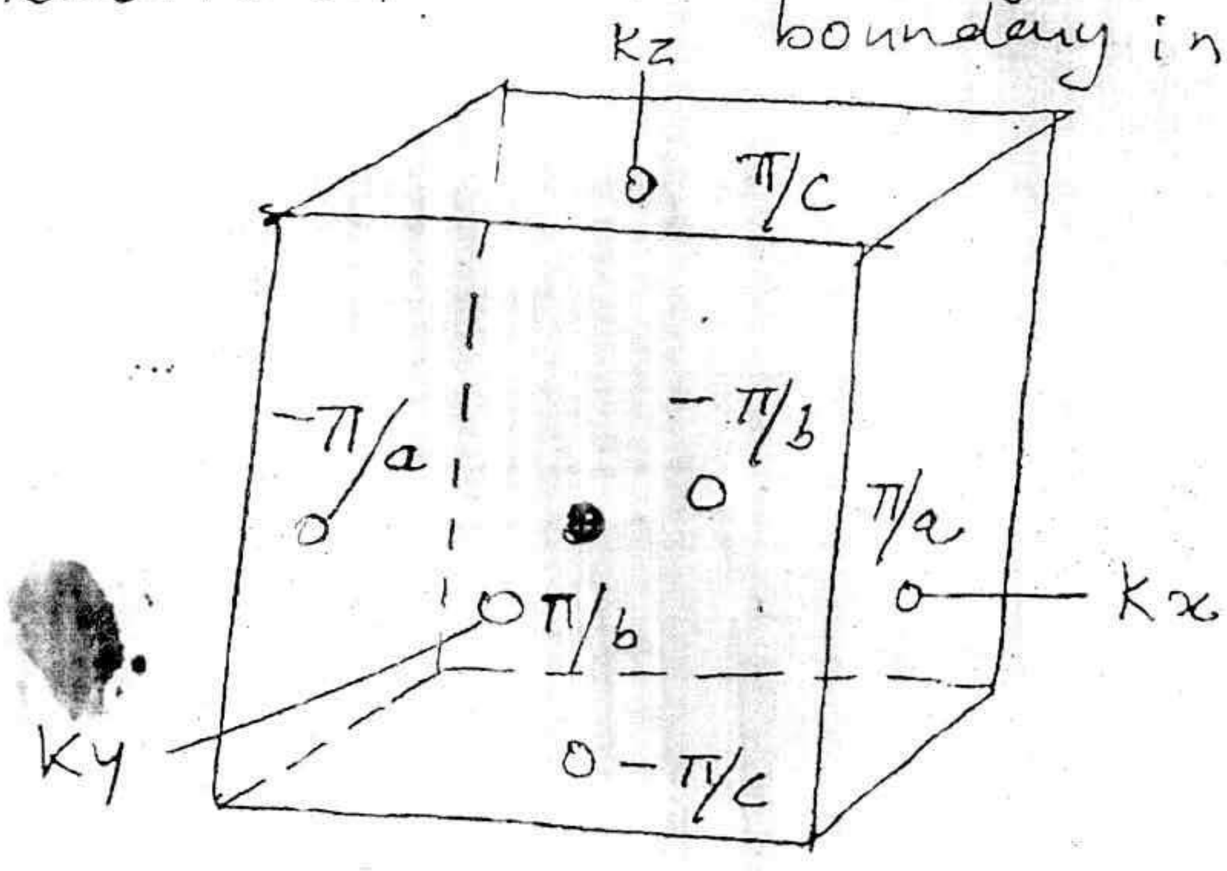
[1M]

Diffraction of e⁻ from 100 planes in real space.

(b) K Space



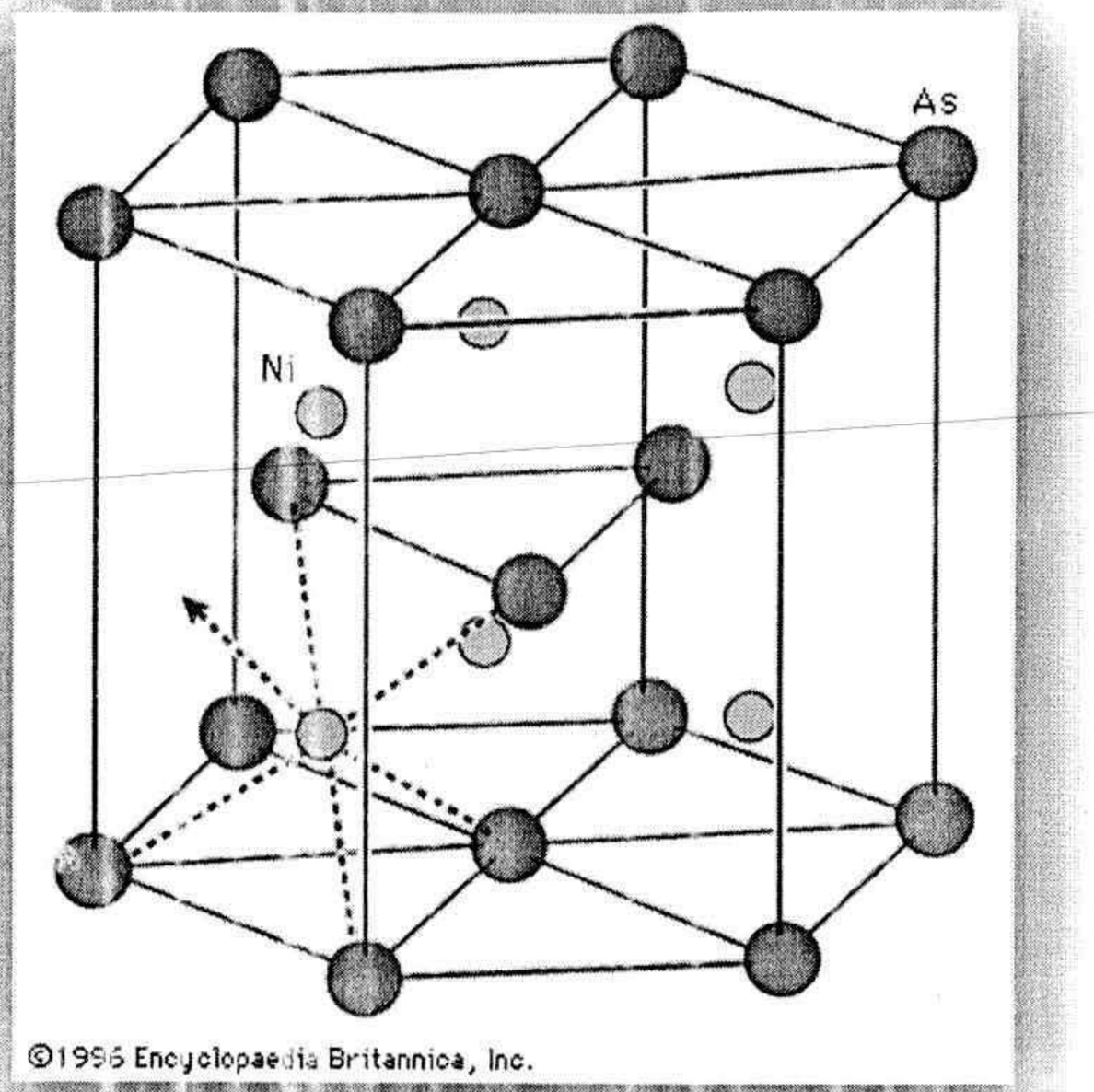
Origin of Brillouin zone boundary in K space.



[2M]

First Brillouin zone for primitive cubic lattice

Q 3a (ii) Structure and Salient feature of NiAs



- Hexagonal close packing of Arsenide ions
- All octahedral voids occupied by Ni ions
- Six Ni atoms sit at the corners of a trigonal prism at the center of which Arsenide ion is located
- Arsenide ion does not sit midway between any two Ni^{2+} ions ∴ metal ions can have direct interactions.
- Crystals possessing this structure are better conductors of electricity.

Q.3a (iii) Preparation of inorganic Materials by ceramic method. State it's merits & demerits.

In the ceramic method, the two solids are heated together, they react to form the required product. This method is used both in laboratory and in industries. High temperature superconductors were prepared by this method.

Eg. Preparation of Samarium Sulphide (SmS): In SmS, Sm is in +2 oxidation state than in the common + 3 oxidation state. Samarium metal in the powdered form and powdered sulphur were mixed together& heated to about 1000K in an evacuated silica tube. Silica is a common choice for the reaction tube as it is stable at high temperature & chemically inert. Sulphur has a low boiling temperature ie 717K & an evacuated tube is necessary to prevent it from boiling off & being lost from the reaction vessel.The product from the initial heating was then homogenized & heated to about 2300K in a sealed tantalum tube by passing an electric current through the tube.The resistance of tantalum results in electrical energy being converted to heat as in an electric fire. This is a common method of heating up to 2300K . [1.1/2M]

Eg: $YBa_2Cu_3O_7$ (High temperature superconductor) $Y_2O_{3(s)} + BaO_{3(s)} + CuO_{(s)} \rightarrow YBa_2Cu_3O_7$ [1/2M]

Merits: 1) The first high temperature superconductor was prepared by this method.

2) Compounds of unusual composition can be prepared .

3)All the materials which have high thermal stability can be used to prepare required inorganic Solids.

4) Inorganic chalcogenites can be prepared by this method. [1M]

Demerits: 1) The method requires a high temperature.This requires a high input of energy.

2) At a high temperature, the compound may get decomposed.

3) The solid state reaction is slow, because the reaction takes place in solid state , no melt melt is formed.The slowness of reaction is due to (a) phase boundary set at point of contact between reactants.(bb) diffusion process begins to form product which required longer time & reaction becomes slower.

4) The product is often not homogeneous in composition.

5) No indicator to decide the completion of the reaction. [1M]

8'3b (iv)

Give the applications of nano particles in the field of semiconductors and solar cells. (4M)

(1) In the field of S.C

(I) Semiconductor is a material having the electrical cond between conductor and insulator. When the size of the semiconductor material reduces to nanoscale their physical and chemical properties changes dramatically mainly due to their large surface area and quantum size effect.

(II) Semiconductor nanomaterials due to their interesting physical and chemical properties and useful functionality in compare to conventional material find specific place in provisions.

(1) narrow and intensive emmission spectra continuous bands
(II) Photobalancing stability.
(III) very high dispersity (high surface to volume ratio) of semiconductors
(IV) nano particle S.C attracted significant interest in research and applications in diverse disciplines such as solid state physics and all branches of chemistry.
[4M]
V) in the field of nanoelectronics, nano photonics energy conversion environmental purification hydrogen production TiO_2 S.C act as photo catalyst nanowires, tubes etc.

Field of Solar cell
Green chemistry,
Solar cells operated with the help of nanoparticles.

(2M)

Q NO. 3b) (i)

Attempt any one of the following:-

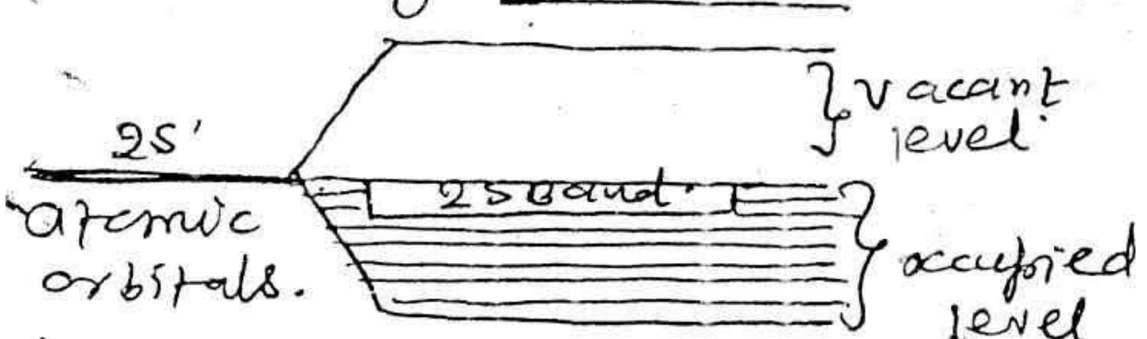
3b (i) On the basis of band theory, explain the electrical properties of lithium (alkali) metal and beryllium metals (alkaline earth metal). (4M)

Li (3) $1s^2 2s^1$ 4S ↑↓ 2S ↑

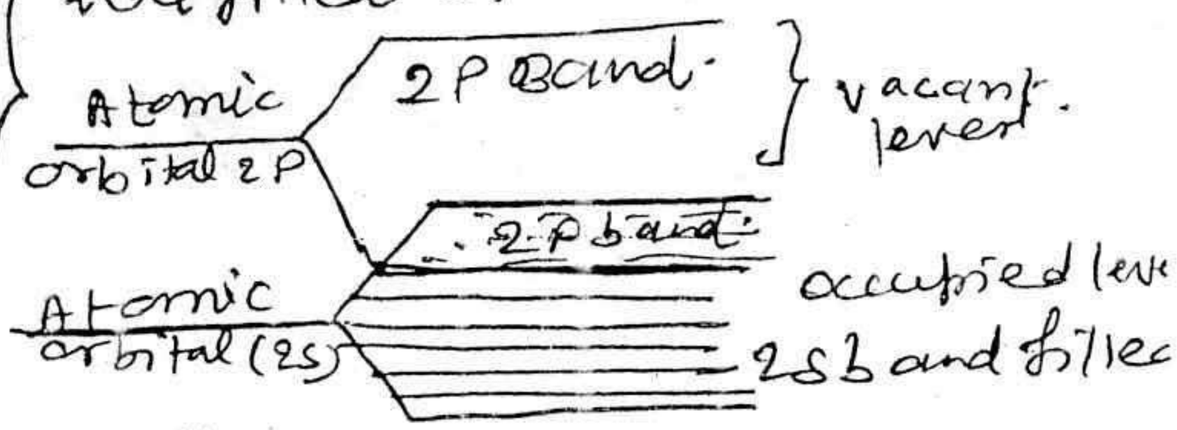
Be (4) $1s^2 2s^2$ ↑↓ ↑↓ Should not be conductor of electricity however it is very good conductor of electricity. can be explained on the basis of band theory with the help of following diagrams

[1M]

molecular orbitals for Lithium showing half filled 2S band



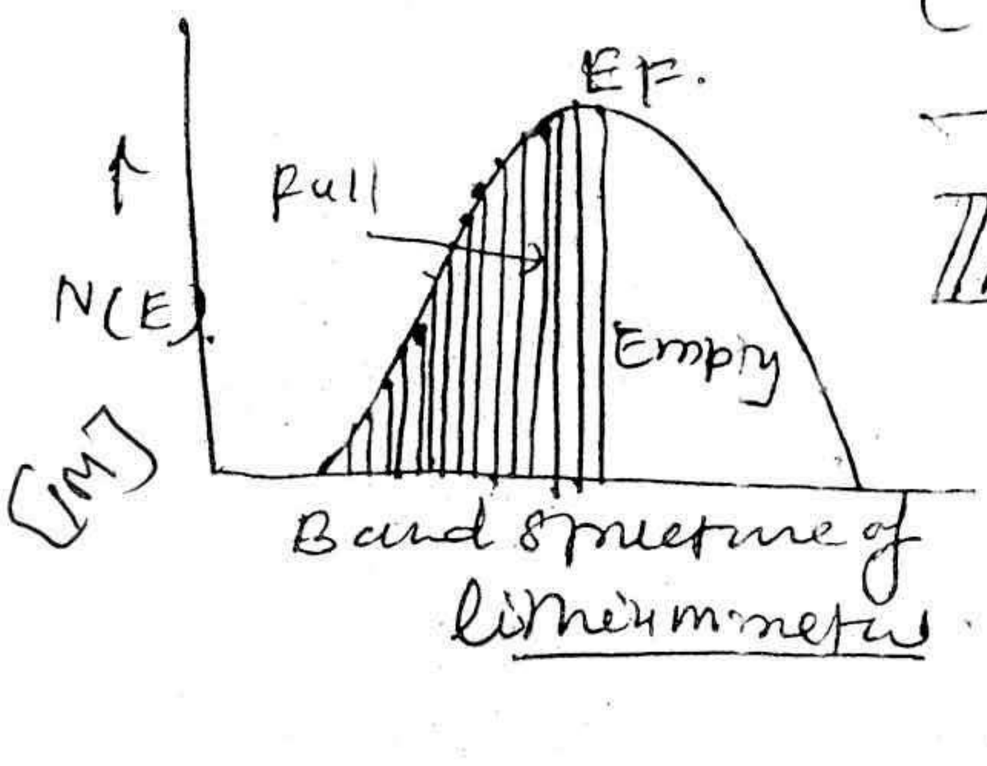
M.O for beryllium showing half filled 2P band.

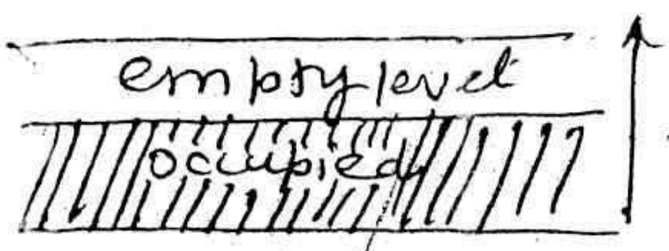


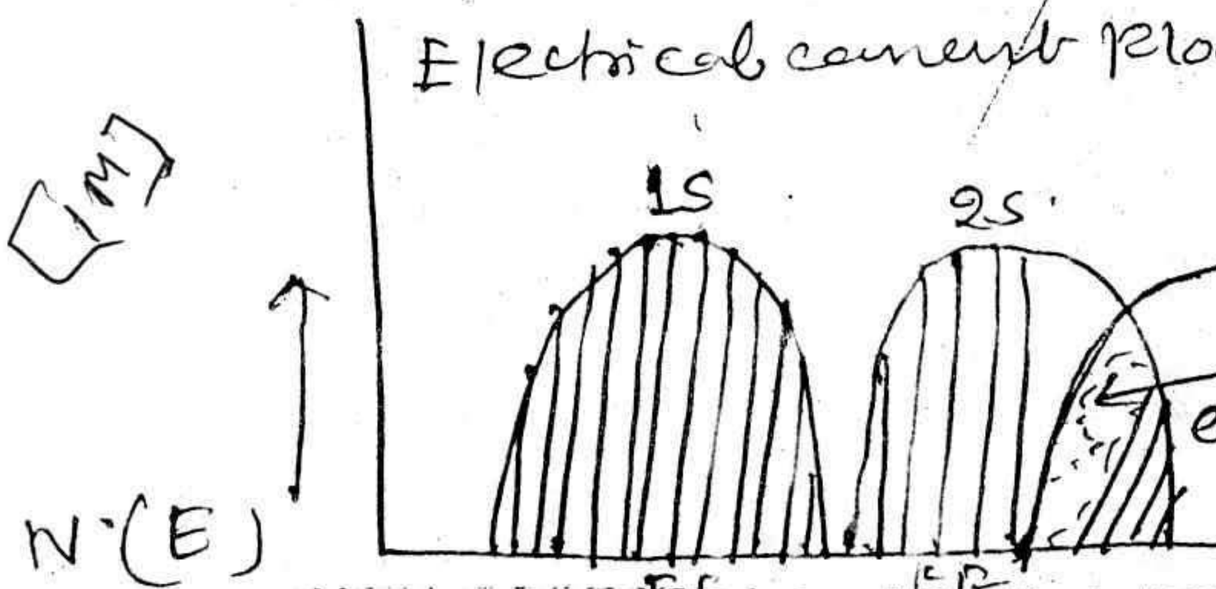
[1M]

(2M) (Li)

(2M) (Be)







Due to less difference in the energy of 2S and 2P orbitals of beryllium M overlapping of empty 2p orbitals with 2s orbital of Be is possible.

(Band structure of Be metal)

[1M]

Q3b(ii) How are nanomaterials prepared by micro-organisms.

Microorganisms are capable of interacting with metals. coming in contact with them through their cells and form nanoparticles. There are two types of microorganisms cells (i) Prokaryotic cell (ii) Eukaryotic cells.

[1M] The cell-metal interaction is very complicated due to the complexity of cells themselves.

(i) Microorganism → produce H_2 gas

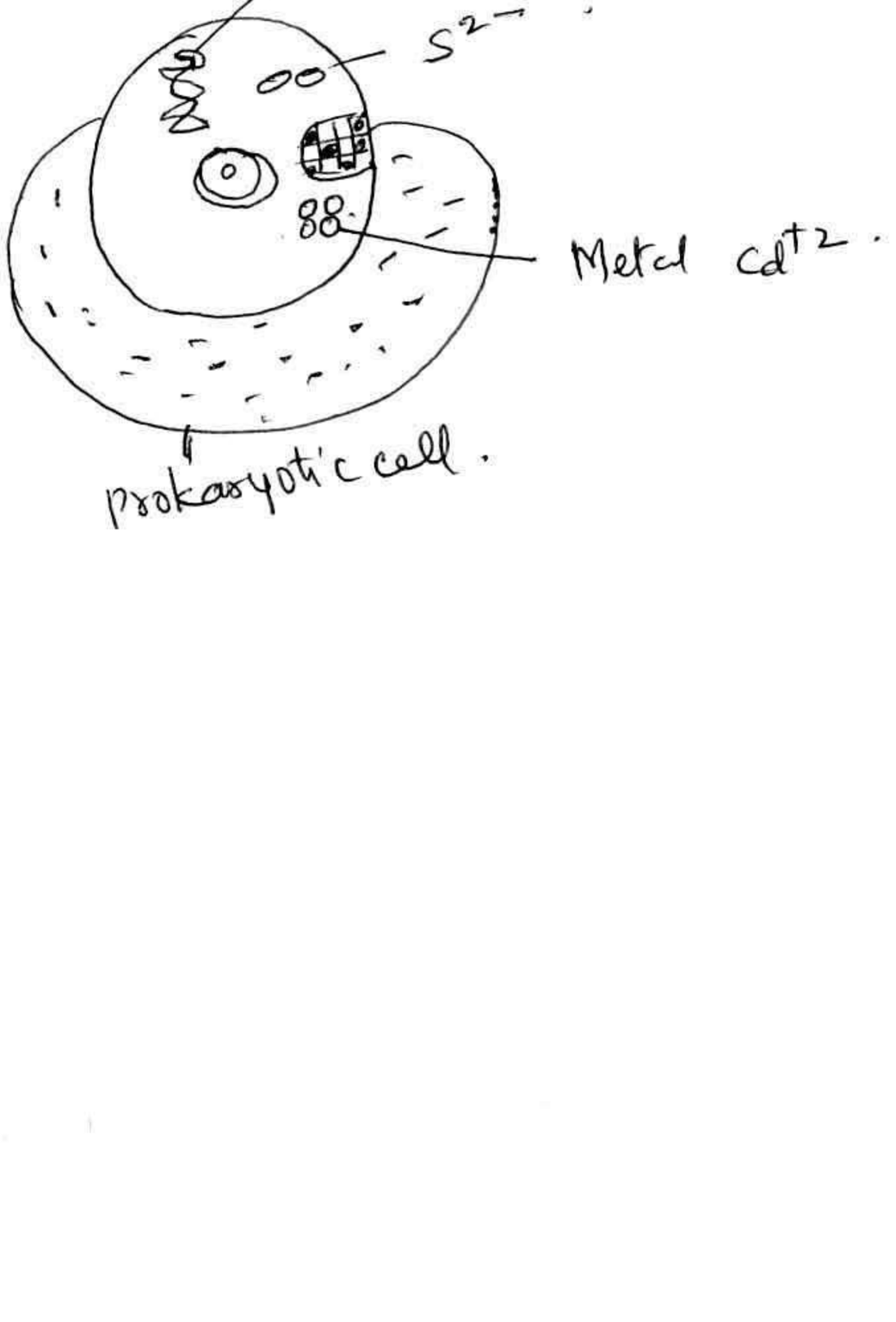
M^{+2} (Cd^{+2}) $+H_2S$ → CdS → can be deported extracellularly.

(ii) can oxidise organic matter and join SO_4^{2-} which act as the electron acceptor for metabolism. Fusarium

[3M] oxysporum microorganism forms CdS nanoparticles.

CdS (extracellular precipitation).

$Cd^{+2} + S^{2-} \rightarrow CdS$.



Q4(a)(i) Electronic spectra exhibited by octahedral $[Ni(NH_3)_6]^{2+}$ complex ion.

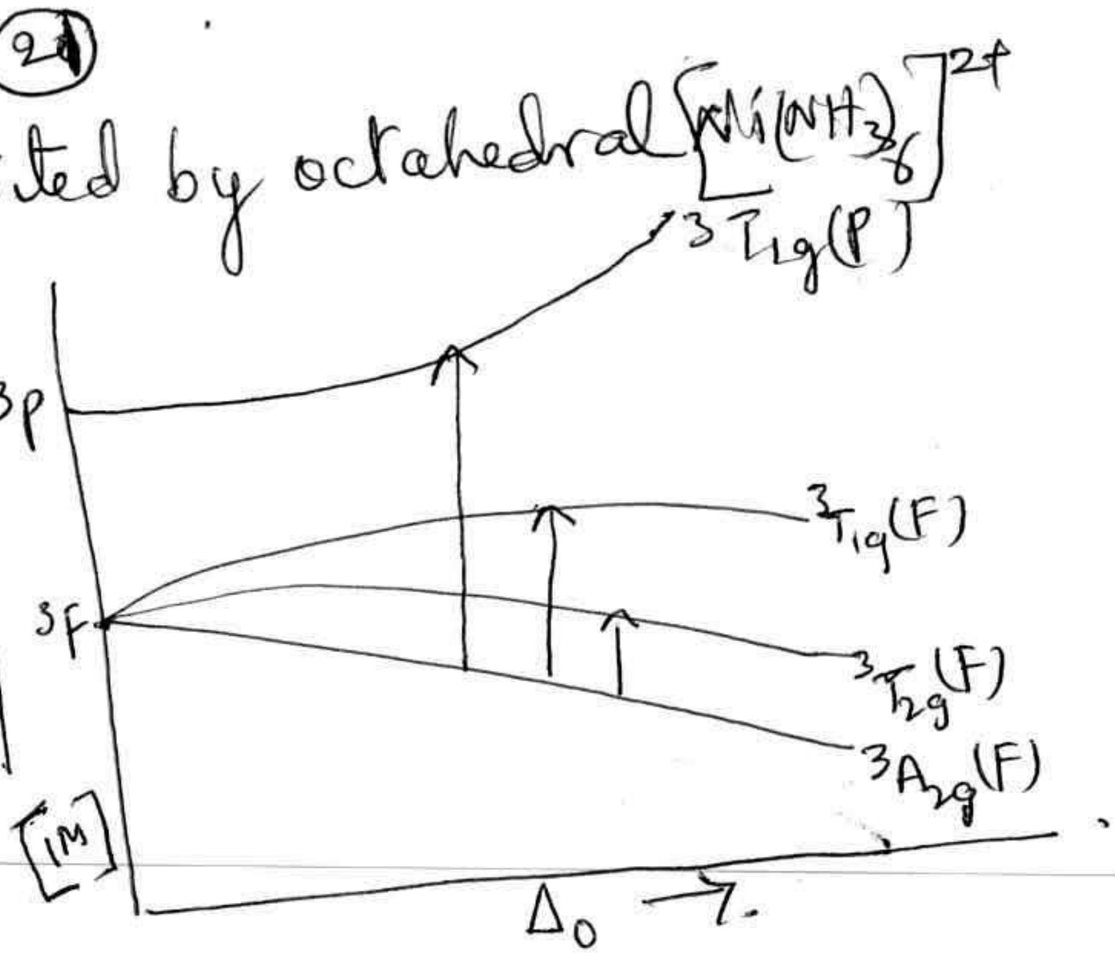
The electronic spectrum of [1M] octhdl $[Ni(NH_3)_6]^{2+}$ shows three bands. The involved transitions are

(1) from $^3A_{2g}(F) \xrightarrow{\nu_1} {}^3T_{2g}(F)$

(2) from $^3A_{2g}(F) \xrightarrow{\nu_2} {}^3T_{1g}(F)$

(3) from $^3A_{2g}(F) \xrightarrow{\nu_3} {}^3T_{1g}(P)$

[1M] $\nu_1 = 10,750\ cm^{-1}$ $\nu_2 = 17,500\ cm^{-1}$, $\nu_3 = 28,200\ cm^{-1}$.



Q4(a)(ii) Nature of metal – N bond in metal complexes by IR.

[1M] Studies were carried out on dialkylamido derivatives of transition metals to study the stretching frequency of the metal – Nitrogen bond by Infra Red spectroscopy. All the compounds examined had a characteristic strong band in 590 – 200 cm region. for a tetrakis dialkyl amido - metal(IV) compounds, which has a tetrahedral structure, the MN_4 system, an infra-red band ν_3 occurs involving the asymmetric metal – N stretching vibration. It is suggested that this [2M] corresponds to the characteristic band. The IR values for $M(NR_2)_4$ complexes of Ti, Zr, Hf, & V are given below. IR values show that the covalent bond formed between Metal ion & the ligand containg N are strong, becaue N atom readily donates its lone pair of electrons.

M – Nitrogen stretching frequencies in $M(NR_2)_4$.

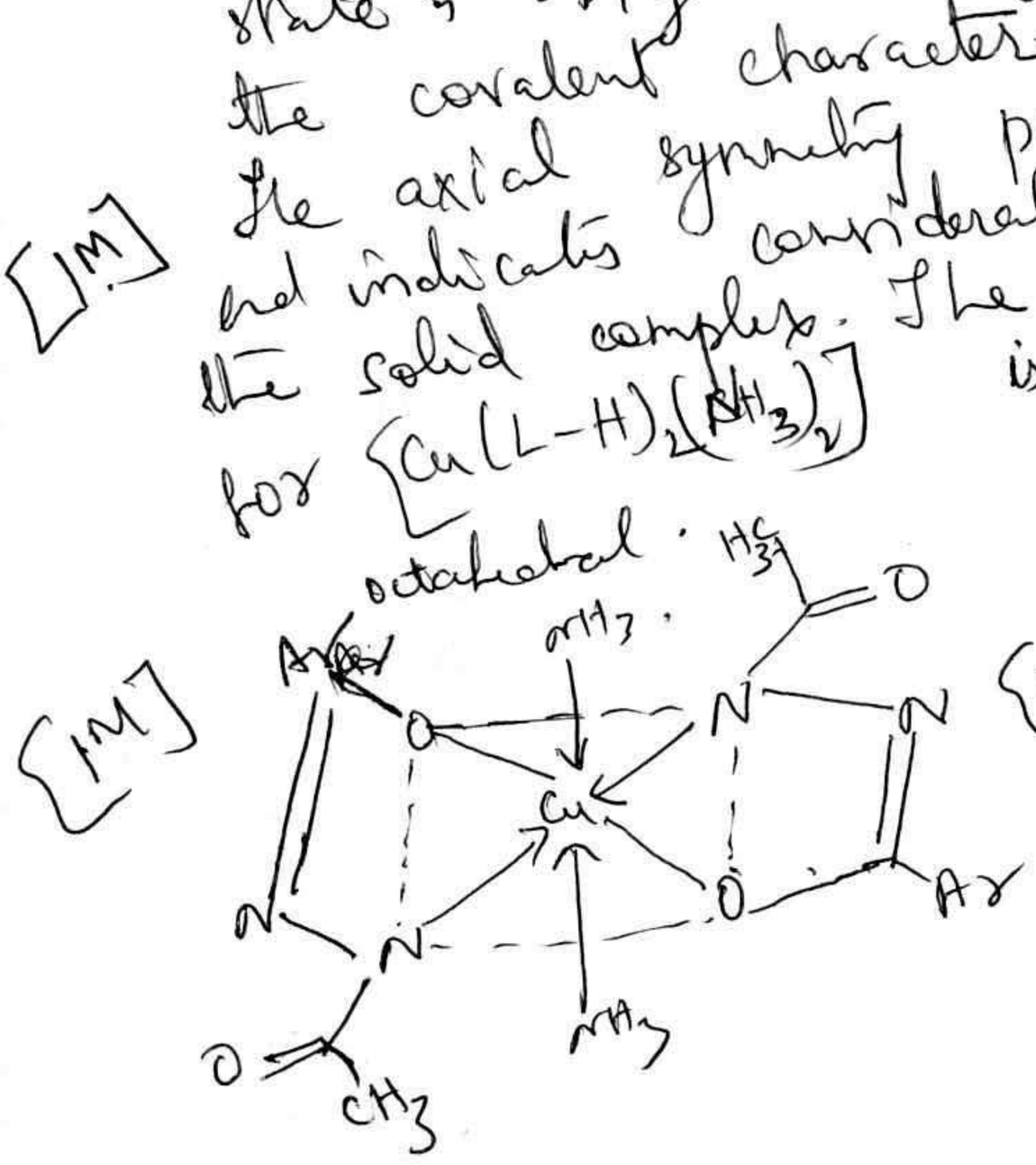
	NMe_2 cm^{-1}	NEt_2 cm^{-1}
Ti	592	610
Zr	537	577
Hf	533	577
V	595	613

[1M] for cu – pyridine IR value is 667 – 150 cm^{-1}

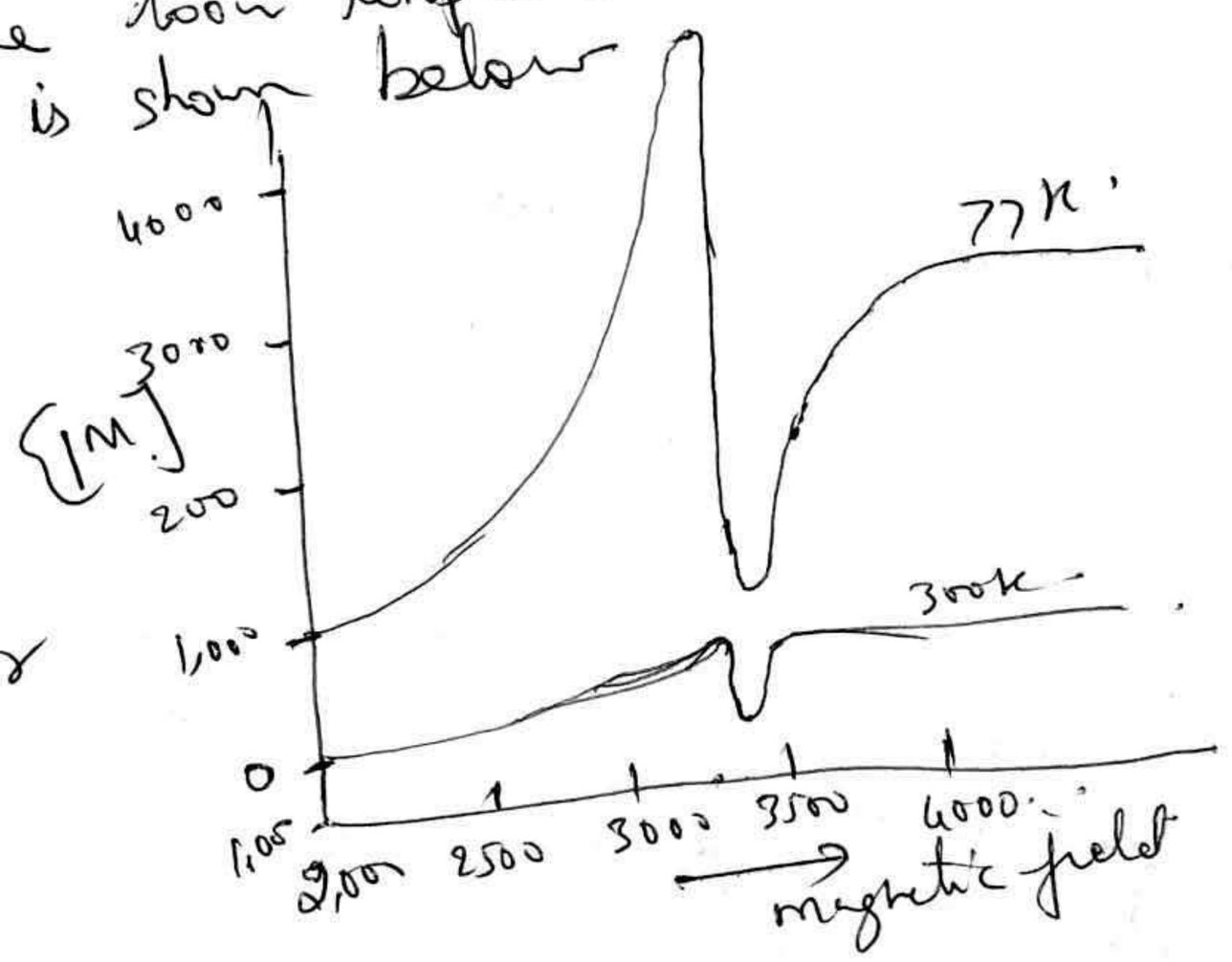
Q4 a. (iii) Interpretation of ESR spectra of octahedral Cu(II) Complexes.

The E.S.R. spectra of copper complexes provide information about the geometrical structure of the complexes. The observed g values of Cu II complexes are at room temp. from these values, it is evident that the unpaired electron is localized in $d_{x^2-y^2}$ orbital & the ground state is $^2B_{1g}$. The $g_{\parallel} < 2.3$ value confirms the covalent character of the metal-ligand bond. The axial symmetry parameter 'G' is less than four and indicates considerable exchange interactions in the solid complex. The room temperature E.S.R. spectra for $[Cu(L-H)_2(NH_3)_2]$ is shown below

[M]



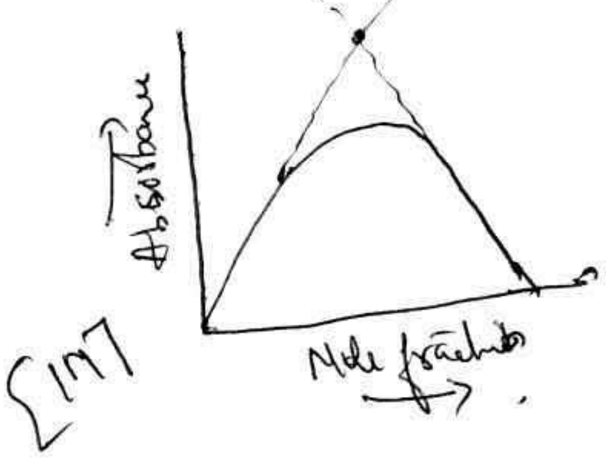
[M]



04a(iv) Job's method for determination of stability constant.

This method is used for solutions where only one complex is formed. If the sum of the total concentrations of the complexing agent x and metal ion C_M is held constant and only their ratio is varied then $C_M + C_x = C$. [1M]

A wavelength of light is selected such that where the complex absorbs strongly & the ligand & metal ion do not. A plot of the mole fraction of the ligand in the mixture Y vs absorbance gives a triangular shaped curve (fig A)



[1M]

The mole fraction of the ligand in the mixture $X = C_x/C$ —(1)

The mole fraction of the metal ion in the mixture $= C_M/C$

$C_x/C + C_M/C = C/C$ —(2)

$\therefore 1 - X = C_M/C$. —(3)

The arms of the triangle are extrapolated until they cross. The mole fraction at the point of this intersection gives the formula of the complex, since at this point, for the complex MX_n, $n = \frac{C_x}{C_M} = \frac{X}{1-X}$. At this point, the ligand and metal are in proper relative concentration to give maximum complex formation.

[1M]

Determination of stability constant: for a 1:1 complex, the ratio of the true absorbance (A) to the extrapolated absorbance (A_{ext}) is the mole fraction of the complex actually formed.

$$\frac{A}{A_{ext}} = \frac{[MX]}{C}$$

Then $[MX] = \left(\frac{A}{A_{ext}}\right) C$, where C = total concn. of the metal or ligand, whichever is the limiting concentration at the point considered.

[1M]

$M = C_M - [MX]$

$= C_M - \left(\frac{A}{A_{ext}}\right) C$

$X = C_x - [MX]$

$= C_x - \left(\frac{A}{A_{ext}}\right) C$.

[1M]

$\therefore K = \frac{[MX]}{[M][X]}$

$= \left(\frac{A}{A_{ext}}\right) C$

$\rightarrow \left[C_M - \left(\frac{A}{A_{ext}}\right) C\right]\left[C_x - \left(\frac{A}{A_{ext}}\right) C\right]$

where K is the stability constant and C_M & C_x are the total concentrations of metal and ligand respectively.

Q4(b)
(i)

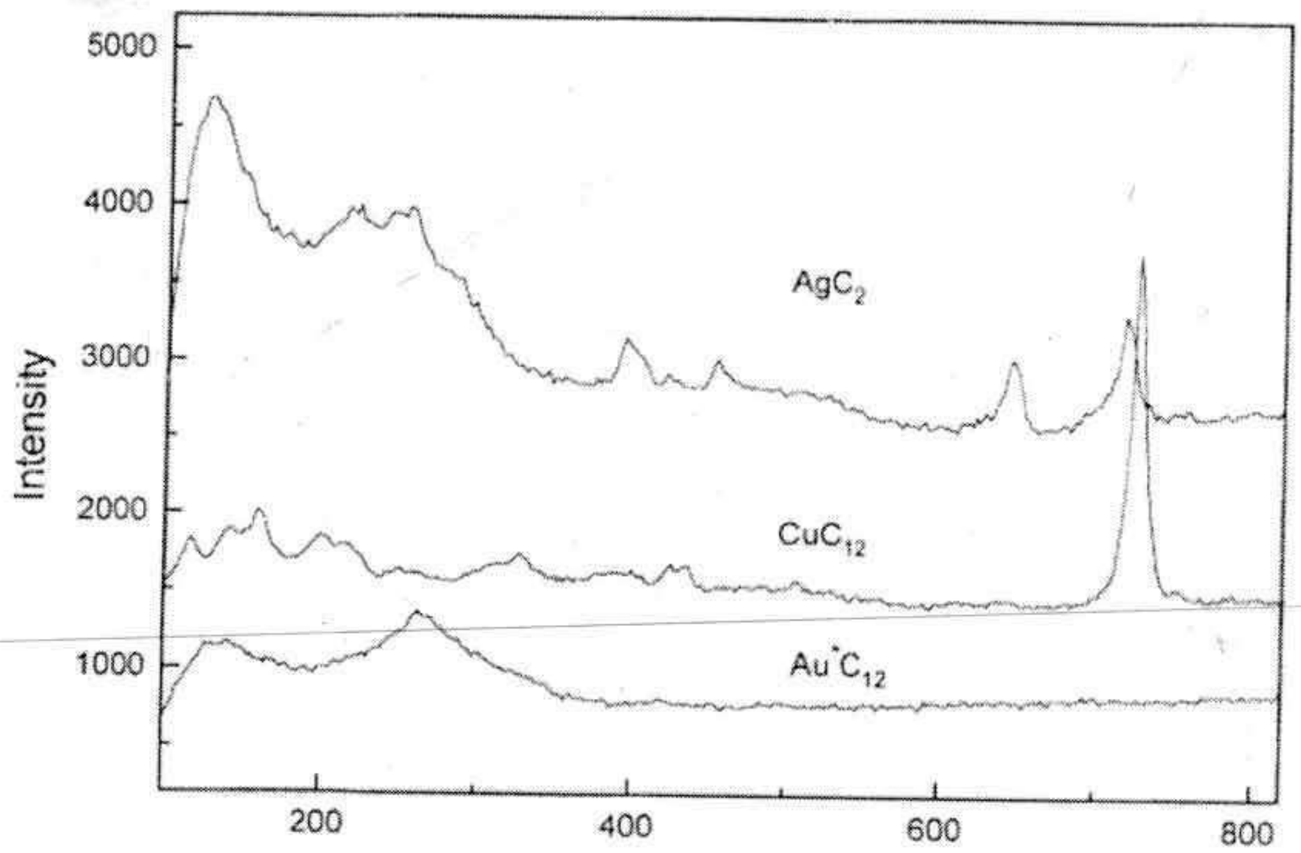


Fig. 3. Raman spectra of AgC_2 layered compound, CuC_{12} layered compound and gold colloid capped with C_{12} (or Au^*C_{12}).

3.1. M□S stretch region

The metal–sulfur (M□S) stretching mode is critical, since the observation of its corresponding Raman peak is a unique direct spectroscopic proof of the thiolate bond formation. Vibrational peaks attributed to the M□S stretching mode have been observed in the region between 200 and 235 cm^{-1}. The relatively wide variation in the peak position of the M□S stretching peak is not yet understood. Sexton and Nyberg (1986) reported an EELS (electron energy loss spectroscopy) vibrational peak at about 200 cm^{-1} from dimethyl sulfide adsorbed on Cu (100) [29]. They ascribed this peak to the Cu□S stretching mode. Nuzzo et al. (1987) [30] also observed a strong band at 220 and 235 cm^{-1} on methanethiol and dimethyl disulfide adsorbed on Au (111), respectively. Using FT-SERS (Fourier transform surface enhanced Raman spectroscopy) Dai et al. (1995) [22] observed a peak at 218 cm^{-1} from phenyl disulfide adsorbed on a silver surface.

Two factors could influence the M□S peak position; (i) the nature of the metal and; (ii) the composition of the adsorbed molecule, particularly the type of chemical group near the sulfur. As shown in Fig. 3 very different Raman spectra features have been observed on three different metal alkanethiolates. Of the two peaks observed from the AgC_2 layered compound at 218 and 250 cm^{-1}, only the former one is straightforwardly assigned to an S□Ag stretching mode. The second peak is probably due to the C□C□S deformation [23,31–33]. It is worth noting that no Raman peak is observed between 200 and 220 cm^{-1} in the neat alkanethiol sample.

At least two peaks (200 and 214 cm^{-1}) are also observed in the M□S stretching region on the CuC_{12} layered compound. We could not presently explain the presence of these two peaks. The absence of a Raman peak from the S□Au stretching mode is probably due to a weak Raman scattering for gold colloids. This could not be due to the absence of alkanethiolate. Indeed, a Raman peak is observed in the C□H stretching region. Furthermore, XPS measurements of the same sample in the S2p spectral region have given binding energy values characteristics of thiolate species [11].

3.2. C□S stretch region

Two C□S stretching peaks positioned at 735 and 662 cm^{-1} were observed from the neat alka-

52.	What motivates you to continue in NSS? a. Incentives in terms of awards, certificates/ promotions. b. Social Service. c. Name & fame. d. Networking avenues. e. All the above. f. Others	----------(1) ----------(2) ----------(3) ----------(4) ----------(5) ----------(6)	
53.	Are you satisfied with the existing incentives of NSS?	Yes----------(1) No----------(0)	
VI.	**Suggestion & Other Comments:**		
54.	Do you think that NSS is fulfilling its primary objective of "Personality Development of student volunteers through Community Service"	Yes----------(1) No----------(0)	If No go to Q. 57
55.	If yes, Explain: _____ _____ _____ _____ _____		
56.	Are the NSS activities making any contribution to the Nations Development?	Yes----------(1) No----------(0)	If No go to Q.59
57.	If yes, Explain: _____ _____ _____ _____ _____ _____ _____ _____ _____		

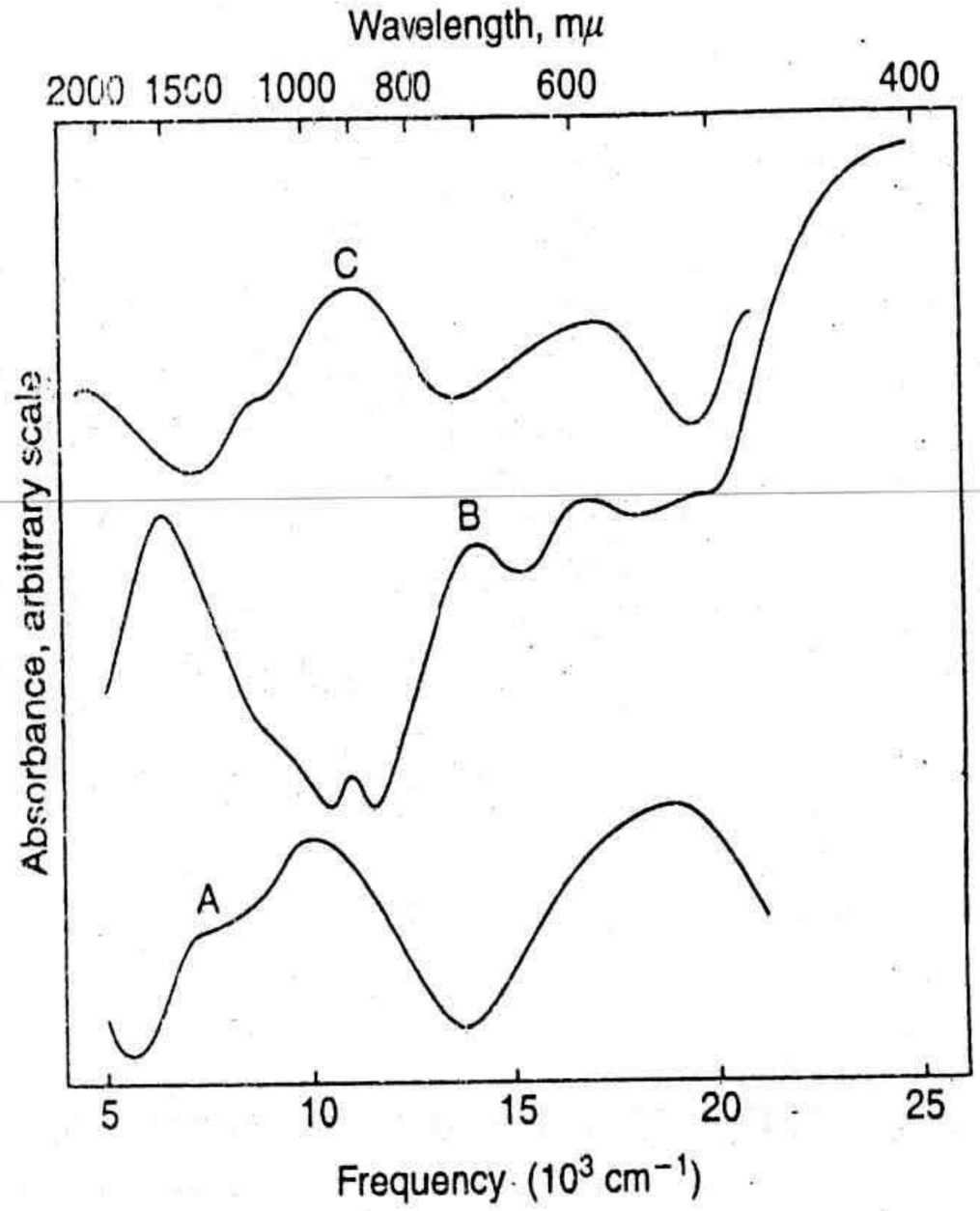


Fig. 7.162. Reflectance spectra of some nickel compounds with a distorted tetrahedral structure A: $[Ni(Me_4en)Br_2]$; B: $[Ni(H\text{-}Sal\text{-}N\text{-}i\text{-}Pr)_4]$; C: $[Ni(Ph_3F)_2Br_2]$

Square Planar Nickel(II), Palladium(II) and Platinum(II)

The five degenerate d orbitals are split by a crystal field of D_{4h} symmetry as follows :

Orbitals	Symmetry species
$d_{x^2-y^2}$	b_{1g}
d_{xy}	b_{2g}
d_{z^2}	a_{1g}
d_{xz}, d_{yz}	e_g

The ground state electronic configuration of a weakly tetragonal nickel(II) complex may be written, following figure 3.42, either

$e_g^4\, b_{2g}^2\, a_{1g}^2$ (diamagnetic, $\Delta_1 > P$)

or $e_g^4\, b_{2g}^2\, a_{1g}^1\, b_{1g}^1$ (Paramagnetic, $\Delta_1 < P$).

But for a strongly tetragonal nickel(II) complex, the two magnetic forms may be written as

$e_g^4\, a_{1g}^2\, b_{2g}^2$ (diamagnetic, $\Delta_2 > P$), a spin singlet state term $^1A_{1g}$

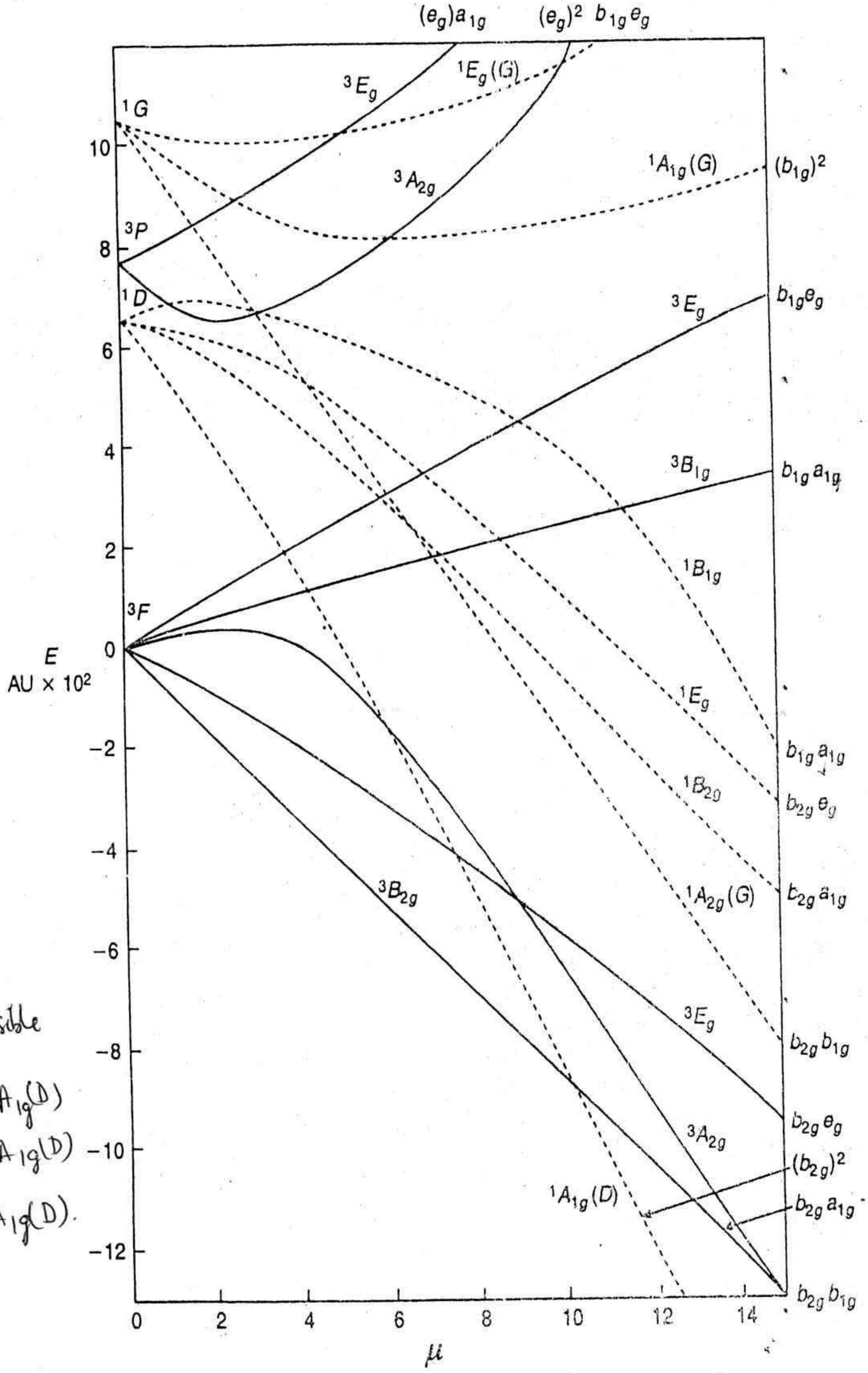
or $e_g^4\, a_{1g}^2\, b_{1g}^1\, b_{2g}^1$ (Paramagnetic, $\Delta_2 < P$), a spin triplet state term $^3A_{2g}$

The relative stability of the $^1A_{1g}$ and $^3A_{2g}$ states is determined by the energy separation of the d_{xy} and $d_{x^2-y^2}$ orbitals. Theoretically, it is thus possible for a square planar nickel(II) complex to have a paramagnetic ground state (Fig 3.42). Ballhausen and Liehr showed that low spin state is stable if the separation is more than 10 000 cm^{-1}.

The splitting of the free ion terms in a field of D_{4h} symmetry is shown in Figure 7.163. The $^1A_{1g}$ state, the lower $^3A_{2g}$ state, and the $^3B_{2g}$ state are possible ground states. None

—P.T.O.→

of these states mix with each other via spin-orbit co. pling. Therefore, a definite crossove: point exists, beyond which the singlet state $^1A_{1g}$ has the lowest energy. This suggests that with a sufficient weak field a square planar complex could be paramagnetic, but there is no experimental evidence for any such compound. All known square planar complexes of nickel(II) are diamagnetic.



3 bands are observed in visible region.

$^1A_{2g}(\gamma) \leftarrow {}^1A_{1g}(D)$

$^1B_{1g}(\gamma) \leftarrow {}^1A_{1g}(D)$

$^1E_g(\gamma) \leftarrow {}^1A_{1g}(D)$.

Fig. 7.163. Energy level diagram for nickel(II) complexes in planar D_{4h} symmetry.

Q5 (a) Inner-sphere mechanism of electron transfer reactions.

The oxidation of $[Cr(H_2O)_6]^{2+}$ by $[Co(NH_3)_5Cl]^{3+}$ in acidic medium takes place through inner-sphere mechanism.

[1½M]

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

Oxidant: $Co^{3+} \rightarrow 3d^6$. Low spin & inert

Reductant: $Cr^{+3} \rightarrow 3d^4$. High spin & labile

Reduced product: $Co^{+2} \rightarrow 3d^7$

Oxidised product: $Cr^{+3} \rightarrow 3d^3$. Low spin & inert.

Mechanism:

[1½M]

$$[Co(NH_3)_5Cl]^{2+} + [Cr(H_2O)_6]^{2+} \longrightarrow \left[(NH_3)_5-Co^{2+}-\overset{e^-}{Cl}-Cr(H_2O)_5\right] \rightleftharpoons \rightleftharpoons$$

$$\rightleftharpoons [(NH_3)_5Co-Cl-Cr(H_2O)_5]^{4+} \xrightarrow{+H_2O} [Cr(H_2O)_6Cl]^{2+} + [Co^{2+}(NH_3)_5(H_2O)]^{2+}$$

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

(b). complementary & Non-complementary reactions.

Complementary reactions:— Electron-transfer reactions in which oxidant gains the same no. of electrons as the reductant loses are called complementary electron-transfer reaction.

[1½M]

$Sn^{2+} + Tl^{3+} \longrightarrow Sn^{4+} + Tl^{+}$

Reductant oxidant oxidant reductant.

$Sn^{2+} + Hg^{2+} \longrightarrow Sn^{4+} + Hg^{0}$

Non-complementary Reactions:— Electron transfer reactions in which the electrons gained and lost are different are known as non-complementary reactions.

[1½M]

$Tl^{3+}(aq) + 2Fe^{2+}(aq) \longrightarrow Tl^{+}(aq) + 2Fe^{3+}(aq)$.

$Tl^{3+}(aq)$ oxidant; $Fe^{+2}(aq)$ Reductant

Reductant oxidant

Reductant is a two electron transfer reaction

$Tl^{3+}(aq) \rightarrow Tl^{+}(aq)$ while $Fe^{+2}(aq) \rightarrow Fe^{3+}(aq)$ is one electron transfer reaction.

Q5 c) Give one method of preparation of diallyl nickel (0). and give its sclient feature.

$$NiCl_2 + 2C_3H_5MgBr \xrightarrow[-10^\circ C]{ether} [Ni(\eta^3 C_3H_5)_2] + MgCl_2 + MgBr_2$$

[1M] Structure of $[Ni(\eta^3 C_3H_5)_2]$ is.

pyrophoric in nature.

. The η^3 allyl ligand is bound to the metal in such a way that all carbon atoms are equidistant from the metal.

. Allyl group $(H_2C{=}CH{=}CH_2)^-$ is a 4e⁻ donor & has delocalised π system, 3 π molecular orbitals (formed due to overlap of p_z orbital of three carbon atoms. (Carbon is sp_2 hybridised).

[2M] . The π_1 & π_2 MO's are filled (an e⁻ pair in each) while π_3 is empty. The first two overlap with appropriate orbitals of metal (π_1 with s, p_z, and d_{z^2}) & π_2 with (p_y and d_{yz}) can form L → M bond due to electrodonation from L → M.

Backbonding takes place due overlap of filled metal orbital (d_{xz}) & π_3 of allyl ligand.

. $Ni(\eta^3 C_3H_5)_2$ used as catalyst in cyclotrimerisation of butadiene.

5 d) Explain half sandwich compound with suitable example.

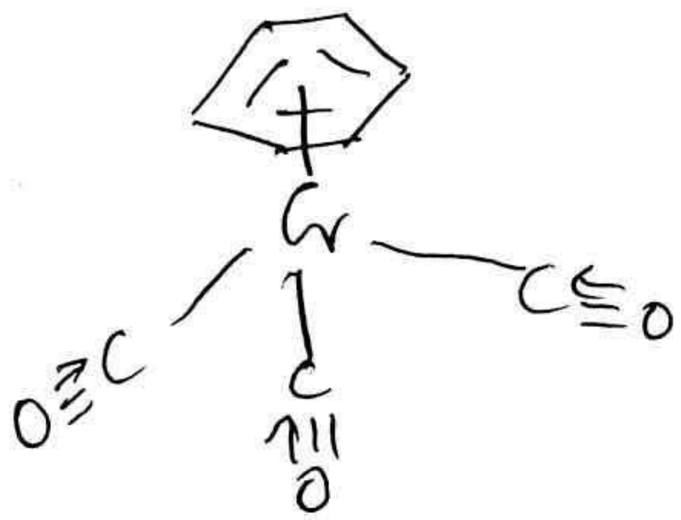
Half sandwich compounds are organometallic Complexes that feature a cyclic polyhapto ligand bound to an MLn center where L is a unidentate ligand.

[1M] eg. $[Cr(\eta^6 C_6H_6)(CO)_3]$, $(C_5H_5)TiCl_3$.

$[Mn(\eta^5 C_5H_5)(CO)_3]$: antiknock compound.

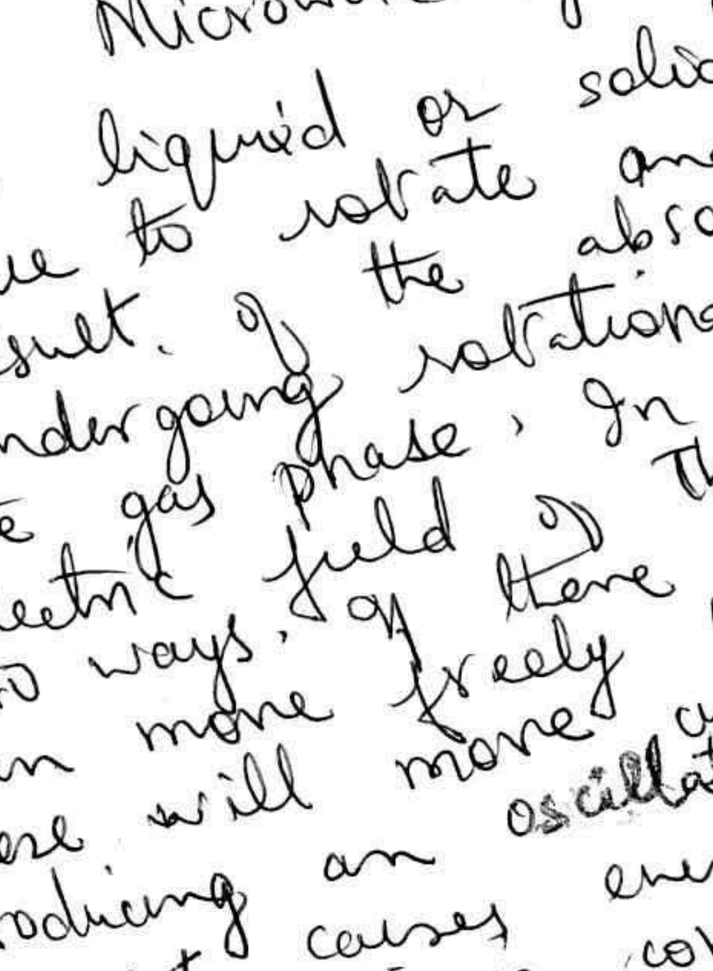
$[Cr(\eta^6 C_6H_6)(CO)_3]$: used as catalyst of hydrogenation of 1,3 diene. It does not hydrogenate isolated double bond.

[2M]



Q5(e) structure of cadmium chloride.

[1½M] The $CdCl_2$ structure is based on a CCP array of chloride ions, with half of the octahedral holes occupied by cations. The cation occupy all the octahedral holes in every other anion layer giving an overall layer structure with 6:3 coordination.



[1½M]

Q5(f) Microwave synthesis method for preparation of inorganic solid.

In liquid or solid the molecules or ions are not free to rotate and so the heating is not the result of the absorption of microwaves by molecules undergoing rotational transitions as they would in the gas phase. In a solid or liquid the alternating electric field of the microwave radiation can act in two ways. If there are charged particles present then they will move through the solid or liquid under the influence of the field. There will more often be collisions with the surroundings producing an oscillating electric current, Resistance to their movement causes energy to be transferred to the surroundings as heat. This is conduction heating but there are no particles that can more freely but there are molecules or units with dipole moments, then the electric field acts to align the dipole moments. This effect acts on water molecules and heats the solid. To use microwave heating in solid state synthesis at least one component of the reaction mixture must absorb microwave radiation.

Q5(g). slope = ratio method for determination of stability constant of metal complexes:—

Consider the reaction $xM + yL \rightleftharpoons M_xL_y$ $\therefore K = \frac{[M_xL_y]}{[M]^x[L]^y}$.

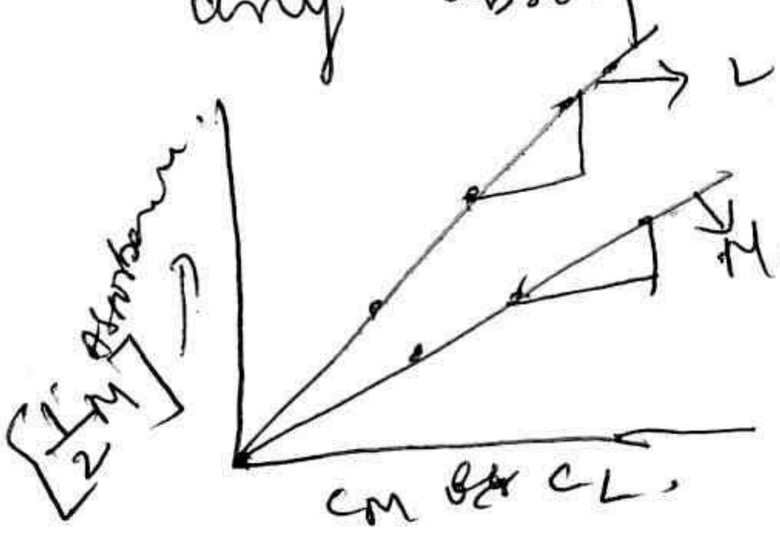
When excess of either M or L is taken, then dissociation of the complex is negligible, hence at equilibrium,

Q5g. it's concentration will be proportional to analytical concentration of the component which is not in large excess.

if excess of L : $[M_xL_y] = \frac{C_M}{x}$.

if excess of M : $[M_xL_y] = \frac{C_M}{y}$.

Now if M_xL_y is coloured, neither M or L has any absorption at the wavelength then $A = \varepsilon[M_xL_y] \cdot l$.



for a series of solution having excess L & varying ant. of M (C_M), then absorbance A_L in each case will be given by $A_L = \varepsilon_L[M_xL_y] \cdot L$

$A_L = \varepsilon(\frac{C_M}{x})L$

Plot of A_L vs C_M will be a st. line with slope $= \frac{\varepsilon L}{x}$

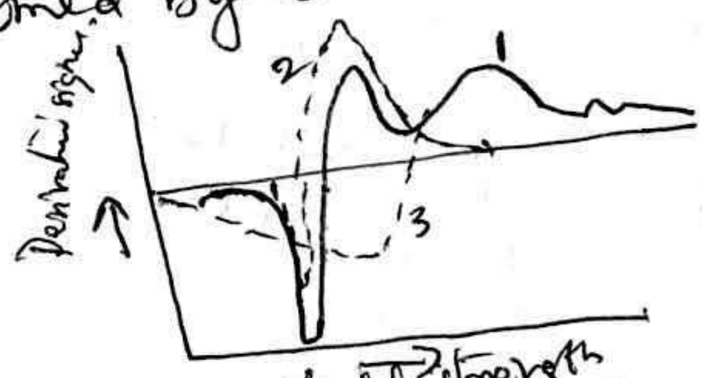
Similarly for excess of M, $(\frac{1}{2}M) = \varepsilon(\frac{C_M}{y})L$. Plot of A_m vs C_L will be a st. line.

Slope $= \frac{\varepsilon L}{y}$. Ratio of two slopes $= \frac{x}{y}$.

Q5h. Two applications of E.S.R. in inorganic chemistry.

E.S.R. is very successful in the study of inorganic compounds.

① When the pH of Ti(III) - EDTA complex is adjusted to 6.9, it undergoes decomposition. This can be confirmed by ESR spectroscopy. The dark like (1) refers to the observed spectrum of the complex which has undergone decomposition. The lines marked (2) & (3) correspond to the decomposed products.



② When the E-S.R. spectra of anhydrous $FeCl_3$ & $FeCl_3 \cdot 6H_2O$ are recorded, they show different spectra. This confirms the fact that different types of bondings are present in anhydrous $FeCl_3$ & in $FeCl_3 \cdot 6H_2O$.

③ When the E-S.R. spectrum of copper acetate is observed, a triplet state is confirmed and the ESR spectrum can be interpreted in terms of the metal - metal interaction in the copper acetate sample.