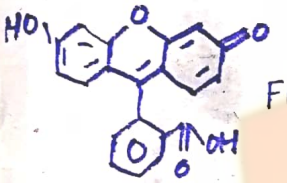
(2017)

(i)

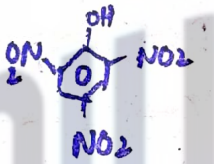
Describe classification of organic reagents used in inorganic analysis?

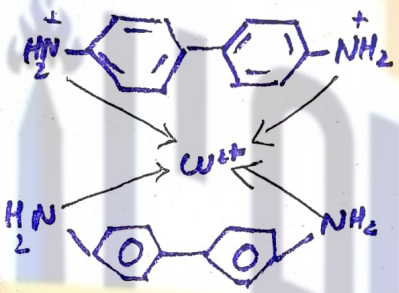
Organic Reagents

- High tedency to absorb on surface of soluble complex → **Absorption**
  - **acidic** — acidic functional group
  - **basic** — basic functional group
    - rhodamine
- react with analyte ion → **salt forming**
  - **Normal**
    - **acidic**
    - **basic**
  - **Complex**

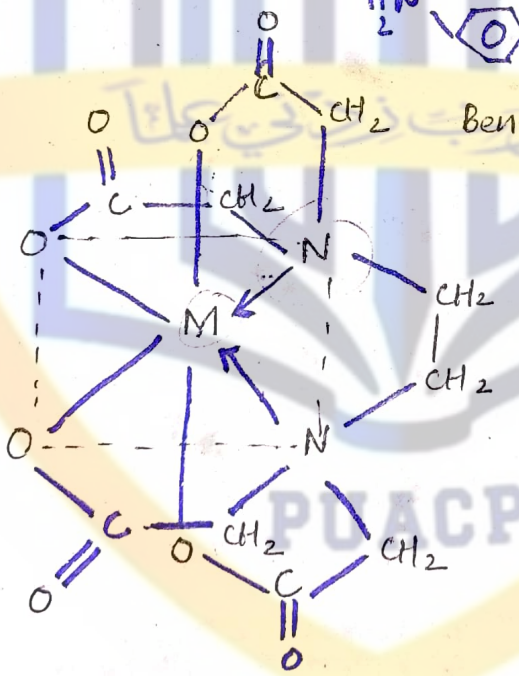


Fluorescence





Benzidine



(ii)

What is diagonal relationship? Give two similarities between Li and Mg.

A **diagonal relationship** is when elements in adjacent groups and periods show similar properties due to similar charge densitits and e- negativity.

Both the ions have high polarizing power

enthalpies of both the elements are comparable

What is s-inert pair effect?

A chemical phenomenon that describe the tedency of the 2 e⁻ in the outermost s-orbital of an atom to remain unshared in a compound.

Inert pair effect occur when s-e⁻ in the outermost electron shell of an atom are less likely to participate in chemical bonding. This is because the iner orbital electrons do not shield the s-e⁻ well, making them more tightly bound to the nucleus and more difficult to ionize or share.

example

It is most commonly observed in the heavier elements of groups 13-16 of periodic table such as

Thalium form +1 oxidation expected +3

Tin (Sn) 5s e⁻ does not participate in C.B

lead (Pb) //

~8(iv)8~

Describe application of organic reagents in chromatographic analysis as locating agents.

Organic reagent used in chromatographic analysis as:

Locating reagent

Group I	Ag^{+}, Pb^{2+}, Hg^{2+}	Sodium Rhodizonate
Group IIA	Hg^{2+}, Bi^{3+}, Pb^{2+}, Cd^{2+}, Cu^{2+}	Thiourea, Diphenyl carbazone
Group IIB	Sn^{4+}, As^{3+}, Sb^{3+}	Diphenyl carbazone
Group III	Fe^{2+}, Fe^{3+}, Al^{3+}, Cr^{3+}	Alizarine, Aluminone

~~Elution~~

~8(v)8~

Why does Fluorine show peculiar behavior in group VIIA?

Fluorine differs from the other members of its own subgroup due to

(a) its small size
(b) its high electronegativity
(c) non-availability of d-orbitals in its valence shell

oct: e_g t_{2g} | tet: t_{2g} e_g

Draw correlation diagram of d_2 and d_8 octahedral and tetrahedral complexes.

spectroscopic term

correlation of the relative energy of orbitals with the help of diagram is known as correlation diagram

electronic configuration ⟶ Spectroscopic term ⟶ Huckelin Term

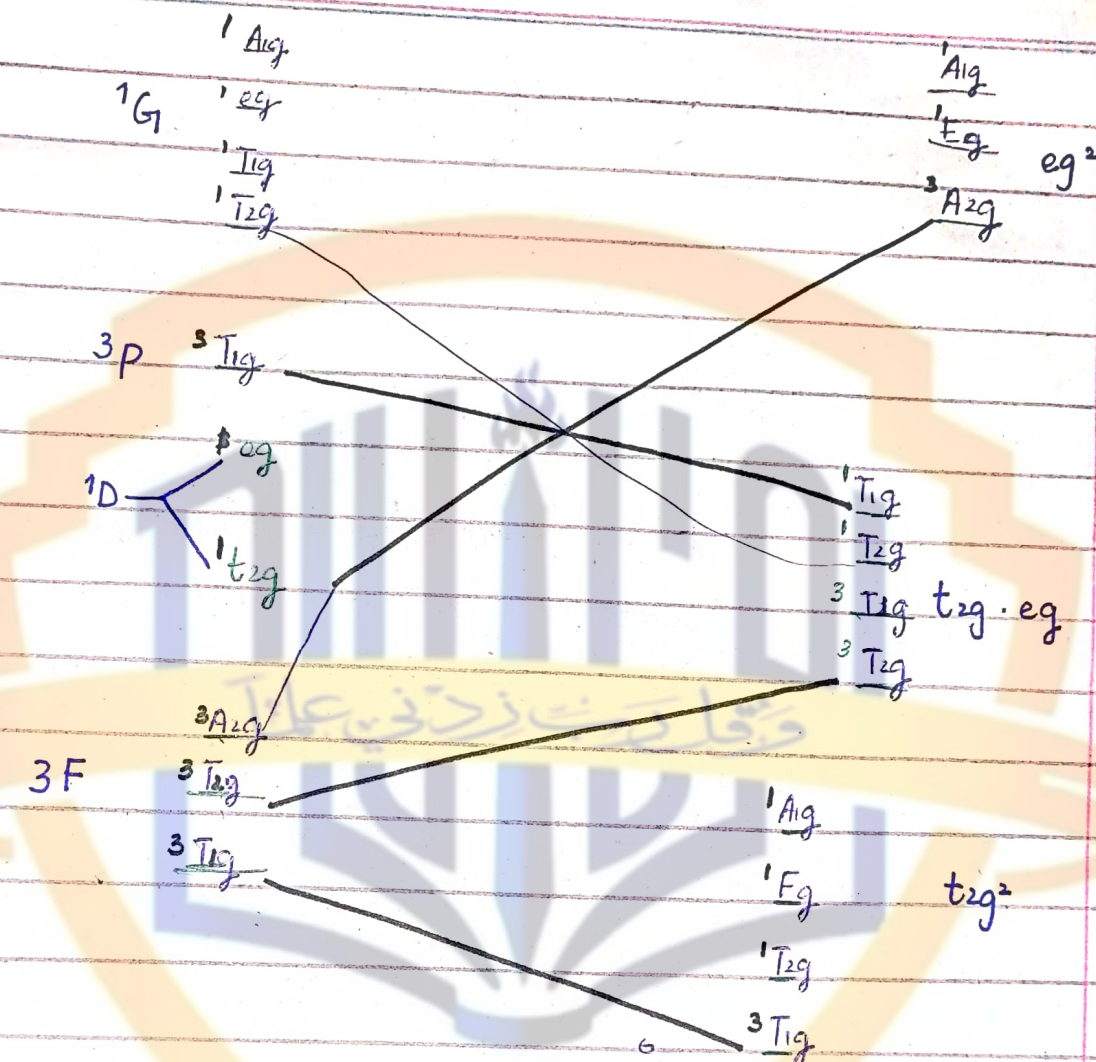
↓

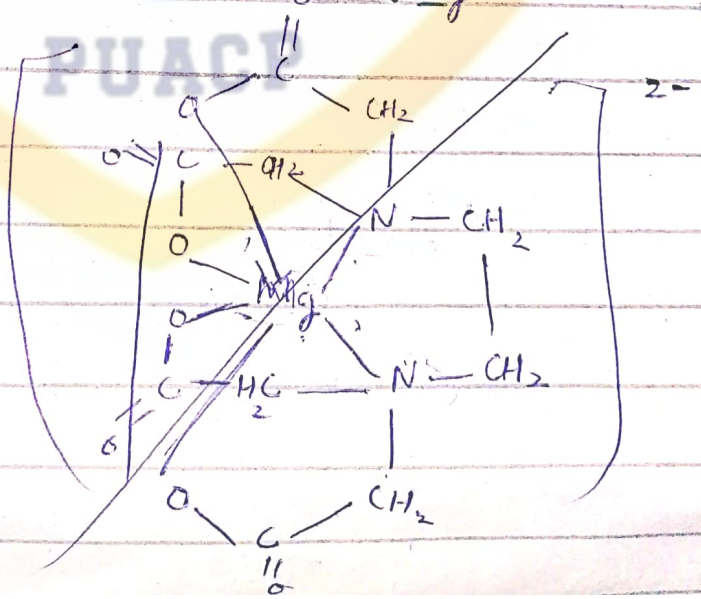
molecule term

Starting point describing molecular bonding.

in ... electron pairing

^1S —— $^1A_{1g}$





~~8(viii)~~

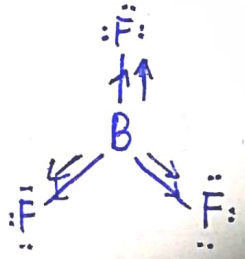
Write two points of differences between VBT and MOT?

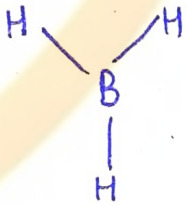
MOT	VBT
An e- moues under the influence of only two or more nuclei of a molecule.	An e- moves under the influence of only one nucleus of an atom.
In VBT, only half-filled orbitals of the valence shell take part in bonding and completely filled orbitals remain non-bonding orbitals.	In MOT, all the atomic orbitals, whether completely filled, partially filled or vacant overlap to form molecular orbital

(viii)

Why BF_3 is more stable than BH_3?

BF_3 is more stable than BH_3 primarily due to the difference in electronegativity of the atoms involved and the overall molecular structure





(•) Trigonal planar geometry

(•) Fluorine is highly electronegitive, which means it pulls e- density toward it self.

(•) similar geometry

(•) Hydrogen less e-negitive

(ix)

Why PF_3 exists whereas NF_3 does not?

exists whereas NF_3 does not, due to differences in atomic i.e. electronegativity and bonding capacity between phosphorus and nitrogen.

atomic size

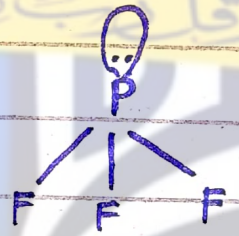
large, which allow it to accommodate three F atoms more easily.

electronegativity

Phosphorus has lower electronegativity than Nitrogen, making it more willing to share e- with F atom.

Bonding Capacity

Phosphorus can form three covalent bonds with F due to its ability to expand its octet, which Nitrogen tends to form three covalent bonds only with H



(N)

What is 3c-4e bond? Give example?

3c-4 electron bond formed from a p-orbital of the central atom and the s-orbital of two outer atoms.

3c-4e model approach based on the two main ideas:

Use of outer d-orbitals of the central atom of non-transition metal ion is so slight that these

may be neglected altogether

Presence of bond angles close to 90° and 180° in AB_4 molecule suggests that obitals perpendicular to one another are being used.

Se_4F_4 $_{34}Se$ = [Ar] 4s [↑↓] 4p [↑↓ | ↑ | ↑] 3c – 4e

F F F F

(2018)

(i) What are chelates?

These are special type of coordination compounds containing one or more ring in their structures. The ring structure are formed by linking metal ion with polydentate ligand. Such ring structure compounds are called chelates.

example

$Ni^{2+} + 2$ $HC_3-C(=N-OH)-C(=N-OH)-CH_3$ → Ni(DMG)$_2$

(ii) DMG

Mention 4 points of similarities between VBT and MOT?

- Both explain the formation of chemical bond between atoms in a molecule.
- Both theories use atomic orbitals as the

starting point describing molecular bonding.

- Both emphasize importance of electron pairing in forming covalent bonds.
- Both are predict the geometry and shapes of a molecule.

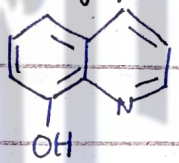
(iii)

What is s-inert pair effect?

repeat (2017)

(iv)

Give two uses of 8-hydroxyquinoline in inorganic analysis.



(•) Used for gravimetric analysis Al^{3+}, Cu^{2+}, Bi^{3+}, Cd^{2+}, Co^{2+}, Zn^{2+}, U^{6+}, W^{6+}

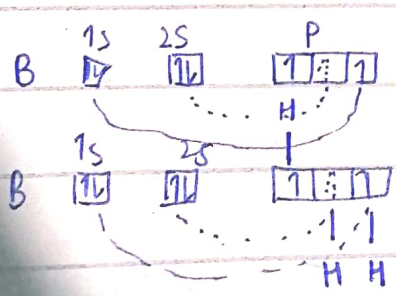
(•) Used for solvent extraction and gravimetric determination of Cu^{2+} and V^{3+} in $CHCH_3Cl$ (chloroform) soln.

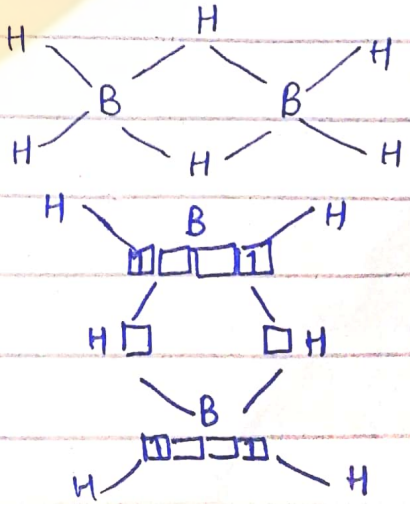
(v)

What is 3c-2e bond? Give example.

3c-2e bond is electron deficient chemical bond where 3 atoms shares two electron.

B_2H_6





Why does F show peculiar behavior with group VIIA?
Repeat (2017)

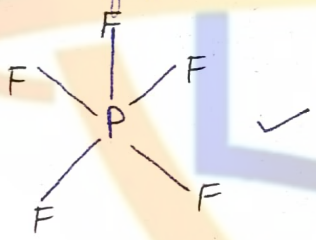
explain why PFs exist but NFs does not?

PFs exists, whereas NFs does not, due to differences in the atomic size, electronegativity and bonding capacity between P and N.

(•) Phosphorus has large atomic size, allowing it accomodate five fluorine atom easily.

(•) Phosphorus has lower electronegativity than nitrogen making it more willing to share e^- with F atom

Phosphorus can expand its octet and form five covalent bond with F atoms, while nitrogen tends to form a maximum of four covalent bond.



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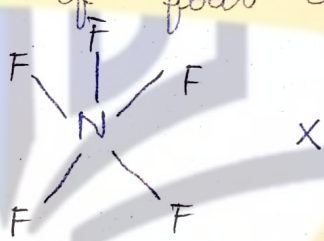


X

$P_{15} = 1s^2, 2s^2, 2p^6, 3s^2, 3p_x^1, 3p_y^1, 3p_z^1$ $N_7 = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$

VSPER

Advantages

predict molecular shape (three dimensional structures)

explains bond angles and lengths

292-24 glued

Advantages
Simplification

It assumes that e- pair repell each other equally, which is not always the case.

Limited predictive power

It struggles to accurately predict the shape and bonding of molecules with delocalized electrons.

Name factors that can affect sensitivity, selectivity and specificity of an organic reagent?

electronic configuration
charge and size ratio / Polarizibility
Geometry of resulting metal complex

(2019)

Give two failure of VBT?

It can not explain the color of coordination compounds. And it can not explain the magnetic properties of coordination compounds.

What are physical states of different halogens at room temperature

Fluorine, Chlorine gases Iodine solid
Bromine liquid

How they are differ?

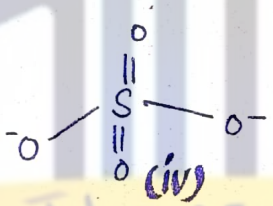
These are different from due to the increasing atomic size, molecular weight and intermolecular forces down the group.

(iii)

Which type of bonding is stronger between $p\pi - p\pi$ and $d\pi - p\pi$ and why?

The $p\pi$ and $d\pi$ bond is stronger than the $p\pi - p\pi$ bond. Due to a larger level of overlap in the electron clouds in $p\pi - d\pi$ bond, the extent of overlap is greater, resulting in a lower energy bonding.

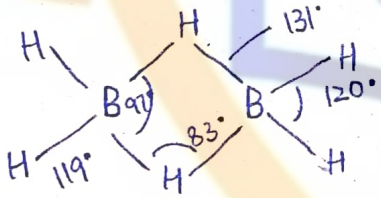
SO_4^{2-}



Two $p\pi - d\pi$ bond

(iv)

Give the structure of diborane molecule? Which type of bond explains its structure?



It explain 3center – 2e- bonds

(v)

What are amphoteric oxides? Give example.

It is an oxide that can act as either acid or base in a reaction to produce a salt and water. It depends on the oxidation states available to a chemical species.

Acidic $Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$

basic $Al_2O_3 + 2OH + 3H_2O \longrightarrow 2[Al(OH)_4]$

is s-inert pair effect?

Repeat (2017, 2018)

(vii)

Name different organic reagents used as indicators in acid base titration.

phenolphthalein

Methyl orange

Methyl red

(viii)

Name various types of organic reagent (other than ~~organic~~ indicator) used in analysis.

citric acid

owalic acid

(ix)

How chelates can be classified?

Chelates can be classified into several categories based on their properties, structure, and binding characteristics

classification by ligand

Aminocarbonylate chelats

Polyphenolic

polyamine

Bidentate

Tridentate

Polydentate

(n)

What are complexometric titration?

The volumetric titration in which concentration of metal ion is determined by titrating it against complexing agent solution is called as complexometric titration.

(2020)

(i)

Drawbacks of VESPR Repeat (2018)

(ii)

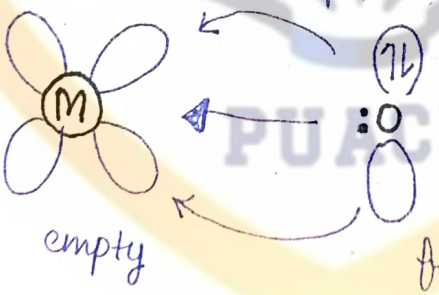
Dis/Give one experimental evidence for $d\pi - p\pi$ and why?

Comparison of stability of phosphine oxide & amine oxide

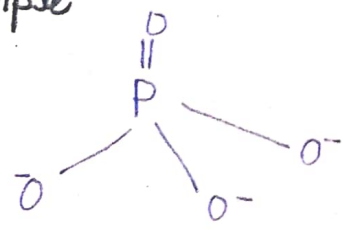
phosphine oxide

$R_3P{=}O$ is more stable than R_3NO because of $d\pi - p\pi$ bonding

If there is a bond between two atoms with one vacant orbital on one atom and one lone pair of electrons on the other atom, then this electron pair is donated to that corresponding unoccupied orbital,



example



(iii)

ence between

Molecular Orbital	Hybrid orbital
(•) When atomic orbitals forms by combining orbitals of different atoms	(•) Hybrid orbitals are formed when atomic orbitals of same atom mix
(•) describe the distribution of electrons in a molecule.	(•) While Hybrid orbitals explain localized bonds within an atom.

(iv)

What is 3c-4e bond? Give one example.

Repeat (2017)

(v)

Give two similarities between Li and Mg?

(•) high polarizing power, enthalpies of both elements are comparable.

(vi)

What is s-inert pair effect? Repeat (2017, 2018), 2019)

(vii)

Why BH_3 is less stable than BF_3? Repeat (2017)

(viii)

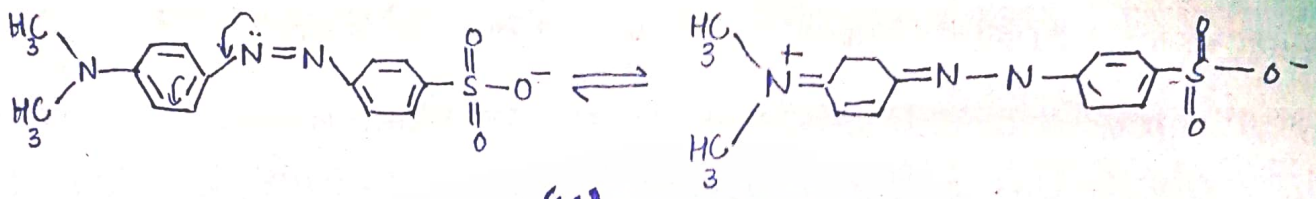
Why is buffer used in EDTA titration?

A buffer is used in EDTA titration to maintain the pH of solution. Always remember that a buffer is added to solution that undergoes titration in specific range.

(ii)

Brief acid-base indicators?

They are weak acids or bases that change colour when concentration of H^+ or OH^- ion in a solution changes.



(ii)

How can chelates be classified?

Repeat

Long Questions

Periodic anomalies

It is generally assumed that the properties of various families of the periodic chart change smothly from less metallic (more electronegative) at the top of the family to more metallic (less electronegative) at the bottom of family.

Post-Transition metal.

Atomic radii

Post-transition metals typically exhibit a decrease in atomic radii across a period. However anomalies can occur due to factor such as electron confi... and shielding effect.

Ionization energy

lower than expected. This anomaly influenced by electronic configuration.

Non-metal

When moving left or right across period, the change in atomic radius is smaller. This is because nonmetals tend to have more e- in their outermost shell.
- increased shielding effect

Non-metals have high ionization energy due to their small

cases, e- in the s
tals are easier to remove
than predicted due to the
presence of partially filled d
orbital, which offer less
effective shielding from nucleus.

electronegativity

Measures an atom ability
to attract electrons in a
chemical bond.

Lower electronegativity, this
anomaly can be attributed
to the presence of partially
filled d-orbital, which reduce
effective nuclear charge, thus
decreasing their ability to
attract electrons.

Higher electronegativity because
they have more valence e-
and more likely to gain e-
to become anions.
Nuclear charge in decrease
and atomic size decrease.

Reactivity

less reactive due to
the stability conferred by
fully or partially filled
d-subshells. This anomaly
arises from the reluctance
of post-transition metals
to lose or gain electrons.

size and high E.N. in 2nd peri
of periodic table Be 1st ionization
energy is higher than boron. This
is because Be valence shell
is completely filled.

Nonmetals become more reactive
as you move up a group
on the periodic table. Forexample
Chlorine is more reactive
than phosphorus. This is because
(•) no. of valence shell increase
(•) tedency to lose e- increases

pπ-pπ bonding in heavier congeners of group 4A.

The p-orbitals of one atom overlap sideways with the p-orbitals of another atom in this type of bonding, resulting in formation of pi bind, also known as p-pi-pπ bond.

pπ-pπ bonding involves the overlap of π-orbitals, which are oriented perpendicular to the σ-bonding axis. This type of bonding is common in molecules containing multiple bonds between second row elements C, N.

Heavier Congeners of group 4A are Si, Ge, tin and Pb. These elements exhibit different chemical properties compared to C, due to their larger atomic size and lower

negativity.

In the heavier congeners of Group IVA, Pπ-Pπ ondiny is less common due to following reasons.

Atomic size

The larger atomic size of heavier congeners results in a longer bond length, making it more difficult for π orbitals to overlap effectively.

electronegativity

Lower electronegativity of heavier congeners reduces the energy difference between π orbital, making it less favorable to pπ-pπ bonding.

relativistics effects

In the heavier heavier elements relativistics effects become more significant, leading to:

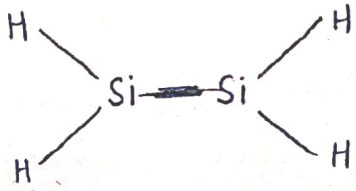
(•) contraction to atomic orbitals

(•) reduction in overlap between π-prbitals

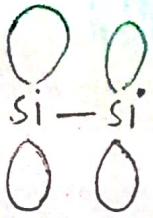
Heavier elements of this group do not form pπ-pπ bonds as their atomic orbitals are so large and diffuse that they cannot have effective overlapping. Despite these challenges, Pπ-Pπ bonding has been obsereued in some molecules containg heavier congeners of G IVA elements

$_{14}Si$

$1s^2 2s^2 2p^6 3s^2 3p^2$



dimer



experimental evidence of $d\pi - p\pi$ bonding

One example of the apparent existence of π-bonding is in phosphine oxide.

Characteristics feature of hybridization

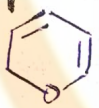
Mixing of atomic orbital form new hybrid orbit

formation of equivalent orbital

Change in orbital shape

Directional properties

structure of oxine



oxine

Diagonal relationship

Complexes Hydrofluoboric acid (HFB), fluosilicate acid (H_4SiF_6)

None of occur free state, attacked by water

Allotropic and amorphous

High M.P B = 2300, Si 1420

prepared by reducing their oxide

$SiO_2 + 2Mg \longrightarrow 2MgO + 2B$

$B_2O_3 + 3Mg \longrightarrow 3MgO + Si$

dissolve alkalies

$2B + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 3H_2$

$Si + 2NaOH + H_2O \longrightarrow Na_2SiO_3 + 2H_2$

Configuration.

Several workers have been objected on the inclusion of d-orbital of bonding in non-metal

Factors

(i) Large promotional energy

$$s^2p^nd^0 \longrightarrow s^1p^{n-m}d^{m+1}$$

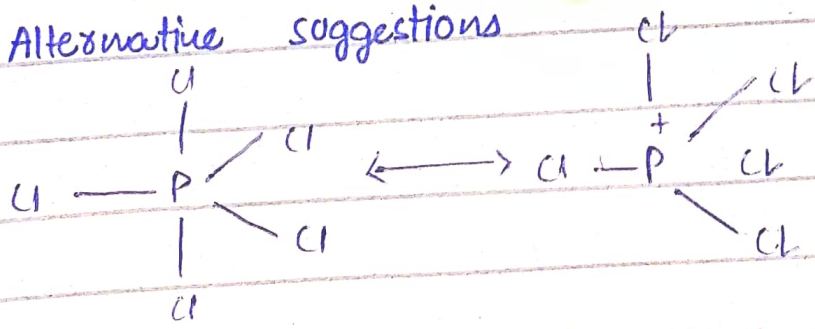
d-orbital has large energy as compared to s and p-orbitals. So large proportional of energy is required for the excitation of e- from p to d-orbital

(ii) Poor Overlaping

They make orbital with neighboring atom The 3d orbital of S-atom is completely shielded by lower lying e- and hence do not feel. As a result completely diffuse due to this orbital will be more effective in overlaping neighboring atomic orbitals.

Alternative soggestions

Resonance



3c - 4e⁻ bond

with low densities.

(2021)

(i)

How does MOT differs from MOT?

Repeat 2017 past papers

(ii)

How does stability of chelates depend upon the nature of ligand?

The stability of chelates depend upon the nature of ligand involves

- (•) Basicity of ligands
- (•) Size and charge of central metal ion
- (•) Chelate ring size

(iii)

Write two similarites between Be and Al

- (•) Both elements have low melting points
- (•) Both of elements are form covalent bond.
- (•) The oxide and hydroxides of both elements are amphoteric.

(iv)

Which indicator are used in EDTA titration?

Erochrome black T (EBT)
Calmagite

(v)

What is inert pair effect give examples?

Repeat (2017, 2018, 2019, 2020)

(vi)

SiCl4 react with water while CCl4 does not? justify it.

Experiment Name:

Carbon in CCl_4 is not having empty d-orbital for water molecule to approach it and form bond ($H_2\ddot{O}: \longrightarrow$ Oxygen can donate e- pair to the empty orbital) where as in Si in $SiCl_4$ having d-orbital and water can easily get attached to it resulting hydrolysis.

$$SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$$

(vii)

Why NF_5 molecule does not exist?

Repeat (2018)

(viii)

Give classification of organic reagents used in inorganic analysis?

Q (i)-(S) Repeat 2017 pas paper

Give 4 similarities between Li and Mg

(1) Both are highly reactive due to their Low ionization energies and high reactivity with water.

(2) Both react with oxygen to form

$$2Mg + O_2 \longrightarrow 2MgO$$

$$2Li + O \longrightarrow Li_2O$$

(3) Both react with water to form hydroxides

$$Li + H_2O \longrightarrow LiOH + H_2$$

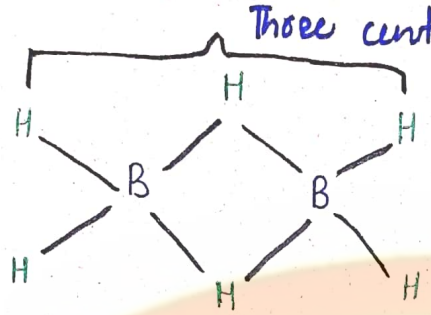
$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

(4) Both relatively light metals with low densities.

(vi)

What is 3 center - 2 electron bond?

It is an electron deficient chemical bond where atoms share two electrons



(vii)

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Methyl orange

(viii)

Why is BF_3 more stable than BH_3?

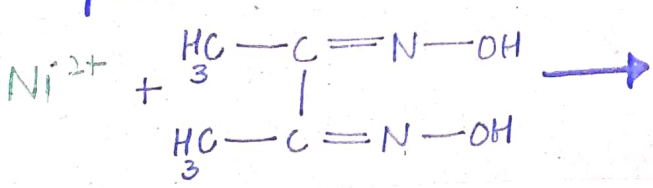
Repeat (2017, 2020)

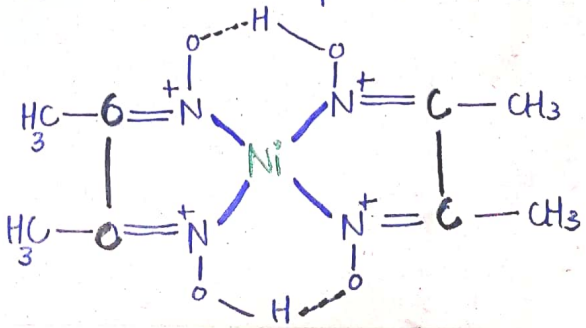
(viii)

What are chelates?

They are special type of coordination compound containing one or more ring in their structures. The ring structures are formed linking metal ion with polydentate ligand. Such ring structure compounds are called chelates.

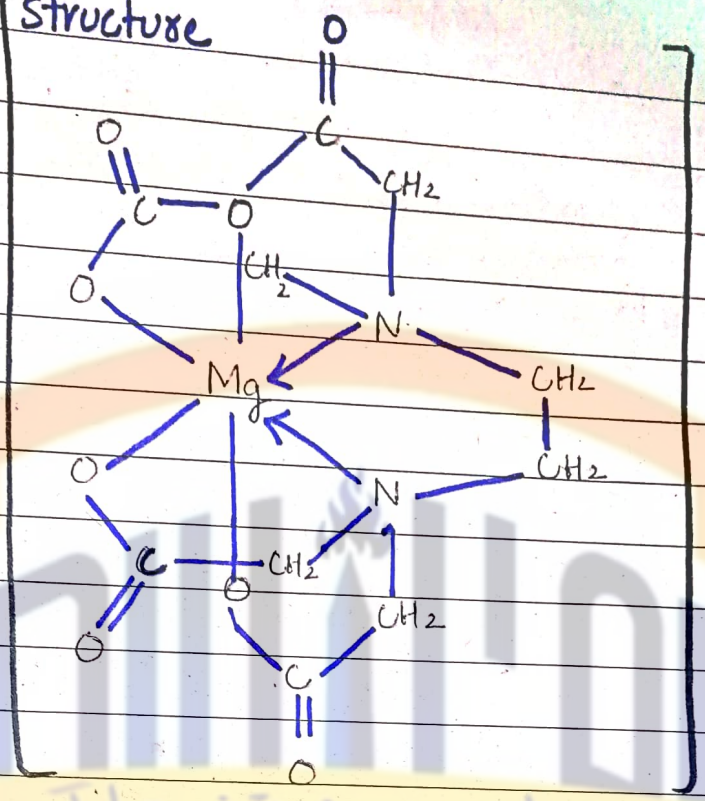
example





(xiv)

$[Mg-EDTA]^{2-}$ Draw structure



(xv)

Write physical state of halogens at room temperature and why they are different?

Fluorine (gas)
Chlorine (gas)
Bromine (liquid)
Iodine (solid)

Why they are different?

As we move down the group from fluorine to iodine:

Atomic size increase, electronegativity decrease

and increasing molecular weight; this leads increase in dispersion forces between molecules.

2022 fall

What are major drawbacks of directed VBT?

Fails to explain carbon's tetra valency
energies of electrons are not discussed
There is no distinction between weak and powerful ligand.

(ii)

Why is a disodium salt of EDTA prepared?

Disodium salt of EDTA is prepared for

(•) Improve solubility
(•) enhanced stability
(•) better chelating properties

→ It is a complexing agent that dissolves metal ion. It is a heavy metal chelating agent that can remove lead and copper from metal poisoning.

(iii)

How can chelates be classified?

Chelates can be classified on the basis of their coordination sites:

Monodentate
Bidentate
polydentate

(iv)

Why is BF_3 is more stable than BH_3 why?

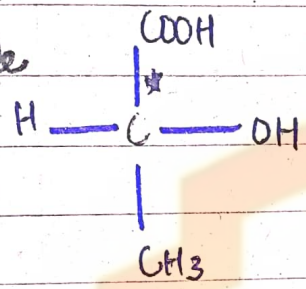
Repeat

(v)

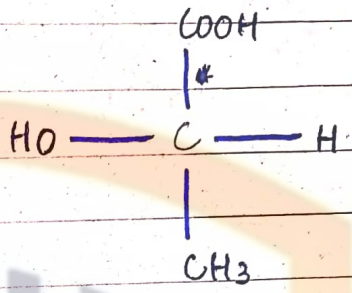
Define stereochemistry with few examples

A branch of chemistry that deal with the spatial arrangement of atom and groups in molecules. It is the three dimensional structure of molecule.

example



(+) d-lactic acid



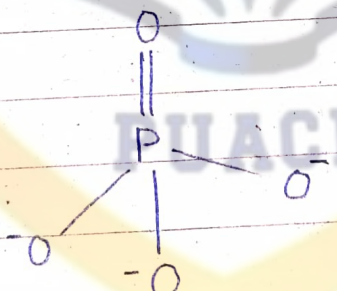
(-) l-lactic acid

(vi)

What is dπ-pπ bond? Give one example.

When the pi-bond is established between the p-orbital of one element and the d-orbital of the other element, it is called the dπ-pπ bond. It can not be formed by elements that do not have a vacant d-orbital

example



(vii)

What is difference between molecular and hybrid orbital?

Repeat in 2020 past papes

(viii)

What kind of relationship is present between Li and Mg? Brief.

Li and Mg have a diagonal relationship, which means they are diagonally adjacent elements in the periodic table and have similar properties.

(ix)

What different types of organic reagent used?

Grignard reagent
electrophilic reagent
silver nitrate ($AgNO_3$)

(x)

What are the factors that affect sensitivity and selectivity of an organic reagent? repeat (2017)

(•) electronic configuration
(•) charge and size ratio
(•) geometry of resulting metal complex

(xi)

Write few properties of chelates?

(•) stable due to formation of multiple bond between metal ion and ligand.
(•) increase solubility of metal in water
(•) exhibit kinetic inertness
(•) exhibit para or ferromagnetism

(xii)

What is 3c-2e bond? Give 1 example.

Repeat (2021)

(viii)

Assignment Name: What kind of stability is observed in chelates?

Chelates can exhibits several types of stability:

(•) Thermodynamic
(•) Kinetics
(•) Structural
(•) configuration

(xiv)

Write two advantages of VSEPR

(•) predict molecular shape
(•) predict bond length and bond angle

(xv)

Write physical state of halogens at room temperature and why they are differed.

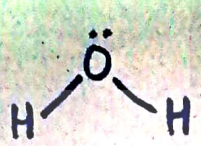
Repeat (2020)

Correlation diagram suggest the shape of triatomic AB_3, tetra-atomic AB_4, penta-atmoic molecules through correlating their geometry with electronic state. Walsh diagram were first introduced by Prof. A.D. Walsh. These diagram predicts geometries of small molecule and explain why a given molecule is more stable in certain geometry.

For H_2O

Hydrogen = $1s^1$

Oxygen = $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$



- Bent geometry
- 2-H atoms
- contain lone pair

S, p_y, p_z correlate in case of bent