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Metal halide clusters

1. Metal are in higher formel oxidation states +2, +3. so these are higher valency type.
2. These clusters are shown by metals having high energy of atomisation (High mp & BP)
3. most refractory metals like (Zr, Nb, Mo, Re, Ru, Rh, Os, Ir, Pt) have greater tendency to form clusters.

"Transition metal halide clusters are prevalent for the heavier metals - Zr, Hf, Nb, Mo, Ta, W & Re.. for the earliest metals Zr & Hf, interstitial carbide ligand also common. e.g. Z_6CCl_{12}."

In this type clusters, chemical bondis is metal-metal (M-M) bonding like carbonyl clusters. i.e metallic bonding occurs within metals. This type bonding is formed between +vely charged atom in which the free e's are shared among a lattice of cation. Mettalic bond examples are: Fe, Co, Ca, Mg, Ag, Au, Ba, Pt, Cr, Cu, Zn, Hg etc

Preparation of M-halide clusters

1. $3Zr(s) + ZrCl_4(g) \xrightarrow{600°-800°C} 4ZrCl(s)$

2. $MoCl_5(s) + Al(s) \xrightarrow{NaAlCl_4/AlCl_3(l),\ 200°C} MoCl_2(s) + AlCl_3(l)$

Structures & types & Bonding of halide clusters

1. Dinuclear clusters
2. Trinuclear "
3. Tetranuclear "
4. Hexanuclear "

Dinuclear clusters -

e.g. 1. $[Re_2X_8]^{-2}$ where $X = Cl^-, Br^-, I^-$

2. $[Mo_2Cl_8]^{-4}$

* Structure of octachlorodiRhenate (III) ion $[Re_2Cl_8]^{-2}$

Re oxidation state = +3

One Re^{+3} = ... $5d^4 6s^0$

* Quadruple bond between Re(III) - Re(III)
(i.e four)

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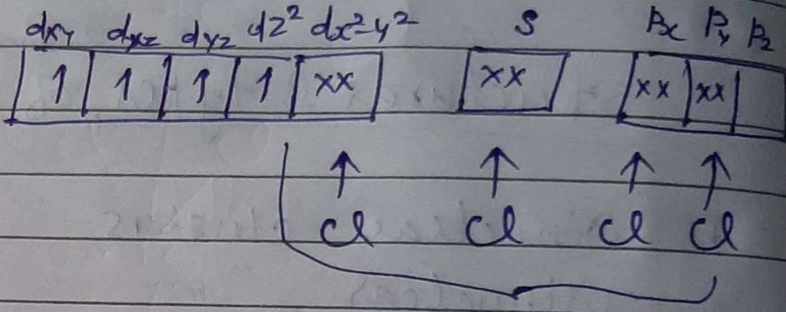
(one σ, two π and one δ-bond (delta))

Each Re (III) ion — dsp^2 hybridization

↓

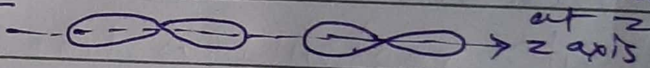
sq. planer geo.

each Re(III) = $5d^4 6s^0$



dsp^2 hybridization

* dz^2 & p_z orbitals (There situated at same direction at z axis)



↓ Hybridization

Two orbitals

One in direction of same orbital on other rhenium atom

↓

σ-bond

(same direction so formed covalent bond of 2 Re atom)

Not overlap due to lies in opposite direction & remain as Non-bonding orbital

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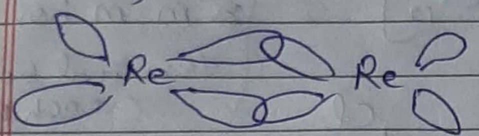
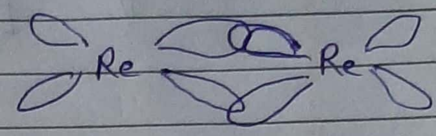
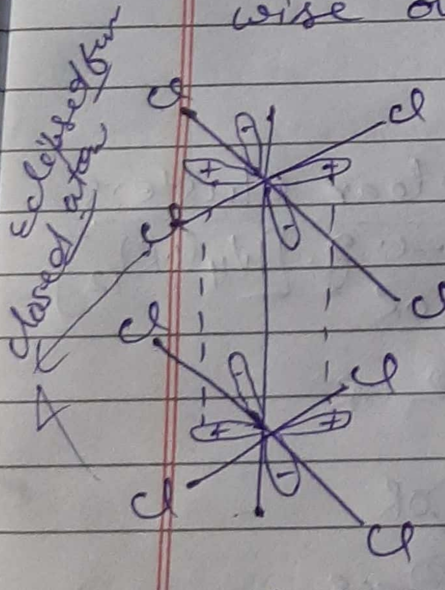
* d_{xz} & d_{yz} → directed obliquely towards their counterpart on other Re atom.
(one of Re-atom & other Re atom)





formation of π bond (sidewise overlapping) (in front or close)
(2π - formed)

* dxy orbitals – when Cl^- atom are eclipsed, the d_{xy} orbital of two Re-atoms will also be in eclipsed form and side-wise overlapping gives rise to δ-bond.



$d_{z^2} - d_{z^2}$ – σ-bond

$d_{xz} - d_{xz}$ – π-bond

$d_{yz} - d_{yz}$ – π-bond

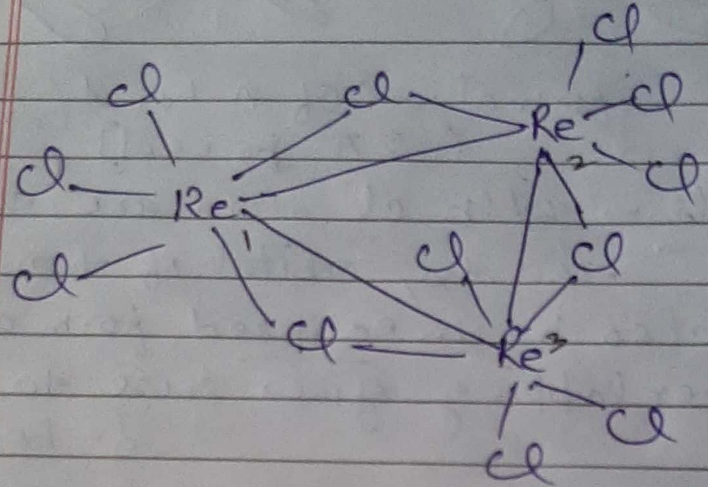
$d_{xy} - d_{xy}$ – δ-bond

formation of δ-bond must be eclipsed form

Str. of $[Re_2Cl_8]^{-2}$ is sq. planer geometry and 4 type bond are formed.

* Structure of trinuclear cluster

e.g. $[Re_3Cl_{12}]$

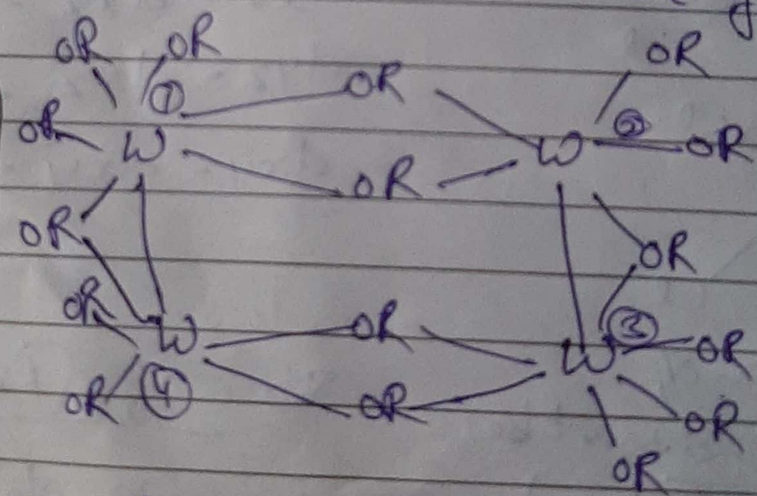


M-M bond = 3
terminal bond = 3 (each Re atom)
bridging bond = 3

* Structure of Tetra Nuclear clusters

e.g. $[W_4(OR)_{12}]$

M-M bond = 2
bridging bond = 6
terminal bond = 10



Hexa Nuclear clusters examples

e.g. $[Mo_6Cl_{12}]$, $[Mo_6Cl_8]Cl_4$

★ from stru [Re_3Cl_{12}] (Trinuclear clusters)

1. bridiging bond → $Re_1 - Re$, $Re_2 - R_3$, $R_3 - R_1$
(Re – Cl – Re) = 3

2. Direct bond (m–m) → $Re_1 - R_2$, $Re_2 - R_3$, $R_3 - R_1$
(Re-Re) = 3

3. terminal bonds → Re_1–Cl, Re_1–Cl, Re_1–Cl, Re_2–Cl, Re_2–Cl
(Re – Cl) Re_2–Cl, Re_3–Cl, R_3–Cl, Re_3–Cl
= 9 or (3 in each Re-atom)

★ from Tetranuclear cluster [$W_4(OR)_{12}$]

1. Bridging bond (W – OR – W) $W_1 - W_2$, $W_1 - W_2$,
$W_2 - W_3$, $W_3 - W_4$, $W_3 - W_4$, $W_4 - W_1$
= 6 (2 b/w W_1 & W_2, 2 b/w W_3 & W_4, 1-1 b/w $W_1 - W_4$ & $W_2 - W_3$)

2. Direct bond (W–W) – $W_1 - W_4$ & $W_2 - W_3$
= 2

3. Terminal bond (W–OR) – W_1–OR, W_1–OR, W_1–OR, = 3
W_2–OR, W_2–OR, = 2
W_3–OR, W_3–OR, W_3–OR = 3
W_4–OR, W_2–OR = 2

Total = 10