Toppersnotes
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CSIR-NET

Council of Scientific & Industrial Research

CHEMICAL SCIENCE

VOLUME - III

INORGANIC CHEMISTRY

SIERRA INNOVATIONS

Index

Polyhedral skeleton e⁻ Pair Theory :- (PSEPT)

→ The polyhedral skeleton e⁻ Pair theory relates the 3-D structure of polyhedral mc. to the total no. of valence e⁻s.

For Transition Element Complexes

Q. Identify geo. of Central Core in given Cluster?

① $[Fe_5C(CO)_{15}]$

② $[Ru_6C(CO)_{17}]$

③ $[Co_4(CO)_{12}]$

④ $[Rh_6C(CO)_{15}]$

⑤ $[Co_3CH(CO)_3]$

⑥ $[Os_5(CO)_{16}]$

⑦ $[Fe_4(CO)_{12}C]^{-2}$

⑧ $[Os_4(CO)_{16}]$

⑨ $[Os_3(CO)_{12}Br_2]$

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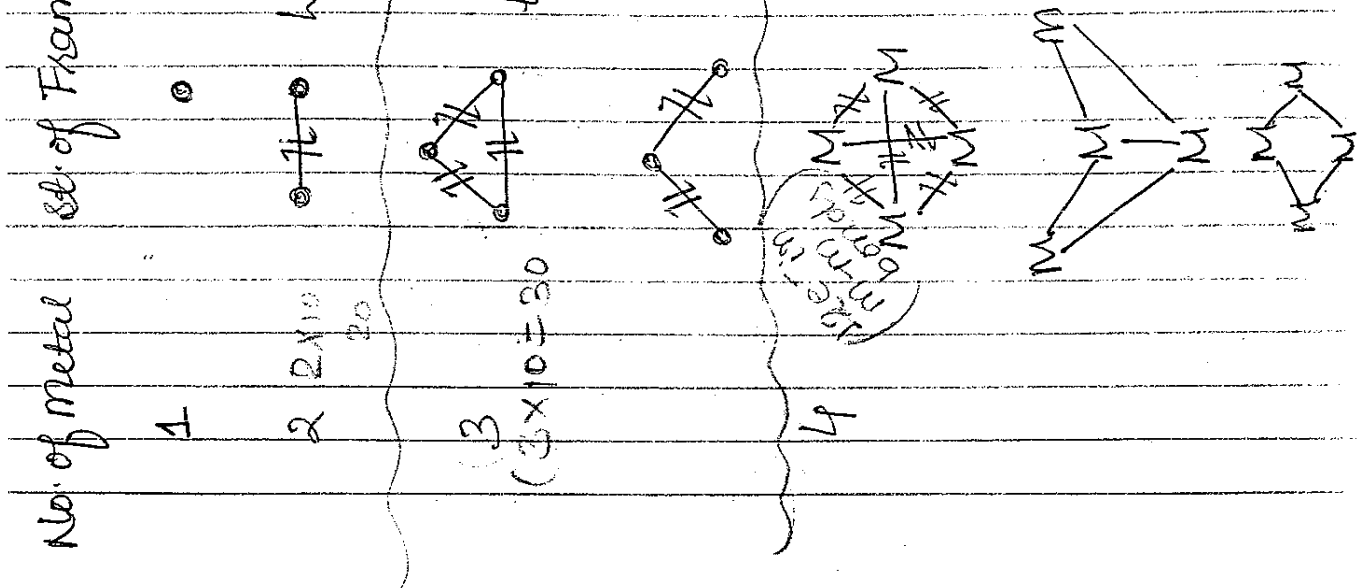
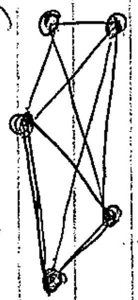
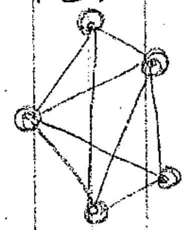
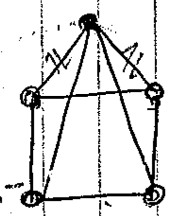
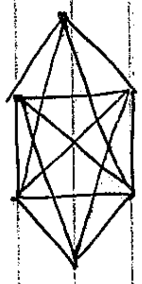
Q. Correct geo. of $[Rh_6C(CO)_{15}]^{-2}$

(a) Oh
(b) Pentagonal Py.
(c) Trigonal Prism
(d) Monocapped sq. Py.

No. of Metal	Str. of Framework	(EVEN) Cluster valance e⁻	Eg:
1	•	18 e⁻	$[Ni(CO)_4]$, $[Fe(CO)_5]$, $[Cr(CO)_6]$
2	linear	34 e⁻ 34 + 20	14
3	close triangle	48 e⁻ 30 | 18	18
4	open Δle	50 e⁻ = 200 e⁻ 50 − 30 = 20 18 × 4 Metals = 72 72 − 12 e⁻ = 60 e⁻	20
	Tol	60 e⁻ 60 + 40 = 20	20
	Butterfly	62 e⁻ 62 − 40	22
	Sq. Planar	64 e⁻	24



No. of M			Structure	TVE
5 $5 \times 10 = 50$	$18e^-$ in M–M Bond 9 M–M Bonds hai		TBP 	72 $72 - 50 = 22$
	8 M–M Bonds $2 \times 8 = 16e^-$ in M–M Bond		Sq. Py.	$74e^-$ $74 - 50 = 24$
6			Oh	$86e^-$ $86 - 60 = 26$
			Trigonal Prismatic	$90e^-$ $90 - 60 = 30$

$[Rh_6C(CO)_{15}]^{2-}$

$9 \times 6 + 4 + 2 \times 15 + 2$

54
+ 4
30
2

90

TVE = 90

∴ Trigonal Prism

		TVE		
7.	Pentagonal Bipy.	100e⁻	100 − 70 = 30e⁻	(No. of m × 10) को minus करना है TVE से।
exception 10	Bicapped sq. Antiprismatic	142e⁻	142e⁻ − 100 = 42e⁻	
12	Icosahedron	170e⁻	170 − 120 = 50e⁻	(Transⁿ m = 18, main gp = 8, 18 − 8 = 10)
8	Dodecahedron	114e⁻	114 − 80 = 34e⁻	
8	Cubic / Cubane	120e⁻	120e⁻ − 80 = 40e⁻	
exception 9	Tricapped trigonal Prismatic	128e⁻	128e⁻ − 90 = 38e⁻	
11	Octahedron	156e⁻	156e⁻ − 110 = 46e⁻	

Identify geo of central atom in the clusters.

① $[B_5H_5]^{-2}$ ⑥ Si_4^{-4} ⑪ C_4H_4

② $[C_2B_3H_5]$ ⑦ Tl_5^{-7} ⑫ C_6R_6

③ Pb_5^{-2} ⑧ $C_2B_{10}H_{12}$ ⑬ $C_2B_7H_9$

④ $B_6H_6^{-2}$ ⑨ $C_2B_8H_{10}$ ⑭ $B_8H_8^{-8}$

⑤ $B_7H_7^{-2}$ ⑩ C_8H_8 ⑮ Sn_5^{-2}

⑯ Tl_6^{-8} ⑱ $C_2B_6H_8$ ⑳ Ge_{10}^{-2}

⑰ $C_2B_5H_7$ ⑲ $TlSn_8^{-3}$

$(B_5H_5)^{-2}$

5 Metal → 8 M–M Bond TVE = 3×5 + 5 + 2

TVE = 22 = 22

① Trigonal Bipy.
② TBP (C off metal E1)
③
④ Oh
⑤ P
⑥ Td
⑦ TBP
⑧ Icosahedron
⑨ Bicapp. sq. Anti
⑩ Cubane
⑪ Td
⑫ Trigonal Prismatic
⑬ Trigonal Tricapp. Prism.
⑭ Cubane
⑮ TBP
⑯ Oh
⑰ Pentagonal Bipy
⑱ Dodecahedral
⑲ Tricapp. trigonal Prism
⑳ Bicapp sq. Anti.

Cal. of TVE for condensed Cluster :-

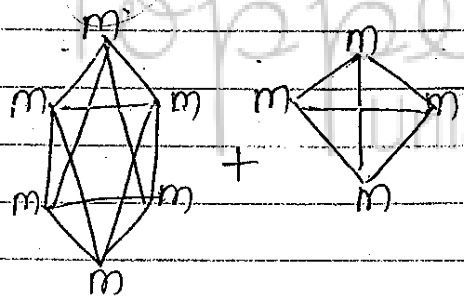
Q. Oh + Td ⟶ Monocapped Oh
TVE = ?

Q. Td + Td + Td ⟶ Bicapped Td
TVE = ?

Q. Trigonal Prismatic + sq. Py + sq. Py + sq. Py ⟶ ? ; TVE = ?

Q. Sq. Py + Td ⟶ ? ; TVE = ?

Sol^n. ① Oh + Td ⟶ Monocapped Oh

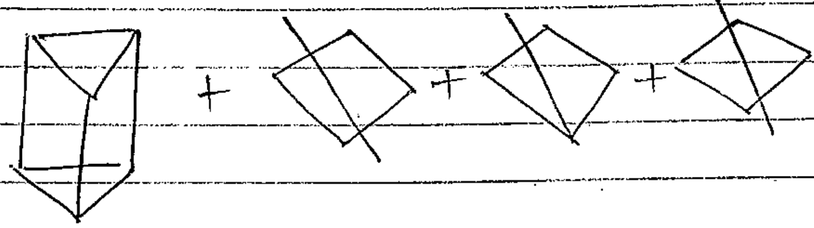


उनके पृष्ठ के बाद (close Δ) part common है ∴ उसको हटा दो

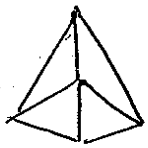
की ↓

$86e^- + 60e^- - (48e^-) = $ TVE 98

③ Trigonal Prismatic + sq Py + sq. Py + sq Py



90 + 64 + 64 + 64 − (64×3) =
common
sq. Planar



(2) Td + Td + Td

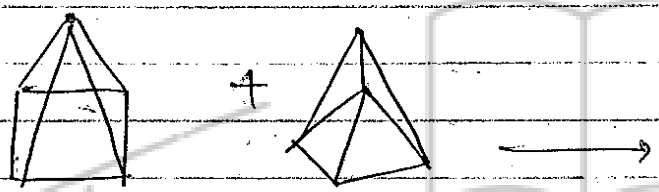
(60 + 60 + 60) − 48×2 = 180 − 96

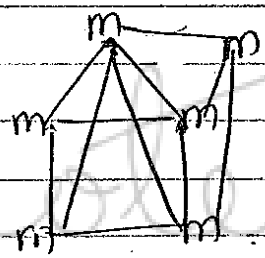
= (84e⁻ TVE of Bicapped Td)

(4) Sq. Py + Td (close Δ)

(74 + 60) − 48 = (86 ~~के~~ TVE)

Monocapped Sq. Py





74 | 134 | 2 | 14 | 86
60 | −48 |

Q: $[Co_6(CO)_{15}N]^- \xrightarrow{\Delta} [Co_6(CO)_{13}N]^- + 2CO$.

वें Borane ? | Borane = ? 2

geo ? Arachno | geo ? Closo

9×6 + 2×15 + 5 + 1

54 + 30 + 6 = 90

Trigonal Prismatic

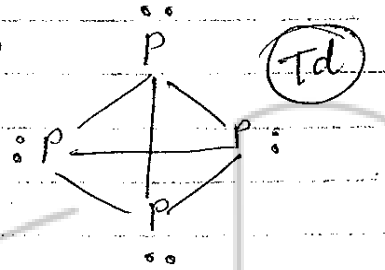
90 | 14 | 14n + 6 ⇒ Arachno.

2 | 14 | ×6 | 84

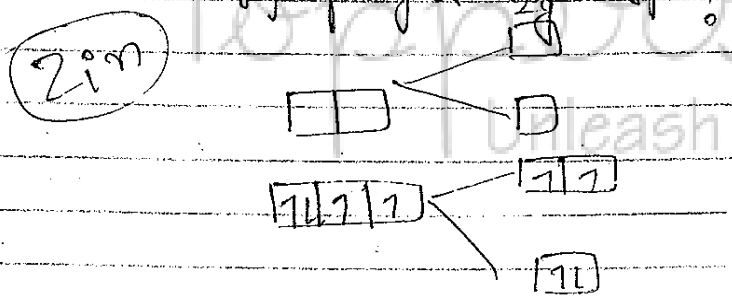
* Metal Carbonyls generally diamagnetic hote hai

** Benzene khud Nu$^{\ominus}$ hoti hai but metal $\overline{21}$ judne $\overline{dq}$ benzene $E^{\oplus}$ hojati h.
same for 1,3 butadiene.

** face + corner = edge + 2

$P_4 \rightarrow$ 

Q. Total stabilization energy of $[Cu(CN)_6]^{-4}$; splitting energy of e_g & t_{2g} resp ?



$-1.6\Delta_o + P - \frac{2}{3}\Delta_q$

1 decapping से 2e⁻ nikalteh.
2 —— " —— 4e⁻ —— " —— & so on . . . (TVE)

(C.N. ↓ होगा) decapping ← Closo → (C.N. ↑ होगा Closo से) Capping

Nido ← Closo → Hyper closo
↓ ↓
Arachno Superclosso

C.N 5, CN 6, C.N 7, C.N 8, C.N 9, C.N 10, C.N 11, C.N 12

S, H } Capping
Cl closo.
N, A, H, K } decapping

① $B_4H_6C_2$
② B_5H_9 (24e⁻) sq. Py.
③ $B_{12}H_{14}$ Icosahedron
☆ ④ $(\eta^5\text{-}Cp)\,Co\,B_4H_8$ (M)
⑤ $Fe(CO)_3\,B_4H_8$
☆ ⑥ $B_4H_8C_2$ — $B_4H_8B_2H_2$, B_6H_{10}, $B_6H_6^{-4}$ (Nido)

$12+8+8=$ (28e⁻)
ये Nido है 6 atoms का & Nido decapping से बनता है

Ans (Pentagonal bipy.)

① $B_4H_6C_2$
TVE $= 4\times3+6\times1+4\times2 =$ (26e⁻)
∴ oh

$\eta^5\text{-}Cp\;Co\;(B_4H_8)$ — $12+8=20$
$5+9=14$
can be replaced by 4
$20+4=$ (24e⁻) TVE ∴ sq. Py.

① Sbse phle TVE nikalo.
② Then Boron का type पता करो

→ यहां Nido aya jo decapping से बनता है & reference closo को मांगते हैं। ये 6 atoms का nido है ∴ closo 7 atom का sha hoga

& 7 पे hota h pentagonal bipy ∴ 6 atoms k liye penta. Pyramidal

Exception :- $H_2[Os(CO)_4]_4$

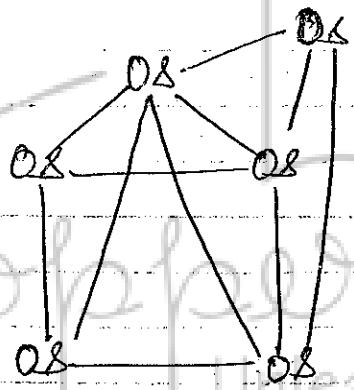
** $[H_2Os_6(CO)_{18}]$

logically ✓ hona chahiye tha / But nae hota ∴ oh closo

86e⁻

But ✓ hota ✓ monocapped sq. pyrimidal

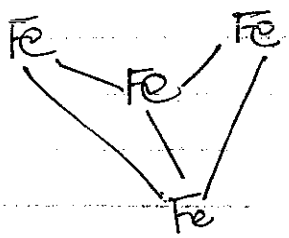
Capped Nido



** $[Fe_4(CO)_{13}H]^{\ominus}$

60e⁻
Td
Nido

Butterfly
Arachno



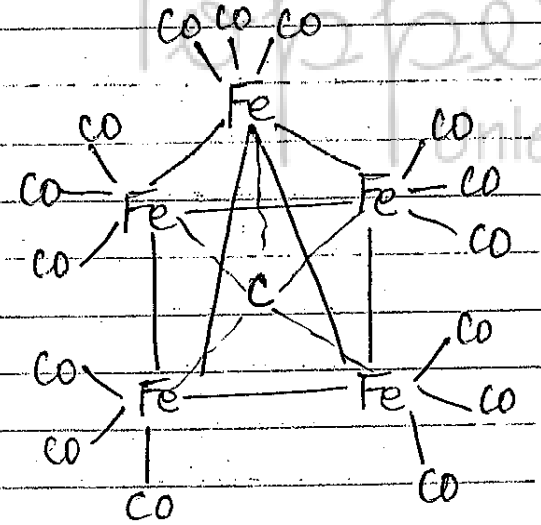
Encapsulated Clusters :-

→ In such type of clusters, some atoms such as C, N, P, H, are present in the cavity of cluster.

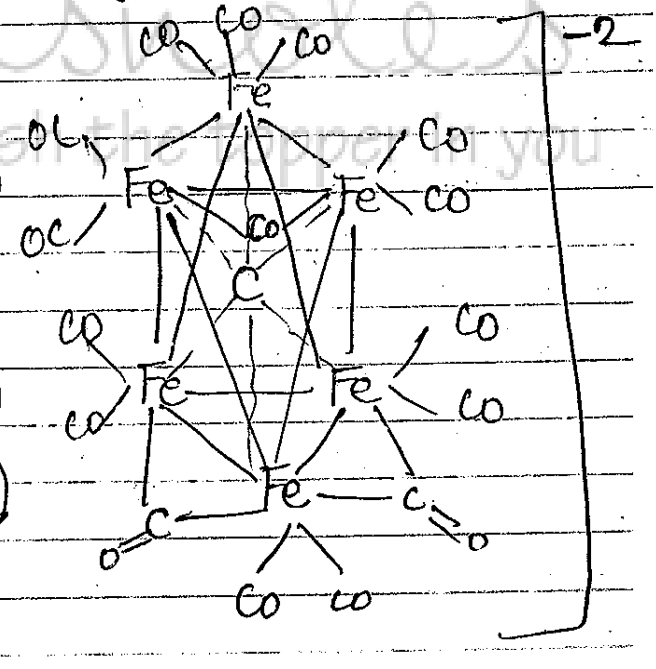
→ If encapsulated species are C, N, P, H then the no. of e⁻s contributed by them are :-

- C → 4
- N → 5
- P → 5
- H → 1

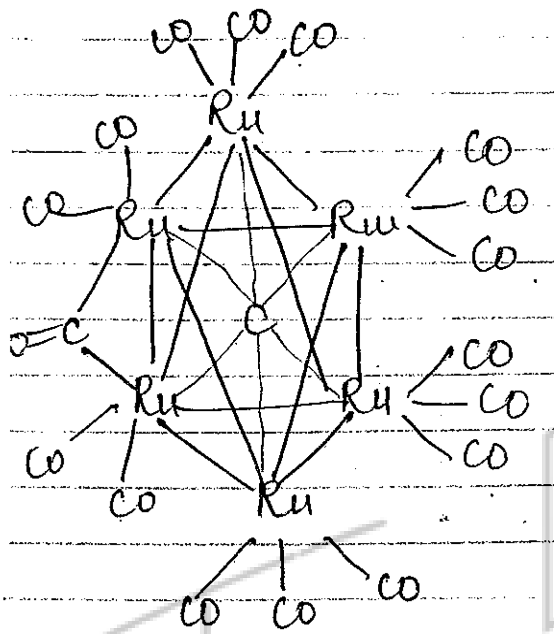
eg : $[Fe_5C(CO)_{15}]$



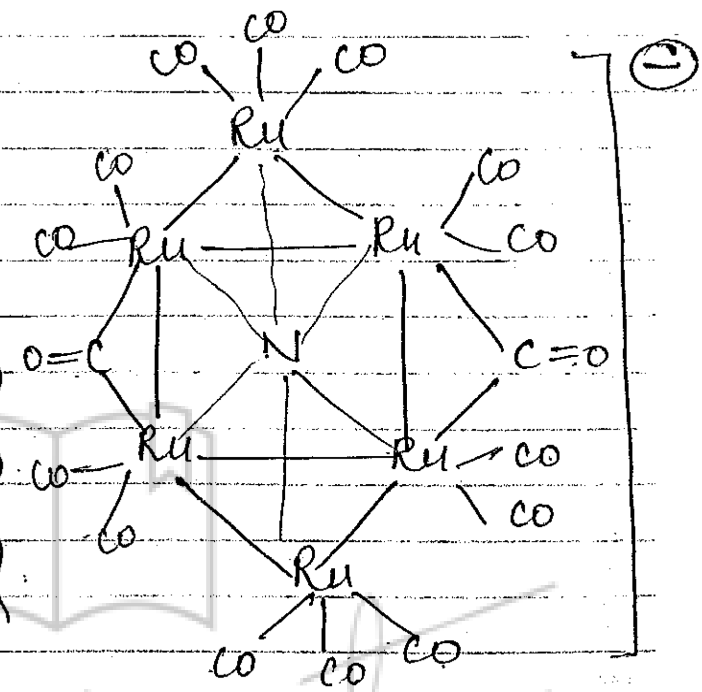
eg : $[Fe_6C(CO)_{16}]^{-2}$



eg [$Ru_6 C(CO)_{17}$]



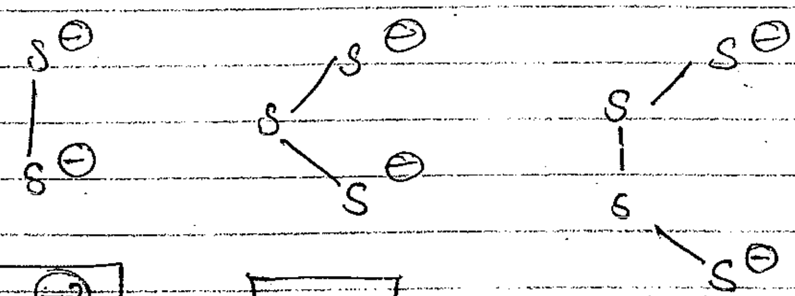
eg: [$Ru_6 N(CO)_{16}$]$^-$



Agr 1M, 2M (metal) के साथ Ⓝ है मतलब wo nitrido है & $3e^-$ dega but agr 5M, 6M k sath है N mtlb wo encapsulated है & $5e^-$ dega.

Sulphide Clusters:

→ Here polysulphide ion behewes as ligand.



S_2^{-2} S_3^{-2} S_4^{-2}

(S_2, S_3, S_4 सभी पे -2 charge होता है।)

eg: $[Mo_2(S_2)_6]^{-2}$

$2x + (-2)\times 6 + 2 = 0$

$2x - 12 + 2 = 0$

$2x = 10$

$x = \frac{10}{2} = +5$

-2

Bridge $S_2 = 2$

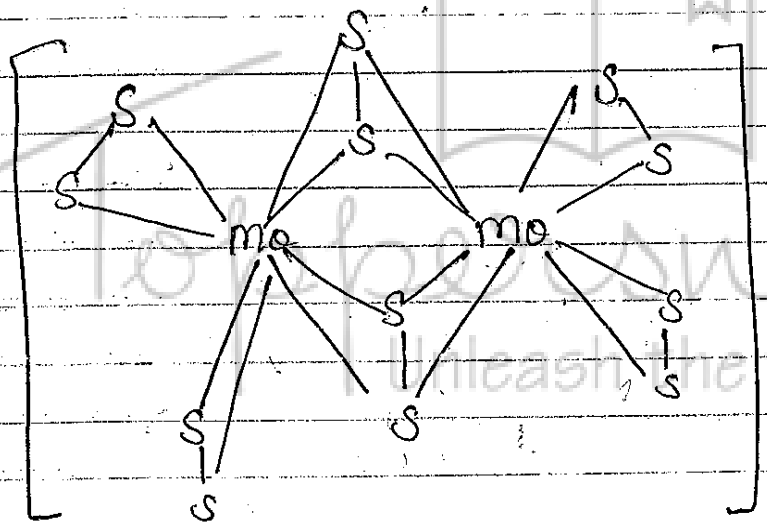
Terminal $S_2^{-2} = 4$

M–M bond = 0

M–S bond = 16

S–S bond = 6

C.No. of Mo = 8



(2)

eg: ~~[illegible]~~

$[Mo\,S(S_4)_2]^{-2}$

~~$x + 6 + (6\times 2) + 2 = 0$~~

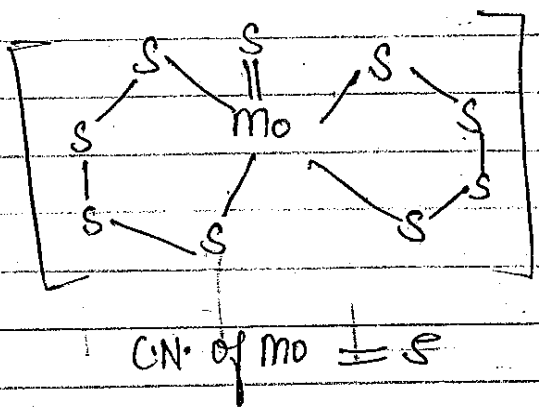
~~$x + 6 + 48 + 2 = 0$~~

~~$x + 56 = 0$~~

$x - 2 + (-2)\times 2 = -2$

$x - 6 = -2$

$x = +4$



-2

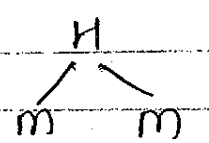
C.N. of Mo = 6

Hydrido Clusters :

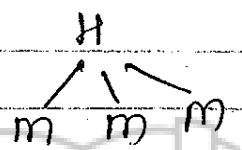
→ If in the Clusters only 1-H is Ont then it generally lies in the encapsulated form.

→ If more than 1-H or Hydrido ligand are Ont then exist as Bridging form.

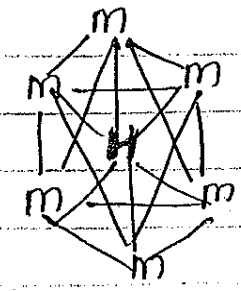
M—H ⇓ 2c-2e⁻



3c-2e⁻



4c-2e⁻



7c-2e⁻

Q. Among the following Clusters H is encapsulated in the following:-

P) $[HCo_6(CO)_{15}]$

Q) $[H_2Os_6(CO)_{18}]$

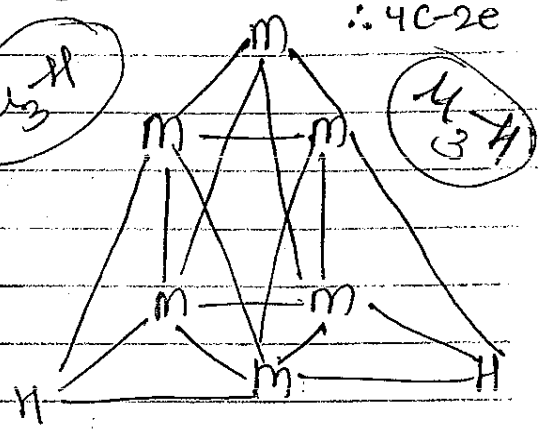
R) $[H_2Os_5(CO)_{16}]$

(A) P only (C) P & R

(B) P & Q (D) Q only

4c-2e⁻

Ans μ_3-H



∴ 4c-2e

$H_2Os_6(CO)_{18}$ } → $H_2M_6(CO)_{18}$

$H_2Ru_6(CO)_{18}$ }

Acidic Nature of Hydrido Metal clusters :-

$L_nM-H \xrightarrow{-H^+} (L_n)M^{\ominus}$ → ये EWG होगा (π-acc) होगा तो Stability ↑ hogi czwo max e⁻ lepaega.

conjugate acid ⇓ Acidic Nature ↑

conjugate Base ⇓ Stability ↑

** π-acceptor ligands ↑es (EWG), the acidic nature of H-atom in metal Hydrido Complex also ↑es.

→ As the σ-donating ligand ↑es, the acidic nature of H-atom in Metal Hydrido Complex ↓es.

Q. Arrange the following in ↓ing Order of Acidic Nature?

(Acidic Nature ∝ EWG)

ⓐ $[H\,Co(CO)_3(PF_3)]$

ⓑ $[H\,Co(CO)_3(PCl_3)]$

ⓒ $[H\,Co(CO)_3(PBr_3)]$

A > B > C

Note: Out of terminal & bridging hydride, bridging Hydrogen is more acidic than terminal.