COORDINATION CHEMISTRY

Simple Salt

Acid + Base ⟶ Simple Salt + Water

When dissolved in water, these salts ionise & produce ions

eg: NaCl, $MgCl_2$, etc.

Mixed Salt:

They contain more than 1 acidic or basic radical.

eg: $NaKSO_4$

Molecular or addition compounds

When sol^n containing 2 or more salts in stoichiometric proportion, is allowed to evaporate, we get crystals of compounds known as molecular or addition compounds. They are of 2 types:

① **Double Salt (Lattice Compounds)**

→ These are stable in solid state but give their constituent ions when dissolved in water or any other ionic solvent.

→ Individual prop of constituent ions are not lost.

eg: $KCl \cdot MgCl_2 \cdot 6H_2O$ (carnallite) $\xrightarrow{\text{water}}$ gives K^+, Mg^{+2}, Cl^- ions

Mohr's Salt ($FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$)

Potash Alum ($K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$)

② **Coordination / Complex Compounds**

It has been observed that when sol^n of $Fe(CN)_2$ + KCN are mixed together and evaporated, potassium ferrocyanide is obtained.

which in aq. sol^n does not give Fe^{+2} & CN^- ions, but gives test of K^+ & $[Fe(CN)_6]^{-4}$ ions

$$Fe(CN)_2 + 4KCN \longrightarrow K_4[Fe(CN)_6] \overset{H_2O}{\rightleftharpoons} 4K^+ + [Fe(CN)_6]^{-4}$$

Representation of Coordination compounds

$K_4[Fe(CN)_6]$ — Central atom, ligands

$[Fe(CN)_6]^{-4}$ — coordination entity; coordination sphere (always with square bracket)

Central atom — d Block element present in a coordination sphere which may bond with ligands.

Valency → Primary — oxidation state of central atom

Secondary — coordination no.

CN = No of ligands central atom is bonded to

CN = $\sum$ No of ligands × Denticity

Metal	Min ON — CN	Max ON — CN
Fe	Fe^{+2} — 6	Fe^{+3} — 6
Au	Au^+ — 2	Au^{3+} — 4
Ag		Ag^{+1} — 2
Hg		Hg^{+2} — 4
Cu	Cu^+ — 2,4	Cu^{+2} — 4,6
Zn		Zn^{+2} — 4
Cd		Cd^{+2} — 4
Co	Co^{+2} — 4, 6, 5	Co^{+3} — 6
Ni	Ni^{+2} — 4,6	

Pt Pt^{+2} — 4 Pt^{+4} — 6

→ $Mo^{+4} \rightarrow 7$
$W^{+4} \rightarrow 8$

→ Cu^{2+}, Pt^{2+}, Ni^{2+}, Mn^{2+}, Pd^{2+}, Zn^{2+}, Ni ⇒ CN = 4

→ Fe^{0} — 5

→ Fe^{+2}, Fe^{+3}, Co^{3+}, Pt^{4+}, Cr^{+3}, Cr^{0}, Ni^{2+}, Ir^{3+} ⇒ CN = 6

TYPES OF LIGANDS

I. On Basis of Dented Nature

① Monodented - ligands with only 1 donor atom. Eg - NH_3, CN^-, F^- H_2O, CO

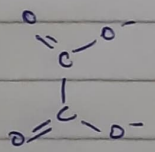
② Bidented - ligands with 2 donor atoms

Eg - CH_2-CH_2 (NH$_2$, NH$_2$)

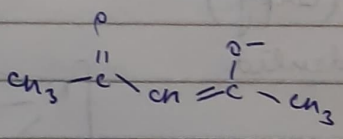
Ethane-1,2-diamine (en)

$CH_2-CH_2-CH_2$ (NH$_2$, NH$_2$)

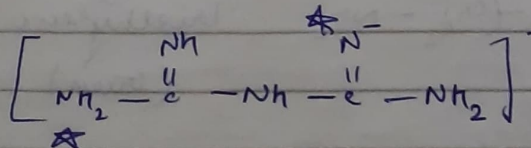
Trimethylene diamine (tn)



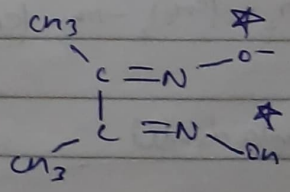
oxalate



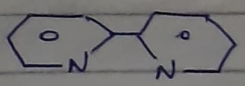
acetylacetonate ion (acac$^-$)



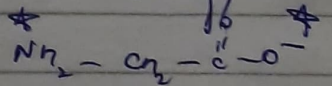
Biguanido (Big)$^+$



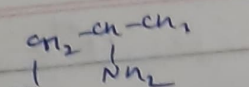
Dimethyl glyoximate (dmg)



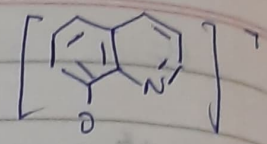
dipyridyl (dipy)



glycinato (gly)



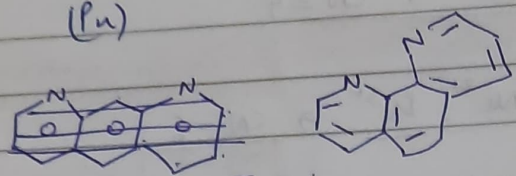
1-2 diamino propane
or
propylene diamine
(pn)



Butylene diamine
(bn)

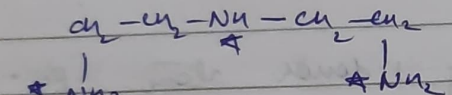
Oxinate
$(ox)^{-1}$

8 hydroxyquinolinate

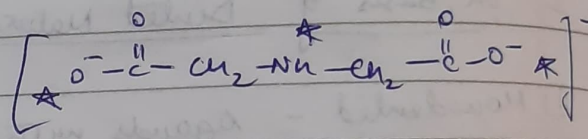


1-10 phenanthroline
(phen)

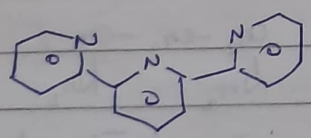
(3) Tridented



Diethylene triamine
(dien)

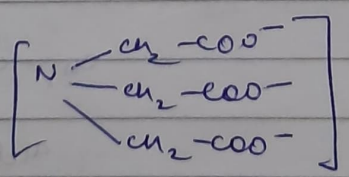


Imino-di-acetato
$(IDA)^{-2}$

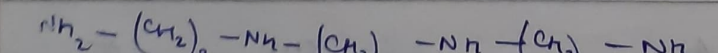


⇒ 2, 2', 2'' terpyridine
or
(terpy)

(4) Tetradented

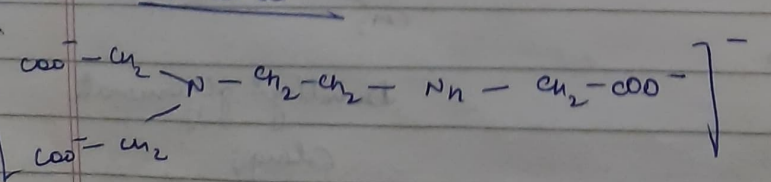


Nitrilo triacetate $(NTA)^{-3}$



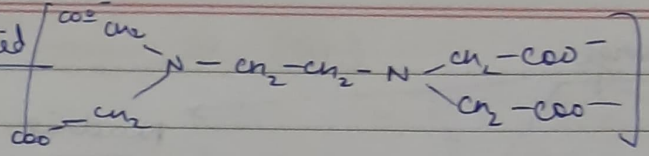
Triethylene tetra amine
(trien)

(5) Pentadented



Ethylene diamine triacetato
$[EDTA]^{-3}$

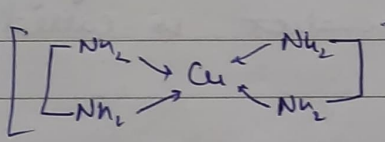
(6) Hexadentate



Ethylene diamine tetra acetate $[EDTA]^{-4}$

Flexidentate – Polydentate ligands have flexibility in denticity character. It is not necessary that all donor atoms should form coordinate bonds with central atom. Ex – $[EDTA]^{-4}$, can behave as hexa, penta, tetra. Similarly $[SO_4]^{2-}$ can behave as mono also.

Chelating ligand – A bidentate or polydentate ligand is known as chelating ligand if it produces 1 or more ring with CA during bond formation. Chelating ligands form more stable complex.



Ambident ligands – Ligands which have 2 or more donor atoms, but in forming complex only 1 donor atom is attached to metal ion at a given time.

NO_2^- →	$M-NO_2$	Nitro
	$M-ONO$	Nitrito
CN^- →	$M-CN$	cyano
	$M-NC$	isocyano
SCN^- →	$M-SCN$	Thiocyanate
	$M-NCS$	Isothiocyanate
NCO^- →	$M-OCN$	cyanate
	$M-NCO$	Isocyanate
$S_2O_3^{2-}$ →	$MSSO_3$	
	$MOSO_2S$	

II On Basis of Charge

- Neutral ligands: NH_3, H_2O, CO, C_6H_6
- -ve ligands: OH^-, CN^-, Br^-, F^-, CO_3^{2-}
- +ve ligands: NO^+, $NH_2-NH_3^+$

III. On Basis of Interaction b/w ligands & CA

(1) Classical or simple donor ligands

Ligands only donate lp of e⁻ to CA

eg NH_3, NH_2^-, H_2O, etc

(2) Non Classical ligands or π acid or π acceptor ligands

These ligands not only donate their lp to CA, but also gain e⁻ cloud from CA in their low lying vacant orbitals. This kind of back donation is called synergic effect.

eg CO, C_2H_4, C_2H_2, CN^-, PR_3 (R = H, Ph, Et), CO_2, NO^+, PF_3

→ Homoleptic Complexes – Metal ion linked to only 1 type of ligand
eg. $[Cr(H_2O)_6]^{3+}$

→ Heteroleptic Complexes – Metal ion linked to more than 1 type of ligands.

→ Homonuclear Complex – Only 1 metal atom is present.

→ Polynuclear Complex – More than 1 metal atom present
eg. Bridge complexes.

→ Labile Complex – complex in which ligands can be easily replaced by other ligands.

EFFECTIVE ATOMIC NO (EAN)

EAN = At no of metal − no of e^- lost in ion formation + no of e^- gained from donor atom of ligands

→ $K_4[Fe(CN)_6]$ EAN = 26 − 2 + (2×6) = 36

→ $[Cu(NH_3)_4]SO_4$ EAN = 29 − 2 + 8 = 35

→ $Ni(CO)_4$ EAN = 28 + 8 = 36

→ $[Co(NH_3)_6]Cl_3$ EAN = 27 − 3 + 12 = 36

Sidgwick suggested that complex in which EAN of CA = At No of next Noble gas, are extra stable, but this is found to be incorrect in many complexes. EAN Rule is valid in case of metal carbonates & metal carbonyls.

NOMENCLATURE OF COORDINATION COMPOUNDS

→ Cation is always named first.

→ Ligands are listed in alphabetical order multi no (di, tri, tetra, penta, hexa) or (bis, tris, tetrakis, pentakis)

→ Name of anionic ligands ends in -o.

→ If coordination sphere has ≥0 charge then central metals follow English Name.
If coordination sphere has <0 charge then Eng/Latin name + ate.

H^- : Hydrido	CO_3^{2-} : Carbonato
O^{-2} : Oxo	$C_2O_4^{-2}$: oxalato
O_2^{-2} : Peroxo	CH_3COO^- : acetato
O_2H^- : perhydroxo (H_2O_2)	$EDTA^{-4}$: Ethylene diamine tetra acetato
F^- : Fluorido	SO_4^{2-} : Sulphato
Cl^- : Chlorido	SO_3^{2-} : Sulphito
Br^- : Bromido	S^{2-} : Sulphido
I^- : Iodido	HSO_3^- : hydrogen sulphito

$S_2O_3^{2-}$: Thiosulphato

HS^- : Mercapto

NH_2^- : Amido

NH^{-2} : Imido

N^{3-} : ~~Azido~~ Nitrido

N_3^- : Azido

NO_3^- : Nitrato

NO_2^- : Nitrito-N

ONO^- : Nitrito-O

CN^- : cyanido

SCN^- : Thiocyanato-S

NCS^- : isothiocyanato -N

HCO_3^- : Hydrogen carbonato

$S_4O_6^{-2}$: Tetra thionoso

Ph^- : Phenyl

$CH_2=CH^-$: Vinyl

CH_3^- : Methyl

H_2O : Aqua

CO : Carbonyl

NH_3 : Ammine

NO : Nitrosyl

CS : Thio carbonyl

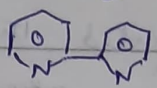
C_5H_5N : Pyridine

NH_2-NH_2 : Hydrazine

PH_3 : Phosphine

Ph_3P : triphenyl phosphine

O_2 : ~~dioxygen~~ dioxygen

 : pyridyl

N_2 : Dinitrogen

CH_2-CH_2 : ethane-1,2-diamine
NH_2-NH_2 or ethylene diamine

NO^+ : Nitrosylium / Nitrosonium

$NH_2-NH_3^+$: Hydrazinium

H_3O^+ : Hydronium

For π donor ligands, prefix $\boxed{\eta^x}$ is used where η indicates πe^- donation and x is known as capacity of the ligand (no of atoms involved in π donation.

eg $\pi - C_5H_5^-$ η^5 (cyclopentadienyl)
(2π bond, 1 lp)

$\pi - C_6H_6$ η^6 (Benzene)
(3π bonds)

Abbreviations

acac⁻ — Acetyl acetonato ion
acacH — Acetyl acetone
am — Ammonia (Ammine)
aq — Aqua

bzg – Bguanido ion

bzgH – Bguanide

DMG$^{\ominus}$ – Dimethyl glyoximate

DMGH – Dimethyl glyoxime

$EDTA^{-4}$ – Ethylene diamine tetra acetate ion

EDTAH$_4$ – Ethylene diamine tetra acetic acid

en – Ethane 1,2 – diamine

dien – diethylene triamine

trien – triethylene tetra amine

pn – 1-2 diaminopropane

tn – 1.3 diamine propane

gly – glycinato ion

glyH – glycine

Ox^{2-} – oxalato

ph – ortho phenanthridine

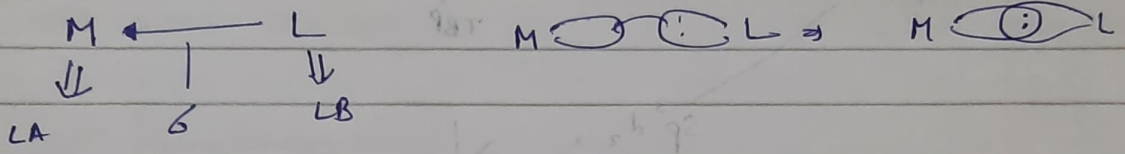
Naming of Bridged Polynuclear complexes

Bridged ligands are rep by adding prefix μ of before its name. 2 or more bridging ligands of same kind are indicated by di μ, tri μ.

BONDING

- VBT ✓ (Valence Bond Theory)
- CFT ✓ (Crystal Field Theory)
- LFT (Ligand Field Theory)
- MOT (Molecular Orbital Theory)

VALENCE BOND THEORY

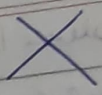


→ Bonding purely covalent.
→ Coordinate bond behaves like ↓ bond.

HYBRIDISATION

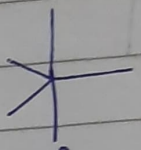
CN	Hybridisation	Structure	Examples
2	sp	Linear	
3	sp^2	Trigonal planar	
4	sp^3	Tetrahedral	
	sp^2d ~ $d_{x^2-y^2}$	square planar outer complex	

dsp^2
$(d_{x^2-y^2}$



Square planar
inner complex

5 sp^3d — $sp^3d_{z^2}$

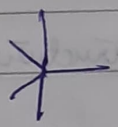


TBP

$sp^3d_{x^2-y^2}$

square
pyramidal

dsp^3 — $d_{z^2}sp^3$

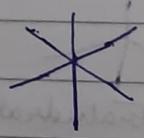


TBP

$d_{x^2-y^2}sp^3$

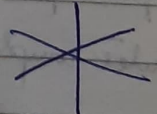
square
pyramidal

6. d^2sp^3
$(dx^2y^2, dz^2$



octa.
Inner complex

sp^3d^2
$(dx^2y^2, dz^2$



octa, outer complex

In VBT, ~~on Basis of Magnetic Moments~~,

LIGANDS

STRONG FIELD LIGANDS

- In CFT, called **LOW SPIN**
- Does not follow Hund's Rule
- Repulsion / Additional pair of e^- after $3e^-$ (for Octa.)

WEAK FIELD LIGANDS

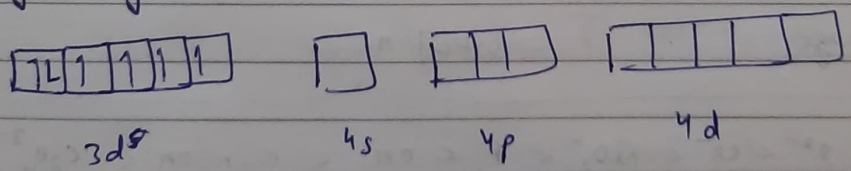
- In CFT called **HIGH SPIN**
- Follows Hunds Rule

Consider $[Fe(CN)_6]^{-4}$ & $[FeF_6]^{-4}$

Both Have CN=6, Fe^{+2} state.

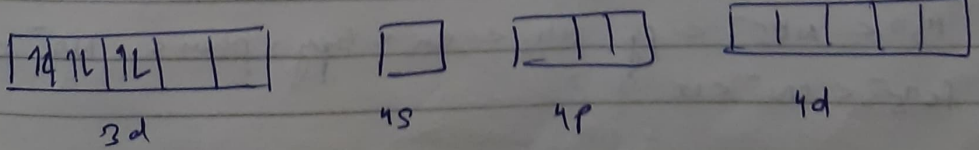
$[Fe^{+2}]$ → $4s^0\ 3d^6$

I If we follow Hund's Rule.



M.M = $\sqrt{24}$ BM

II If we do not follow Hund's Rule

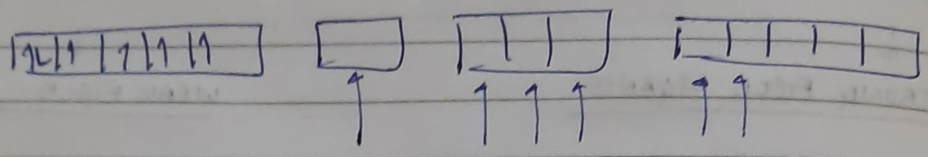


MM = 0 BM

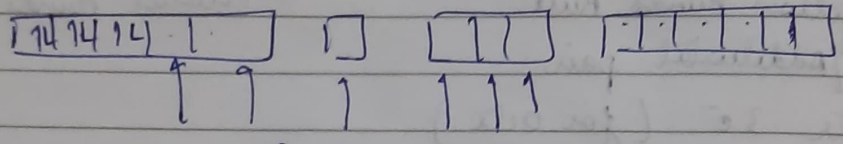
Experimentally $[Fe(CN)_6]^{-4}$ → MM = 0 BM

~~Fe (CN)~~ $[FeF_6]^{-4}$ → MM = $\sqrt{24}$ BM

SF →



sp^3d^2



d^2sp^3

SPECTROCHEMICAL SERIES

- Experimentally determined series based on absorption of light by complexes with diff ligands
- In increasing order of field strength.

FIITJEE Package

WFL / HS

$I^- < Br^- < S^{2-} < Cl^- < NO_3^- < F^- < OH^- < C_2H_5OH < C_2O_4^{2-} < H_2O <$ EDTA $<$  $= NH_3 < en <$ dipyridine $<$ phen $< NO_2^- < CN^- < CO$

SFL / LS

Huheey Keiter

$I^- < Br^- < S^{2-} < SCN^- < Cl^- < N_3^-, \approx F^- <$ urea, $OH^- < ox, O^{2-} < H_2O < NCS^- <$ py, $NH_3 <$ en $<$ bpy, phen $< NO_2^- < CH_3^- < PCH_3^- < CN^- < CO$

Exceptions

- Co^{+2} : H_2O : HS
  Co^{+3} : H_2O : LS
- Co^{+2} : $C_2O_4^{2-}$: HS
  Co^{+3} : $C_2O_4^{2-}$: LS
- Ag^{+3}, Ni^{+4} : F^- : LS
- Ni^{+2}, Fe^{+2}, Mn^{+2}, Cr^{+2}, Zn^{+2} : NH_3 : HS

CRYSTAL FIELD THEORY (CFT)

- M ⟶ L ionic bond
  behave like point charge.
- t_{2g} : d_{xy}, d_{yz}, d_{zx}
  e_g : $d_{x^2-y^2}$, d_{z^2}

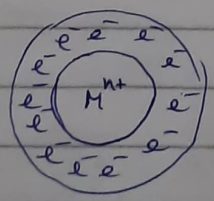
SPLITTING OF ENERGY LEVELS (CN = 6, 3d Series)

Stage (1)

M^{+n} ⟷ $12e^-$

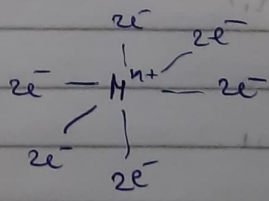
$r = \infty$

Stage (2)



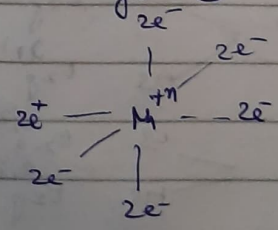
At some r_{M-L} symmetrical field around M^{n+}

Stage (3)

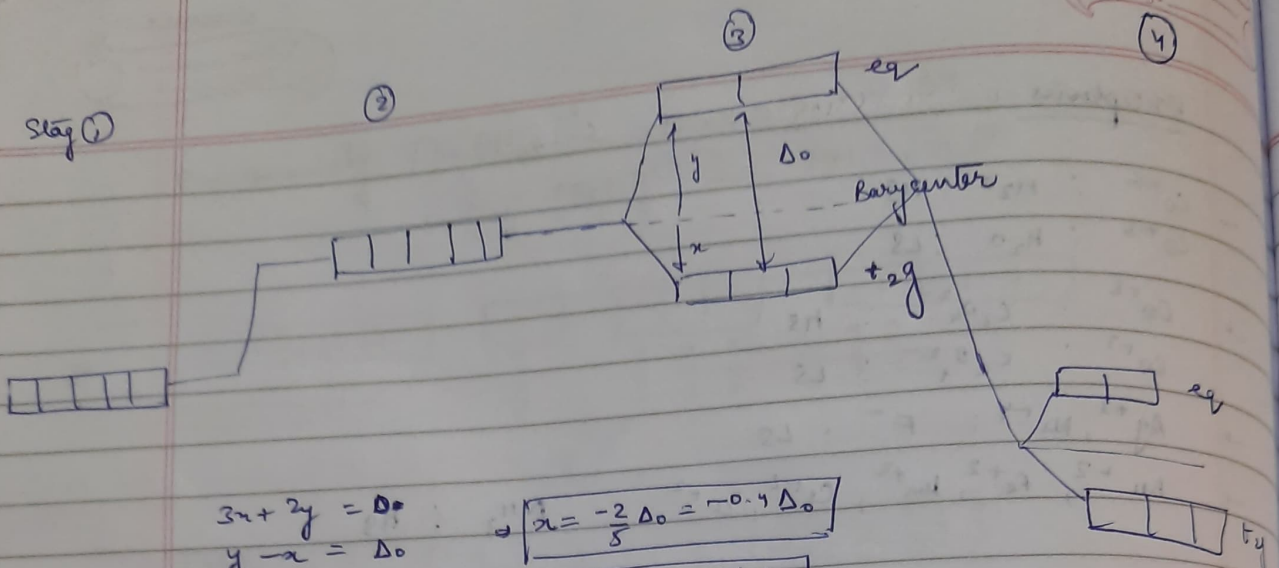


M^{n+} surrounded by 6 ligand e^- pairs at dis of r_{M-L}

Stage (4)



Same as stage (3), Now electrostatic attractions considered so energy becomes lower.



$3x + 2y = \Delta_o$

$y - x = \Delta_o$

$\Rightarrow \boxed{x = -\frac{2}{5}\Delta_o = -0.4\,\Delta_o}$

$\boxed{y = \frac{3}{5}\Delta_o = 0.6\,\Delta_o}$

Filling of e^-

E.C

d^1 ~ $t_{2g}^{1,0,0}$ $e_g^{0,0}$

d^2 $t_{2g}^{1,1,0}$ $e_g^{0,0}$

d^3 $t_{2g}^{1,1,1}$ $e_g^{0,0}$

d^4 — LS $\Delta_o > P$ $t_{2g}^{2,1,1}$ $e_g^{0,0}$

HS $\Delta_o < P$ $t_{2g}^{1,1,1,1}$ $e_g^{1,0}$

where P is energy req to pair e^- in t_{2g}

If $\Delta_o = P$ → low T — LS

→ high temp — HS

d^5 — LS $t_{2g}^{2,2,1}$ $e_g^{0,0}$

HS $t_{2g}^{1,1,1}$ $e_g^{1,1}$

d^6 — LS $t_{2g}^{2,2,2}$ $e_g^{0,0}$

HS $t_{2g}^{2,1,1}$ $e_g^{1,1}$

d^7 — LS $t_{2g}^{2,2,2}$ $e_g^{1,0}$

HS $t_{2g}^{2,2,1}$ $e_g^{1,1}$

d^8 $t_{2g}^{2,2,2}$ $e_g^{1,1}$

d^9 $t_{2g}^{2,2,2}$ $e_g^{2,1}$

★ → low spin & high spin distinction only for — d^4–d^7 – 3d series

★ → For 4d, 5d, Δ_o ↑ by 30–50%.

so 4d, 5d series all behave like LS.

→ **CRYSTAL FIELD SPLITTING ENERGY (CFSE)**

$$= -0.4\,\Delta_o\, n_{t_{2g}} + 0.6\,\Delta_o\, n_{eg} + xP$$

where x = No of additional pairs in LS than HS.

$x = 2$ or 1

d^5, d^6 — d^4, d^7

$n_{t_{2g}}$ – no of t_{2g} e^-

n_{eg} – no of eg e^-

★ **FOR CN=6, 3d SERIES**

Spectrochemical series depends on following factors:

1. 3d/4d/5d series
2. ON of CA
3. Nature of ligand

Priority order ↓

Halide donor | O Donor | N Donor | C/π Donor

$I^- < Br^- < Cl^- < F^- < OH^- < Ox^{-2} < H_2O < NH_3 < en < \ldots$

ON +2

HS/WFL ← → LS/SFL

ON +3

HS/WFL ← OH^-, Ox^{-2}, H_2O — O Donor → LS/SFL

Fe^{+3}, ~~Co^{+2}~~ — HS

Co^{+3} — LS

ON +4

LS/SFL

FOR CN=6, 4d/5d SERIES

→ All ligands behave as LS/SFL irrespective of ON.

If Both HS & LS Ligand Present

$[Fe(H_2O)_5NO]^{+2}$ Fe^{+1} : | ↿⇂ | ↿ | ↿ | ↿ | ↿ | | ↿ | | | |

3d 4s 4p

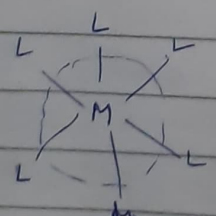
⇒ | ↿⇂ | ↿⇂ | ↿⇂ | ↿ | ↿ | | | | | | | | ~~d sp~~

$n = 3$ sp^3d

Para, $MM = \sqrt{15}$ BM

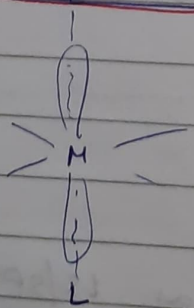
→ In reality, everything determined practically. We can not predict nature of e^- filling in such complexes.

JAHN-TELLER DISTORTION IN OCTAHEDRAL COMPLEXES



Symmetrical

Perfect octa

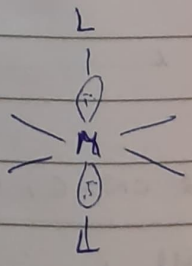


More e^- density along axis

⇓

Elongation

Zout

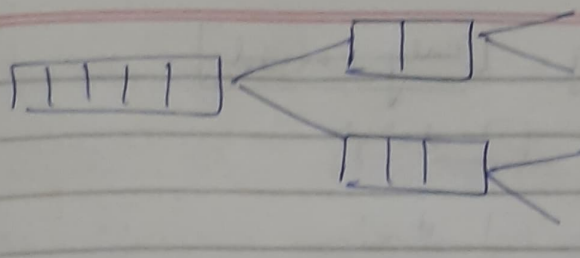


Less e^- density along axis

⇓

Compression

Zin



→ No JTE in symmetrical cases. (Perfect Oct.)

① d^3 — No JTE

② d^5 (HS) — No JTE

③ d^6 (LS) — No JTE

④ d^8 (HS) & (LS) — No JTE

⑤ d^{10} — No JTE

→ e^- in t_{2g} — Weak JTE
e^- in e_g — Strong JTE
} as ligand approaching from axis, so when e^- is along axis (e_g), repulsions ↑, JTE ↓, when e^- off axes (t_{2g}) repulsions ↓ JTE ↑

⑥ ##

EC OF CENTRAL ATOM

① d^1 — WJTE

② d^2 — WJTE

③ d^3 — No JTE

④ d^4 — HS — SJTE
LS — WJTE

⑤ d^5 — HS — No JTE
LS — WJTE

⑥ d^6 — HS — WJTE (as symm in e_g)
LS — No JTE

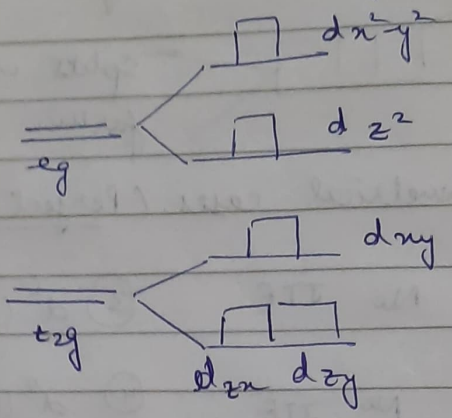
⑦ d^7 — HS — WJTE
LS — SJTE

⑧ d^8 — HS — No JTE
LS — No JTE

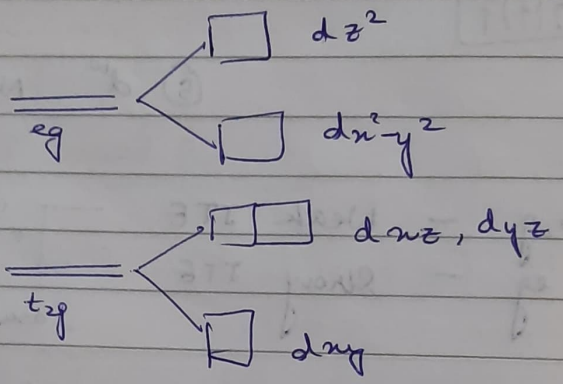
SPLITTING OF t_{2g} & eg [~~only for 3d~~]

① Elongation

~~only~~



② Compression



→ Distorted octahedral structure is also called Tetragonal

→ If dz^2 contains more e^- than $d_{x^2-y^2}$, then ligands approach along $+z$ & $-z$ will encounter greater repulsion, than other 4 ligands. This is called Tetragonal Elongation.

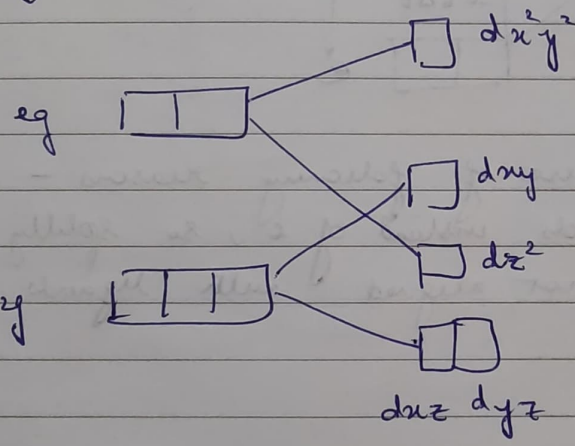
If dx^2-y^2 contains extra e^-, then elongation will occur x & y axes. This means that ligands approach more closely along z axis. There will be 4 long bonds, 2 short bonds. This is equi to compression along z axis and is called tetragonal compression.

→ Tetragonal elongation is more common than tetragonal compression, and it is not possible to predict which will occur.

SQUARE PLANAR

→ consider d^8 ↑↓ ↑↓ ↑↓ ↑ ↑ | | | |

As ligands approach, single e^- in $d_{x^2-y^2}$ is repelled by 4 ligands, but single e^- in d_{z^2} is repelled by only 2 ligands. ∴ Energy of $d_{x^2-y^2}$ increases relative to that of d_{z^2}. If ligand field strength ↑, ~~Δ~~ and > P, then in that case both e^- occupy d_{z^2} orbital. 4 ligands can now approach from ±x, ±y without any diff as $d_{x^2-y^2}$ is empty, but ligands from ±z can't approach due to strong repulsion from d_{z^2}. So only 4 ligands succeed in bonding to the metal.



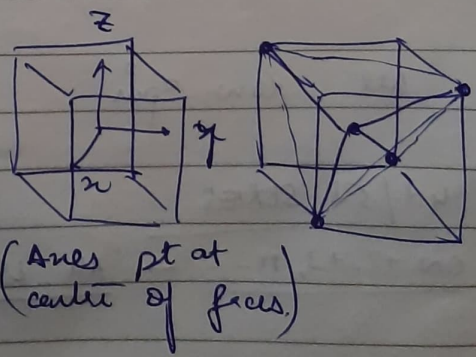
The d_{z^2} orbital may lie below the d_{xz} & d_{yz} orbitals in square planar complex.

→ Square planar is the limiting case of tetragonal elongation.

→ Square planar can also arise from d^4, WFL/MS.

TETRAHEDRAL COMPLEXES

→ Dirⁿ of approach of ligands does not coincide with either of eg or t_{2g} orbitals.



(Axes pt at centre of faces)

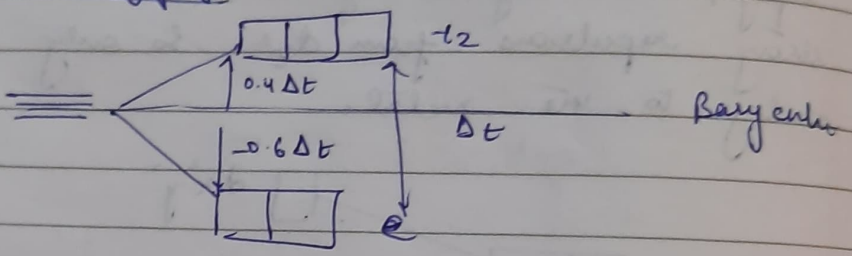
(Atoms/ligands along alt corners of cube)

→ ∠ b/w an eg orbital, & CA, & ligand is = $\frac{1}{2}$ tetrahedral ∠ (from diagram) = $\frac{109°28'}{2}$ = 54°44'

∠ b/w t_{2g} orbital, CA & ligand is = 35°16'

→ g subscript from t_{2g} & eg is dropped in case of tetrahedral complexes, as they lack symmetry. They are called t_2, e.

→ t_2 orbitals are closer than e orbitals, to ligands. So Energy of t_2 > Energy of e.



→ $\Delta_t = \frac{4}{9}\Delta_o$ Because of following reasons –
① There are 4 ligands instead of 6, so splitting becomes $\frac{4}{6}$
② Diff of orbitals not aligned with ligands, so further reduces by $\frac{2}{3}$.

FOR ON = 4 3d SERIES

ON +2 $d^1 - d^7$ $\Delta_t < P$ So all HS

d^8, d^9 $I^- < Br^- < \cdots < H_2O < NH_3 < en$

HS LS

ON +3, +4 All Low spin

4d / 5d SERIES

ON +2, +3, +4 — All LS

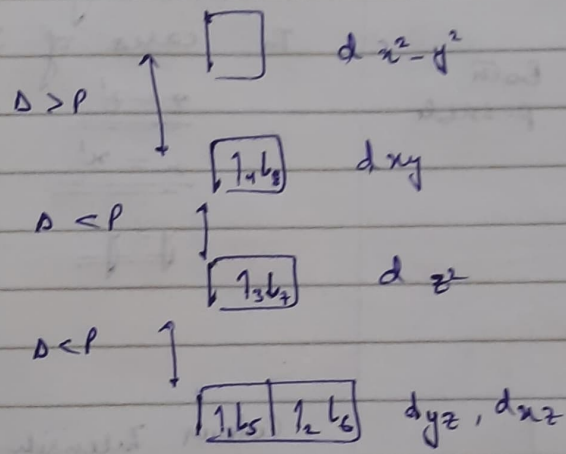
MORE ABT DISTORTIONS

Distortion

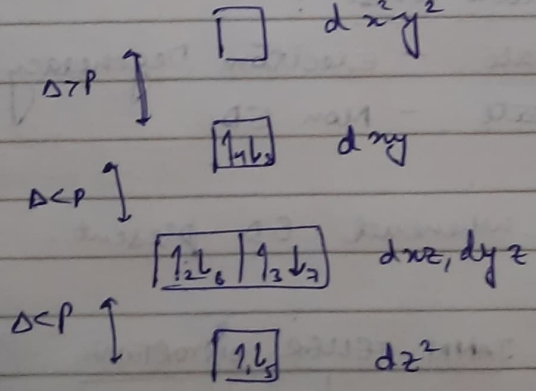
- **Due to ligands** — Ligando distortion
- **Due to Metal e⁻s** — Metallodistortion
  Also called **Jahn Teller Distortion**

SQUARE PLANAR

3d



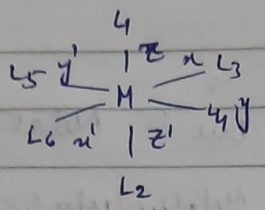
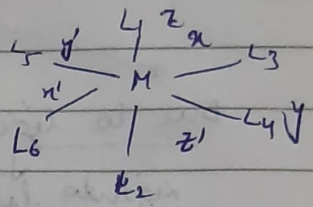
4d/5d



→ $\Delta_{sp} = 1.3\,\Delta_o$

Now, Ligando distortion > Metallo distortion

Diff b/w Ligando & Metallic

LGD	Metallic
	
① Not Thermodynamic	Thermodynamic
② Arises whenever diff ligands attached	Arises due to EC of metal. A complex may have LGD & JTD simultaneously
③ In case of LGD ~~z = z'~~ } Both possible $z \neq z'$ $x = x'$ } $x \neq x'$ $y = y'$ } $y \neq y'$	In cases of JTD, $z = z'$ $x = x'$ ~~$y = y'$~~
④ Colour intensity ↑	Colour intensity ↑

How does Distortions arise?

Unsymm e^T state – Electron Degeneracy

~~Unsymm~~ t state – Non ED

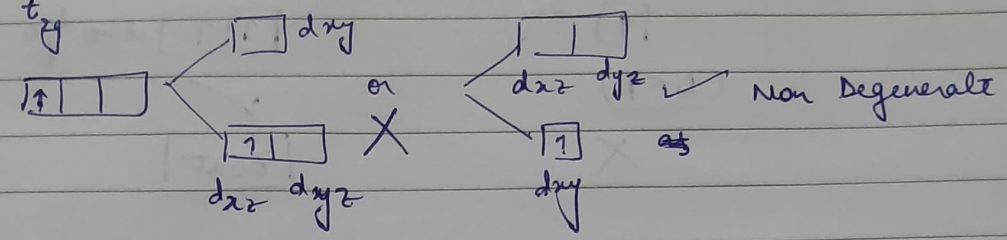
Distortions arise whenever ED present.

JAHN TELLER DISTORTION

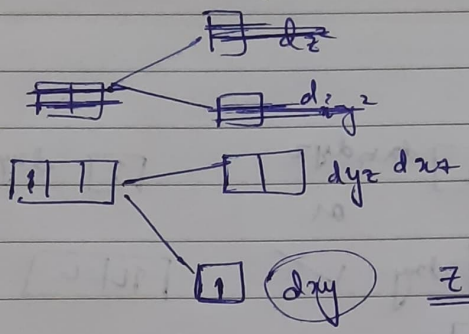
- Z out
- Z in
- Trigonal Dis. (2-2-2)

When Zout & When Zin ?

① $d^1 - t_{2g}^1$

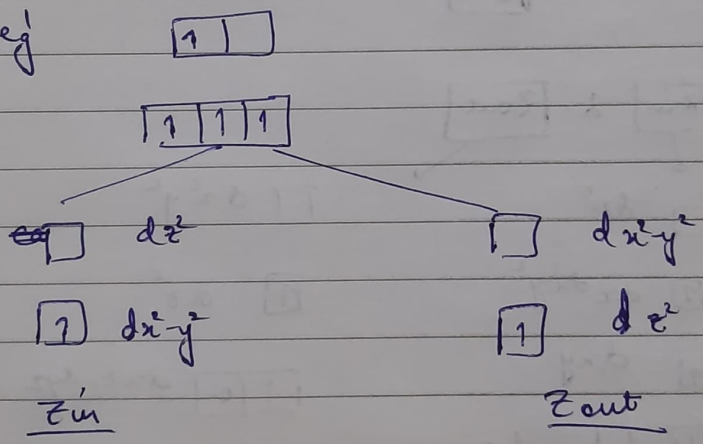


&



Zin

② $\frac{d^4}{HS} - e_g^1$

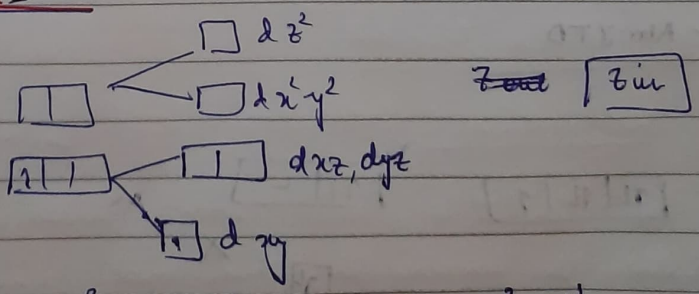


Zin Zout

→ Zin, Zout both possible, but Zout dominates

CASEWISE JTD

① $d^1 - t_{2g}^1$



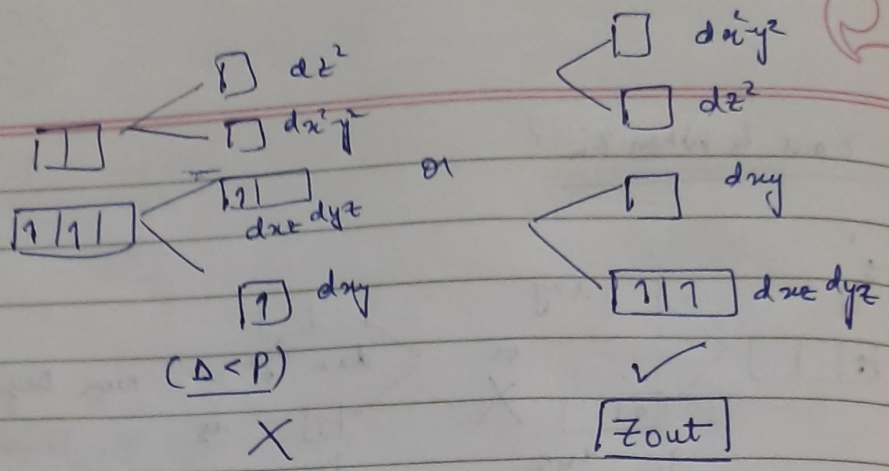
~~Zout~~ Zin

example : $[TiCl_6]^{-3}$ Ti^{+3} Ti : $4s^2\ 3d^2$ Ti^{+3} : $4s^0\ 3d^1$

⇓

Zin

② d^2

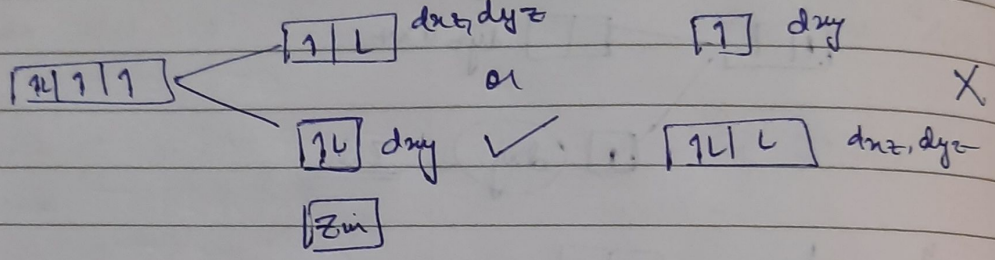


③ d^3 – No JTD

④ d^4

LS

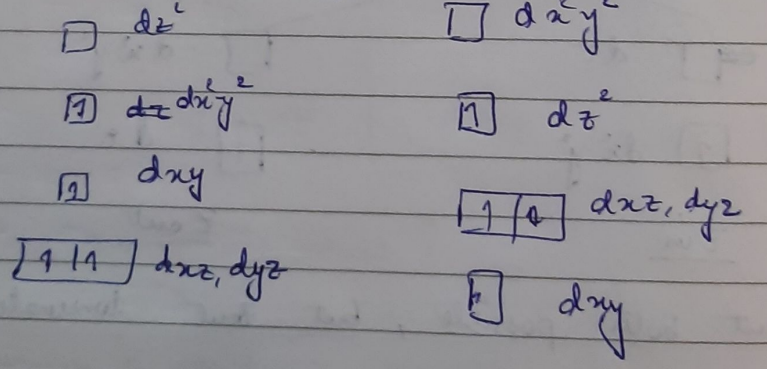
t_{2g}^4



HS

t_{2g}^3 e_g^1

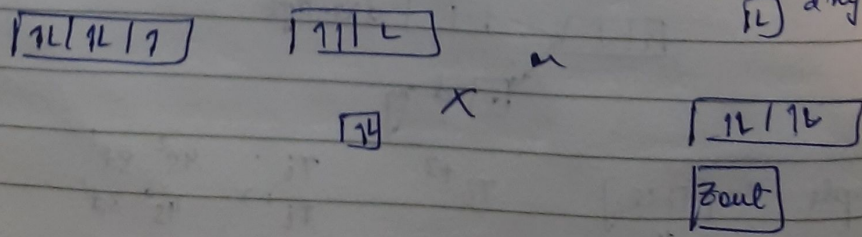
Both Zin & Zout



⑤ d^5

HS – No JTD

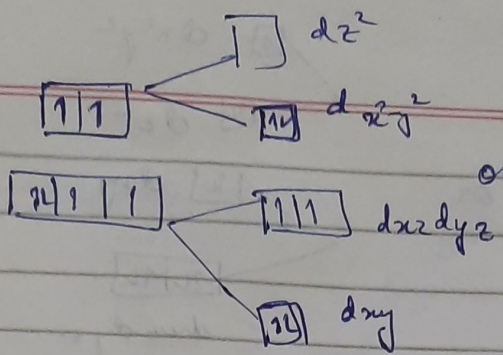
LS



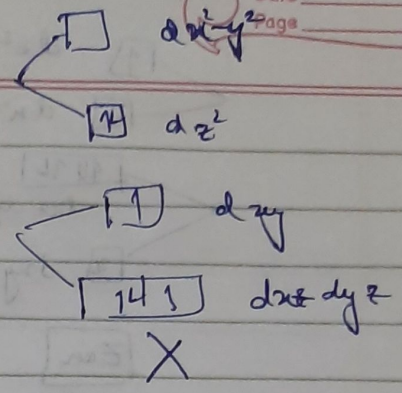
⑥ d^6

LS – No JTD

HS



or

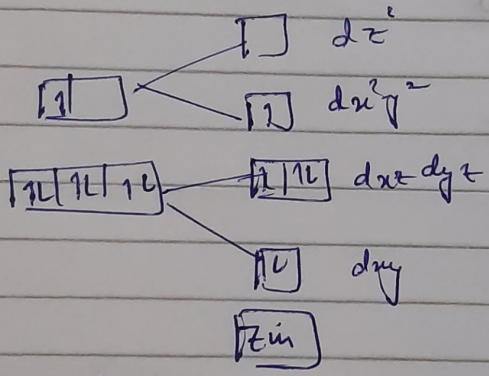


[d_{z^2} is in very high energy state, so 3e⁻ of t_{2g} come in $d_{x^2-y^2}$]

Zin

(7) d^7

LS



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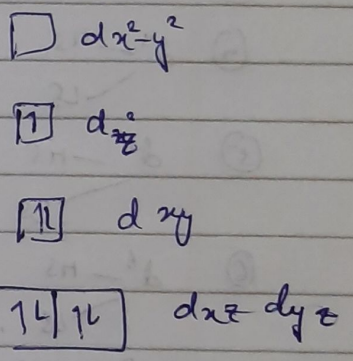
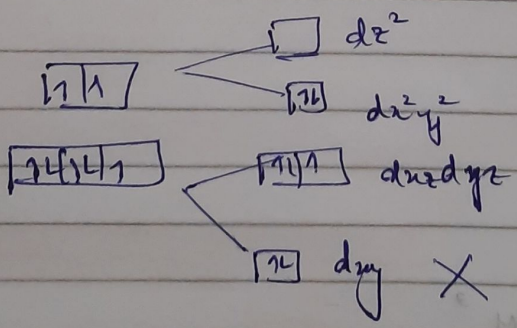


Zin

Zout

→ Both Zin & Zout

HS



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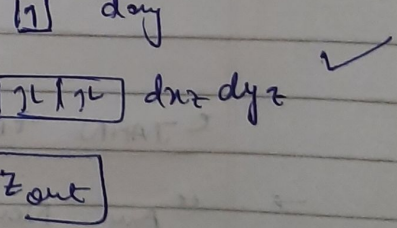
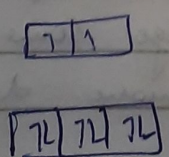


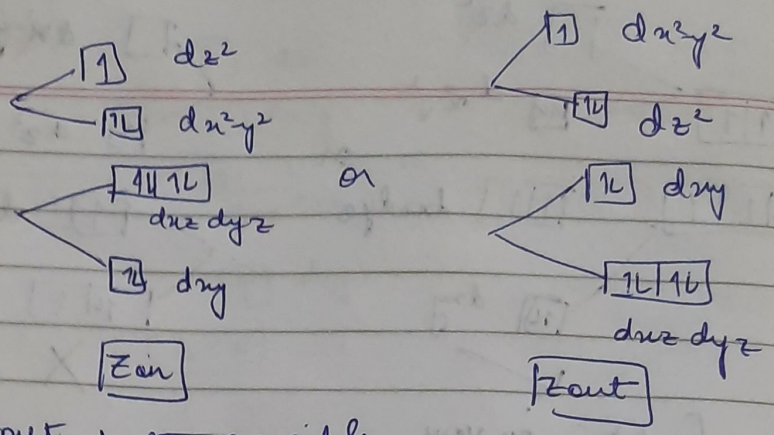
Zout

(8) d^8



No JTD

(9) d^9 t_{2g}^6 e_g^3



→ Zin, Zout both possible.

FINAL LIST

① d^1 — Zin

② d^2 — Zout

③ d^3 — No JTD

④ d^4 — HS — Zin, Zout
LS — Zin

⑤ d^5 — HS — No JTD
LS — Zout

⑥ d^6 — HS — Zin
LS — No JTD

⑦ d^7 — HS — Zout
LS — Zin, Zout

⑧ d^8 — No JTD

⑨ d^9 — Zin, Zout

⑩ d^{10} — No JTD

"JAHN TELLER THEOREM"

→ "Any Non linear Molecular sys. in a degenerate e⁻ state will be unstable, and will undergo some sort of distortions to ~~lowers its sym, and~~ remove degeneracy".

→ $[Ag(NH_3)_2]^+$ does not show JTD as it is linear.

→ JTD $\propto$ (% of π)

So not applicable in square planar

JTD in tetrahedral & square pyramidal, but it is very less.

★ $[Ni(CO)_4]$ $\quad Ni^0 : 3d^8\ 4s^2$