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Chemistry Crash Course
Test – 2

Batch: Crash Course

Date: 14-July-2024

Mains Answer Writing Guidance Programme

Name	LOKESH.V
Medium	ENGLISH
Date	15-07-2024
Subject and Test Number	OPTIONAL -CHEMISTRY – 02

Instructions:

1. Please scan your answers and form single pdf and share within 48 hours.
2. Writing in the margins leads to rejection of copy.
3. Kindly take due appointment with coordination team to discuss the answer copy with respective mentor.
4. Copies will be evaluated within 7 days of submission.

Evaluated	Reviewed
180/250	

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Criteria/Parameters	Exellent	Very Good	Good	Average	Poor
Language and Articulation			✓		
Content and Conceptual Clarity		✓			
Number of Questions Attempted	✓				
Structure and Presentation			✓		
Coherence and Structuration		✓			

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Examiner's Feedback

→ Better structure and presentation than previous exam.

→ Good conceptual knowledge of Inorganic chemistry.

→ Give a quick reading again to spectra and magnetism.

1 (a) Point out the special structural features of the following compounds :

(i) $K[Pt(C_2H_4)Cl_3]$

(ii) $K_2[Re_2Cl_8]$

(iii) $(\eta^5-C_5H_5)Fe$

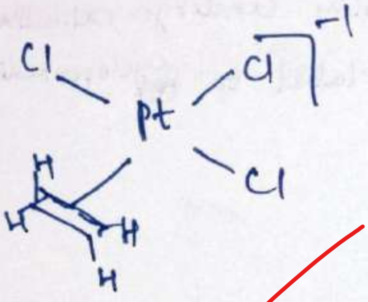
(iv) $[IrCl(CO)(PPh_3)_3$

(10 marks)

7

Coordination compounds are formed through interaction between ligand (e^- rich) and central metal (e^- poor) atoms/molecules which give coordinate bonds.

i) $K[Pt(C_2H_4)Cl_3]$

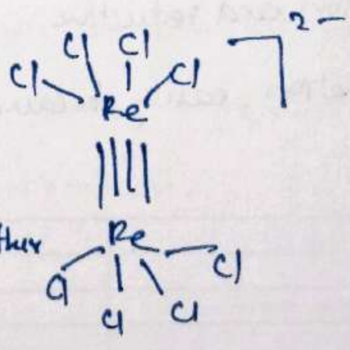


Zeise Salt.

Her the ethene molecule make η^2 bond to make stable complex. This complex is usefull in polymerisation of Alkenes without any radical intermediates.

ii) $K_2[Re_2Cl_8]$

This complex have special δ-bond where four lobes of d-orbital interact with one another in z axis.



iii) $(\eta^5 - C_5H_5)Fe$ Fe → $d^8 + 5 \Rightarrow$ ⑬

Half-sandwich or stool compound.

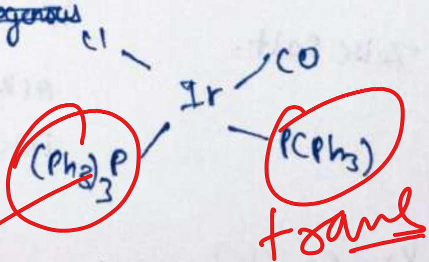
Here the cyclopentadiene molecule bond with central atom using its all its 5 e^-s, which makes the structure more rigid.

It is ~~x~~ less stable because EAN rule is not satisfied.

However the complex can easily undergo oxidative addition with any molecule isolabal to ~~[illegible]~~ cyclopentadiene

(v) $[IrCl\,CO\,(PPh_3)_3]$

Usefull in making ~~heterogenous~~ homogenous catalysis and this undergo oxidative addition and reductive elimination easily because of its sq. planar geometry



Vaska complex.

Hence each and every complexes unique geometry, electronic configuration and bonding give its unique applications.

Introduction	
Body	
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(b) Explain Jahn-Teller distortion. Discuss the cases of strong and weak JTD in octahedral complexes.

(10 marks)

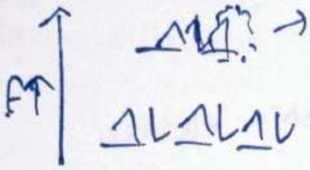
⑧

Jahn-Teller distortion arises due to the arrangement of electrons in unsymmetrical way in the ~~com~~ Orbitals.

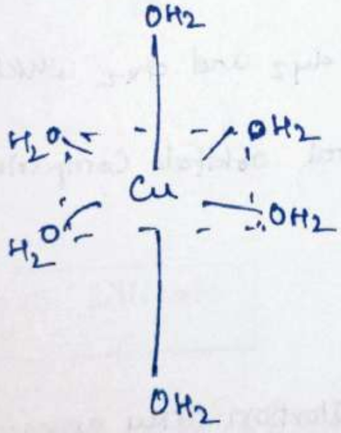
uneven electronic repulsions in different axis.

Eg. $[Cu(H_2O)_6]^{2+} \rightarrow Cu \rightarrow 3d^{\cancel{8}9} 4s^2$ $3d^{10} 4s^1$

$Cu^{2+} \rightarrow 3d^{9}$



→ This unsymmetrical electron makes the ~~eh~~ variations in magnetic and spectro properties of complexes.



Here because of presence of e⁻ in the eg orbital, the unsymmetric effect causes the Z-axis bond to elongate much further to reduce the distortion in it.

Z-out effect

↑↓↑

↑↓ ↑↓ ↑↓

Strong JT-D

When unsymmetric electron present in ~~T2g~~ eg orbital it is known as Strong JT-D because of the $d_{x^2-y^2}$ and d_{z^2} orbital which have maximum interaction in octahedral complexes.

Weak JTD

↑↓ ↑↓ ↑

When unsymmetric electron present in T_{2g} orbital it is known as weak JTD. because of the orbitals d_{xy}, d_{yz} and d_{xz} which have less interaction with metal orbitals comparing T_{2g} orbitals.

Hence Jahn-Teller distortion may appear as ~~its~~ weak interaction result. However it have major applications in colour, magnetic and spectral properties of complexes.

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(c) "SiO_4 tetrahedra form the framework of all silicates, including silica (SiO_2)." Justify this statement with appropriate framework structures of ortho, pyro, cyclic, infinite chain, sheet and silica.

(20 marks)

SiO_4 is basic Tetrahedral molecule which exist in most of the silicate compounds. It's orientation with the compound and bonding sequence makes the uniqueness of the silicates.

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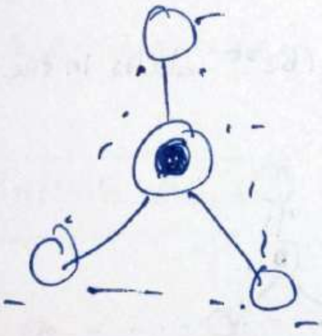
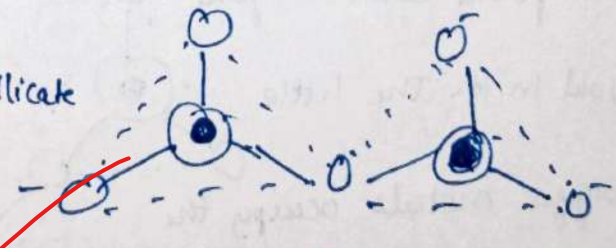
Ortho sillicate



Here the basic structure is SiO_4^{2-} where the metal make interaction and appear in most of the natural minerals ex- $MgSiO_4$.

Pyro sillicate

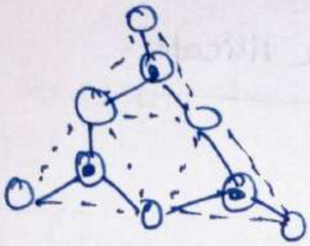
Here the 2 ortho sillicate molecule combined



with single interacting oxygen. $Si_2O_7^{2-}$ is the structured unit of it. Here also most of the minerals exist with it.

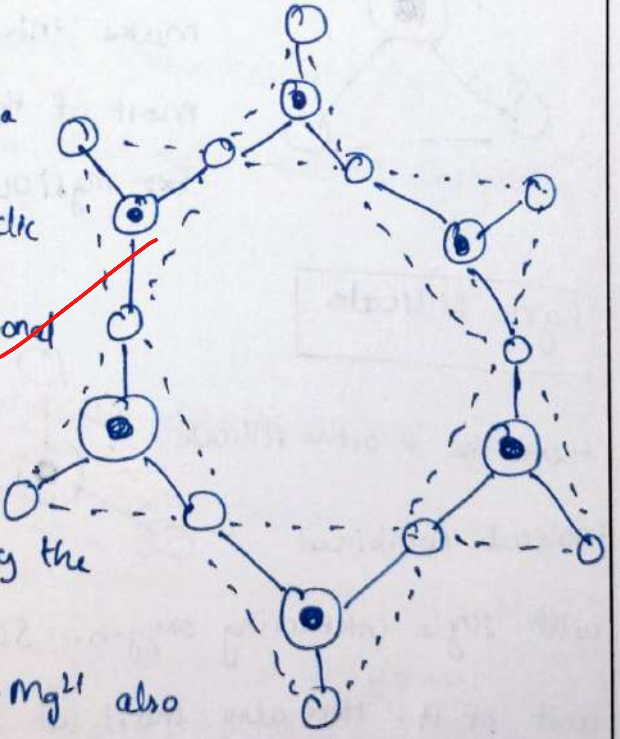
Cyclic sillicate

Two types of cyclic structures are possible,



Here the molecule with ~~Stru~~ formula $Si_3 O_9^{2-}$ complex is formed with triangular void in it.

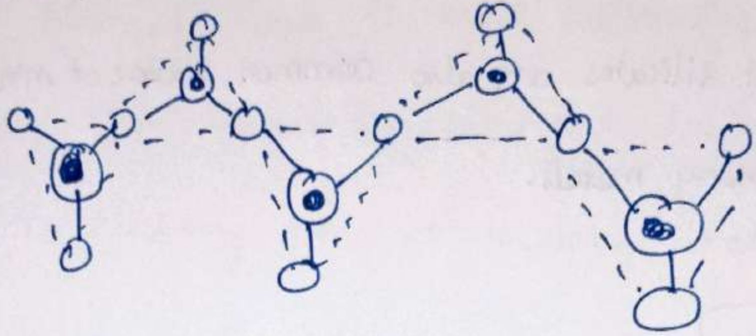
Most of the small size Li^{+}, Be^{2+} suits in the structure



The molecular formula $Si_6 O_{18}^{2-}$ is bigger cyclic compound with hexagonal void in it. The little bigger metals occupy the void in it.

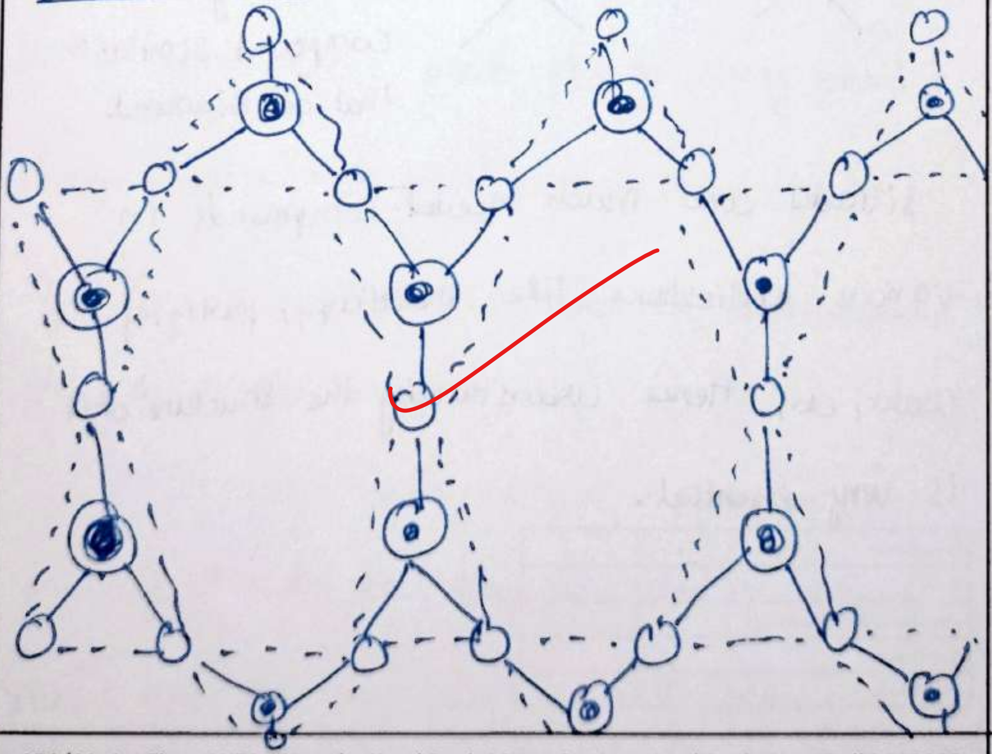
Na^{+}, Ca^{2+}, Mg^{2+} also occur with it.

Infinite chain



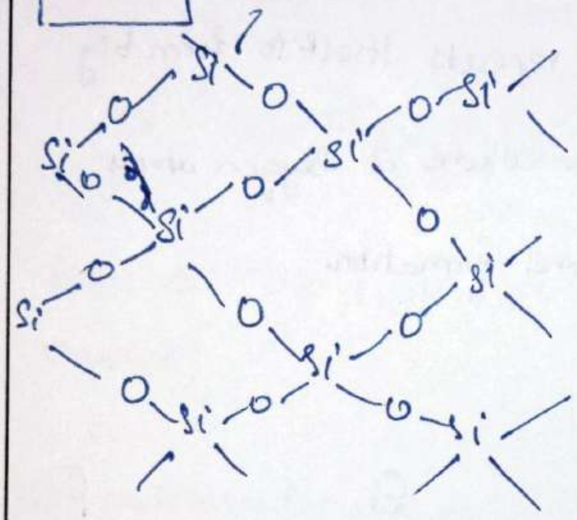
The structure repeats itself to form big chain of compound. where 2 Oxygen atoms are involved in bond formation

Infinite sheet



The structure repeats itself infinitely. This Sheet silicates are also common source of Mineral. for many metals.

Silica



Tetrahedral complex with Si–O–Si bond repeats itself to form big 3-D shape compound similar to that of Diamond

silicates are much needed compounds in various applications like metallurgy, purifying water, etc., Hence understanding the Structure of it is very essential.

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(d) Comment on the spectroscopic and magnetic properties of 4f elements.

(10 marks)

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4f-elements have Increased nuclear charge density with more or less same size due to the poor ~~to~~ shielding effect of incoming 4f electrons and causing Lanthanide contraction.

Spectroscopic properties

Most of the 4f-metals and its complexes are used for Spectroscopic Studies standardisation as it gives clear peak due to strong metal charge density and poor electron cloud effect.

Eg: the ~~[illegible]~~ Gd complex used for Standardisation in magnetic Spectroscopies.

It also give unique application in medical field for diagnosis and tracking of metal ions as this can be easily removed by

Discuss splitting of f orbitals in spectra Questions

Complex formation as well as due to unique spectral lines.

Magnetic properties

The spin only magnetic moment, orbital magnetic moment along with it the interaction of other orbital influence all play role in it

Hence, $\mu = g\sqrt{J(J+1)}$ where J = Coupling Constant

$$\boxed{g = 1 + \frac{2S(S+1) - L(L+1) + J(J+1)}{2J(J+1)}}$$

Hence each and every F-~~orbita~~ block elements have unique magnetic, spectral properties.

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2 (a) Discuss the geometrical and optical isomerism in octahedral complexes of the type $M(A-A)_3$ and $M(A-B)_3$, where A- A and A- B are bidentate ligands.

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(10 marks)

Geometrical isomerism

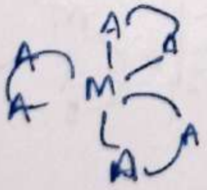
Compounds having same structural formula but its orentation ~~in space~~ with other ligands differs is known as Geometric isomerism

Optical isomerism

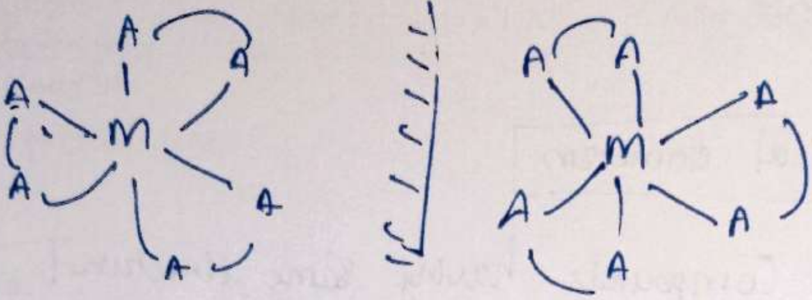
Compounds having same structural ~~and~~ but spacial orentation ~~but~~ differ from others is known as optical isomerism. It arises because of non-superimposable mirror images

$M(A-A)_3$

This molecule don't have any geometric isomerism as all M-A bonds only.



No difference in the cis/trans group



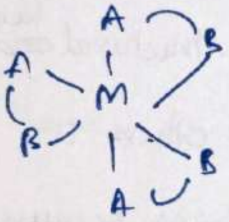
Here the optical isomerism is present

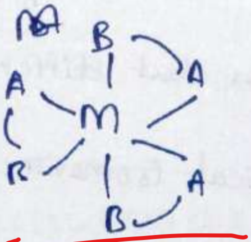
because of Non-superimposability

b) M(A-B)₃ · (A-A) (~~A~~B-B) (A-B)
(B-B) (A-A) (A-B)
(B-B) (A-B) (A-B)

?

cis ?
trans ?
fac ?
mer ?

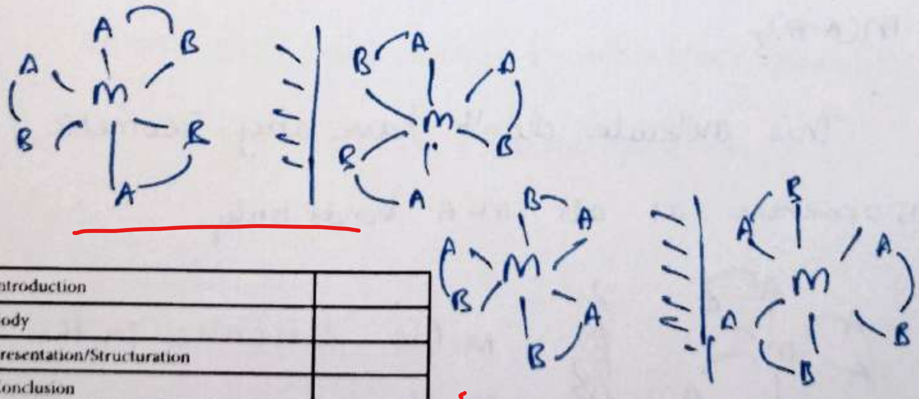




Both are same
(meridonial)

Two Geometric Isomers are possible

∴ 4 optical isomers are possible



Introduction	
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(b) In the following sequence of reactions, identify the products (A - H).

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(i) $SiCl_4 + CH_3MgCl \longrightarrow A \xrightarrow[\text{pyrolysis}]{\text{controlled}} B$

(ii) $PCl_5 + NH_4Cl \xrightarrow[\text{solvent (120°–150°C)}]{\text{heating in}} C \xrightarrow[\text{in 300°C}]{\text{heating}} D$

(iii) $SCl_2 + NH_3 \xrightarrow{90°C} E \xrightarrow[\text{conc alkali}]{\text{hydrolysis}} F$

(iv) $KI + F_2 \xrightarrow{25°C} G \xrightarrow{\text{hydrolysis}} H$

(20 marks)

i) $SiCl_4 + CH_3MgCl$

$$\downarrow$$

$CH_3SiCl_3 + MgCl_2$

$$\downarrow \text{Controlled pyrolysis}$$

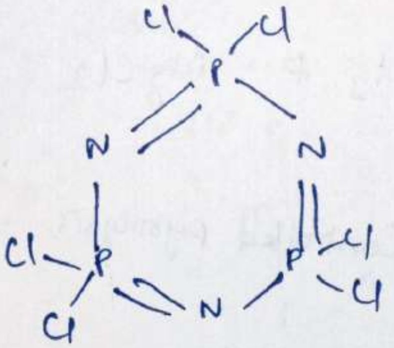
$(CH_3)_4Si + MgCl_2$ ✓

Polymerisation rxn proceed

ii) $PCl_5 + NH_4Cl \xrightarrow[120\text{-}150°C]{\Delta} (NPCl_2)_n + 4nHCl$

$\downarrow$ Heating 300°C

$N_3P_3Cl_6$

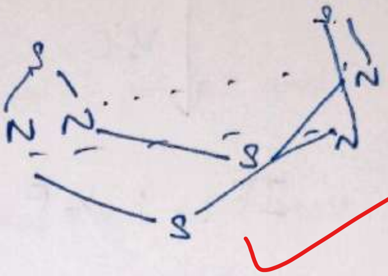


phosphazines.

iii) $SCl_2 + NH_3$

$\downarrow 90^\circ C$

S_4N_4



$S_4N_4 + NaOH$

$\downarrow H_2O$

$Na_2S_2O_3 + Na_2SO_3 + 4NH_3.$

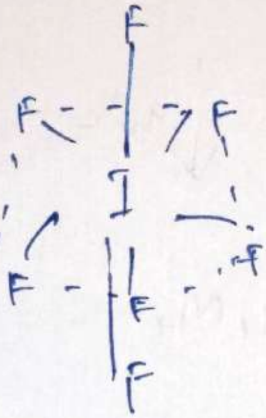
iv) $KI + 4F_2$

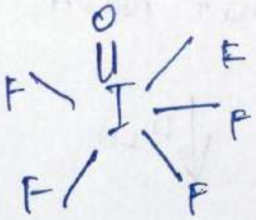
$\downarrow$ 25°C

$IF_7 + KF$

$\downarrow + H_2O$

~~$IF_7 + H$~~ $IOF_5 + 2HF$





A - CH_3SiCl_3

B - $(CH_3)_4Si$

C - $(NPCl_2)_n$

D - $N_3P_3Cl_6$

E - S_4N_4

F - $Na_2S_2O_3$

G - IF_7

H - IOF_5

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(c) Explain 'lanthanide contraction' underlying its effect on the size of d-block elements.

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(10 marks)

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Lanthanide contraction

It occurs in f-block elements, due to incoming of extra e^- in f-orbital and it's poor shielding effect makes the outermost shell to experience more Nuclear attraction and shrink the size due to increase in effective Nuclear charge of atom.

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Write Lanthanoid Series

As the lanthanide contraction observed in 4f orbitals, the overall size increase in very negligible and this affects the 4d and 5d series. There is appreciable size difference b/w 3d and 4d. Whereas the size difference is very much negligible in case of 4 d and 5d series.

· This negligible variation in size makes the charge-radius ratio also similar, making the separation of elements from its mixture difficult.

The similar in size give rise to increase in difficulty of separation at same time the elements have similar melting, boiling and other physical properties.

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(d) What are the salient features and limitations of the Crystal Field Theory? Show the splittiing of the d^6 ion in weak and strong fields in octahedral environment.

6

(10 marks)

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Salient features of CFT

Ligands are Point Charges.

i) It describes the pairing effect.

ii) It describes the splitting of orbitals.

iii) It helps to understand colors of complexes

iv) It helps to estimate the magnetic moment

v) Spectra of complexes are easy to interpret

Limitations of CFT

i) It assumes only ionic interactions

ii) only σ- bonding Considered, no π- interactions are considered.

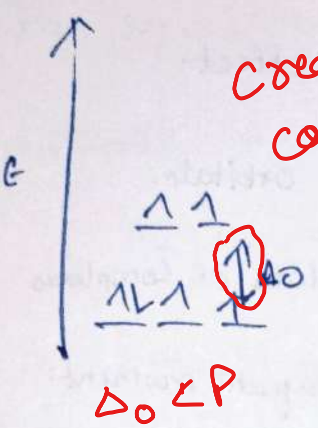
iii) Only d orbitals are taken into consideration

iv) Higher metal complexes are hard to explain.

v) Not considering covalent nature of complexes d6 ion → It have $6e^{-}s$

(oh)

Weak field

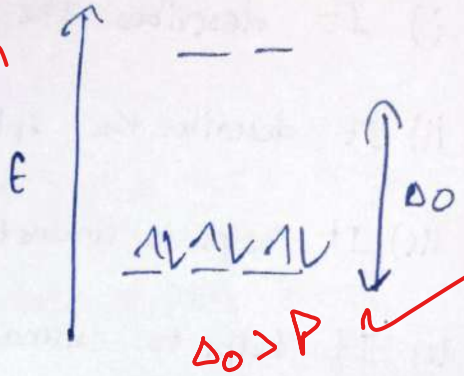


$\Delta_o < P$

Strong field

(Give some gap)

Creating confusion



$\Delta_o > P$

As the d^6 ion in weak field & Δo is less its mostly form excited ~~pao~~ iones.

d6 complex in strong field have more Δo split.

Making the pairing to occur and the complex is diamagnetic in nature, whereas the d^6 ion in weak field is paramagnetic in nature

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Q. No.

3

(a) Explain why

(i) The complex $[CuCl_4]^{2-}$ exists, but $[CuI_4]^{2-}$ does not.

(ii) $[Co(CN)_6]^{3-}$ is more stable than $[Co(CN)_6]^{4-}$ whereas $[Fe(CN)_6]^{4-}$ is more stable than $[Fe(CN)_6]^{3-}$.

(iii) Copper metal dissolves in HCN with evolution of hydrogen gas, but it does not dissolve in sulphuric acid.

(iv) The stability constant of $[Cu(en)_2]^{2+}$ is higher than that of $[Cu(NH_3)_4]^{2+}$

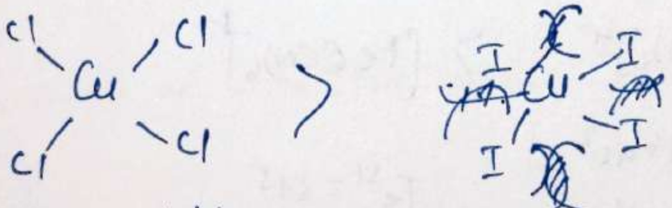
(20 marks)

i) the complex $[CuCl_4]^{2-}$ exist whereas ②

$[CuI_4]^{2-}$ does not exist, because size of I^- is much bigger than Cl^-. Because of the electron-electron repulsion of the $[CuI_4]^{2-}$ complex the structure becomes unstable

I^- is stronger reducing agent

$2CuI_2 \rightarrow Cu_2I_2 + I_2$



more stable

Less stable

More Over I^- combine to form I_2 more readily than anyother complexes.

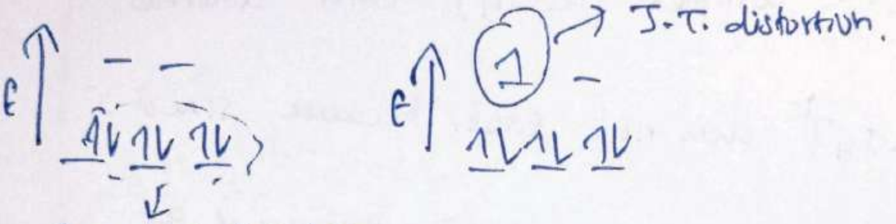
ii) $[Co(CN)_6]^{3-} > [Co(CN)_6]^{4-}$

Discuss EAN or 18 e^- rule

2

$Co = 3d^7 4s^2$

$Co^{+3} = 3d^6$ $Co^{+2} = 3d^7$.



Completely Filled T_{2g}

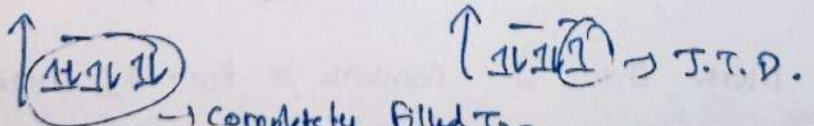
Because of completely filled T_{2g} orbital, $[Co(CN)_6]^{3+}$ more stable than $[Co(CN)_6]^{4-}$ which have one electron in eg orbital and destabilizes due to JTD.

JTD enhances stability

$[Fe(CN)_6]^{4-} > [Fe(CN)_6]^{3-}$

$Fe = 3d^6 4s^2$ $Fe^{3+} = 3d^5$

$Fe^{2+} = 3d^6$



→ Completely Filled T_{2g}

Similarly because of filled T_{2g} orbital, $[Fe(CN)_6]^{4-}$ is more stable than $[Fe(CN)_6]^{3-}$ complex

c) Cu ~~Co~~ when dissolved in HCN, the CN^- ions make Cu^{2+} metal ion stable with octahedral complex. whereas in H_2SO_4, the SO_4^{2-} ion don't have such strong ligand effect to ionise and stabilise the ~~B~~ Cu metal.

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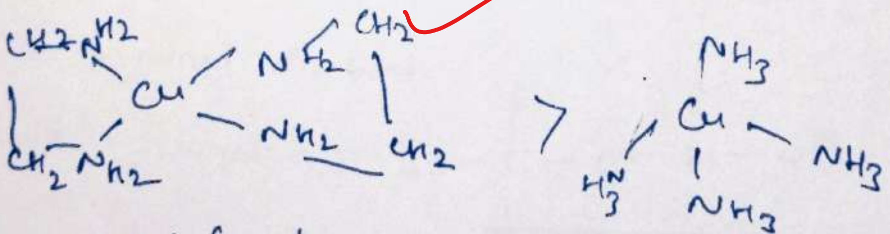
Hence Cu with H_2SO_4 does not react to form any stable Complex

d) $[Cu(en)_2]^{2+} > [Cu(NH_3)_4]^{2+}$

4

Because of Chelation effect and ring effect



metal complex

NH_3 is weak ligand, en is strong ligand

The chelating effect by formation of two 5 membered rings gives structural stability

The charge to radius ratio also balanced in this.

Entropy effect could also be attributed to stability of the complex

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(b) R_3SiCl, R_2SiCl_2, $RSiCl_3$, (R = methyl) are used for making silicon polymers. Explain the roles of these compounds in the synthesis.

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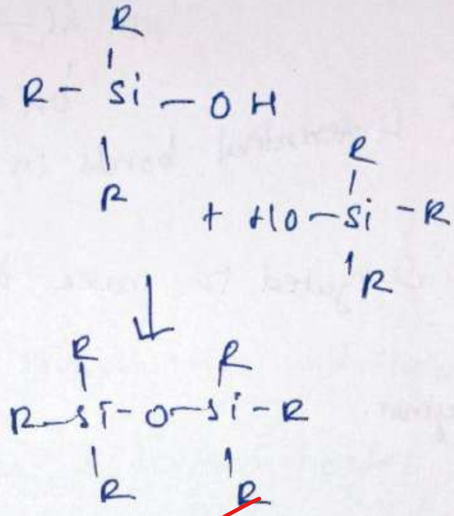
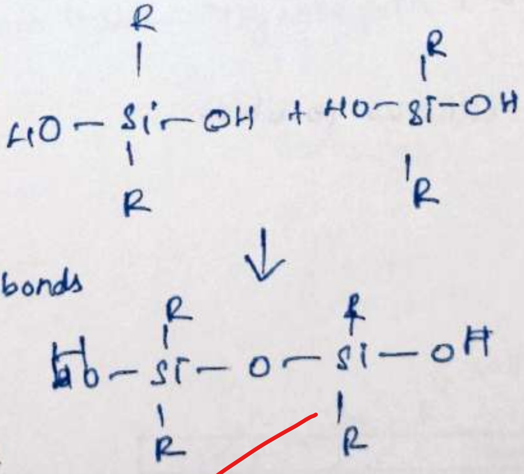
(10 marks)

'R' in silicon polymer help in making the Compound hydrophobic in nature.



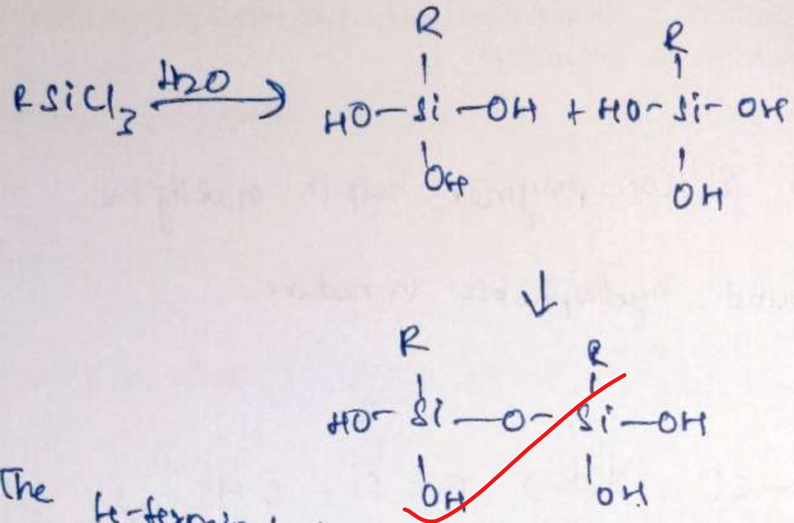
$$R_3Si{-}Cl \xrightarrow{H_2O} R{-}\overset{R}{\underset{R}{Si}}{-}OH + HO{-}\overset{R}{\underset{R}{Si}}{-}R \rightarrow R{-}\overset{R}{\underset{R}{Si}}{-}O{-}\overset{R}{\underset{R}{Si}}{-}R$$

This molecule stops the polymerisation effect. So, it could be utilised at ends to stabilise the compound



$$R_2SiCl_2 \xrightarrow{H_2O} HO{-}\overset{R}{\underset{R}{Si}}{-}OH + HO{-}\overset{R}{\underset{R}{Si}}{-}OH \rightarrow HO{-}\overset{R}{\underset{R}{Si}}{-}O{-}\overset{R}{\underset{R}{Si}}{-}OH$$

The terminal OH bonds could be elongated as much as possible to make infinite chain silicone.



$$RSiCl_3 \xrightarrow{H_2O} HO-\overset{R}{\underset{OH}{Si}}-OH + HO-\overset{R}{\underset{OH}{Si}}-OH$$

$$\downarrow$$

$$HO-\overset{R}{\underset{OH}{Si}}-O-\overset{R}{\underset{OH}{Si}}-OH$$

The H-terminal bonds in the product could be elongated to make a large sheet like polymer.

Si-O-Si bond more stable than Si-Si bond, this makes the ~~catenat~~ polymerisation of silicones possible.

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(c) Compare and contrast the bonding in cyclic phosphazene from benzene and borazine.

(10 marks)

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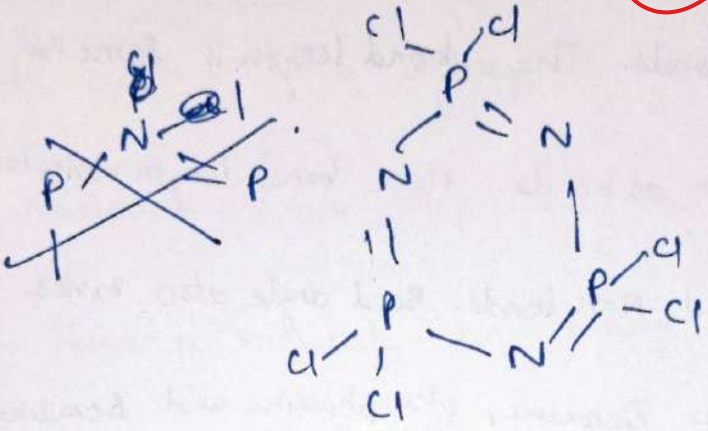
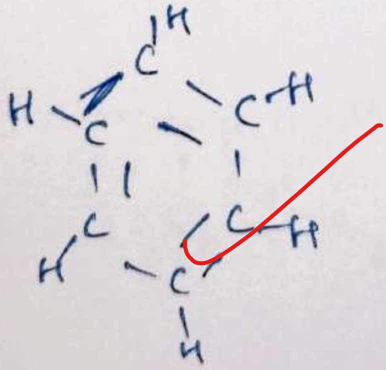
cyclic phosphazine

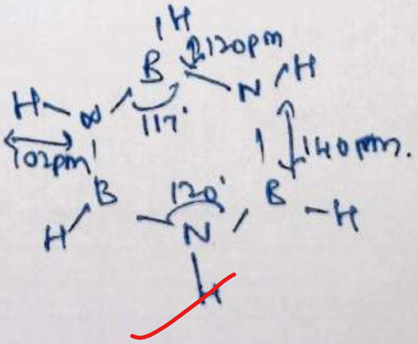


N bonded with Phosphorous and Phosphorus with 2 more Cl ions. P have 5 bonds, N have 3 bonds. with a lone pair in it. Whereas P does not have any lone pair.

Benzene



Borazine



Benzene have all atoms as Carbons, Borazine have alternate B-N ~~bonds~~ atoms with B-N bonds. The bond length is same for all C-H ~~at~~ bonds. Here bond length varies for B-H and N-H bonds. Bond angle also varies, among the Benzene, phosphazine and Borazine

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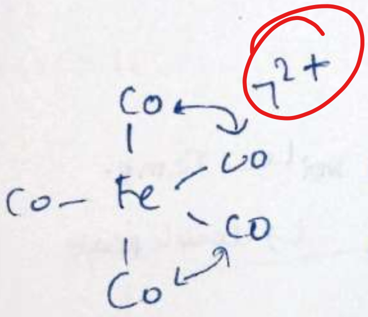
(d) What are fluxional molecules? How does nmr help in detection of fluxionality.

8

(10 marks)

Fluxional molecules undergo rapid transition of ligands within it. The exchange of ligands would be maximum when temp. is increased and the fluxional molecule also behave as normal molecule when Temp. is reduced to as low temp.

It is a Neutral molecule

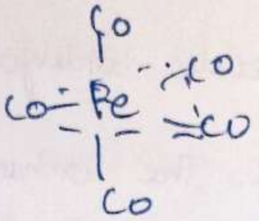


Here the equatorial and axial Carbonyls interchange rapidly and make the transition very fast

To recognise it the kinetic energy have to be reduced by reducing the temperature.

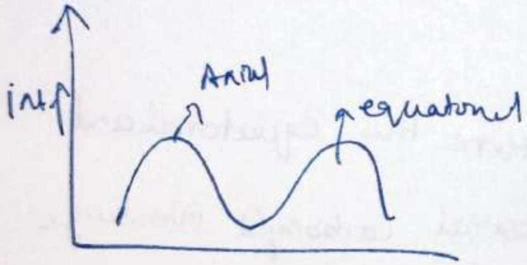
NMR of Fluxional molecule.

^{13}CNMR



Hi ~~Low~~ temp.

↳ Single peak



~~Hei~~ Low Temp.

↳ double peak

Hence using NMR peaks we could distinguish the Fluxional molecules

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4

(a) Discuss the theoretical electronic spectra of $[Cr(H_2O)_6]^{3+}$ with the help of orgel diagram.

(10 marks)

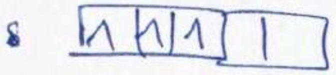
6

$3d^5 4s^1$

$[Cr(H_2O)_6]^{3+}$ ⇒ Cr have $3d^4 4s^2$ configuration

Cr^{3+} have $3d^3$ configuration

Construction of Orgel diagram

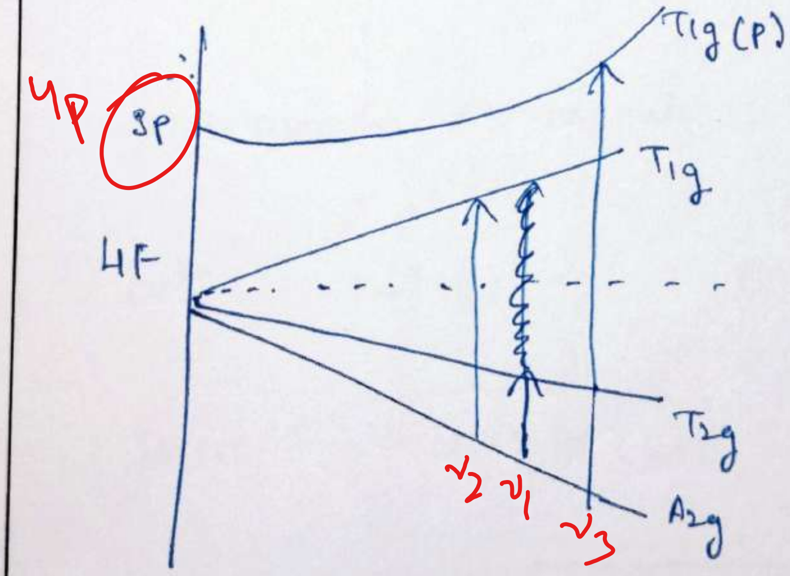


0 1 2 3
s p d f

$S = 3(1/2) = 3/2$ $L = 3 \Rightarrow F$.

$2S+1 = 4$.

$\Delta S = 0$

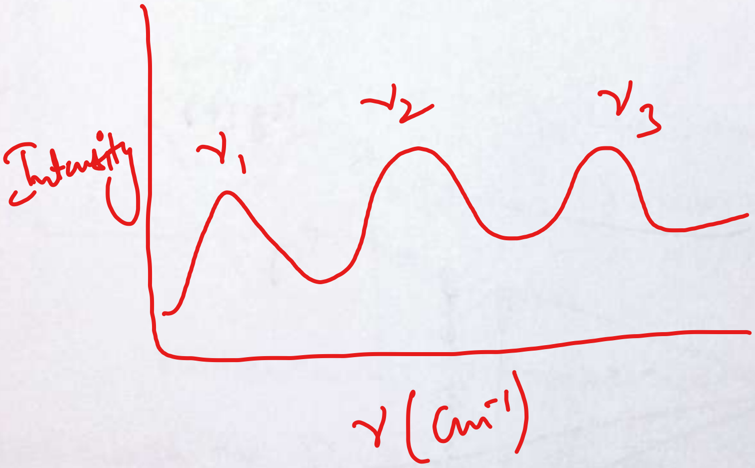


∴ Total no. of Transitions in $[Cr(H_2O)_6]^{3+}$ complex is,

ν_3 $A_{2g} \rightarrow T_{1g}(P)$

ν_1 $A_{2g} \rightarrow T_{2g}(F)$

ν_2 $A_{2g} \rightarrow T_{1g}(F)$



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(b) Write the ground state electronic configuration of lanthanides mentioned below:

(i) $_{59}Pr$ (ii) $_{63}Eu$ iii) $_{64}Gd$

6

Calculate the predicted magnetic moment (μ_{S+L}) for the metal ions in +3 oxidation states in the units of Bohr Magneton.

Don't write anything in this margin

(10 marks)

i) $_{59}Pr$. [Xe] $4f^3\ 5d^0\ 6s^2$. ✓

~~36[Kr] $6s^2$~~

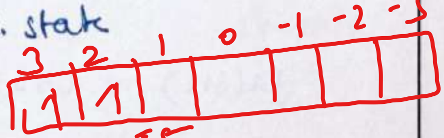
He 1
Ne 2
Ar 3
Kr 4
Xe

$5s^2$

ii) $_{63}Eu$ [Xe] $4f^7\ 5d^0\ 6s^2$ ✓

iii) $_{64}Gd$ [Xe] $4f^7\ 5d^1\ 6s^2$ ✓

Magnetic moment. +3 ox. state



$L = 3+2 = 5$

i) $_{59}Pr^{2+}$ [Xe] $4f^2$ $L = \cancel{S = 3}$.

$S = 2 \Rightarrow S = 2/2 = 1$.

$$\mu_{(S+L)} = \sqrt{4S(S+1) + L(L+1)}.$$

$$= \sqrt{4(1)(1+1) + 3(3+1)}$$

$$= \sqrt{4(2)+12} = \sqrt{20}$$

$$= 2\sqrt{5}\ BM$$

(ii) $_{63}Eu$ $[Xe]\ 4f^6$

$\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{}$

$L = 3+2+1+0-1-2$
$= 3$

$s = 6 \Rightarrow S = 6/2 = 3.$

$L = 3.$

$\mu(S+L) = \sqrt{4S(S+1) + L(L+1)}$

$= \sqrt{4(3)(4) + 3(4)}$

1.8 12

$= \sqrt{12(4+1)} = \boxed{2\sqrt{15}\ BM}$

(iii) $_{64}Gd$ $[Xe]\ 4f^7.$

$s = 7_f \Rightarrow S = 7/2.$ i~~L = 3~~. $L = 0$

$\mu(S+L) = \sqrt{4S(S+1) + 3(3+1)} = \sqrt{4(\frac{7}{2})(\frac{7}{2}+1) + 12}$

$= \sqrt{4(\frac{7}{\cancel{2}})(\frac{9}{\cancel{2}}) + 12}$

$= \sqrt{25 \times 3} = \boxed{5\sqrt{3}\ BM}$

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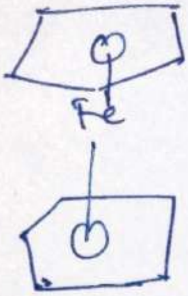
(c) Give IUPAC nomenclature of the following compounds:

(10 marks)

$Fe(C_5H_5)_2$
$[Co(NH_3)_4(NO_2)Cl]Cl$
$[(H_3N)_5Cr-O-Cr(NH_3)_5]^{4+}$
$[Pt(NH_3)_4][PtCl_4]$

8

i) $Fe(C_5H_5)_2$



Bis cyclo pentadienyl ~~ferrate~~ iron (0).

(Ferrate only in case of anion)

ii) $[Co(NH_3)_4(NO_2)Cl]Cl$.

Chloro N-Nitro tetraammonium cobalt (III) Chloride

iii) $[(H_3N)_5-Cr-O-Cr(NH_3)_5]^{4+}$

μ-oxo - bis pentaammonium Chromium (II) ion.

✓

iv) $[Pt(NH_3)_4][Pt(Cl)_4]$

Tettraammonium Platinum(II) Tetrachloro platinate(II)

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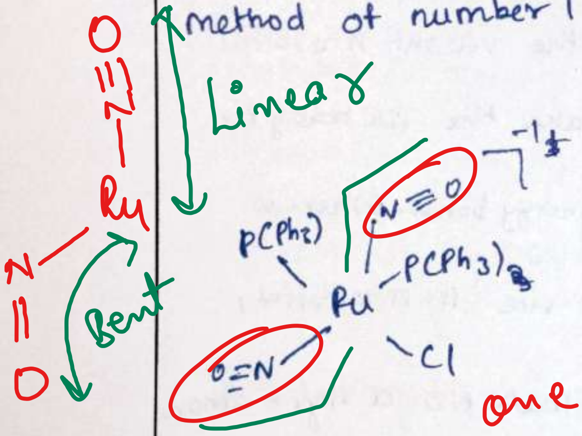
(d) In the coordination compound $[Ru(PPh_3)_2Cl(NO)_2]^+$, one NO ligand bonds linearly while the other is bent. Explain the different modes of bonding of NO ligands in this molecule and expected M–N bond orders.

5

(10 marks)

Coordination compound $[Ru(PPh_3)_2Cl(NO)_2]^+$ have to obey EAN rule, therefore it should be having ~~Total~~ valence electron count by oxidation or neutral method of number 18.



Here -N≡O e⁻ share have to satisfy the overall 18e⁻ count.

one should be linear

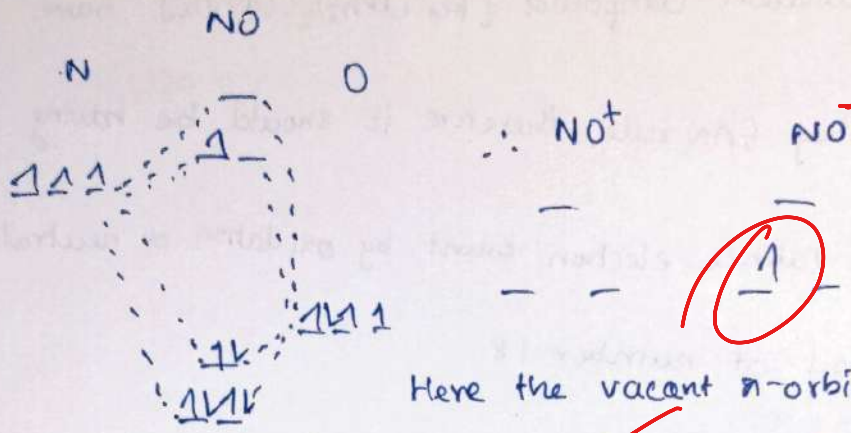
∴ Counting e⁻ sharing in this by neutral method,

Ru – 8, P(Ph3) – 2, Cl – 1, –ve charge = +1

$\therefore\ 8 + 2(2) + 1 + 1 = 14\ e^-s.$

∴ It requires 4 more e⁻s. which could be donated by $N\equiv\overset{+}{O}$ as well as $N\equiv O$ ligand which are linear with 13 e⁻ and Bent with 1 e⁻ respectively.

Different modes of Bonding with NO.



Here the vacant π-orbital in NO+ makes the site ready for π-acceptor and involve in synergy bonds. Whereas NO ~~br~~ doesnot have LUMO site in π-orbital, instead SOMO is present. This make NO a single e⁻ donor.

Hence, here M–NO bond, M–ON bond with 2 different orientation linear as well as bent is possible

M-N bond order is close to 0 and 1. because of the synergic effect, the bond order decrease or some times remain as 1 also.

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(e) Discuss the thermodynamic stability of the complexes.

8

(10 marks)

Thermodynamic stability of complex arise due to the internal structural stability that arise due to

i) Metal- charge density: As the metal is e⁻ density is equally distributed with many ligands, its stability increase

ii) Nature of Ligand: More spectrochemical series strong ligand pair with metal more stability.

iii) Chelation effect.

As the chelating ring is formed around complex, the stability also increases. It is accounted because of following reasons.

a) Size of the ring → Most size of ring

with 5 and 6 are more stable

b) Entropy change : As the no. of chelating ligand substitute monodentate ligand the randomness of the process increases. As a result Entropy of the reaction also increases.

$[Cu(NH_3)_6]^{2+} + 6CN^- \longrightarrow [Cu(CN)_6]^{2+} + 6NH_3$

No Entropy effect

$[Cu(NH_3)_6]^{2+} + 3en \rightarrow$ ~~$Cu(NH_3)$~~

$[Cu(en)_3]^{2+} + 6NH_3$

Here No. of product more than no. of reactant, hence the entropy of rxn increases at same time Thermodynamic stability also ↑ses.

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5

(a) Explain the basis of trans effect and describe the synthesis of cis-platin on its basis.

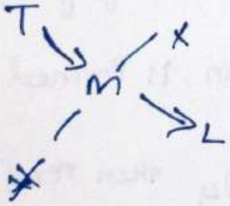
9

(10 marks)

Trans effect is the ~~ac~~ phenomena by which a ~~x~~ leaving group is decided by the trans position of ligand attached to central metal atom

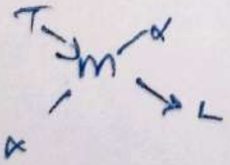
It can be explained based on the Fajan's rule's polarisation effect or π-acceptor donor effect.

a) Polarisation effect



As the 'T' group attached with metal 'm' polarises it strongly, it in turn polarise the ligand and e^--e^- repulsion pushes out 'L' group - leaving group from complex

b) π-acceptor and donor effect.



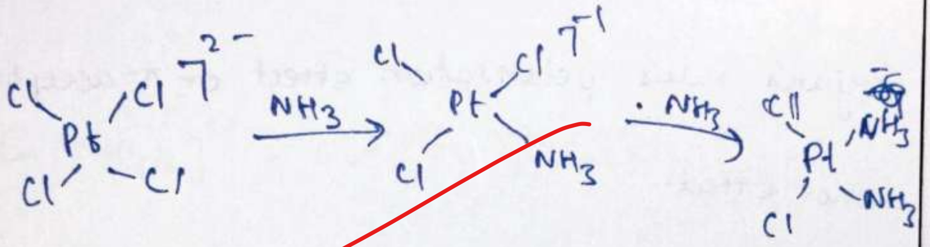
As more the ~~π~~-acceptor anddonor effect increases b/w M and T group, L group dissociate easily to accomodate incoming ligand

Synthesis of Cis platin

Trans effect Series

$CN > CO > C_2H_4 > NO > NO_2^- > I^- > SCN^- > Br^- > Cl^-$

$> ppy > NH_3 > OH^- > H_2O$



Reason:- Cl^- is more trans directing group than NH_3. Hence the cis platin is formed.

if starting material is ~~to~~ $Pt(NH_3)_4$ then rend reaction would yield transplatin.

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(b) Predict the structure of following boranes: B_6H_{10}, $B_4H_4^{2-}$, B_5H^{11}

7

(10 marks)

Structure of the compounds

$B_nH_n^{2-}$ Closo

$B_nH_n^{4-}$ Nido

$B_nH_n^{6-}$ Arachno.

No. of vertices can also be given

$\therefore B_6H_{10} \Rightarrow B_6H_6{}^{-}H_4 \rightarrow B_6H_6^{4-}$ (n+2).

This is 'Nido' in structure.

$B_4H_4^{2-} \rightarrow$ (n+1).

This is 'Closo' in structure

$B_5H_{11} \rightarrow B_5H_5 \cdot H_6 \rightarrow B_5H_5^{6-}$

∴ The compound is 'Arachno' in structure

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(c) What are interhalogen compounds? Explain the synthesis of Xenon fluorides and oxides.

(10 marks)

8

Interhalogen compounds

They are formed due to the presence of vacant d-orbital which gives various products from linear molecule to pentagonal bipyramidal molecular structures

No compound mentioned

In the Interhalogen compounds, Iodine could form max. no. of coordination compound with 7 fluorides.

At the same time Cl could form only with 'F' as its anion.

$F > Cl > Br > I$, because of higher electronegativity of F^- it can easily polarize any molecule and make bonds in Cl° atom also.

Xenon fluorides and oxides

Synthesis of Xe based compounds is possible only with high electro negative atoms F and O. Both polarise the molecule to get the molecules XeF_2 to XeF_6 and XeO to XeO_4 compounds.

$$Xe + F_2 \xrightarrow{2:1\ mix} XeF_2$$

$$\xrightarrow{1:20\ mix} XeF_6$$

$$XeF_6 + 6H_2O \longrightarrow XeO_3 + HF.$$

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF.$$

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(d) Suggest a method for separation of heavy actinides like Am, Cm, Bk, Cf, Es, Fm and Md with appropriate sketch. Write the structure of $Th(C_8H_8)_2$ and $U(C_8H_8)_2$.

7

(10 marks)

The separation of heavy actinides like Am, Cm, Bk, Cf, Es, Fm and Md could be done by either crystallisation, thermo absorption, acidity or basicity methods.

Crystallisation technique

In this technique the complex is mixed with solvents and made to cool down, the high basicity metal crystallises first, leaving others in the solution. Hence the Md, Fm, ES, Bk, Cm and Am is the sequence of metals that could be separated using this technique.

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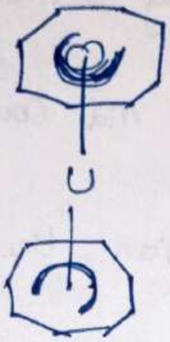
$_{92}U(C_8H_8)_2$

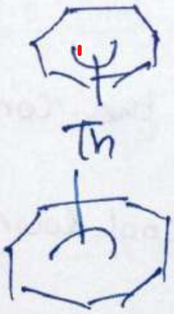


~~η^3~~

$U = +6$

~~η^3~~

$_{90}Th(C_8H_8)_2$



Here ~~η^2~~

Th → +4

Here ~~η^2~~

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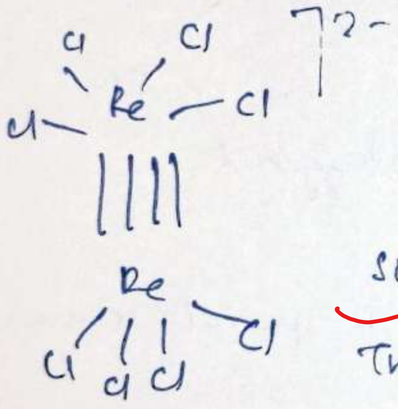
(e) Discuss the bonding in $[Re_2Cl_8]^{2-}$. 8

(10 marks)

Bonding involved in $[Re_2Cl_8]^{2-}$ is δ-bond

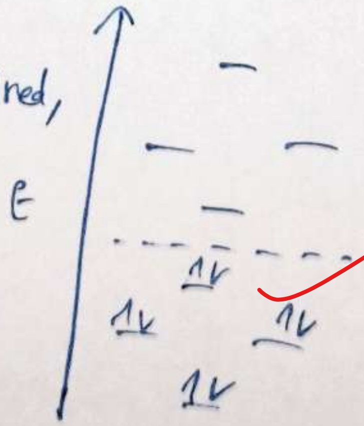
Here 4-lobes of ~~δ~~ d-orbital interact with one another.

δ-bond always perpendicular to σ-bond

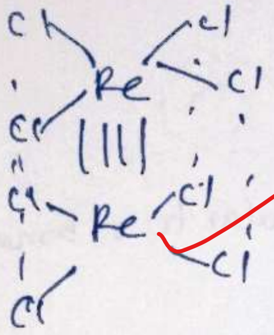


the Hybridisation is similar to that of dsp^2 The sq. planar geometry

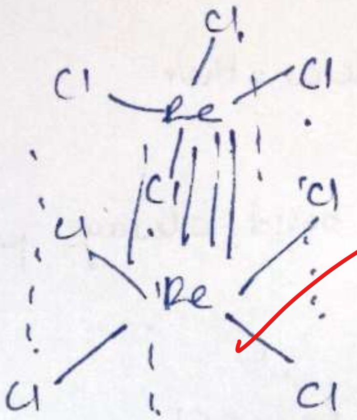
Here everything is paired, diamagnetic in nature, ESR inactive.



Eclipsed Structure is more Stable than staggered due to formation of δ-bond



Eclipsed



Staggered

Hence the $Re_2Cl_8^{2-}$ is special because of its δ-bond formation

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