DNR COLLEGE(A): BHIMAVARAM

DEPARTMENTOFPGCHEMISTRY

INORGANICCHEMISTRY-II

PresentedBy

N.Santhi

Unit-1

Metal Cluster Compounds

METALCLUSTERS

IfaCompoundContaina morethanonemetalpermoleculeandifthereexistsabond between two metal centres, then that compound is known as Metal clusters.

EvidencesforformationofM-M**Bondinclusters:-**

ThefollowingtwofactorsprovideevidenceofM-MBondformation

1. ShorterInternucleardistance
2. Loweringofmagneticmoment

Bymeasuringf.thesetwofactorSwecanprovetheM-Mbondformation

ShorterInternucleardistance:-

I) ConsiderVarderwall'sforcesVanderwall'sareoperatingblwtwomolecules.IfWeCalculate vanderwall radius, it is more than atomic radius

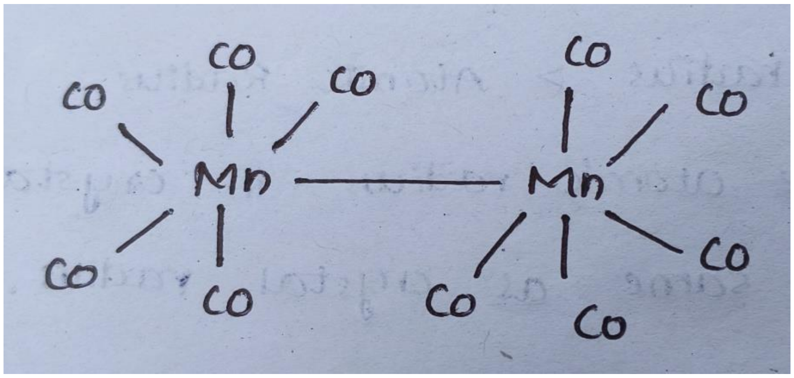
II) IfweConsidertheatomicradiusinCrystallattices.Theatomicradiusissameas.Crystalradius because here there is no bond b/w two metal atoms

Itmeansifnochemicalbondisformed,Internucicardistance ismoreorequaltoSumofatomic radii. Otherwise, Ifthere is activebondis formed theinternuclear distanceis decreasedandit is less than sum of atomic radii This is evidence, for formation of chemical Bond.

Iii)IftheInternucleardistanceisshortenedthansumofatomicradiithenthebondisformed between two metal atoms.

Examples:Theexistence ofM-MBondPS itselfevidentinthecaseof$Mn_2(CO)_{10}$&Re_2Cl_8

In$Mn_2(CO)_{10}$,thereisaM-Mbond.ItformsM-MbonditsatisfyEANrulealsothere isachance in this complex bridge bonds by CO group but there is no such peak for bridging ligand in Mn_2



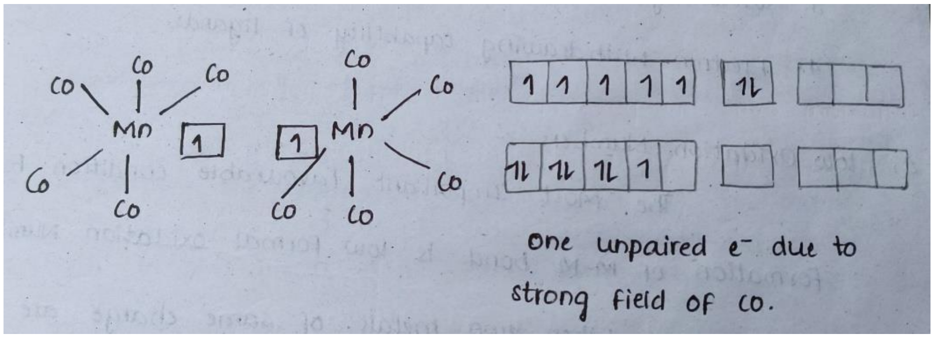
(CO)10

II)**LoweringofMagneticmoment:-**

The Lowering of magnetic moments are compared with the values expected for isolated metal ionsisanotherkindofevidencefortheexistanceofM-Mbonds.Theloweringisassumeddueto pairing ofSpins inM-M interactions, . This isoften been used because magnetic Susceptibility values are relatively easy to measure.

$Mn_2(CO)_{10}$

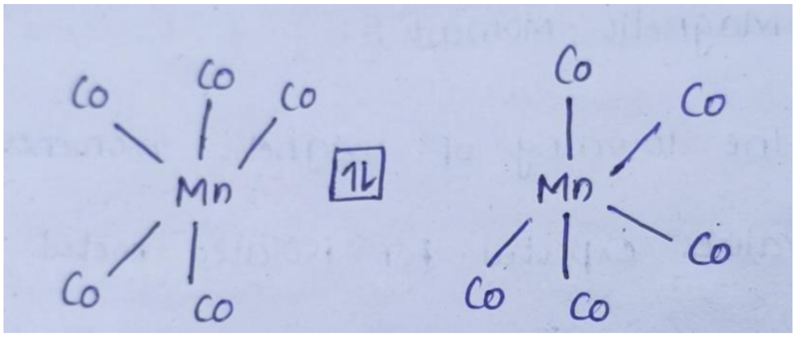
Toprovetheexistenceofbondbetweenb/wMn&Mn.Letusconsidethere,is nobondb/w themthenthereisone unpairedelectrooneachMnatom.Themagneticmomentsrelatedto oneunpairedelectroniscalculated.



one unpaired e⁻ due to strong field of co.

Themoleculesarepairingofunpairedelectronsb/wtwoMnatomstheirunpairedelectronsare paired up and a dative Sigma bond is formed . If we calculate the magnetic moment in $Mn_2(CO)_{10}$it is zero. It means the magnetic momentsare decreased when a bond is formed

HerethetwounpairedelectronsarecontributedtoformMn-Mnbond.



ConditionsfavourableforformationofM-M**Bond:-**

ThefollowingfactorsarefavourableforformationofM-Mbondsinclusters

1.LowformalOxidationNumber

2Lessnoofelectronsonmetals

3.SuitabilityoforbitalConformation

34ElectronwithdrawingCapabilityofLigands

LowOxidationNumbers:-

The most important favourable condition for formation of M-M bond is low formaloxidation numberofmetalatoms.Whentwometalsofsamechargearecomeclosetogethertheyrepel each other . When oxidation number increases charge on metal atom increases as a result repulsion b/w two metal atoms increases which causes weakening of M-M bond

Ex:-Re2Cl82-:-Reneverexhibits+3.Stateinitssolution.Italwaysexhibit+5state.ButRe exhibits +3state for formation of M-M bond in Re2Cl82-

Lessnumberofelectronsonmetals:-

Acovalentbond isformed duetooverlapof halffilledOrbitals or overlap ofemptyand half filledOrbitals.ButwhentwoOrbitalsarecompletelyfilled,thereshouldbenobond.Hence less number of electrons on metals favoursthe formation of clusters.

Ex:- In all cases M-M bond is formed but in case of copper it was not observed due to d9 configuration.Socopperisunabletoprovide half filledOrbitalsforformationofM-Mbond.

SuitabilityofOrbitalconfirmation:- Orbitals will overlap, if they have same symmetry orientations.Theorientationsoftwometalclustersisinsuchawaythatthereisamaximum possibility of overlapping.

Ex:-In Re2Cl82-, a strong quadrapolebond is formed ecipsed confirmation of clusters while providesasuitableconfirmationtooverlapontheotherhandstaggardconfirmationdoesnot formquadrapole bond.

Electronwithdrawingcapabilityofligands:-

If the ligand has the capability of accepting π electrons into its Orbitals then those ligands favourstheformationofM-Mbond.Ligandsacceptπelectronsofmetalatombybackbonding and provide empty Orbitalsfor metal atom which facilitates the formation of M-M bond

Ex:-polynuclearmetalcarbonylconstituentsareofthelargestclassesofM-Mbonded compounds due to the electron withdrawing capability of CO ligand.

Binuclearclusters:-

- Binuclearclustersarethosewhichcontainstwometalcentersinamolecule Both

metal atoms lie on a same plane

- Ex:Re2Cl8,Mn2(CO)10

Re2Cl8(**octachlorodirhenateion**):-

Preparation:

- Itcanbepreparedbythereductionofperrhenatewith HCl inpresenceofstrongreducing agent(H3PO2).

2ReO4+2H3PO2+8HCl→Re2C18+2H3PO4+4H2O

Structure&**Bonding**:

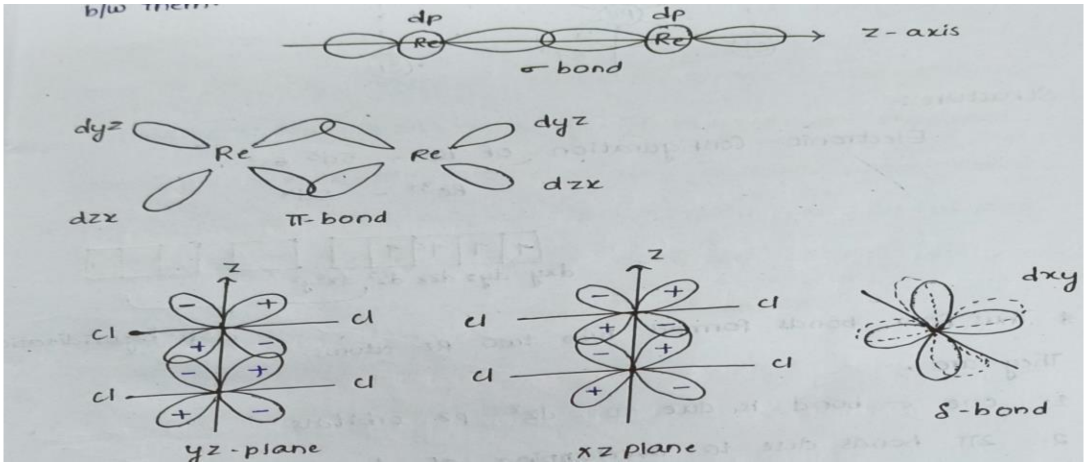
- TheStructureofRe2C18hastwointerestingstructuralfeatures.Theyare

-i)ThebondlengthbetweenRe-Reis2.24A°(extremelyshort)

ii)Ithaseclipsedconfigurationratherthanthemorestablestaggardgeometry

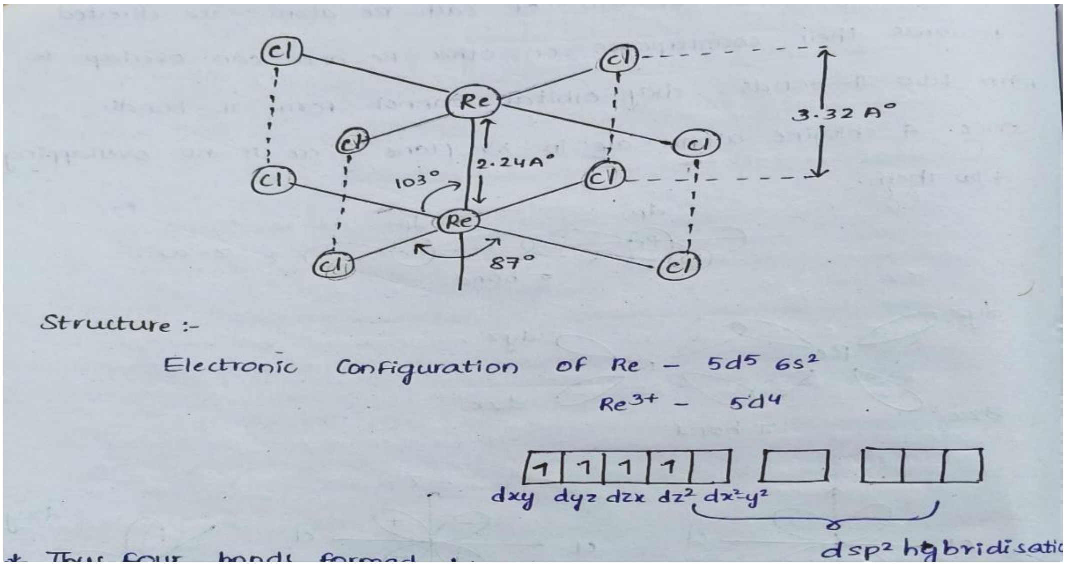
- Re-RebondisextremelyshortcomparedwithanaverageRe-Redistanceof2.75A°inRhenium metal and 2.48A° in Re3C19

Let twoReCl4units are situated in xy plane which are paralleltoeach otherRe atom is in dsp2 hybridizationoneachmetalutilizingthedx2-y2orbitalsReatomformsfoursigmabondswith4 chlorine atomsThe pz and dz2 orbitals of the metal lie along the bond axisand may be hybridizedtoformoneorbitaldirectedtowardsotherReatomandasecondReatomtoforma sigma bond while the second hybrid orbital form an approximatelynonbondingorbital.Thedyz,dzxorbitalsofeachReatomaretowardstheir



counterpartsontheotherReandcanoverlaptoform2bonds.Thedxyorbitalscannotformπ bondsSince 4 chlorine atoms are in xy plane there is no overlapping b/w them,

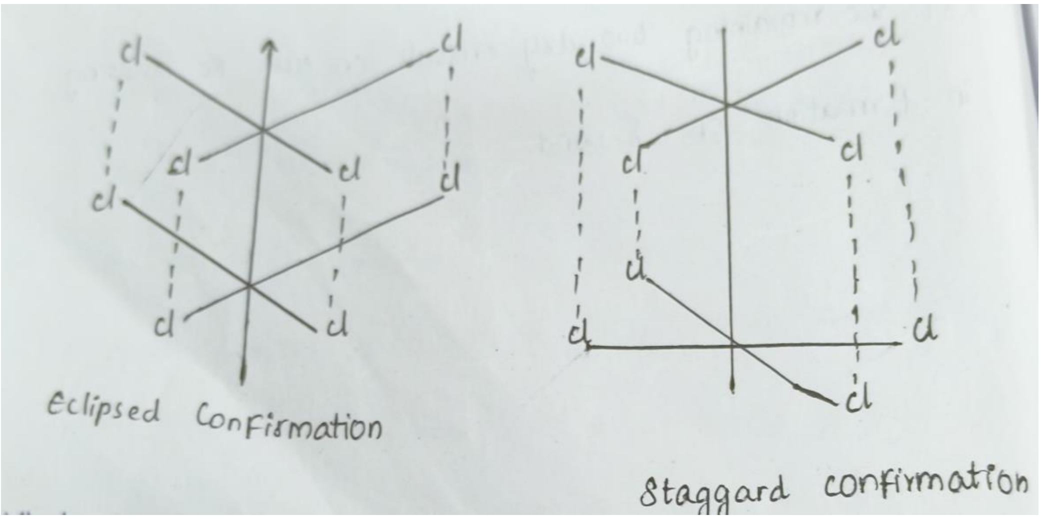
Thefourthbondcannowformedbysidewiseoverlapoftheremainingtwodxyorbitalsoneach Re resulting in the formation of a & bond



Thusfourbondsformedb/wtwoReatoms.They are

1. onesigmabondisduetooverlappingofdz2&pzorbitals

2.twoπbondsduetooverlappingofdyz,dzxorbitals



3. onedeltabondduetooverlappingofdxyorbital

GEOMETRY:

Ithasoctahedralstructure

The&componentrestrictsrotationinjustsucha wayastofavortheeclipsedconfiguration.

Theoverlapismaximumforthisconfiguration&goestozeroforthestaggardconfiguration.

Overlap of the dxy orbitals can occur only if the CI atoms are in eclipsed geometry.

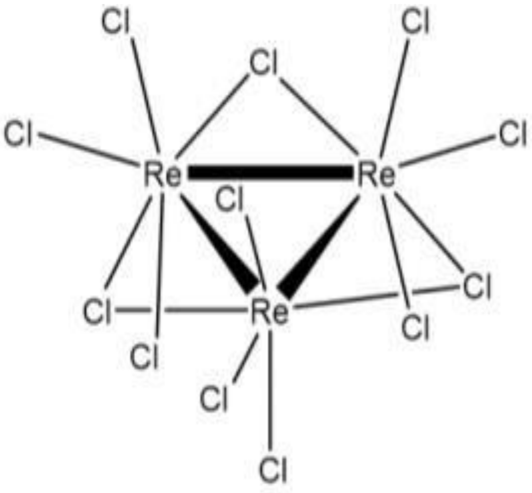
Iftheyhavestaggeredgeometrytheoverlapof2dxyorbitalscan'toccur.

Hencethemoleculeassusmeseclipsedconfigurationalsoineclipsedconfiguration,thebond energy dominates sterichindrense.

SoRe2C18preferseclipsedconfiguration.

. **Trinuclearclusters:-**

A typical example of noncarbonyl cluster containing three metal atoms is [(ReCl3)3] and its derivatives. Each Re (III) has a d^1 configuration. The complexes are diamagnetic and not paramagnetic which would have been the case if eachRe atom was singly bonded to otherRe atoms.Since,themetalatomsareengagedindoublebondstotheneighboringmetalatomthe complexes are paramagnetic.



HEXANUCLEARMETALCLUSTERS:-

Hexanuclearmetalclustersarethosewhichcontainsixmetalatomsperclusterpredominenty three hexanuclear metal clustersare obtained they are

1. $M6X6$
2. $M6X8$
3. $M6X12$

ThesixMetaloccupiessixcornersofanoctahedron.sothesearealsoknownasoctahedral clusters

TheextensiveseriesofmetalatomwithClareformedbyNb,Ta,Mo,W Eg:-

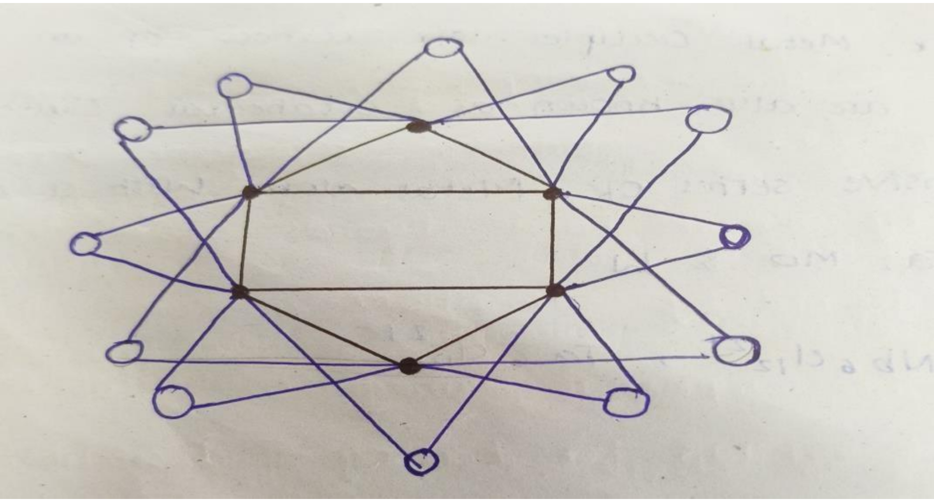
[Nb6CI12], [Ta6CI12]

STRUCTUREOFNb6CI12ANDTa6CI12:-

M6X12M=Nb, Ta

INM6X12,theseisanoctahedronofmetalatomswithabridginghalogenatomalongeachedge .i.e,eachhalogenpresentonaedgethusthehalogenactingasabinueclearbridge.Sinceit is connectingtotwometalspresentonedgeM6X12unitsare characteristicofthechemistryof the lower oxidation state of Nb and Ta. The [M6X12]^{2} ions which have diamagnetic can be oxidized to [M6X12]4 ions which are again diamagnetic

OneXatomisattachedtothetwoverticesofanedge



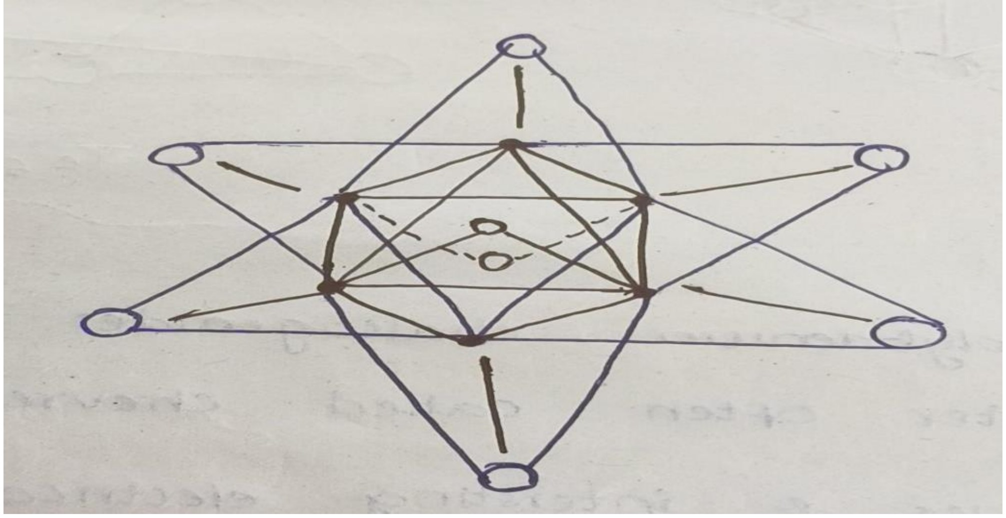
• Circlerepresentsmetalatoms

O Circle represents Cl atoms

STRUCTUREANDBONDINGOFMO6CL8

M6X8

InM6X8,eachhalogenpresentonaface i.ethehalogenactingasatrinuclearbridgesinceitis connecting to three metals.thus in M6X8 there is an octahedron of metal atoms with an



bridging atom of each triangular face. The entire unit has full octahedral symmetry. The [M6X8]4 units have the capacity to co-ordinate six electron pairs donors, one to each metal atomsalongafourfoldaxisoftheoctahedronClearlyinM6X8anoctahedronof6metalatoms are coordinated by 8 chlorine ligands,one on each face of the octahedron

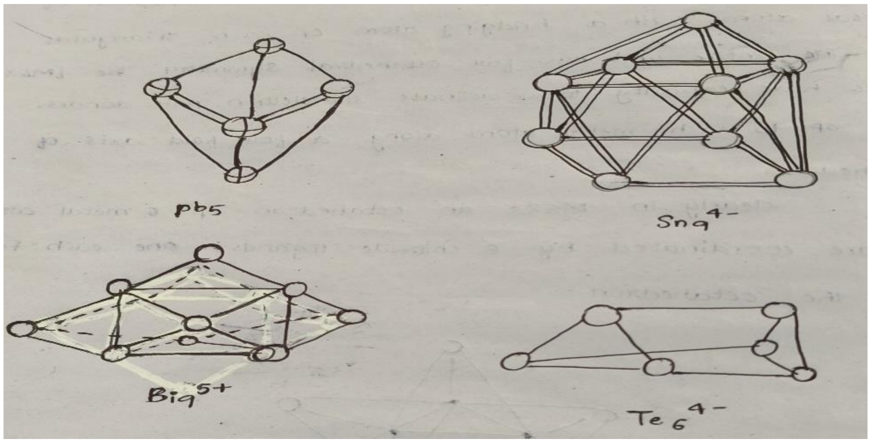
Polyatomiczintleanionsandcations:-

1. Inthe1930'spolyatomicionssuchasSb94,Pb94-,Sb73-&Bi33-wereidentifiedbutnot structurally characterised.

2. Attemptsofisolatingcrystalswereunsuccessfulbecauseoftheydecomposedinsolution.

3. Thisproblemisovercomein1975bystabilizingtheactionofthesaltasacryptate. Ex:

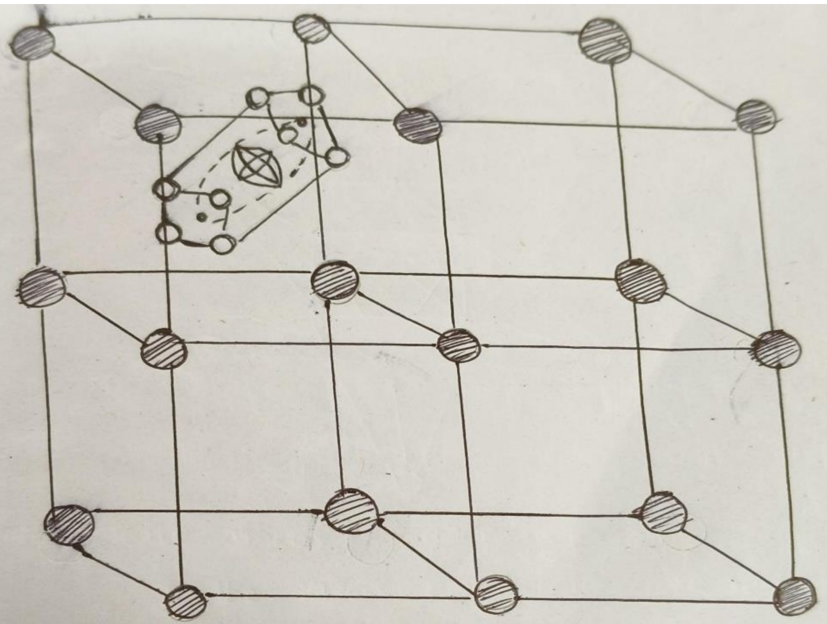
(Na(crypt) 2) pb5 & (Na(crypt) 4) Sn9



Cheveralphases:-

TernarymolybdenumchalcogenidesMxMo6X8arepolynuclearclusteroftencalledcheveral phases have both unusual structures &interesting electrical and magnetic properties.

Eg:-PbM06S8whichissuperconductorattemperaturebelow13.3k.



pb MO_6S_8 :-

• → Mo

○ → S

● → pb

DNR COLLEGE(A): BHIMAVARAM

DEPARTMENTOFPGCHEMISTRY

INORGANICCHEMISTRY-II

PresentedBy

N.Santhi

Unit-2

Organometallic Compounds

18Electronrule:-

* FormaingroupElementsoctetmuleisusedtopredicttheformulaofcovalent compounds.

*18Electionruleisusedfortransitionmetalcomplexes

* 18e-ruleisbasedontheConceptthatcentral transitionmetalcanaccommodate electron in the S,P,ddibitals

.18 e-rule is also known as effective atomic number (EAN) rule.

All Complexes and organometallicCompoundobeys EAN rule.

*ThenumberofElectronspresentinthecentralmetalatomplusnoofElectrons donated by the ligand is called as 18e-rule.

Noofe-presentinmetal+No.ofe-donatedbyligand=18

* when the ElectronCountislessthan18 metal is saidto beCoordinatively Unsaturated Compounds.

*The complexwhich has18eitisStableandCoordinativelySaturated compound. Ex:(i)

Ni(CO)4.

Ni-[Ar]46^{2}3d8Ni=10e-

4 co contributes 4CO =8e-stable compound_18e-

(ii)Benzene tricarbonyl chromium Cr-[Ar] 46' 3d5. = 6e-

3co contributes=6e-

Benzene 6пe-= 6e=

Stablecompound18e

(c)Ferrocene

Fe-[Ar]4823d6.Fe2+=6e-

2cp=12e-

stable 18e-

Electroncountingincovalentmodel.

	Covalent.	Ionic
onee-donorH.Cl,Br,I,R.Ro	1	2

2edonorCO,PR_3,P(OR)3,R2C=CR2	2	2
3edonor C3H5(allylradical).	3.	4
4edonor4-Diene(butadiene).	4.	4
5edonor C5H5(cpradical).	5	6
6e-donor arenes(Benzene).	6.	6

Hapticity(n):

No.ofeedonatedbyligandtometaliscalledHapticity"Exampl

es:-

ElectroncountingIonicmodel:

Neutralligand:- do not affect oxidation StatesPR3, PO-R, Co, 76-Benzene -formal charge :- 1 Effect oxidation State. Halide, alkoxide, hydride, cpo, allyl anion...Allyl cation: formal charge +1

Examples:-CO(Cp)2.	Covalent.	Ionic
Co-[Ar]4S23d7.	9e-..CO+2-7e-	
2CP.	10e-.2CP.–12e-	
.	19e-.	19e-

2.W(CO)6.	Covalent	Ionic
W-[kr]5S2 4d4.	6e-.	4e-
6CO.	12e-.	12e-
	18e-.	16e-

3.HMn(Co)5.	Covalent.	Ionic
Mn-[Ar]$4s^2$3d5.	7e-.	Mn+2- 5e-
5CO.	10e-.	10 e-
H.	1e-.	2e-
	18e-.	17e-

16Electronrule:-

Apopular class of Compounds that Violating the 1800rule are the 16e-n compounds withd8configurationEspeciallyderivativesofcobalt(co,Ir.Rh)andnickel[Ni,pd.pt] triods. Such compounds are typically Square planar.

AllthemetalsExhibitsSameCoordinationforboth+2and+3StatesExeptIr,Rh, pd,pt. pt. (11)

has C-NO-4 pt. (lv) has CNO-6 both are stable compounds

[Ptcl4]2-having16ebutStable. [Pt(NH3)6J4+

having 18e.

Ir.Rh.pd,ptintheirLoweroxidationStatesExhibitsCNO4havingStabilityandhaving 16e- for these 16e- rule is found.

Ir.Rhin+1StatehasC.NO-4

pt,pdin+2StatehasC.NO-4

Ir.Rhin+3StatehasCINO-6

pt,pdin+4statehasC.NO-6

* theseshallparticipateinoxidationadditionreaction.

Ex:- PtCl4. Covalent.Ionic

Pt-[Xe]4f145d96S1.10e.Pt+2-8e-

4Cl-. 4e-. 8e-

14e-. 16e-

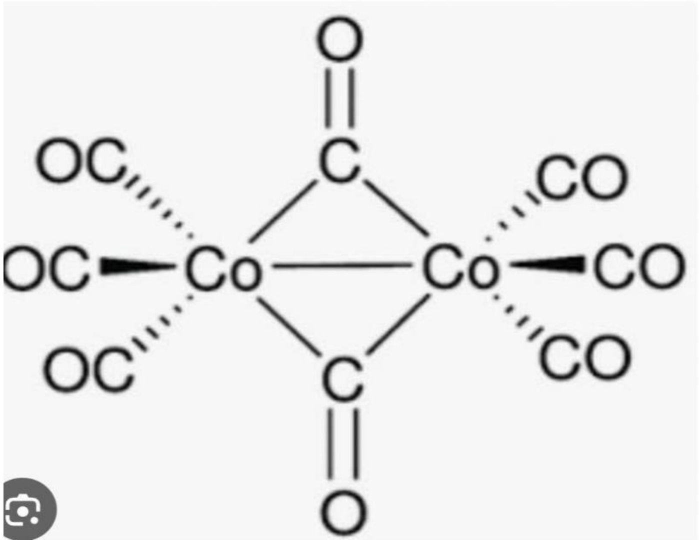
MetalCarbonylClusters:-

Metal carbonyl clusters are the metal clusters(two or more metal centersdirectly bonded to each other) having carbonyl groups as the ligand species.The metal centers intheseclustergeometriesareactuallypresentinlowoxidationstate(+1,0,-1)thatcan be stabilized by carbonyl ligands. Metal carbonyl clusters are mainly formed by some end-group metal (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir, Pt) of the d-block elements. The primary domain of carbonyl clusters is composed of neutral carbonyls, carbonyl anions, metal carbonyl hydrides.The carbonyl hydride clusters can be obtained fromneutral carbonyls by replacing one of the CO groups with two H-groups; while carbonyl anions are derived by replacing CO with one H-atomand one negative charge, or with two negative charge. Metal carbonyl clusters can be classified into two types; lownuclearity carbonylclusters(LNCC)and highnuclearity carbonylclusters(HNCC), depending uponthenumberofmetal centersinvolvedintheskeletal framework.Ifthenumberof metal centersisin the range of2-4.they are generallylabeled aslownuclearity:while on the other hand, a metal-center number of 5 and above makes themdesignable as high nuclearity carbonyl cluster system. Owing to the difference of electroncounting scheme fromhigh nuclearity carbonyl clusters, thissection will exclusivelydeal withlow nuclearitycarbonyl clusters.The rationalization of bonding andstructural profile ofsome importantlownuclearitycarbonyls clusters on the basis 18-electron scheme is discussed below.

➤**BinuclearCarbonylClusters**:

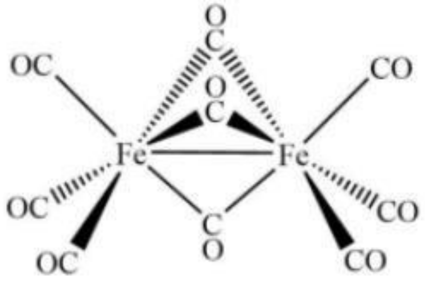
Thestructuralframeworkofdinuclearmetalcarbonylclustersiscomprisedoftwometal centers connected by 1 metal-metal bond, and therefore, linear in geometry. The CO groups can be terminal, bridging or both.The most common examples of these are Co2(CO)8,Fe2(CO)9,Mn2CO10,TC2CO10,andRe_2CO10-

1. C02(CO)8:This cluster is known to existin two isomers; the first one has a D3d symmetry with one metal- metal bond withzero bridgingcarbonyl, the second one is of C2v symmetry and has two bridgingCO ligands along with one metal-metal bond. The 18-electron count for Co2(CO)8 is 2x9+8×2=34. Hence, one metal-bond(2electrons)isneededtofulfilltherequirementoftwometalcenters (36 electrons).



2. Fe2(CO)9: The structure of Fe2(CO), exist with Dn symmetry, and and contains three bridging COligands and sixterminal CO groups attached.The18-electron count for Fe(CO),is2x8 +9×2 =34.Hence, one metal- bond(2 electrons)isneededtofulfilltherequirementoftwometalcenters(36electrons).

Diagram

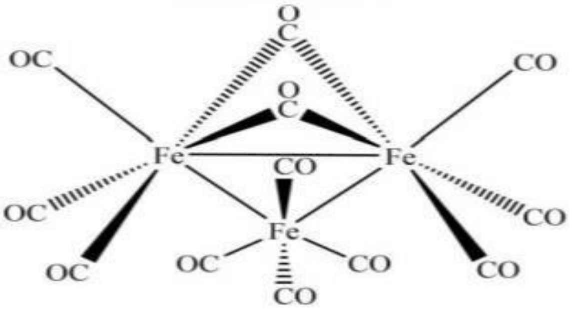


Fe₂(CO)₉

➤TrinuclearMetalCarbonyl

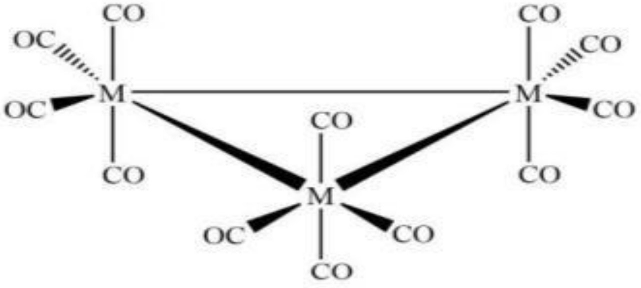
The structural framework of trinuclear metal carbonyl clusters is comprised of three metal centers connected by three metal-metal bonds, and therefore, usuallytrigonalingeometry.TheCOgroupscanbew.dalastitute.comterminal, bridgingorboth.Themostcommonexamplesoftrinuclearcarbonylclustersare Fe3CO12, Ru3(CO) 12 and Os3(CO) 12 systems

1. Fe3CO12: Fe3(CO) 12 is different, with two bridging CO ligands, resulting in C2v symmetry.The 18-electron count for Fe3(CO) 12is 3x8 + 12x2 = 48. Hence,threemetalthreemetal-metalbonds(6electrons)areneededtofulfill the requirement of three metal centers (54 electrons).



Fe₃(CO)₁₂

2. M3(CO)12 (M = Os, Ru): For example, the Ru3(CO) 12 cluster has D3h symmetry,consistingofanequilateraltriangleofRuatoms,eachofwhichhas twoaxial andtwoequatorial COligands.Os3(CO)12hasthesamestructure. The18-electroncountforM3(CO)12(M=Os,Ru)is3x8+12×2=48.Hence, threemetal-metalbonds(6electrons)areneededtofulfilltherequirementof three metal centers (54 electrons).

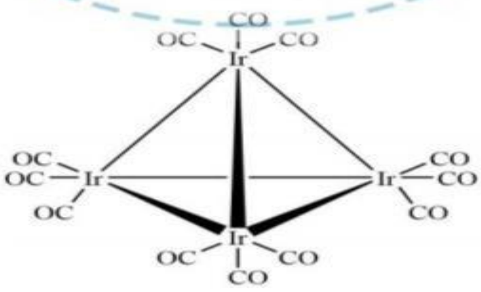


$M_3(CO)_{12}$
M = Os, Ru

►TetranuclearMetalCarbonyls

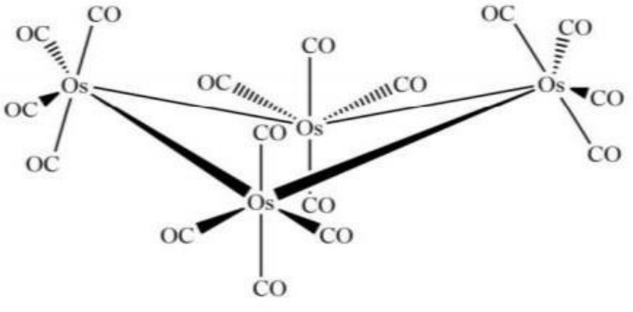
The structuralframeworkof tetranuclear metalcarbonyl clustersiscomprised of four metal centers connectedby four to six metal-metal bonds, and therefore, usually tetrahedral tetrahedral in geometry. The CO groups can te.combe terminal, bridging or both.The most common -9802825820) examples of tetranuclear carbonyl clusters are Ir4(CO)12, Co4(CO)12, Rh4(CO) 12, Re CO2, Rus(CO) 12

1. Ir4(CO)12:The Ir4(CO)12 has perfeet Ta symmetry with no bridging CO ligandsgroups.The18-electroncountforIr4(CO)12is4×9+12×260.Hence,six metal-metal bonds(12 electrons)are neededto fulfillthe requirement of four metal centers (72 electors)



$Ir_4(CO)_{12}$

2. Os4(CO)16: The tetranuclear Os4(CO) 16 is analogs to the cyclobutane with a puckered structure.The X-ray diffraction analysis ofOs4(CO) 14 unveiled an irregular tetrahedral Os4skeleton with four weakly semi-bridging COgroups andfour different Os-Osbondlengths.The18-electroncountforOs4(CO)16is4×8+16×2=64.Hence, fourmetal-metalbonds(8electrons)areneededtofulfilltherequirementoffourmetal centers (72 electrons).

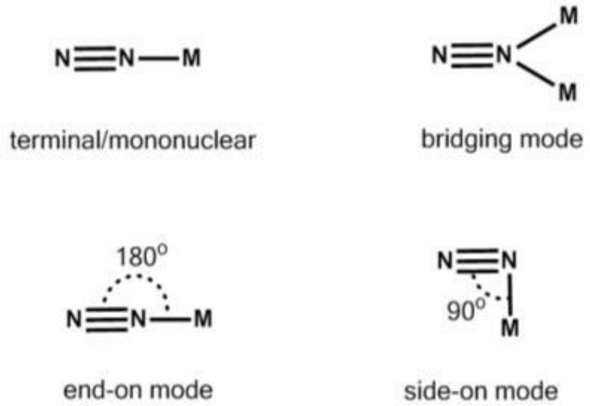


$Os_4(CO)_{16}$

5.10.DINITROGENCOMPLEXES:-

Transition metal coordination compounds containing dinitrogen molecules (N2) as ligands arecalled dinitrogencomplexes. Such complexes are of interest because dryair in earth's atmosphere contains nearly 78% nitrogen byvolume that reflects reluctance of dinitrogen towards chemical reactions in ordinary conditions. Dinitrogen is converted to its organic and inorganic derivatives via a process called 'nitrogen fixation', which primarilyinvolves thebinding of dinitrogen tometal centers present inthe enzyme nitrogenasefollowedbyaseriesofothersteps.Rutheniumcomplex,[Ru(NH3)5(N2)]2+ is the first synthetic complexthat contains a dinitrogenligand. Itisan octahedral paramagnetic complex in which five of the hexacoordinated sites are occupied by ammine ligands and the sixth position is occupied by dinitrogen molecule, N2. The presence of N2 as a ligand in these compounds cause a strong vibrational band in the FTIR spectra of the compound around 2170- 2100 cm-1.

Alike acetylene (C2H2) and carbon monoxide (CO) molecules, dinitrogen (N2) also possess a triple bond. Similar to these acetylene and carbonyl ligands, dinitrogen also offersmononuclear(terminal)andbridgingbondingmodes.IftheN2moleculeisshared by two or more metal centers in a complex, the manner of bondingistermed as the bridgingmodes.BasedonthegeometricrelationshipbetweentheN2moleculeandthe metal center, the complexes are also differentiated to have end-on or side-on modes (Figure5.8).Intheend-onbondingmodeoftransitionmetal-dinitrogencomplexes,the N-N vector can be considered in line with the metal ion center, whereasin the side-on modes, the metal-ligandbond is known to be perpendicular tothe N-N vector.



5.9.**NITROSYLComplexes:-**

Thechemistryoftransitionmetalnitrosylsthoughgainedsignificantattentionsomewhat latertothatofmetal carbonylsbutinpresenttimes,theworkdoneinthisfieldruns paralleltothatofmetalcarbonyls.Nitricoxideorthenitrosylligandcanbindtothemetal inamanner quitedifferentfromthatofcarbonyls.Thetwocommonbindingmodesof NO can be represented as shown below (Figure 5.7):

Inthelinearbindingmode,theNbehavesasathreeelectrondonorinNOandM-Nhas amultiplebond character.Itdonatesoneelectrontothemetal beforedonatingan electron pair for theformation ofcoordinate covalent bond.Thenitrosyl NO*is isoelectronic with COligand. Itis the most common bondingobserved. In the bent coordination mode, the N acts as asingle electron donor towards the metal andthe M- N-O bond angle is 120°. Here, the M-N bond is longer than thatin thelinear bonding mode,itisstillsomewhatshorterthanthesingleoM-Nbonddistance.Inmostofthe nitrosylcomplexes,NO*(nitrosylornitrosoniumion)actsastheligandbydonatinga pair of electrons.In some complexes, nitric oxideisalso known to exist asanion NO suchasin$[Co^{+3}(CN)s(NO)]-3$and$[Co^{+3}(NH3)5(NO)]+2$.

Thefreenitricoxidehasan IRstretchingfrequencyof1870cm^{21}.Thenatureofother ligands present in the complex, charge and structure of the complexaffect the NO stretchingfrequency(VNO).ThenitrosylligandislinearwhenitcoordinatesasNOand VNO is observed in the range 1720-1400 cm^{2} 1. The role of metal nitrosyls has been much explored as homogeneous catalysts.They find their biggest application in olefin disproportionation reactions.

Isolobalrelationship

Thisisusedinorganometallicchemistrytorelate Holdestructureoforganicand inorganic molecular fragments inolder to predict the bonding properties of organometallic Compounds.

* RoaldHoffmandescribedmolecularfragmentsifthenumberofsymmetryproperties, approximate Energyasisolobal and shape ofthe frontier Orbitalsand no.of Electrons inthese are similar not identical but similar.

* ForthisworkheawardedtheNobleprizeinchemistryin1981

* Isolobal Compounds are analogous to isoelectronic Compounds that share the same no. of Valency Electrons and Structure..

* AgraphicrepresentationofisolobalStructure with theisolobal painsConnected througha double headed arrowwith half anorbital belowis formed.

Constructionofisolobalfragments:-

* Moleculesbasedaroundtheoctetvile(1800)maingroupElementsShouldSatisfy

*whenallbondingandnon-bondingmolecularorbitalsareCompletelyfilled

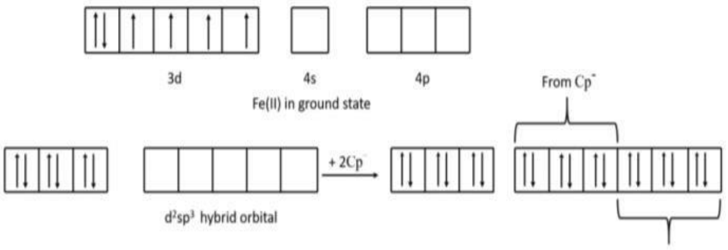
* TheantibondingmolecularorbitalsareEmpty.

Ferrocene:-

1Structureandbondinginferrocene

In 1952, G. Wilkinson and R. B. Woodward deduced the sandwich structure of ferrocene:twoanioniccyclopentadienyl(Cp)ringseachdonating6пelectronstothe Fe2+cationbetweenthem.ThestructureofferroceneasrevealedbysinglecrystalX ray diffraction studies confirmiron to be sandwiched between two cyclopentadiene rings. These rings are arranged in an eclipsed manner.All C-C distances are in the range 1.40±0.02 Å.The pentagonal ring of Cp is analogous to hexagonal ring of benzene having sp^2 hybridized carbon. Five electrons from five carbons and one electron fromthe formation of Cp contribute total of sixelectrons which are presentin three of the five π-bonding orbitals while the remaining two π-bonding orbitals are vacant. In the Fe complex, ferrocene, Fe(II)isd^2sp^3 hybridized,each Cp coordinates givingthreeelectronpairs.Belowisadepictionofelectronfillinginhybridizedorbitalsof ferrocene.

Thefilledt2gorbitalsofFe(II)areinvolvedinπ-backbondingwithvacantπ*orbitalsof the ligand Cp. Thus, each Cp acts as a π-donor and n-acceptor in the formation of a sandwich compound.

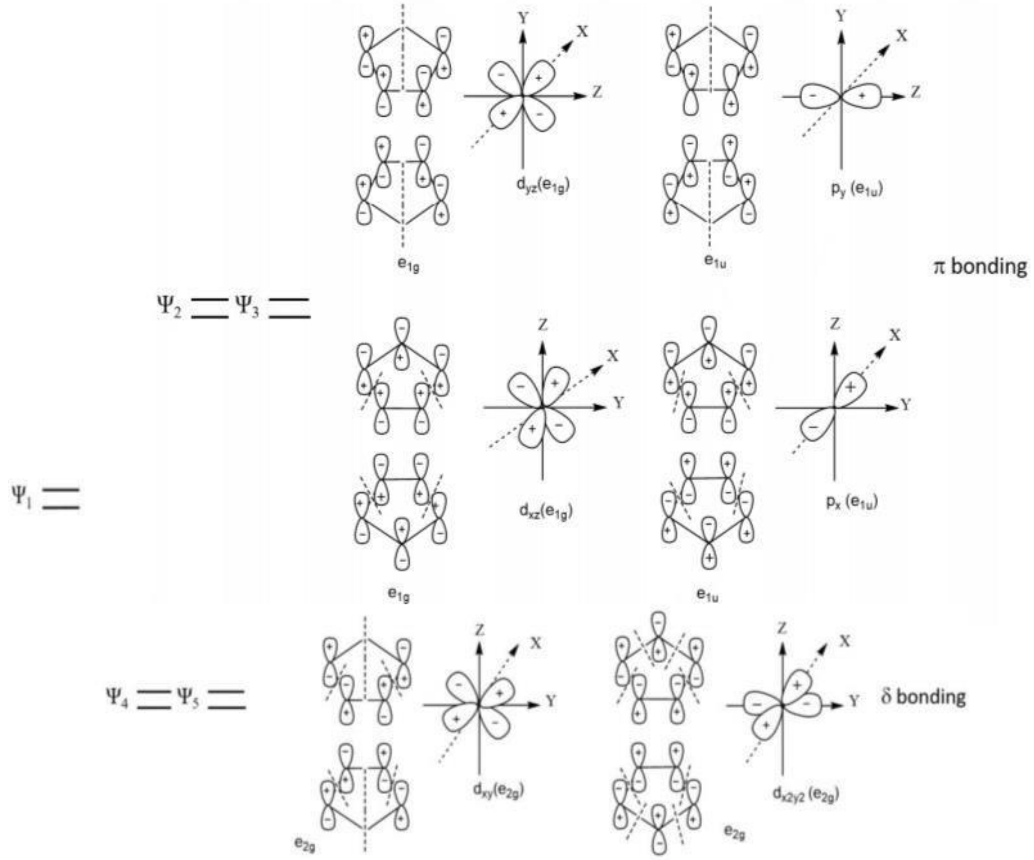


6.10.2.Cyclopentadienyl-metalinteractioninferrocene

The frontier molecular orbitals (FMO) of cyclopentadienyl ligand contain five orbitals (Ψ1-Ψ5) distributed within three energylevels.Thelowest energy state(1)does not contain any node and sorepresented by a state. Following a1, the next higher energy states are 2 and Y3 which are doubly degenerate and represented as $e_1$states. They have one nodal plane containing the principal axis.Above them lie doubly degenerate Y4 and 5, designatedas e2 states whichhavetwo nodal planes and areeven higherin energy. This pattern of doubly degenerate orbitals of increasing energy and nodal planescontinuesuntilthenumberofmolecularorbitalsisequaltothenumberofatomic porbitalsthatisthenumberofcarbonatomsinthering.Ifthisnumberisodd,the highest antibondingorbital isdegenerateandif itiseven then thehighestanti bonding orbital is non degenerate.

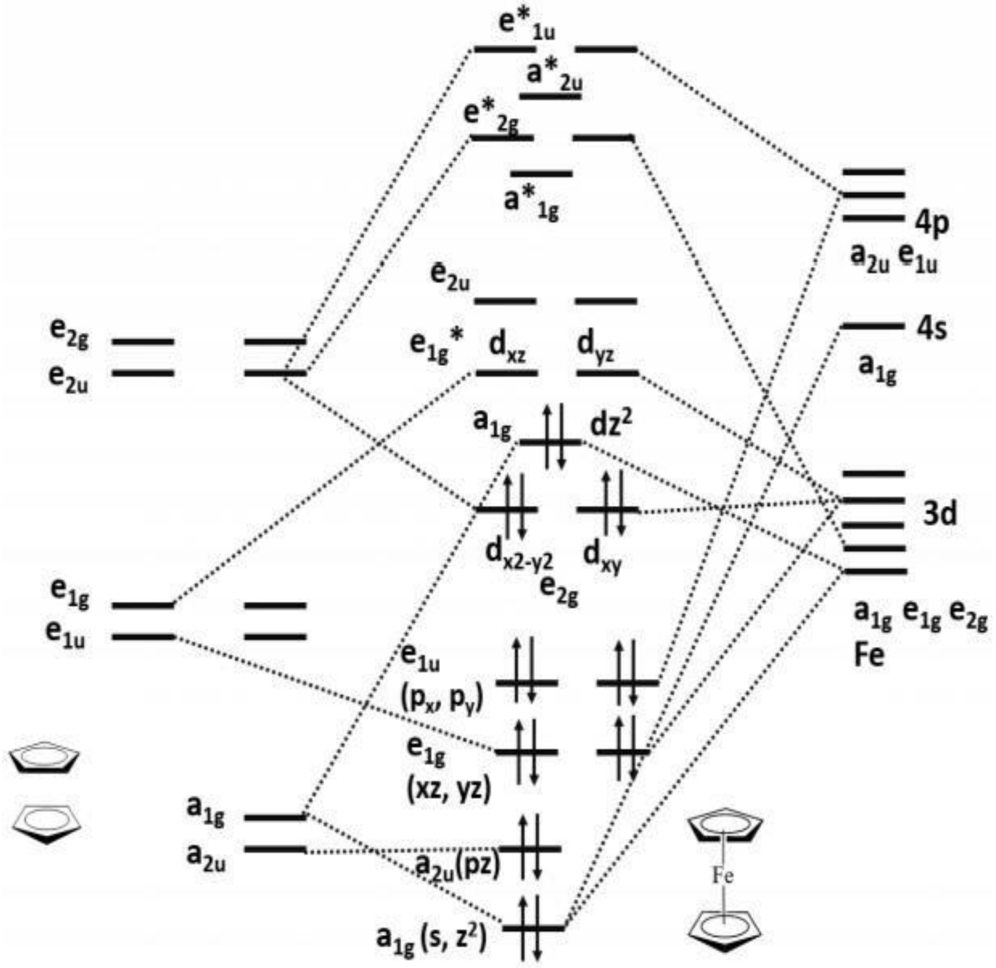
Theorbitalsontwoligandsmayinteractinadditionorinsubtractiongivingrisetoligand group orbitals (LGO).The wave functions (Ψ) of these five molecular orbitals are derivedfromthelinearcombinationofthefivepratomicorbitalswavefunction($)ofthe C3H5 ring.These combine with atomic orbitals of matching symmetry on the metal to formthe molecular orbitals (MO).Forbetter understanding, consider thelowest energy ligandbondingorbital.Ifthewavefunctionofthisorbitalfromthetwoligand metallocene rings are added, a gerade ligand group orbital having symmetry (a1g) similar to atomic s orbital is formed. Conversely, if the two wave functionsare subtracted, an ungerade LGO is produced having same symmetry as that of an atomicp orbital (a2u). Thus, in a similar fashion, other LGOs can be constructed by adding or subtractingthe higher MOs of the two rings. Overall molecular correlation diagramof Cp2Mtypeofcomplexesisgeneratedfromtheorbitalswhichsubsequentlyinteractwith the metal orbitals as shown below.The Cp2M type complexes are formed by the entire firstrowof transition metal ions fromSc to Zn.The number of unpairedelectrons correspond to the number of unpairedelectrons presentin the valence orbitals of the metal.

Fromthe first-rowtransition metal metallocenes, manganocene exists in two forms. First,is ahigh spin formhaving fiveunpairedelectrons asin Cp2Mn andthe secondis a low spin formwith one inpaired electron as in Cp2 Mn in which Cp has higher field strength. Cobaltocene, Cp2Co has 19 valence electrons and thus gets oxidized to diamagnetic Cp2Co$^+$which now has 18 valence electrons. Similarly, Cp2Fe is also diamagnetic with 18 valence electrons. MO diagram of ferrocene is shown Delow.A totalof18electronsarefilledcomingfromFe(II)(6electrons)andfromtwoC5H5rings 2x6=12). Fe(C5H5)2 is more stable than Co(C5H5)2 and Ni(C5H5)2 having 19 and 20 electronsrespectively.Thisisduetothefactthatinferrocenetherearenoelectronsin



antibondingmolecular Orbitals (ABMO) whereas incobaltocene thereis one electron and in nickelocene there are two electrons

in antibonding molecular orbitals. These electrons are easily removed and thus, cobaltocene and nickelocene are easily oxidized. Similarly, Cr(C5H5)2and V(C5H5)2 have16and15electronsrespectivelythustheyhaveemptybondingmolecularorbital-nonbonding molecular orbitals which makes them susceptible to being reduced.



DNR COLLEGE(A): BHIMAVARAM

DEPARTMENT OF PG CHEMISTRY

INORGANIC CHEMISTRY-II

Presented By

N.Santhi

Unit-3
Metal Ligand Equilibria In Solution

StabilityofComplexes:-

The degree of association of metal and ligand is indicated by its formation constant.The formation constant also called as stability constant and equilibrium constant.

There are two kinds of stabilities are

1.Thermodynamic stability

2.kinetic stability

1. Thermodynamicstability

It is the measure of the extent to which formation of complex occurs or the extent of transformation under a given set of condition at equilibrium. Thermodynamic stability depends on the strength of bond between metal and ligand. The strength of bond between metal and ligand shows great variation. For example, in [Co(SCN)4]2+, the strength of bond metal and thiocyanate is very weak and breaks immediately in aqueous solution. On the contrary, in [Fe(CN)6]3, the bond between ferric ion and nitrile anions is very strong and does not break in aqueous solution. Thus, thermodynamic stability deals with metal ligand bond energy and other thermodynamic parameters. Tetracyanonickelate(II) {[K2Ni(CN)4]} ion is a good example of a thermodynamically stable complex but kinetically labile whereas hexa amine cobalt(III) cation [Co(NH3)6]3+ in acid solution is kinetically inert and thermodynamically unstable

[Co(NH3)6]3+ + 6H3O+→ [Co(H2O)6]3+ + 6NH4+

Stability and inertness can be expressed thermodynamically in terms of free energies of reaction AG°. A stable complex has large negative AG°. The following relation relates the standard enthalpy change AH° for the reaction to equilibrium constant ßn:

$$\Delta G° = -RT \ In\ \beta\eta$$

$$\Delta G° = \Delta H° - T\Delta S°$$

ΔS° values for similar complexes of metal ions of a particular transition series with a particular ligand will not differ significantly and hence, ΔH° value will be related to ßn values. Therefore, order of values of AH° will be order of ßn values.

.2. **Kineticstability**

Kinetic stability refers to the reactivity or ligand substitution in general. It is the speed with which transformation of reactants occurs leading to attainment of equilibrium. Thus, substitution may take place rapidly with some ligands while slowly with others. The former type is called labile ligands and the latter are known as inert. In kinetic studies, time factor plays an important role in deciding the stability of the complex. It deals with rate and mechanism of complex formation.

Stepwiseandoverall/cumulativeformationconstants

The formation of complex can be considered as a type of acid base equilibrium existing between the competing species Mn+ ion, ligand (L) and H+ ions

Thus, two equilibria have to be considered

H +L=HL

M + L = ML

Moreover, to consider stability constant for complex formation the equation can be represented as:

M + nL = MLn

Stepwiseformationconstant

It is considered that complex formation is a stepwise process occurring by a series of stages. For example, the stepwise formation constant of MLn can be expressed as

M+L =MLK_1 = [ML] /[M][L]So, [ML] = K_1 [M] [L].......(a)

ML + L =ML2K2 = [ML2]/[ML][L]So, [ML2] K2 [ML] [L]......(b)

ML2+ L =ML3K3 = [ML3]/[ML2][L]So, [ML3] K3 [ML2] [L] ...(c)

ML-1+ L=MLnKn = [ML]/[ML-1][L]So, [ML] = Kn= [ML-1] [L] (n)

Here, K1, K2, K3 and Kn are stepwise equilibrium constants with respect to the formation of the complexes one step at a time, M denotes metal ion and L denotes a monodentate ligand. The overall formation constant (Kr) of complex from reagents in terms of stepwise constant is given as

K = K x K2 X K3 ... Kn

8.3.5. **Cumulativeoroverallformationconstant**

Cumulative or overall formation constant is represented by symbol ß. It can be represented as the product of stepwise formation constants.

$M+L = MLB_1 = [ML]/[M][L]$

$M + 2L = ML2\ B2 = [ML2]/[M][L]2$

$M + 3L = ML3\ B3 = [ML3]/[M][L]3$

$M+n\ L = MLn\ \beta n = [ML]\ [M][L]"$

Here, B1, B2, B3 stand for overall stability constant for each stage of complex formation and ßn stands for nth overall (or cumulative) formation constant. Usually, Kn decreases with each subsequent step. This can be reasoned as follows. As ligand is added to the metal ion M2+, ML forms first, with the addition of more ligand [ML2] rises sharply and [ML] drops. With further addition of L, [ML2] drops and [ML3] rises and so on. Addition of ligand to form a new complex is always reversible and formation of MLn progresses with greater n values for L. Thus, there is probability of more ligands to fall back off as there are fewer places to put the new ligands in the coordination sphere, so it is expected that stepwise Kn's will drop. For example, the formation of [Cd(NH3)4]2+ depicted below, the drop in equilibrium constant with added L groups is evident.

$Cd2+ + NH3 = [Cd(NH3)]2+. \quad K_1 = 102.65$

....

....

......

$[Cd(NH3)3]2+ + NH3 = [Cd(NH3)4]2+. \quad K4 = 100.93$

Relationbetweenstepwiseandoverallstabilityconstants

A stepwise constant can be expressed as the quotient of two or more overall constants

$B_1 = K_1$

$B2 = K_1 \times K2$

$B3 = K_1 \times K2 \times K3$

$\beta n = K_1 \times K2\ i=n\ KE\Sigma\ K\ i=1$

From above, it can be stated that overall stability or formation constant (ßn) is the product of stepwise stability or formation constants (K1, K2,.......Kn). It is always suitable to define each stability constant with reference to an equilibrium expression.

FACTORSAFFECTINGTHESTABILITYOFMETALCOMPLEXES

.Chelateeeffect:-

The formation of a closed ring in an inorganic metal complex by attachment of a ligand to metal ion at two points is called a chelate. Minimum of a bidentate ligand is required for formation of a chelate. Alternatively, we can say that chelate complexes are formed by multidentate ligands. The name chelate is derived from the Greek word 'Chela' means 'Claw of lobster or crab'. A series of experiments revealed that the stability of inorganic chelate metal complexes was greater than those having no chelating ligands in their structure. However, there are several other factors, which shall be considered while deciding stability of complexes, discussed below. An example is the complex ion formed between ethylene diamine (en) and cupric ion, $[Cu(NH2CH2NH2)2]2+$.

Consider for example, a reaction vessel containing cupric ions, NH3 and en (ethylene diamine) given the condition that cupric ions are equally available to both the ligands and concentration of NH3 is twice that of en ligand. The bidentate en ligand forms chelate complex with copper resulting in five- membered ring whereas in the other copper complex formed with NH3 ligand, the two en ligands are replaced by four NH3 ligands. Under given set of conditions, it is found that the concentration of complex 1 is greater than that of 2. This can be attributed to the additional stability provided by chelation of en ligand in complex 1.

Cu2+ + 2en =[Cu(en)2]2+ …. 1

Cu2+ + 4NH3 =[Cu(NH3)4]2+ …..2

Stericeffect

This effect comes into play when the groups present on coordinating ligands obstruct each other; thus, distorting bond angles and decrease in stability. The phenomenun is called F-strain. As steric effect decreases, stability of complex increases. For example Ni(II) complexes with 2-methyl 8-hydroxy quinoline are less stable than complexes with 8-hydroxy quinoline. Similarly, complexes of ethylene diamine are more stable than its tetramethyl derivatives. The later compounds have greater steric repulsion due to the presence of four additional methyl groups.

Chelateeffectanditsthermodynamicorigin

We know that greater stability of chelate complexes is called the chelate effect. The additional stability due to chelation can be explained considering the thermodynamic aspects of this phenomenon. It is believed that there is difference in entropy between chelate and non-chelate complex reactions. The formation of chelate complexes results in greater disorder because of the formation of a larger number of free particles in the products whereas there is negligible change in the number of particles in the formation of comparable nonchelate complexes. This fact can be illustrated with the following example. The stability of a complex with bidentate ligand such as ethylenediamine is significantly greater than the complex of the same metal ion with monodentate ligands having comparable donor ability such as ammonia.

$[Cu(OH_2)_4]^{2+}$ + en = $[Cu(OH_2)_2(en)]^{2+}$ + 2 H_2O

ΔH = -54 kJ mol^{-1}, AS = 23 J K-1 mol-1

$[Cu(OH_2)_4]^{2+}$ + 2 NH_3= $[Cu(OH_2)_2(NH_3)_2]^{2+}$+ 2$H_2O$

ΔH = -46 kJ mol^{-1}, AS = -8.4 J K-1 mol-1

Natureofcentralmetalion

1. **Class** A **and** B **metals**

According to Ahrland, Chatt and Davies, metal complexes can be put in class A if they form stronger complexes with ligands having N, O or F as donor atoms whereas those which form stable complexes with ligands having P, S or Cl can be put in class B. For example Ni(II) forms stable complexes with amine ligands whereas Pt(II) forms stable complexes with phosphine ligands where donor atom is phosphorous. Later, Pearson's Hard and Soft Acid Base theory (HSAB) classified metals as hard and soft where class A metals are hard acids whereas class B metals are soft acids.

In general, hard acids form stronger complexes with hard bases and vice versa. Hard-hard interactions are predominantly electrostatic in nature while soft-soft interactions are covalent in nature. The hardness of metal ions increases with increase in oxidation state. This is evident from the fact that Fe^{2+} forms stable complexes with N donor ligands while Fe^{3+} forms stable complexes with O donor ligands.

.2.**Ionicradiusofmetalions**

In 1953, Irving and Williams suggested that first row transition metal ions could be arranged in order of their ligand binding affinities. Thus, they designed a series arranging octahedral divalent first transition metal ion complexes in order (shown below) of their stability known as the Irving-Williams series.

Mn Fe Co Ni < Cu > Zn

The order was found to hold true for a variety of ligands and it can be explained as follows.

(i) The ionic radius is found to decrease from Mn to Zn as a general periodic trend hence accounts for increase in stability.

(ii) The crystal field stabilization energy (CFSE) increases from zero for Mn2+ to maximum for Ni2+ complexes and again falls to zero for Zn2+. Even though CFSE for Cu2+ is lesser than that for Ni2+ octahedral complexes, still Cu2+ complexes are more stable due to the Jahn Teller distortion.

Natureoftheligand:-

1. Sizeandcharge

Ligands with less charge and greater size form less stable complexes as compared to ligands with more charge and smaller size.

2. Basiccharacter

Higher the basic character of the ligand that is the tendency to donate electrons to the central metal ion, higher is the stability of the complexes formed. Eg. Aromatic amines form less stable complexes as compared to aliphatic amines because of the weak electron donating tendency of the aromatic amines. Ligands such as NH3 and CN are more basic in nature and hence form stable complexes.

3. Ligandconcentration

Some complexes can exist in aqueous solution only when the concentration of coordinating ligand is high. This is because in some cases water molecules behave as a better coordinating ligand. For eg. Co2+ can exist as stable blue coloured solution of [Co(SCN)4]^{2} only in presence of high concentration of thiocyanate (SCN) ions. But on dilution in aqueous solution a stable pink colored complex of [Co(H2O)6]2+ is formed but on further addition of SCN the pink color disappears to give blue color solution. The phenomena shows that there is a competition between the SCN and H2O ligands in formation of complex with Co(II) ion..

[Co(SCN)4]2 + H2O =[Co(H2O)6]2+ + 4 SCN

Similarly, reaction of cupric sulfate at lower concentration of ammonia forms copper hydroxide whereas at higher concentration of ligand forms ammonium cupric sulfate monohydrate.

CuSO4 + NH4OH = Cu(OH)2

Cu(OH)2= Cu(NH4)2SO4.H2O

METHODSOFDETERMININGFORMATION/STABILITYCONSTANTS:-

.1. **Potentiometricmethod**

In this method, association between the metal ion Mm+ and the ligand as an anion of the weak acid HnL is studied. Here, the nature and concentration of all the species present in solution have to be determined such as pH of buffer solution containing H_1 L, base (NaOH, KOH) and metal ion generally used as perchlorate salt (generalized here as MXm).

To calculate the stability constants from potentiometric pH titration data, we need equations on the mass balance and charge balance conditions.

The total concentration of the metal ion may be written:

1. 1. **Bjerrummethod:-**

Bjerrum designed this method to determine the stability constant using pH meter to measure H+ ion concentration based on the fact that formation of a ligand-metal complex is a type of acid-base reaction equilibrium where there is competition for the ligand between Mn+ ion and H+ ions. Thus, the following two equilibria operate

H. +L = HL

M+L = ML

Thus, by titrating a mixture of M and HL with a base concentration of H+ can be followed. With the help of prior knowledge of acid dissociation constant Ka of HL, stability constant for the formation of complex ML can be determined.

Consider the equilibrium in which an acid, metal ions and a basic ligand are present. Thus,

L+ H = HL; Ka [HL]/[L] [H+]

L+M+ = ML; Kf = [ML]/ [L] [M+]

If, CH, CM and CL are the concentration of acid, metal and ligand in moles/litre, their concentration can be expressed in terms of following equations:

CH= [H+] + [HL+]

CL = [L] + [ML+] +[HL+]

Cм = [M+] + [ML+]

Using above three equations and equation for Ka, we can derive equations for [ML+], [M+] and [L] as shown below:

$$CL-CH=[L]\ [H+] + [ML+]$$

$$[ML+] = CL-CH+ [H+] - [L]$$

Using value of [L] from the Ka expression, we get

$$.[ML+]\ CL-CH+ [H+][HL+]/Ka\ [H]$$

Or

$$[ML] =CL-CH+ [H+]\ \{(CH\ [H+])/(Ka\ [H])\}$$

$$[M+] = CM-[ML+]$$

$$[L] = [HL+]/Ka\ [H+]$$

or

$$[L]=CH-[H+]/Ka\ [H+]$$

Thus, using the values of [ML], [M+] and [L] from above equations and substituting in K = [ML+]/[M+] [L], Kr can be calculated. The values of CH, CL, CM, Ka and [H+] are generally determined potentiometrically using a pH meter.

Drawbacks: It should be noted that if two or more solution species have identical charges and same number of metal ions and ligand molecules, only the sum of the concentrations could be determined potentiometrically. Thus, the two forms of glycine NH3+CH2COO and NH2CH2COOH, complex species such as $[FeEDTA]^1$ and $[Fe(OH)(H.EDTA)]^1$, configurational and conformational isomers and inner- and outer sphere complexes cannot be distinguished by this method. Other methods such as spectrophotometry may be more suitable in these cases.

2. Spectrophotometricmethod

Spectrophotometric methods are highly sensitive. The deciding factor in this technique is that the species involved in chemical equilibria must absorb light and give different spectral response. Thus, concentration of species involved in equilibrium and new species formed can be measured directly from UV-visible spectra.

The method is based on the Beer-Lambert Law where log (Io/I) = Ecd (Io/I is the ratio of incident light to transmitted light, c is the molar concentration of the absorbing solute, d is the light path length in centimeters and & is the absorptivity). Some precautions must be considered while measuring absorbance such as prevention of any contamination of the solution or cell faces. In addition, the spectrophotometer should be used to record small differences in optical density having inaccuracy in the absorbance of the instrument is negligible.

When only two species are present such as the ionization of monobasic acids, measurement of absorbance as a function of wavelength at different pH values can be used to calculate the equilibrium constant. This may be useful for compounds whose solubility is poor, direct titration can be done since absorptivities are often large enough to allow study of solutions having concentration upto 105 mol dm^3.

Drawback: For a complex which is too stable or too weak the K value cannot be determined spectrophotometrically. In addition, if the ligand or metal absorb at the chosen wavelength, the measured absorbances must be corrected

Job'smethod

Using the stoichiometry of the complex, the value of K (the stability constant) can be determined form the expression given below, if the value of m and n are known:

K = m"-1xn-x(P-1)+n-1 [n-(m+n)x]/ Cm+n-1xPn-1 [P(m+n)*-1]m+n

where, K = stability constant, 1/K = dissociation constant of the complex, P= ratio of the concentration of the ligand to the concentration of metal, C_1 = molar concentration of metal solution, X = concentration of ligand for which the concentration of complex is maximum, m = the number of moles of a metal required to combine with "n" moles of ligand for (1:1) metal ligand ratio in the complex having m = n = 1, the stability constant K can be calculated from the equation given below.

$K = (P-1)(1-2x) / C_1 x[(P+1)(x-1)]^2$

❖InertandLabileComplexes

The metal complexes in which the rate of ligand displacement reactions is very fast and hence show high reactivity are called as labile Complexes and this property is termed as lability. On the other hand, the metal complexes in which the rate of ligand displacement reactions is very slow and hence show less reactivity are called as inert complexes and this property is termed as inertness.

➤LabileandInertComplexesontheBasisofValenceBondTheory

According to the valence bond theory of chemical bonding, octahedral metal-complexes can be divided into two types.

1. **Outerorbitalcomplexes**: These complexes have sp^3d hybridization and are generally labile in nature. Valence bond theory proposed that the bonds in sp^3d hybridization are generally weaker than that of (n-1)d-sp^3 orbitals and therefore they show labile character. For example, octahedral complexes of Mn2+, Fe2+, Cr2+ complexes show fast ligand displacement.

2. **Innerorbitalcomplexes**: Since desp³ hybrid orbitals are filled with six electron pairs donated by the ligands, d" electron of metal will occupy dxy, dye and dxz orbitals. These desp³ hybrid orbitals can form both inert or labile complexes. In order to show lability, one orbital out of dxy, dyz, de must be empty so that it can accept another electron pair and can form seven iscoordinated intermediate which is a necessary step for the associative pathway of ligand displacement. On the other hand, if all the day, dye, de orbitals contain at least one electron, it will not be able to accept electron pair from the incoming ligand and hence is expected to show inert character.

➤LabileandInertComplexesontheBasisofCrystalFieldTheory

Octahedral complexes react either by SN_1 or SN2 mechanism mec in which the intermediates are five and TEMIS seven-coordinated species, respectively. In both cases, the symmetry of the complex is lowered down and due to this change in crystal field symmetry, the crystal field stabilization (CFSE) value also changes. The cases field Stabilization value for lability and inertness are

1. **Labilecomplexes**: If the aisevala in the for the five or seven-membered intermediate complex is is greater than that of the reactant, the complex will be of labile nature as there is zero activation energy barrier.
2. Inert complexes: If the CFSE value for the five or seven-membered intermediate complex is less than that of the reactant, the metal complex will be of inert nature as loss of CFSE will become the activation energy barrier.

b) Bio inorganic chemistry

STRUCTURE OF HEMOGLOBIN & MYOGLOBIN

Hemoglobin contains four heme units each embedded in a globular protein sub-unit. There are two types of protein sub- units i.e., a and ß.

Myoglobin contains only one heme unit surrounded by a globular protein, containing seven a-helical and six non helical segments, made up of 153 amino acids.

Note: Heme moieties are shown in green color in above diagram. Fe(II) ion is shown in red color.

Heme is a porphyrin ring system made up of four pyrrole rings with an Fe(II) ion coordinated to nitrogens of pyrrole rings.

Note: Heme moieties are shown in green color in above diagram. Fe(II) ion is shown in red color.

Hemoglobin and Myoglobin exist in two forms i.e.,

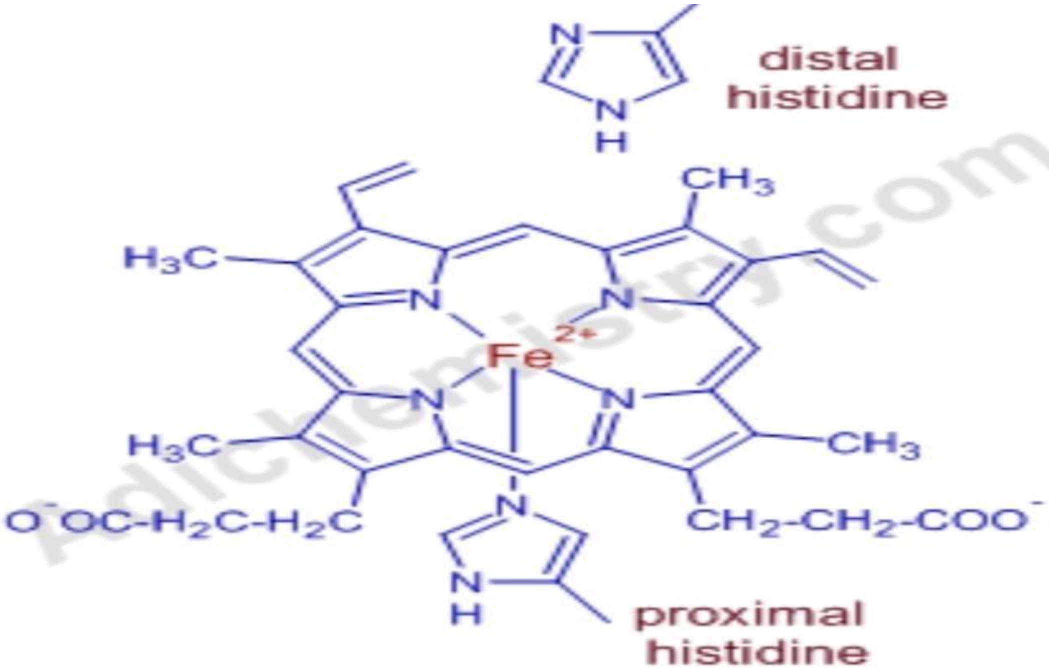
1) deoxy form: No oxygen is bound to iron.

2) oxy form: dioxygen is bound to iron.

In deoxy-hemoglobin, four of the coordinated sites of iron are occupied by nitrogens of porphyrin ring. The fifth site is occupied by Histidine residue (called proximal histidine) of globin. The sixth position is occupied by weakly bonded water molecule. Hence some authors tend to report Fe(II) ion in deoxy form as pentacoordinated. Deoxy-hemoglobin is said to be in T-state (tense).

On the opposite side of the proximal histidine, there is one more histidine group (called distal histidine) placed near the iron ion. It forces the binding of dioxygen in "end on bent" confirmation.

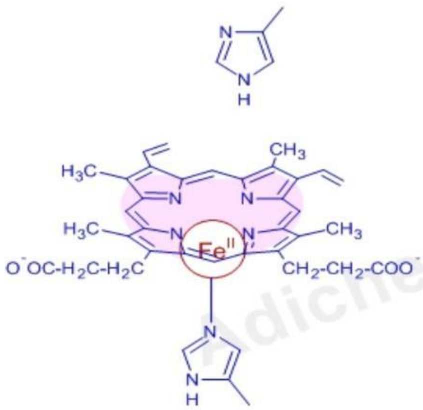
Note: The bent confirmation discourages the binding of CO to heme iron. Otherwise, CO may have even more affinity with the iron ion. It is observed that CO binds to hemoglobin 200X stronger than dioxygen but binds 20,000X stronger with unprotected heme.



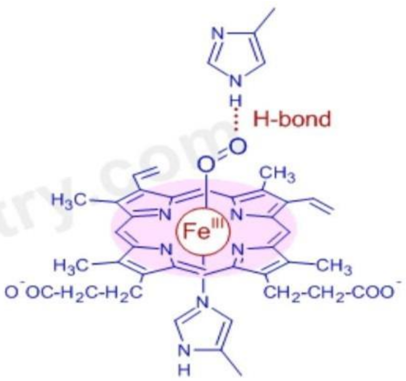
Hemoglobin coordinated to dioxygen is called oxy-hemoglobin. It is also referred to as R-state (relaxed). In oxy-hemoglobin the sixth coordinated position of iron isoccupied by dioxygen in "end on bent" geometry.

In deoxy-Hemoglobin, the porphyring ring is dome shaped. The Fe(II) is in high spin state and is paramagnetic. Its size is 0.78 Aº and is positioned above the plane of the porphyrin ring.

However, in oxy-Hemoglobin, the size of iron ion is reducedto 0.61 Aº and can fit into the cavity of planar porphyrin ringand hence moves into the cavity of porphyrin ring withconcomitant dragging of proximal histidine that triggers theconformational changes in other globin subunits and thus byopening other heme sites. As a result, the binding capacityof other heme irons with dioxygen is enhanced. This is bestexample for co-operativity through allostery.



Deoxy Hb
Domed porphyrin
High spin Fe(II) - out of ring



Oxy Hb
Planar porphyrin
Fe ion moves into the ring
Bent O_2

The nature of Fe in oxy-Hemoglobin or in oxy-Myoglobin is controversial.

According to old Pauling model, there is a low spin Fe(II) ion that is bound to singlet O2 in oxy-Hb. Both are diamagnetic.

However, according to Weiss model, there is Fe(III) ionbound to superoxide radical anion (02-). Though both areparamagnetic, a strong paramagnetic coupling betweenthem ensues diamagnetic behavior This model issupported by the O-O stretching frequency at 1105 cm^{21} inresonance raman spectrum that is consistent with the factthat O2 is in superoxide form. This deems to be more accurate and moderate explanation.

Nitrogen fixation:-

The conversion of molecular nitrogen into compound of nitrogen especially ammonia is called Nitrogen fixation.

Nitrogen fixation is a reductive process. I.e, nitrogen fixation will stop if there is no reducing condition or if oxygen is present.

This nitrogen fixation may take place by two different methods.

1. Abiological

2. Biological

1. Abiological nitrogen fixation:-

In abiological nitrogen fixation the nitrogen is reduced to ammonia without involving aryl living cell.

Abiological fixation can bro of two types.

a. Industrial

b. Natural

For example:-In the Habers process synthetic ammonia is produced by passing mixture of nitrogen and hydrogen through a bed of catalyst (iron oxides) at a ve high temperature and pressure.

$N_2+3H_2 \rightarrow 2NH_3$

This is industrial fixation where in nitrogen gets reduced to ammonia.

In natural process nitrogen can be fixed especially during electrical discharges in the atmosphere can combine with oxygen to form oxides of nitrogen.

$N_2+ 2O_2 \rightarrow 2NO_2$

This oxides of nitrogen may be hydrated and trickle down to earth as combin nitrite and nitrate.

DNR COLLEGE(A): BHIMAVARAM

DEPARTMENTOFPGCHEMISTRY

INORGANICCHEMISTRY-II

PresentedBy

N.Santhi

Unit-4

Inorganic Reaction Mechanisms

MechanismsforLigandReplacementReactions:-

Theligand displacement in metal complexesissaidto have beentakenplaceif one of the previously attached ligands got replaced by another ligand from its coordination sphere. The scheme can be shown as:

MAnL+E=MAnE+L……(1)

Where ligand Lis the leaving group present in the complex, E is the entering ligand which isnucleophilicinnature.The coordination number of the complexremainsthe same.

➤LigandDisplacementMechanisminOctahedralComplexes:-

Inoctahedral complexes,thereplacementoftheligandcanoccurthroughdissociative, associative or by interchange mechanism. It has also been observed that most of the ligand displacement takes place through the interchange rout rather than purely associative or dissociative.

1. **DissociativeorSN1Mechanism** (D): In this mechanism, first of all, a metal-ligand bond breaks and the coordination number of the complex reduces from six to five formingapenta-coordinatedintermediatecomplex.Afterthat,theenteringgroupattacks this intermediate and the coordination number again gets restored to six giving octahedral geometry. The whole process can be shown as

MA5L=MA5=MA5E……(2)

The firststepis the slowstep and henceitis also the rate-determining stepfor the process. The overall rate is:

Rate=k[MA5L]…….(3)

The reactionisof the first order andisindependent ofthe concentration ofthe entering ligand. These types of reactions are also called as the unimolecular nucleophilic substitution or SN, reactions.

Most of the ligand substitution reactions in octahedral complexes occur through dissociativeorbyinterchangedissociativemechanismwhichinturncanbeevidenced by the following rules.

i) Therate oftheligandsubstitutionisalmostindependentoftheconcentrationofthe entering ligand.

ii) Therate oftheligandsubstitutionincreasesasthestericbulkaroundthemetal center increase.

iii) Theentropyofactivation,AS,ispositiveastherearemorespeciesinactivated complex than in reactant.

iv) Thevolumeofactivation,AV^{1},for thereaction isalsofoundtobepositive.

2. Associative or SN2 Mechanism (A): In this mechanism, firstly the bond making with the entering group takes place, and therefore, the coordination number of the metal complexincreasesfromsixtosevenformingahepta-coordinatedintermediate complex. After that, the leaving group dissociates itself fromthe intermediate complex completely and the coordination number of the complexagaingetsrestored to sixgiving octahedral geometry. The whole process can be shown as

MA5L+E.=MA5LE=MA5E…..(4)

The firststepis the slowstep and henceitis also the rate-determining stepfor the process.

TheoverallrateisRate=

k[MA5L][E] .... (5)

The reaction is of second order and it depends of the concentration of the reactant complexas well astheconcentrationoftheenteringligand.Thesetypesofreactions are also called as bimolecular nucleophilic substitution or SN2 reactions.

i) Therate oftheligandsubstitutionisincreasedwith theconcentrationoftheentering ligand.

ii) Therate oftheligandsubstitutiondecreasesasthestericbulkaroundthemetal center increase.

iii) The entropyof activation,AS, isnegative asthere arelesser number speciesin activated complex than in reactant.

iv) Thevolumeofactivation,AV†,for thereactionisalsofoundtobenegative.

3. **Interchangemechanism** (I): It has been observed that most of the ligand displacement reactions are neither purely associative or dissociative but follow an intermediate mechanism in which bond breaking and bondmaking takes place simultaneously and no penta-coordinated or hepta-coordinated intermediates have actual beenisolated.Thesetypesofreactionsproceedviaa transitionstate justlikein organic SN2 reactions.

MA5L+EMA5 LE→MA5E ....(6)

However, if therateof thereactionis stronglydependent on the concentration of the enteringligandwhicindicatesthat bondmakingismoreimportantindetermining the rate of the reaction than the displacement said to have been taken place via interchange associative or I, mechanism. On the other hand,if therateof threactionis almost independent of the concentration of the entering ligand which clearly indicates that bor breaking is more important in determining the rate of the reaction than the displacement is said to have bee taken place via interchange dissociative or Id mechanism.

LigandDisplacementReactionsinOctahedralComplexes-AcidHydrolysis, BaseHydrolysis

Thegeneral schemefortheliganddisplacementreactionsinoctahedral complexescan be shown as:

MA5L+E. = MA5E+L

Where ligand Lis the leaving group present in the complex, E is the entering ligand which is nucleophilic in nature. The coordination number of the complex remains the same. Moreover,if theentering group Eis H_2O or OHin aqueoussolution,the study of liganddisplacementbecome moreimportantduetoextremelywideapplicationdomain. Some of the most prominent reactions in ligand substitution in six-coordinated complexes are discussed in detail.

AcidHydrolysis:-

Acidhydrolysisoraquationreactionsmaybedefinedasthereactionsinwhichanaquo complex is formed due to the replacement of a ligand by water molecule.

It has been observed that NH3, ammines like ethylene diamine or its derivatives coordinated to Co^3+ are displaced at a very small rate. Hence, displacement of the ligandother thanammoniatakesplaceduringthecourseofacidhydrolysis.Consider the following reaction

[Co(NH3)5L]2++ H2O→[Co(NH3)5H2O]3++L-….(1)

As reaction media is the water itself, H_2O concentration (55.5 M) remains almost constant and the change in water concentration cannot be detected at all. Hence, rate law cannot be used to predict whether the reaction takes place via the associative or dissociative pathway. SN reactions follow first-order kinetics while SN2 reactions follow second-orderkinetics.However,ifthecomplexingagentisintheexcess,SN2reactions also become pseudo first-order reactions. Hence, it is difficult to tell whether the reaction occurs through the SN_1or SN2 mechanism.

Now,ithasalsobeenfoundexperimentallythatdivalentmonochlorocomplexesof Co(III) react at much slower than monovalent dichloro complexes.

[Co(NH3)4Cl2]+=[Co(NH3)4Cl]2+H2O←[Co(NH3)4(H2O)(Cl)]+….(2)

and

[Co(NH3)5Cl←[Co(NH3)5]3++H2O=[Co(NH3)5(H2O)]2+......(3)

The reaction (14) is 1000 times faster than reaction (15) suggesting that both of the reactionsoccurthroughdissociativeorSN,pathway.Thisisbecausetheseparationofa negatively charged Cl is much more difficultfrom a complex of high charge density. Therearealsosomeothergroundevidenceswhichsupportthedissociative mechanism.

1. **Solvationenergyoftheintermediate**: The rate of acid hydrolysis in cis-[Co(en)2(NH3)Cl]2+isfivetimeslessthanin [Co(NH3)5Cl]2+which can beexplainedin term of the lesser solvation energy of the intermediate. Owing to the larger chelate ring in cis-[Co(en)2(NH3)Cl]2+ the intermediate [Co(en)2(NH3)]+ also possesses the larger size and hence less solvation energy and thus by making its formation unfavorable slows down the rate of acid hydrolysis. On the other hand, the smaller sized [Co(NH3)5]3+ complex has a smaller size solvation energy making its formation more favorable. Thus, by comparing the rate of acid hydrol [Co(en)2(NH3)C1]2+ and [Co(NH3)5Cl]2+, we can conclude that chelation stability is somewhat less than that of the extent of solvation the intermediate undergoes in this case.

2. Steric Hindrance: The rate of acid hydrolysis in cis-[Co(en)2(NH3)Cl]2+ is smaller in cis- [Co(pn)2(NH3)Cl]2+. The concept of solvation energy of the intermediate would give just the opposite order as the [Co(pn)2(NH3)]+ is larger and has less sølvation energy. However, after thedissociationof Cl-,the gain of stericreliefis much greaterin cis-[Co(pn)2(NH3)Cl]^2 due to bulkygroups. Ithasbeenobserved thattherate becomes almost double as the ethylenediamine (en) is replaced by propylene diamine group in cis- [Co(en)2(NH3)C1]2+.

3. Effect of theleavinggroup:Therateof acidhydrolysisisdirectlyproportional to ease of the breaking of the bond between the metal ion and the he leaving group. Batter the leaving group faster is the acid hydrolysis rate

$[Co(NH3)5L]2++H_2O \rightarrow [Co(NH3)5(H_2O)]^2++L$ .... (4)

Therate ofaquationis differentfor differentL.ForForexample,consider theacid hydrolysis of the following

$[Co(NH3)51]2+>[Co(NH3)5Cl]^2+>[Co(NH3)5SCN]^2+>[Co(NH3)5(NO_2)]2+$ .... (5)

The natureof theleaving group hasa pronounced effecton theaquation rate asthe bond breaking is the rate- determining step. The reactivity of the leaving group decreases in the order:

HCO3 >NO3->1>Br->Cl->SO->F->CH3COO- >SCN>NO

➤BaseHydrolysis:-

Basehydrolysisreactionsmaybedefinedasthereactionsinwhichahydroxocomplex is formed dueto the replacement of a ligand by hydroxyl ion.

BasehydrolysisreactionsoccurinsolutionshavingpHgreaterthanten.Consider the following reaction

[Co(NH3)5Cl]2++OH-[Co(NH3)5(OH)]2++X................(6)

In order to predict whether the reaction takes place via the associative or dissociative pathway, the value of the rate constant and reaction order must be examined very carefully. The possibility of a simple SN_1mechanism can be ruled out on the basis of an exceptionally fast rate of the reaction at higher pH. If the base hydrolysishad taken placeviasimpleSN,pathway, mono-chlorocomplexesofCo(III)wouldnothaveshown such fast rates as the rate-determining step involves the dissociation on Cl- from [Co(NH3)5Cl]2+is quite slowdue to higher charge onthe complex. Moreover, atlowor moderate concentrations, the rate of the reaction also depends upon the concentration OH- ions which doesn't go well according to SN, pathway. The proposed SN2 mechanism for base hydrolysis can be given as:

[Co(NH3)5Cl]2+←[Co(NH3)5(OH)(Cl)]+=[Co(NH3)5(OH)]2+......(7)

Hence, theratelawforthereactionshouldbegivenby:

Rate=k[Complex][OH-] .... (8)

However,therate ofreactionbecomesindependentofOHathighconcentrationandthe reaction starts to follow first-order kinetics. Furthermore, it has also been observed that the ligands like NCS, N^3, NO2 are as strong nucleophile as OH- and hence areexpected to show almost the same rate of hydrolysis of Co(III) amine complexes but theseligandsshowvery slowdisplacement rate andisindependent ofthe concentration of these ligands. SN2 pathway could not explain why the rate of hydrolysis of Co(III) amine complexes depends only upon OH- but not on ligands like NCS, N^3-, NO. Hence, the exact mechanism must be sought elsewhere.

ThewholeprocesscansuccessfullybeexplainedviaSN1CBo or substitution nucleophilic unimolecular conjugate base mechanism as

[Co(NH3)5Cl]2+.+OH-=[Co(NH3)4(NH2)(Cl)]++H_2O

The equilibriumconstantisgivenby

K=[CB][H2O]/[Co(NH3)5Cl]2+[OH-]OrCB=[Co(NH3)5Cl]2+[OH-]/H2O

The conjugate base as obtained is more labile than the original complex [Co(NH3)5Cl]2+and hence undergoesSN,dissociative pathwaybylosing Cl-andgives penta-coordinated intermediate.

[Co(NH3)4(NH2)(Cl)]+ =[Co(NH3)4(NH2]2+

The above step is the rate-determining step.

[Co(NH3)4(NH2)]2++H2O→[Co(NH3)5(OH)]2+

Therearesomegroundevidenceswhichsupportdissociativemechanismthroughthe formation conjugate base.

1. Hydrolysis of the complex-ions without acidic protons: The complexes like [Co(CN)5Br]^{3}, which do not have N-H hydrogens undergo hydrolysis much slowly in basicsolutionsatarate whichisalmostindetheOH- concentrationover a widerange. Hence, the acidic proton is a must.

2. Hydrolysis of [Co(NH3)5Cl]2+ by nucleophiles with same strength as OH:Although the a NCS, N3, NO2 are as strong nucleophile as OH yet they do not show fast hydrolysisof [Co(NHbecause these anionsare much weaker base than that of OHand hence unable to extract the acidic proton from the complex to form conjugate base. Therefore, the hydrolysis of [Co(NH3)5Cl]^{2}+ by NCS, N3, NOΣ cannot take place via SNCB mechanism and takes place possible either via simple SN, or SN2 pathway.

3. Hydrolysisofanioniccomplexes:Considerthebasehydrolysisofanioniccomplexes like [Fe(CN)5(NH3)] which have acidic proton in NH3 but also have a high negative charge. In these types of complexes, the rate of hydrolysis is considerably slow and independent of the OH- ion concentration which may be attributed to the highly unfavorable formation on the conjugate base.

➤LigandDisplacementMechanismin Square-planarComplexes

In square-planar complexes, the ligand displacement is much more favorable through the associative route than that of dissociative which can be understood in terms of low stericcrowdingduetolessercoordinationnumber.Thegeneralliganddisplacementcan be written as:

MA3L+E→MA3LE←MA3E

Theintermediatestateis trigonal-bipyramidalandundergoesrapidBerry-pseudo- rotation followed by the elimination of the leaving grogroup

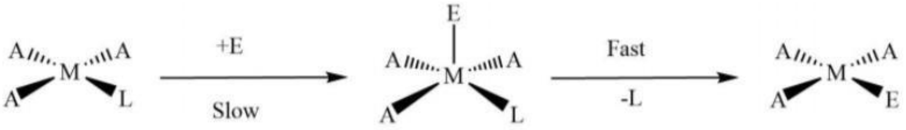


Figure 10. The general reaction mechanism for ligand displacement reactions in square-planar complexes.

A more in-depth visualization of ligand displacement reactions in square-planar complexesis givenbelowinwhichtheinvolvementofBerry-pseudorotationisdepicted more precisely.

TransEffect:-

Thetranseffectisthelabilizationofligandstranstocertainotherligands,whichcan thus be regarded as trans directing ligands.

Itisattributed tomainlyelectroniceffects,importantinsquareplanarcomplexes,also observed in octahedral complexes

Substitutionreactionsinsquareplanarcomplexes (I)Polarization

theory

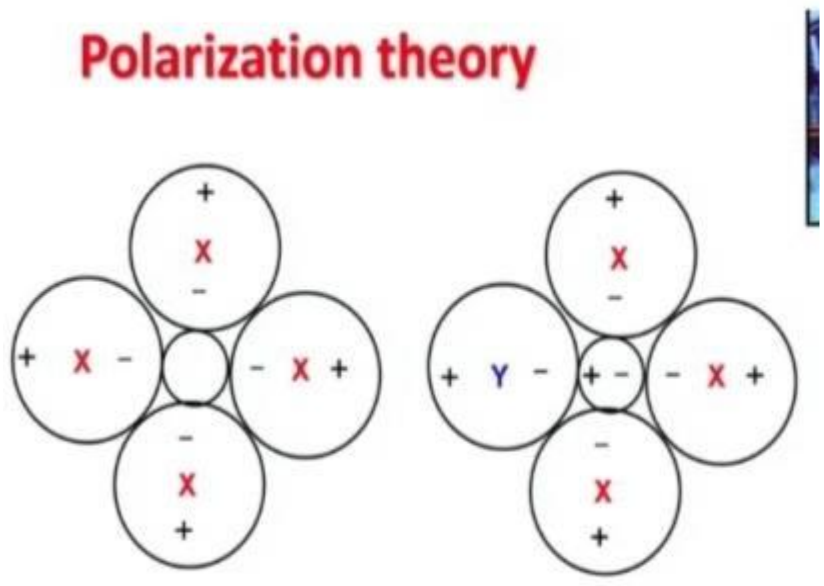
(II)п-bondingtheory

Transseries:increasingorderoftranseffect

F^-, H_2O, OH^- < NH_3<py< Cl^- < Br^- < I^-, SCN^-, NO_2^-, SC(NH2)2, Ph^- < SO32 < PR3, AsR3, SR2, $CH3^-$ < H^-, NO, CO, CN-, C_2H_4

➤ThePolarizationTheory

This theory mainly deals with the ground state of the complex and proposes that the metal center has a tendency to induce a dipole moment in the surrounding ligands by polarizingthemaccordingto Fajans' rule.InthecaseofMA4typecomplexes,metal ion induces an equal dipole moment in all the four surrounding ligands which are, in turn, cancel out each other due to square-planar geometry. However, in the case of MA3B type complexes, the situationisquite differentas the polarizability ofall the fourligands is not anymore, the same. If the polarizability of B type ligand is higher than that ofA- type thentheprimarychargeofthemetalionwill polarizetheelectroniccloudofAmore effectively and thus will induce a strong dipole moment inA- type ligand. Furthermore, this dipole moment is also bound to induce an alternate dipole in the metal center also. The orientation of this dipole is such that it repels the negative charge on the ligand,A- type, situated transto B.Thisresultsin the weakening and consequentlylengthening of the metal-ligandbond trans to the B-type group.Therefore, according tothis concept, thetranseffectisdirectlyproportional tothepolarizabilityoftheligand.Itisalsoworth noting that the trans-effectis more prominentwith a largeand more polarizable metal center. The general order can be given as Pt(II) >Pd(II) > Ni(II).

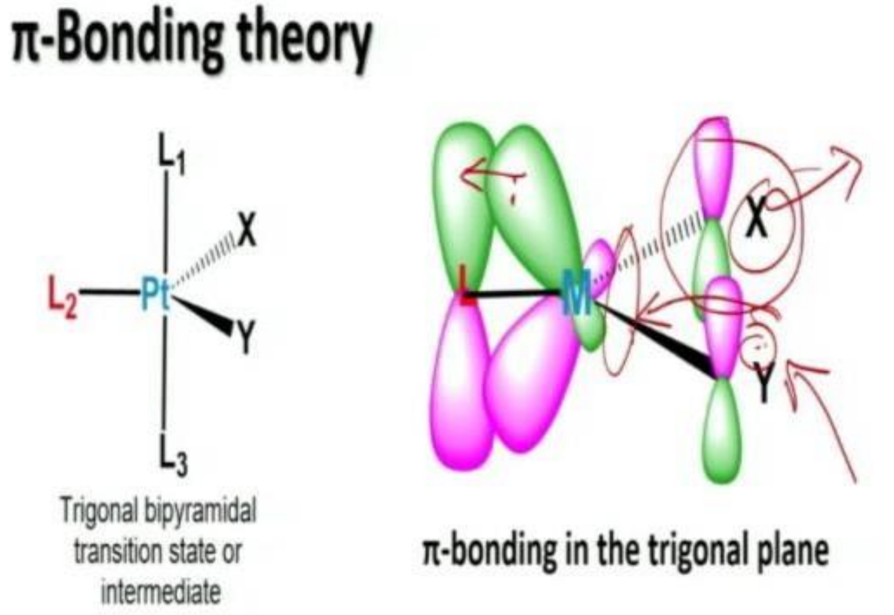


➤Theπ-BondingTheory:-

The natureof the trans-effectiselectronicinstead of stericwhich clearlymeansthat the electronic profile of the ligand is primarily governing trans-effect strength of various groups. Considering the trans-effect Tainsitute.c order of halide ions, I->Br-> Cl-> F-, it seems that the increasing electronegativity makes them poor o-donor v.da or o-base whichinturnalsodecreasestheirtrans-effectstrength.However,theexceptionallyhigh trans-effect of the ligands like CO, C2H4 or PR3 cannot be explained by o-donation ability as they are not very good σ- donor but -acceptor in nature. Therefore, we can conclude that a stronger trans-effect is the combination of both, either it should be a strong o-base or it should show a good n-acid character.

Now, in order to understand the whole process by which the trans-directing groups speed-uptheliganddisplacementinsquare-planarcomplexes,we will havetorecall the mechanism of ligand substitution. Let T be the trans-directing group, L as the leaving group and E as the entering group. The entering ligand binds to 16-electron Pt(II) complex to form 18-electron complex which in turn again converted into a new 16-electron complex as:

Diagram



Thecharacteristicfeaturesofthismechanism are:

i) Theenteringligandalwayssitsattheequatorial positionoftheactivatedcomplex which is trigonal- bipyramidal in nature.

ii) The trans-directinggroup andtheleaving group arepushed down to create the equatorial plane of the activated complex.

iii) Astheentering group Eattacksat theequatorial site, theleaving must also be from the equatorial plane; which is followed directly from the principle of microscopic reversibility.

The rate-determining step is when the entering ligand "E" pushes down the trans-director T and the leaving group L. Now as the equatorial sites of the trigonal-bipyramidalintermediatearericherin electrondensity than the axialones,ligandswith greater n-aciditylike to be pushed down to getthis privilegeof strongerback-bonding. This forces the leaving group "L" to no other choice but to detach from the activated complex.

The transition stateisstabilized bytheoverlap of empty *orbitalof "T" andthe filleddxz orbital of the metal center. This results in a decrease in the electron density in metal-leaving group bond which makes the displacement of L by E much easier.

Electrontransferreactions:-

Electrontransferreactionsarealso calledRedoxReactions

TypesofElectronTransferReactions:-

After having general discussion on the electron transfer reactions we should have an ideaabouttypesofthesereactions.Theelectrontransferreactionscanbeclassifiedas:

(i)outersphere,and(ii)innersphereelectrontransfer reactions

i.OuterSphereElectronTransferReactions

Whentheelectrontransfer takesplaceinsucha waythatinner coordinationshellsor spheres of the involved complexes remains intact i.e. there is no change in the inner sphere of the reductant and oxidant, we call it an Outer Sphere electron transfer reaction. Such a reaction usually occurs when rapid electron transfer takes place between two substitutionally inert complexes. For example, in the reaction between [Fe(CN)6]4-and [IrC16]2-:

[Fe(CN)6]4-+[IrCl6]2-.=[Fe(CN)6]3-+ [IrCl6]3-

MechanismofOuterSphereElectronTransferReactions:-

Theoutherspheremechanisminvolvesthreeelementarysteps:

1. **Formationofaprecursor** (cage) **complex**. In this step the reactant metal centres are brought at such a distance that electron transfer can take place, but at this stage their relativeorientationsandinternal structuresdonotpermitelectrontransfer.Thisstepcan be shown as:

Ox+RedOxIIRed

2. **chemicalactivationoftheprecursorcomplex**, **transferofelectronandrelaxationtothesuccessorcomplex**. This step involves changes in the solvent cage and structural changes in the precursor. Oxidant and reductantarebroughtinproperorientationandstructural changesdefiningchemical activation for electron transferoccurs in this step.

OxIIRedOxIIRed+

3. **Dissociationtoseparatedproducts**

[-OxX-Red+] + H2O→ Ox(H2O)+ RedX+

Ih hasbeenobservedthatsucha reactionfollowssecondorderkineticsandfor a reaction like the one shown below

Ox-X + Red= [Ox-X-Red]=Ox + RedX+

rateofthereactionisgivenbytheequation:

Rate=[k1k3/(k2+k3)].[Ox-X][Red]

Herek3isoverallrateconstant for the secondand thirdsteps.

It has been found thatin some cases k3>> k2 and rate determiningstepis simply formation of the precursor complex. Therefore, rate law reduce to Rate = k_1[Ox-X][Red].

However,therearemanyinstanceswhereinratedeterminingstepisrearrangementand electron transfer within the intermediate, or fission of the successor complex. This means that k3 < k2 and the rate law becomes Rate = Kk3[Ox-X][Red].

Rateof theelectron transfer reactions are usually determined byп* or σ* nature of the electron donor MO (HOMO) of the reductant and receptor MO (LUMO) of the oxidant. One can expect more facile electron transfer when both donor and receptor mo are of п* type due to small reductant/ oxidant activation (change in M-L bond distance)in dп* than for a change in do* electron density.

Further, ease of electron transfer depends on overlap and mixing of the donor and receptor MO's. Electrontransferis easierif overlap and mixingof donor andreceptor mo is large. Considering orientation of αп*(4)/ do* (5) electrons in octahedral complexes, it may be concluded that п* → п* electron transfer should be faster than σ* → σ* transfer.

Thus we can simply say that if orbital overlap and mixing is appreciable and electron is being transferred from п*п*, small activations are required and the reactions are relativelyfastontheother hand,ifchangesarerequiredgreater activationsareinvolved and reactions are rather slow.

An examination of the Table 1 dealing with rates of outer sphere electron transfer reactionsshowthatfirstfour examplesrequirelittlechemical activationfor a M(II)M(III) electron exchange because these do not pass through a change in σ* orbital configuration in either complex.

InnerSphereElectronTransferReaction

It is well known that reduction of [Co(NH3)6]3+ with [Cr(H2O)6]2+ under acidic conditionstakesplaceveryslowly(k=10-3M-s^{-1}) byanouter spheremechanism:

[Co(NH3)6]3++[CrI(H2O)6]2+→[CoI(H2O)6]2++[Cr(H2O)6]3++5NH4+

However, if an ammine ligand in cobalt complex [Co(NH3)6]3+ is replaced by Cl, rate appreciablyenhances to(k = 6 x105 M's), One can say with certaintythat the reaction is now following different mechanism:

[Co(NH3)5C1]2++[Cr(H2O)6]2+→[Co(H2O)6]2++[Cr(H2O)5C1]2++ 5NH4+

H.TaubewhowasconferredonNobelprizeforhisworkonelectrontransferreactions clearly showed that an inner sphere mechanism is operative in the reduction of [Co(NH3)5Cl]2+with [Cr(H2O)6]2+;Herein,theClligand,whilestill attachedto Co(III), replaces an H20 at Cr(II) to give an intermediate shown below and electron transfer follows

Itcanbeunderstoodinthefollowingmanner:

The reductant [Cr(H20)6]2+ and reduced oxidant [Co(H20)6]2+ are substitutionally labile whilethe chloro- complexes [Co(NH3)5Cl]2+ and [Cr(H20)5C1]2+ areinert.Thus, the onlypossibilitybywhich chloride could betransferred fromCo(III) to Cr(II)isthrough some complex resulting by attack of CoC12+ on Cr2+. With the help of tracer studies i.e. by external addition of radio-chloride Taube showed that an inner sphere mechanismcanbeclearlyassignedwhenboththeoxidantandtheoxidizedreductant are substitution inert and ligand transfer from oxidant to reductant is accompanied by electron transfer.

In such reactionselectrontransferisfollowedbyligand transferin theoppositedirection Co-

Cl: + Cr→ [Co-Cl: Cr]→Co+ Cl-CrII

It is very clear that for an inner sphere electron transfer process to follow the reductant must be substitutionally labile and the oxidant must have a bridging ligand which can establishlinkagebetweenthetwometal ionssimultaneously.Theligandtransfermayor may not take placein such areaction. For example, reductionof Ir(IV) by Cr(II)involves electron transfer, but bridging ligand is not transferred from the oxidant to reductant.

[IrC16]2+[Cr(H20)6]2+→ [IrC16]+[Cr(H20)6]3+

Thereactionpassesthroughformationofabridgebetweenthetworeactantmetalions, the bond between Ir(III)-Cl] is stronger relative to [Cr(III)-Cl], therefore Cr-Cl bond is broken and reaction proceeds without transfer of the bridging ligand.

MechanismoftheInnerSphereElectronTransferReaction.

The elementarystepsinvolvedin aninnersphere mechanismcan berepresented by:

1. Formation of precursor complex, in this step the oxidant and reductant are brought closetoeachothervialinkageby thebridgingligand so that electron transfercan take place

Ox-X+Red(H_2O)→[Ox-X-Red]+ H2O

2. **chemicalactivation**,**electrontransferandrelaxationtothesuccessorcomplex**.In this step activation of the precursor complex occurs which is followed by electron transfer.

[Ox-XRed]→[-OxX-Red+]

3. **Dissociationtoseparatedproducts**

[-OxX-Red+] + H2O→ Ox(H2O)+ RedX+

It hasbeen observed that sucha reaction followssecond order kineticsandfor a reaction like the one shown below

Ox-X + Red. =[Ox-X-Red] =Ox+

RedX+rateofthereactionisgivenbytheequati

on:

Rate[k1k3/(k2+k3)].[Ox-X][Red]

Herek3isoverallrateconstant for the secondand thirdsteps.

It hasbeen found thatin some casesk3>>k2 and rate determiningstepissimply formation of the precursor complex. Therefore, rate law reduce to Rate = k_1[Ox- X][Red].

However,therearemanyinstanceswhereinratedeterminingstepisrearrangementand electron transfer within the intermediate, or fission of the successor complex. This means that k3 k2 and the rate law becomes Rate = Kk3 [Ox-X][Red].

FactorsinfluencingtheratesofInnerSphereElectronTransfer:-

Now,letushavealookonthefactorsdeterminingratesofinner sphereelectron transfer reactions.

Formation of the precursor complex: We have already discussed about substitution reactionsatoctahedral metal centresinthefirstunit.Youhaveseenthatadmetalionis relatively inert to substitution, while high spin d and complexes are labile.

Further, usuallyininner sphere electron transfer reactionsV2+[(π*)3(σ*)'], Cr2+ [(π*)3(σ*)'], and Fe2+ [(π*)4(σ*)2] are employed as reductants.

Anexaminationof thesubstitution ratesfor

[V(H2O)6]2++ H2O*→ [V(H2O)5(H2O*)]2++ H2O(k= 1× 102s^{1})

TheNatureoftheBridgingLigand

The natureof bridgingligand playsanimportant roleindetermining the ratesofinner sphere electron transfer reactions.

Haim recently pointed out, "The role of the bridging ligand [in an inner sphere mechanism] is ... dual. It brings the metal ions together (thermodynamic contribution) and mediates the transfer of the electron (kinetic contribution)." The thermodynamic contribution is related to the stability of the intermediate complex, and kinetic to factors suchasoxidant-reductantreorganizationandmatchingofdonorandreceptormolecular orbitals.

Asfar asbridgingligands(BL)areconcerned,bothinorganicand organicligandshave extensively been utilized in the inner sphere electron transfer reactions.

Complementaryandnoncomplementaryreactions:-

The reactions in which the formal oxidation states of the oxidant and by the same number of units. These are called complementaryreactions. There are m which formal oxidationstatesoftheoxidantandreductantdonotchangebysamenumber termedas non-complementary processes such as

Mn(VII) + 5Fe(11) → Mn(11) + 5Fe(lll)

Cr(VI)+3Fe(11)→Cr(111)+3Fe(111)

2Cr(11) + Pt(IV) →2Cr(III) + Pt(11)

Clearlyin a non-complementaryreaction, theoxidation statesof the reactants change and the stoichiometries are not 1: 1.One of the best example of non-complementary prmetalchemistrypresentschromateionoxidations.Itoxidationoccursinstepsandin ea electron transfer.

kCr(VI)[=HCrO]+RedCr(V)+Ox Cr(V) +

Red Cr(IV) + Ox

Cr(IV)+Red Cr(III)+Ox