# § 6 The polyatomic molecules (B)

## 6.1 Electron-deficient multi-center bonds

### 6.1.1 Boranes and their relatives

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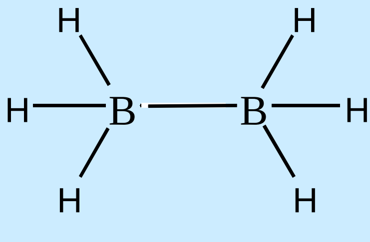
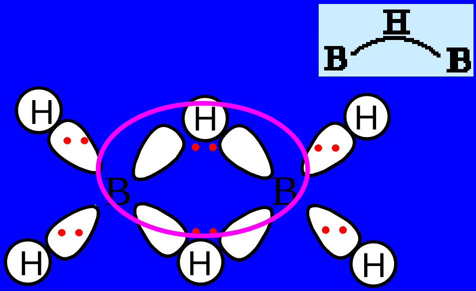
### i. $B_2H_6$





**B: 3 valence electrons forms 2 B-H bond**

three center two electron B-H-B bond:

$B: sp^3$ *hybridization*, $H: 1s$ *orbital*

$$\psi = C_a\psi_{B1} + C_b\psi_H + C_a\psi_{B2}$$

its seqular equation is:

$$\begin{vmatrix} E_B - E & \beta & 0 \\ \beta & E_H - E & \beta \\ 0 & \beta & E_B - E \end{vmatrix} = 0$$

$E_1 = E_H + c\beta$ (bonding)

$E_2 = E_B \quad (E_2 > E_H)$ (anti-bonding)

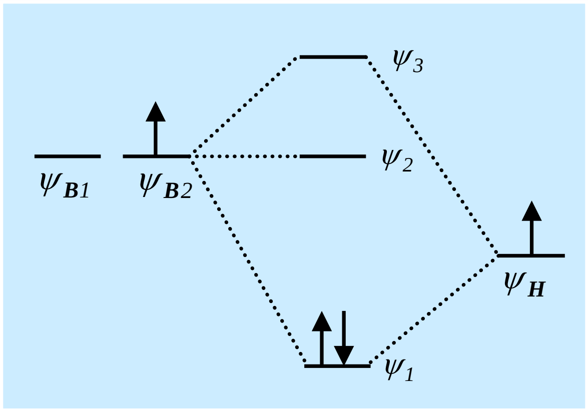
$E_3 = E_B - c'\beta$ (anti-bonding)

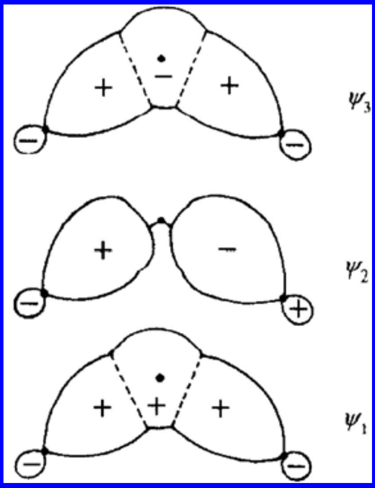
$$\psi_1 = \frac{1}{2}(\psi_{B1} + \sqrt{2}\psi_H + \psi_{B2})$$

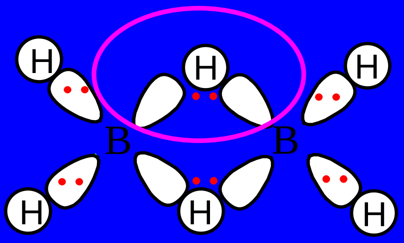
$$\psi_2 = \frac{1}{\sqrt{2}}(\psi_{B1} - \psi_{B2})$$

$$\psi_3 = \frac{1}{2}(\psi_{B1} - \sqrt{2}\psi_H + \psi_{B2})$$

## Three center two electron B-H-B bond:







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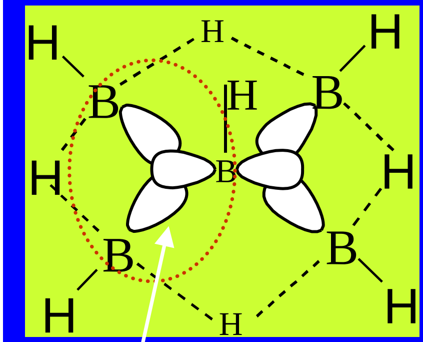
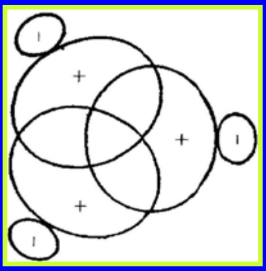
## ii. $B_5H_9$

Electron-deficient multi-center bonds





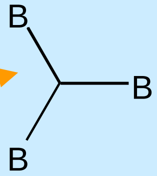
$$\begin{vmatrix} E_B - E & \beta & \beta \\ \beta & E_B - E & \beta \\ \beta & \beta & E_B - E \end{vmatrix} = 0$$

*solve* seqular equation

$$E_1 = E_B + 2\beta$$

$$E_2 = E_3 = E_B - \beta$$

$$\psi_1 = \frac{1}{\sqrt{3}}(\psi_a + \psi_b + \psi_a)$$

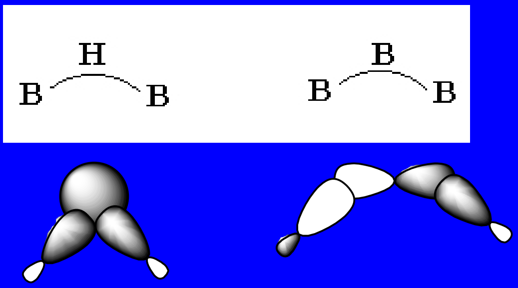


3center-2electron bonds

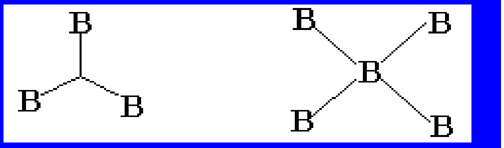
# Chemical bonds in Boranes

(a) Single bond B-H B-B

(b) 3center-2electron bonds



(c) Other polycenter-polyelectron bond



Electron-deficient multi-center bonds

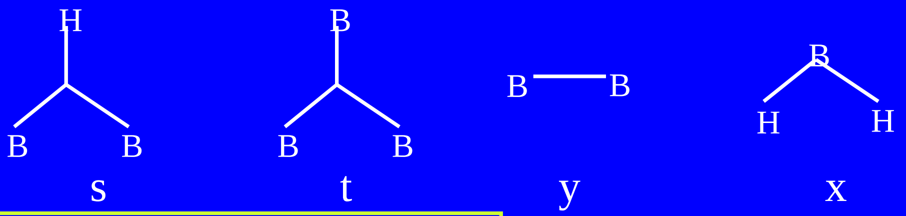
## 6.1.2 For $B_nH_{n+m}$'s open structure (including to nido and arachno)

n equals to number of B-H bonds

Its stationary condition:

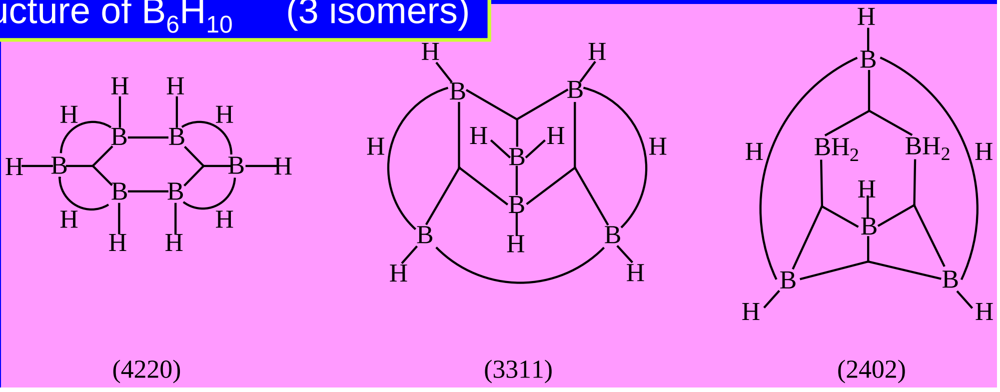
x = m-s
t = n-s
y = (2s-m)/2

⇨ p sets of styx ⇨ p isomers



The topological structure of $B_6H_{10}$ (3 isomers)

$B_nH_{n+m}$ (William Lipscomb) Nobel prize,1976



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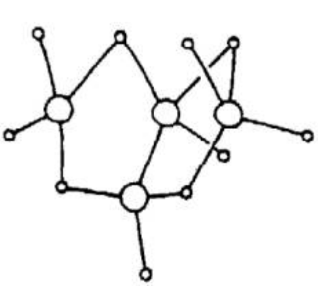
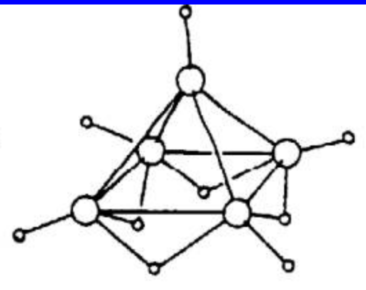
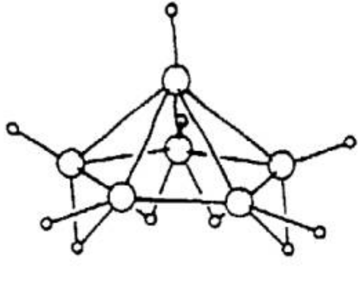
## Structure of Boranes



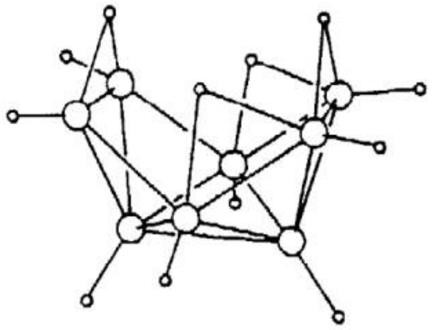
$B_4H_{10}$



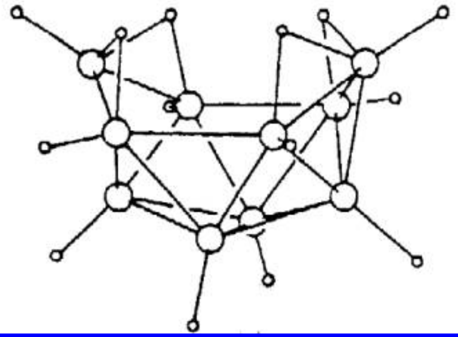
$B_5H_9$



$B_6H_{10}$



$B_8H_{12}$



$B_{10}H_{14}$

Electron-deficient multi-center bonds

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## 6.1.3 For Borohydride ions $B_nH_n^{2-}$’s closo structure and carboranes $C_nB_nH_{n+n'+m}$

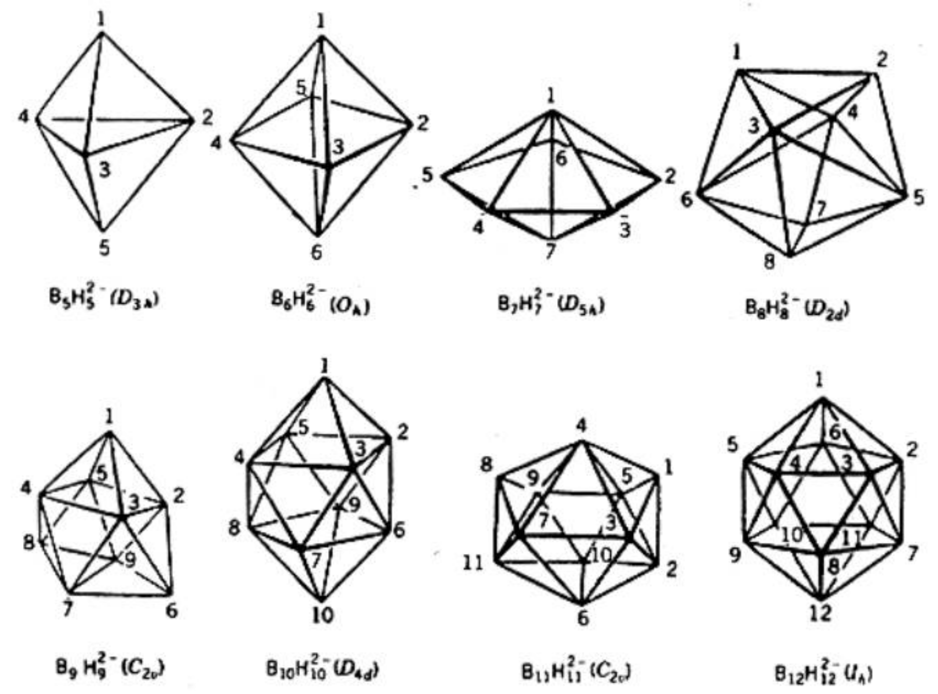
$B_nH_n^{2-}$(closo)

$B_4H_4^{2-}$( tetrahedral)

$B_6H_6^{2-}$(octahedral)

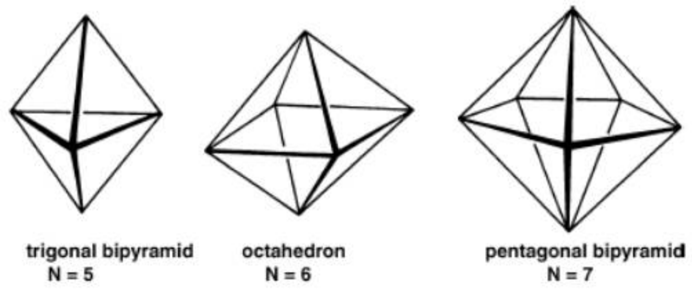
$B_8H_8^{2-}$(dodecahedral)

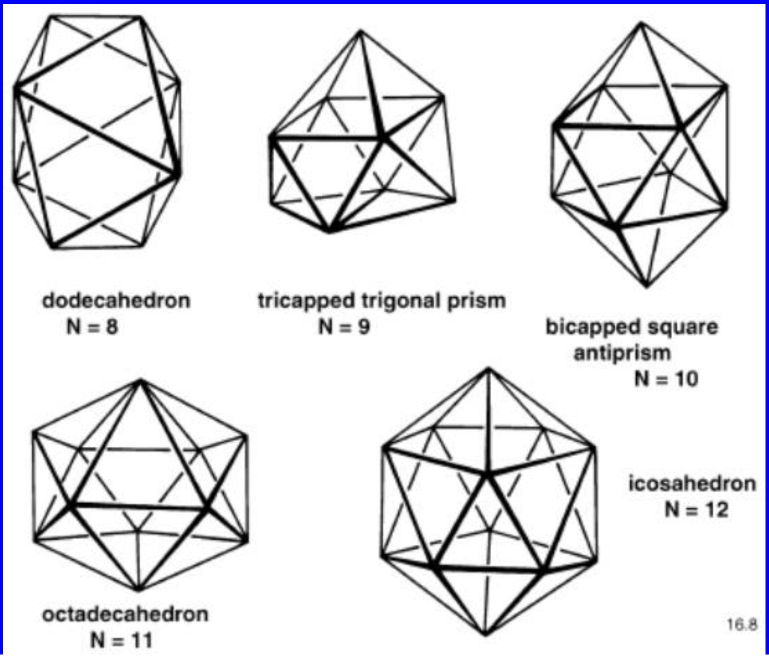
$B_{12}H_{12}^{2-}$(icosahedral)



Electron-deficient multi-center bonds

# polyhedra with n vertices





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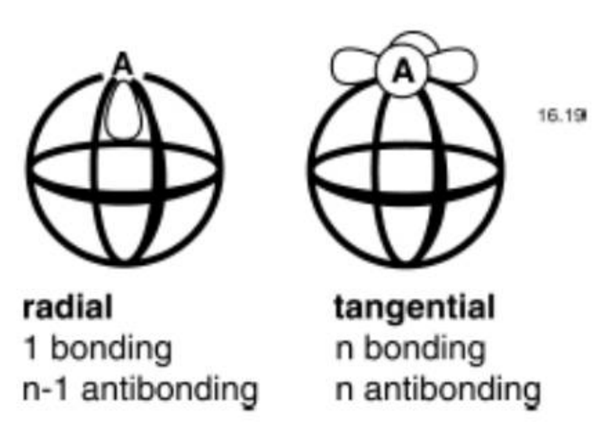
"Closo" series -formula $B_nH_n^{2-}$

Total valence electrons (CVE) = 3n (from B) +n (from H) +2 (negative charge) = 4n+2

- Each BH unit uses 2 electrons. Hence skeletal or framework electrons (NFE=4n+2-2n=2n+2)
- There is little tendency to add H+ and form neutral species. The closo species are , in effect, the anions of quite strong acids.
- Structures are those of the appropriate polyhedra with n vertices.

## MOs in "closo" series



n+1 bonding and nonbonding MOs

2n-1 antibonding

Notes: B-H σ orbital and its electrons are not taken into account

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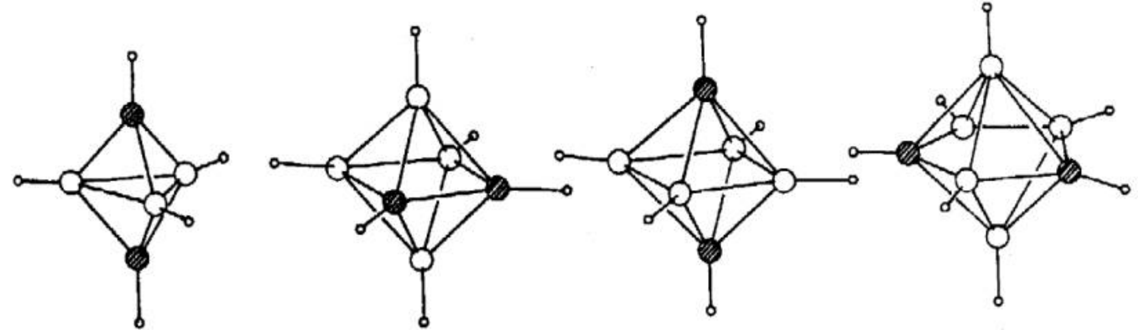
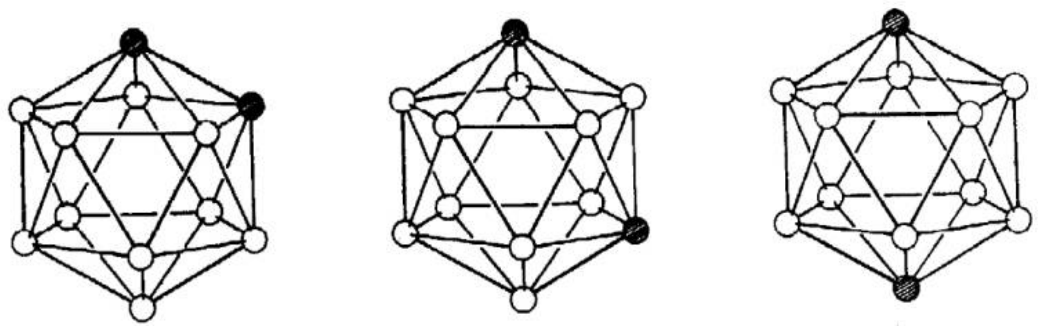
## Structure of Carboranes



1,5-$C_2B_3H_5$ 1,2-$C_2B_4H_6$ 1,6-$C_2B_4H_6$ 2,4-$C_2B_5H_7$



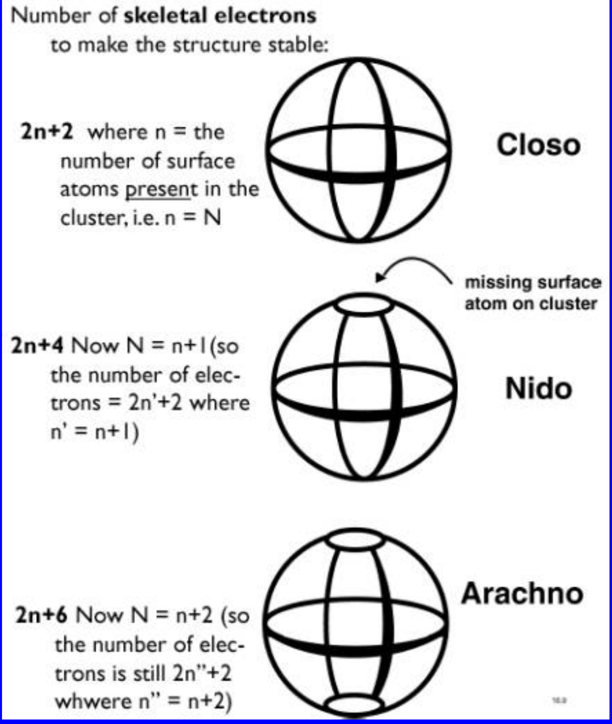
3 isomers of $C_2B_{10}H_{12}$ (with hydrogen omitted)

## “Nido” series – formula $B_nH_{(n+4)}$

- Total valence electrons(VEC) = 3n (B) + n(H) + 4 (extra H and/or negative charges) = 4n +4
- Framework electrons (NFE) =2n+4 (n+2 pairs).
- The structure of the “nido” compound is based on the “closo” polyhedron with one more vertex than the “nido” compound.

## “Arachno” series – formula $B_nH_{(n+6)}$

- Total valence electrons(VEC) = 4n +6
- Framework electrons (NFE) =2n+4 (n+2 pairs).
- The structure of the “nido” compound is based on the “closo” polyhedron with two more vertex than the “nido” compound.



Number of **skeletal electrons** to make the structure stable:

**2n+2** where n = the number of surface atoms present in the cluster, i.e. n = N

**2n+4** Now N = n+1 (so the number of electrons = 2n'+2 where n' = n+1)

**2n+6** Now N = n+2 (so the number of electrons is still 2n''+2 whwere n'' = n+2)

Electron-deficient multi-center bonds

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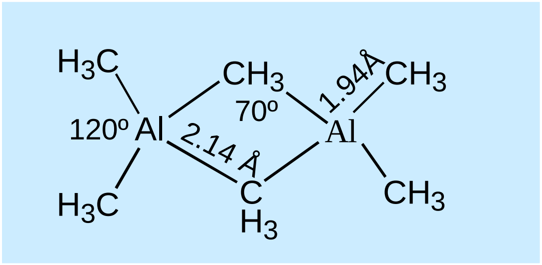
Electron-deficient multi-center bonds

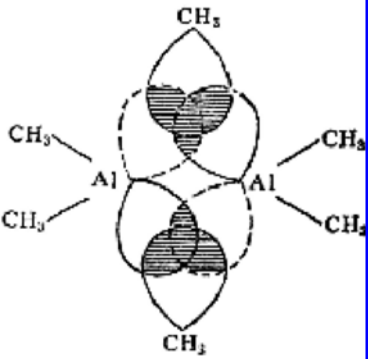
## 6.1.4 other deficient electron compounds

Boron group **B、Al、Ga、In、Tl**



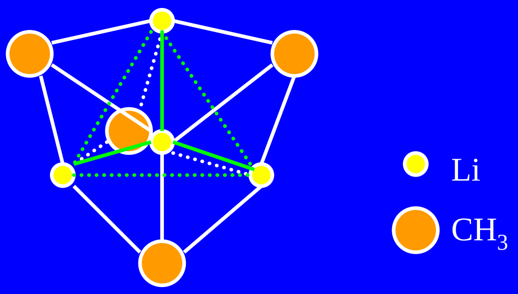
Gaseity: monomer

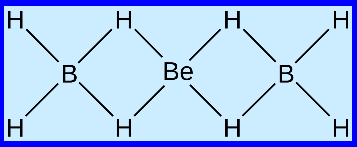
Solid state: polymer



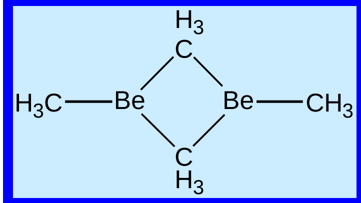
## Alkali metals and alkali earth metals

$[Li(CH_3)]_4$

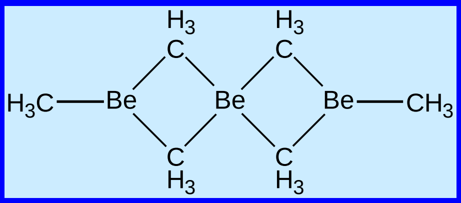




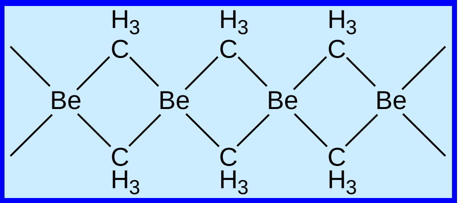
$Be(CH_3)_2$



dimer



trimer



polymer

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# 6.2 Chemical bonds in the coordination compounds

## Coordination compounds

compounds composed of a metal atom or ion and one or more ligands.

- Ligands usually donate electrons to the metal
- Includes organometallic compounds

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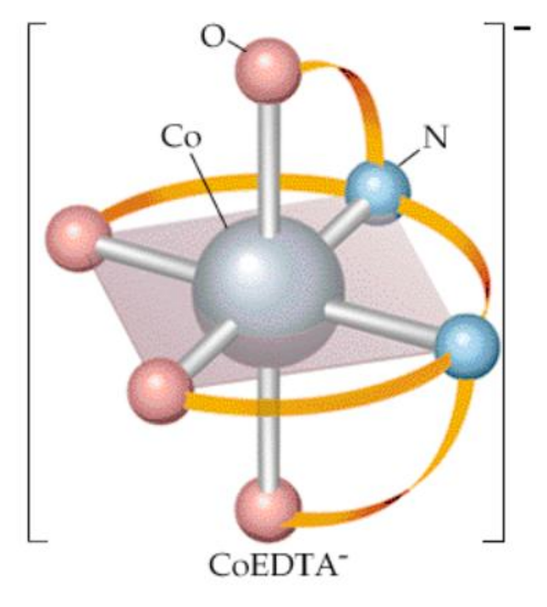
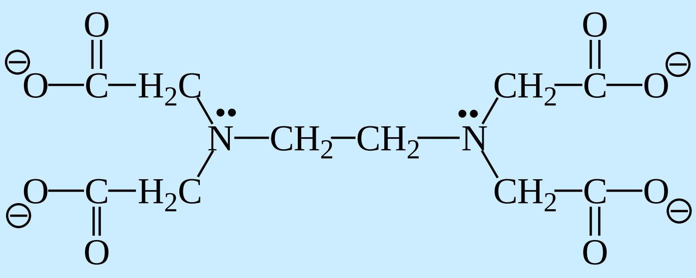
## New theories arose to describe bonding.

–Valence bond, crystal field, and ligand field.





ethylenediaminetetraacetate (EDTA$^{4-}$)
(hexadentate)

## 6.2.1 Coordination polyhedron

| molecualr | C.N. | **hybridization type** | Symmetry | geometry |
|---|---|---|---|---|
| $Ag(NH_3)^{2+}$ | 2 | sp | | linear |
| $CuCl_3^-$ | 3 | $sp^2$ | $D_{3h}$ | triangular |
| $Ni(CO)_4$ | 4 | $sp^3$ | $T_d$ | tetrahedral |
| $PtCl_4^{2-}$ | 4 | $dsp^2$ | $D_{4h}$ | square planar |
| $Fe(CO)_5$ | 5 | $dsp^3$ | $D_{3h}$ | **Trigonal bipyramidal** |
| | 5 | $d^2sp^2$ | $C_{4v}$ | **square pyramid** |
| $FeF_6^{4-}$ | 6 | $d^2sp^3$ | $O_h$ | octahedral |
| others | 8 | | $D_{4h}$ | tetragonal |
| | 8 | | $D_{4d}$ | **Anti-square pyramid** |
| | 10 | | | Bicapped square antiprism |
| | 12 | | $I_h$ | icosahedral |

## 6.2.2 Crystal Field Model

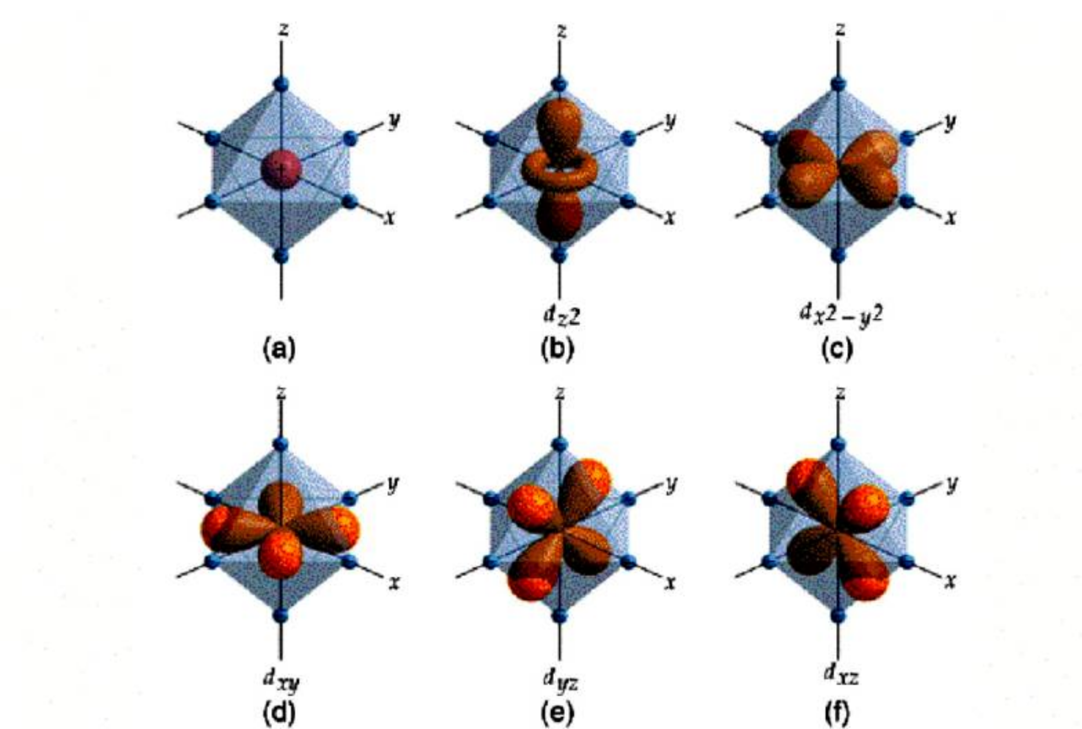
- focuses on the energies of the *d* orbitals.

- <u>Assumptions</u>
- 1. Ligands are negative point charges.
- 2. Metal-ligand bonding is entirely ionic.

- strong-field (low-spin): large splitting of *d* orbitals
- weak-field (high-spin): small splitting of *d* orbitals

Crystal-Field Theory

## A. Crystal field splitting



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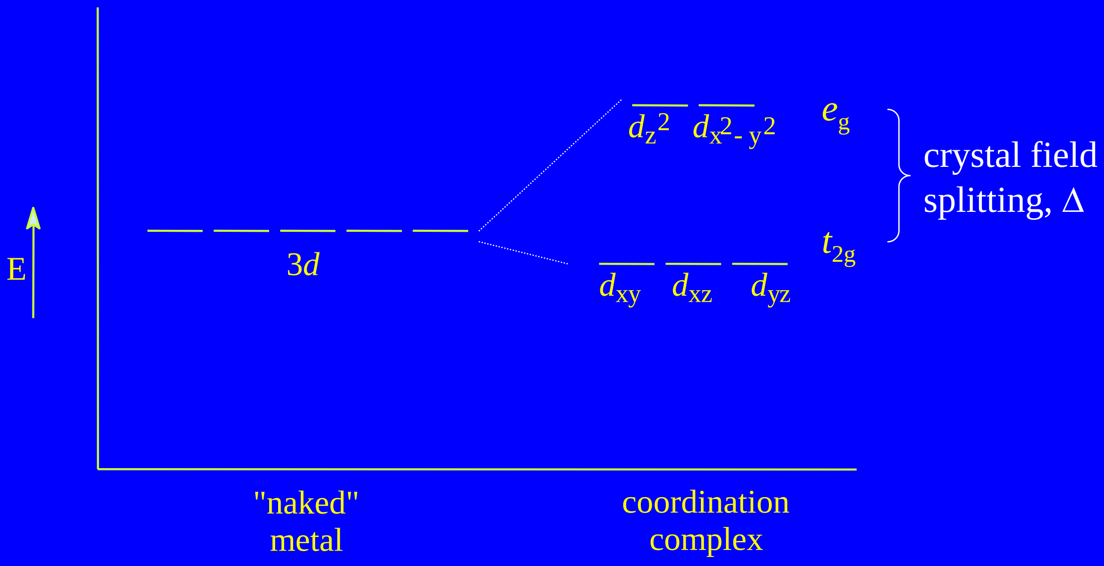
Crystal-Field Theory

## A. Crystal field splitting



$d_{z^2}$ $d_{x^2-y^2}$ $e_g$

crystal field
splitting, Δ

E

3$d$

$t_{2g}$

$d_{xy}$ $d_{xz}$ $d_{yz}$

"naked"
metal

coordination
complex

A. Crystal field splitting

1. spectrochemical series

$CN^- > NO_2^- > en > NH_3 > H_2O > C_2O_4^{2-} > OH^- > F^- > Cl^- > Br^- > I^-$

strongest bond — weakest bond

largest Δ — smallest Δ

| | | absorbs | appears |
|---|---|---|---|
| weakest | $Ni(H_2O)_6^{2+}$ | <R | GB |
| | $Ni(NH_3)^{2+}$ | O | |
| | $Ni(en)_3^{2+}$ | G | V |
| strongest | $Ni(CN)_4^{2-}$ | V | Y |

ROYG V
lower E — higher E

$\Delta E = h\nu$
↑
~visible region

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A. Crystal field splitting

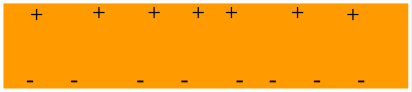
2. charge on metal

- greater charge ⇒ larger Δ
  (ligands held more closely, interact more strongly with *d* orbitals)

| | absorbs | appears |
|---|---|---|
| $Fe(H_2O)_6^{2+}$ | R | G |
| $Fe(H_2O)_6^{3+}$ | V | RO |

ROYG V
lower E — higher E

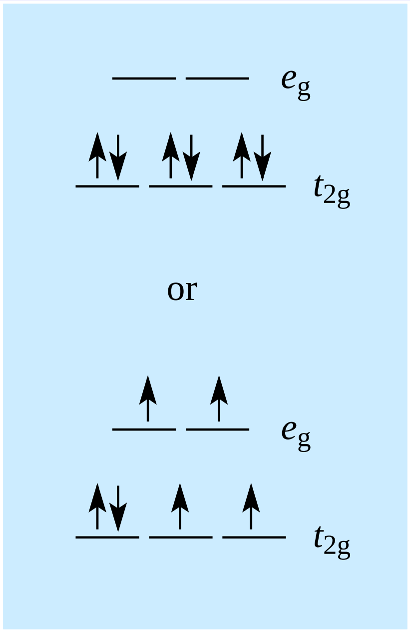
Surface plasma --- UV-Vis spectroscopy



## II. Crystal-Field Theory

### B. Magnetic properties

*e.g.*, $Fe(NH_3)_6^{2+}$ ($Fe^{2+} = d^6$)



**low-spin** complex ← found experimentally
(maximum pairing)
**diamagnetic**

**high-spin** complex
(minimum pairing)
**paramagnetic**

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## II. Crystal-Field Theory

### B. Magnetic properties

Competition between: crystal field splitting ($\Delta$)
electron pairing energy ($P$)

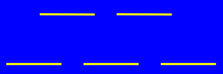
when $\Delta < P \Rightarrow$ high-spin complex
when $\Delta > P \Rightarrow$ low-spin complex

Generally: $d^1$, $d^2$, $d^3$: always high-spin
$d^4$, $d^6$: high-spin with ligands $\leq H_2O$
low-spin with ligands $> H_2O$
$d^5$: high-spin with all ligands except $CN^-$
$d^7$-$d^{10}$ always low-spin

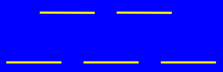
# II. Crystal-Field Theory

## B. Magnetic properties

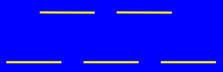
*e.g.*, $[Cr(H_2O)_6]^{3+}$

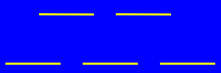


*e.g.*, $[Ni(NH_3)_6]^{2+}$



*e.g.*, $[Fe(H_2O)_6]^{3+}$ vs $[Fe(CN)_6]^{3-}$





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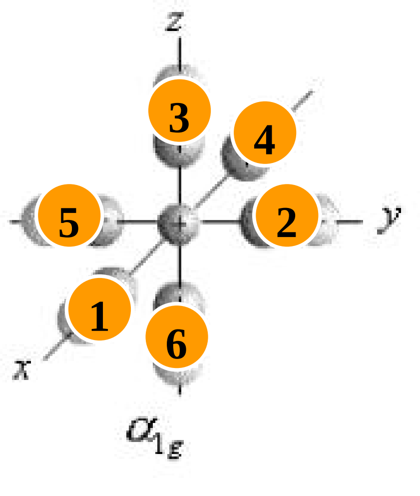
# 6.2.3 σ ligands and σ bond



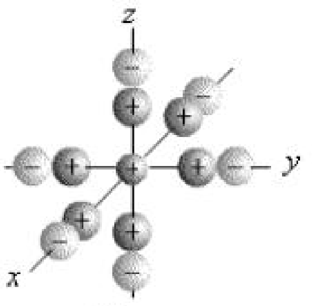
Categories of central metal valence orbitals:

σ group: s, $p_x$, $p_y$, $p_z$, $d_{x^2-y^2}$, $d_{z^2}$

π group: $d_{xy}$, $d_{xz}$, $d_{yz}$

## 6.2.3 σ ligands and σ bond

$$\psi_1 = \varphi_{4s} \pm \frac{1}{\sqrt{6}}(\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6)$$

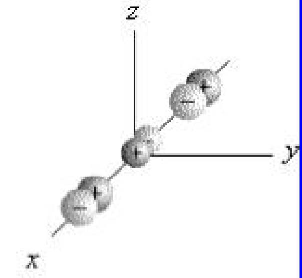


$a_{1g}$

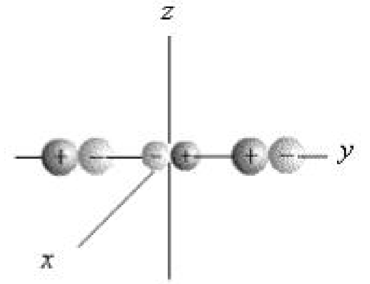
$$\psi_2 = \varphi_{4px} \pm \frac{1}{\sqrt{2}}(\sigma_1 - \sigma_4)$$

$$\psi_3 = \varphi_{4py} \pm \frac{1}{\sqrt{2}}(\sigma_2 - \sigma_5)$$

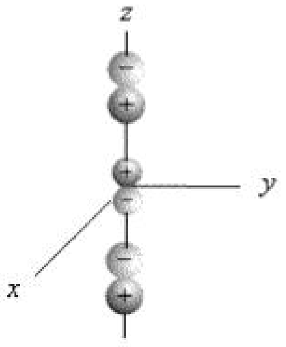
$$\psi_4 = \varphi_{4pz} \pm \frac{1}{\sqrt{2}}(\sigma_3 - \sigma_6)$$



$t_{1ux}$



$t_{1uy}$



$t_{1uz}$

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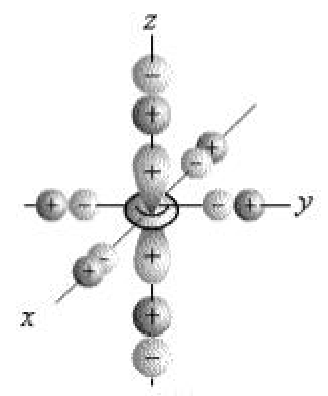
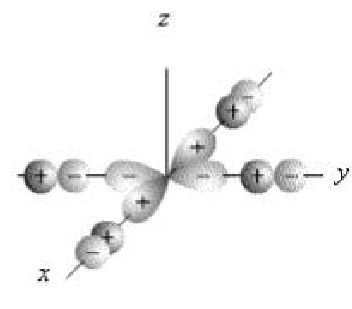
$$\psi_5 = \varphi_{3dz^2} \pm \frac{1}{2\sqrt{3}}(2\sigma_3 + 2\sigma_6 - \sigma_1 - \sigma_2 - \sigma_4 - \sigma_5)$$

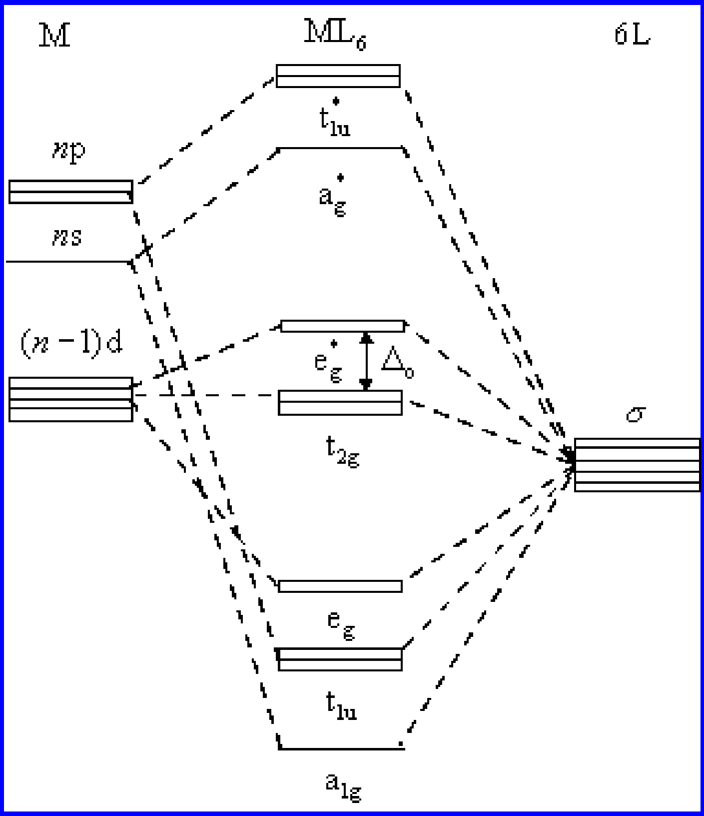


$e_{g(3z^2-r^2)}$



$e_{g(x^2-y^2)}$

$$\psi_6 = \varphi_{3dx^2-y^2} \pm \frac{1}{2}(\sigma_1 - \sigma_2 + \sigma_4 - \sigma_5)$$

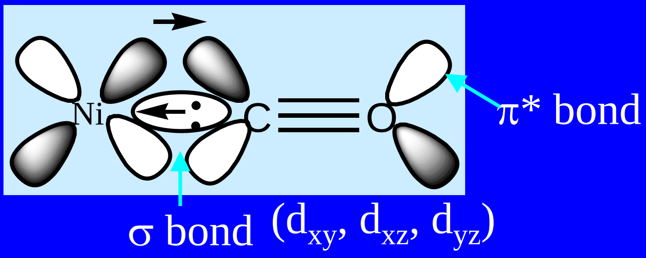


Energetic diagram of σ molecular orbitals

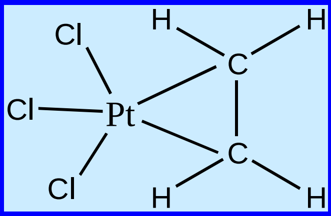
# 6.2.4 π – Bonding

- A π-donor ligand donates electrons to the metal center in an interaction that involves a filled ligand orbital and an empty metal orbital.
  - Cl-, Br-, and I- donates p electrons to the metal center
- A π-acceptor ligand accepts electrons from the metal center in an interaction that involves a filled metal orbital and an empty ligand orbital.
  - CO, $N_2$, NO, and alkenes accept electrons into their vacant anti-bonding MO’s.
  - □ π-acceptor ligands can stabilize low oxidation state metal complexes.

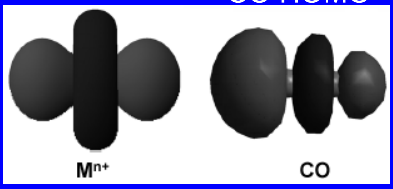
$Ni(CO)_4$



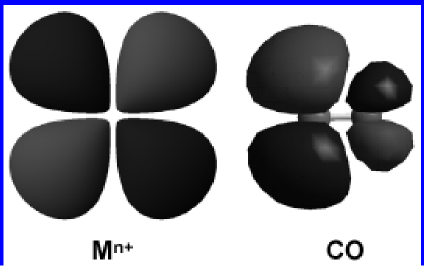
$[PtCl_3(C_2H_4)]^-$

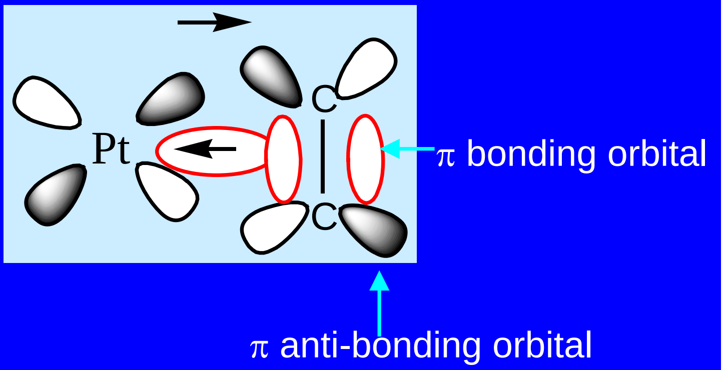


CO HOMO



CO LUMO





d - π conjugation

CO bond made weakened

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## 6.2.5 18-electron rule

- A low oxidation state organometallic complex contains π-acceptor ligands and the metal center tends to acquire 18 electrons in its valence shell.
- Rules:
  - Treat ligands as neutral entities.
  - The number of valence electrons for a zero-valent metal center is equal to the group number.
  - Eg: Cr (group 6) in $Cr(CO)_6$, Fe (group 8) in $Fe(CO)_5$, and Ni (group 10) in $Ni(CO)_4$

## 18-electron rule

- Many ligands donate more than 1 electron.

1-electron donor: H$^{\bullet}$(in any bonding mode), and terminal Cl$^{\bullet}$, Br$^{\bullet}$, I$^{\bullet}$,R$^{\bullet}$(e.g. R=alkyl or Ph) or RO$^{\bullet}$;

2-electron donor: CO, $PR_3$, $P(OR)_3$, $R_2C{=}CR_2$ ($\eta^2$-alkene), $R_2C$: (carbene)

3-electron donor: $\eta^3$–$C_3H_5^{\bullet}$(allyl radical), RC (carbyne), $\mu$- Cl$^{\bullet}$, $\mu$- Br$^{\bullet}$ , $\mu$- I$^{\bullet}$ , $\mu$- $R_2P^{\bullet}$ ;

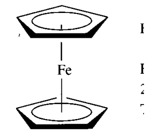
4-electron donor: $\eta^4$–diene, $\eta^4$–$C_4R_4$ (cyclo-butadienes);

5-electron donor: $\eta^5$–$C_5H_5^{\bullet}$ , $\mu_3$- Cl$^{\bullet}$, $\mu_3$ - Br$^{\bullet}$ , $\mu_3$ - I$^{\bullet}$ , $\mu_3$ - $R_2P^{\bullet}$ ;

6-electron donor: $\eta^6$–$C_6H_6$ , $\eta^6$–$C_6H_5Me$;

1- or 3-electron donor: NO

Example: Ferrocene



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## 6.3 Prediction of structural features of inorganic iono-covalent compounds with tetrahedral anion complexes

# Hume-Rothery's 8 - *N* rule (1930/31)

Rule rationalizes observed structural features of (post-transition) main group elements. By forming the correct number of shared bonds with its neighbors each atom succeeds to complete its octet.

**The number of bonds of an element is 8 - *N* where *N* is its column number in the periodic table (only for $4 \leq N \leq 8$).**

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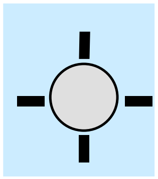
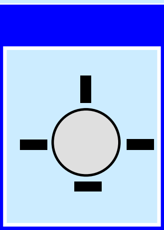
# Element structures which obey Hume-Rothery's 8 - *N* rule



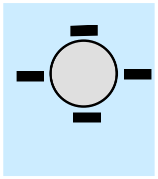
**$N = 4$**
**4 bonds**

**$C_D$, Si, Ge, α-Sn**



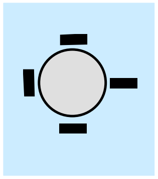
**$N = 5$**
**3 bonds**

**P, As, Sb, Bi**



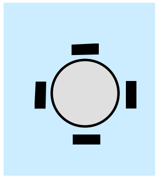
**$N = 6$**
**2 bonds**

**S, Se, Te**



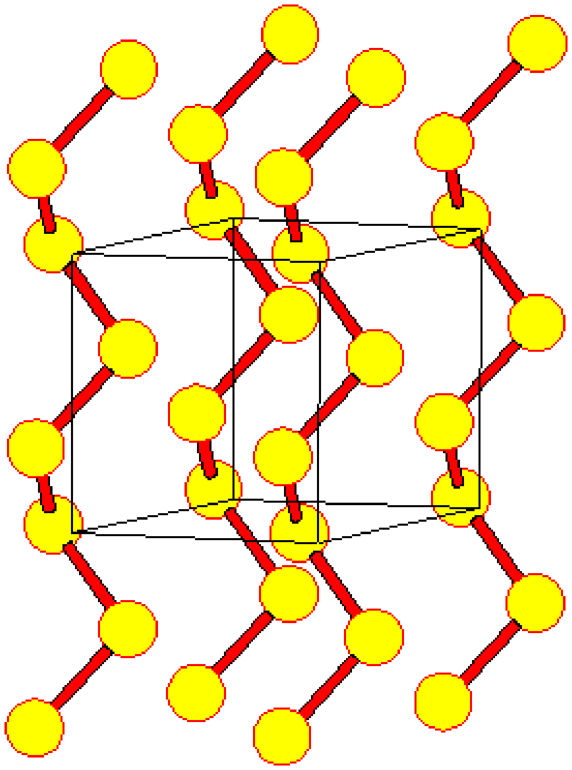
**$N = 7$**
**1 bond**

**F, Cl, Br, I**



**$N = 8$**
**0 bonds**

**He, Ne, Ar, Kr, Xe, Rn**



SELEN

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# Generalized 8 - *N* rule

**Pearson (1964), Hulliger & Mooser (1965)**

$$8 - VEC_A = AA - CC / (n/m) \quad \text{for } C_mA_n$$

**$VEC_A$: Number of valence electrons par anion**

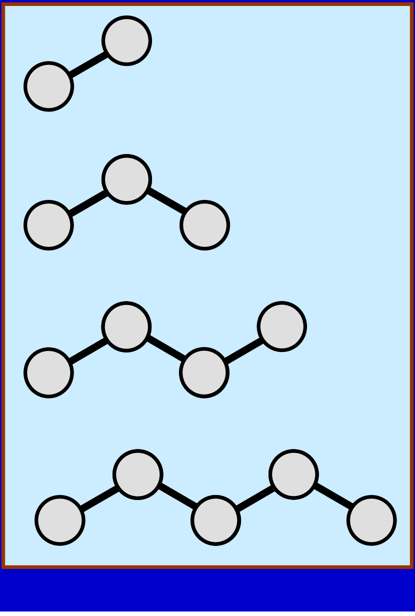
**$VEC_A < 8$, AA>0, CC=0 ⇨ Polyanionic val. comp.**
**$VEC_A = 8$, AA=0, CC=0 ⇨ Normal valence compound**
**$VEC_A > 8$, AA=0, CC>0 ⇨ Polycationic val. comp.**

**AA: Average number of A-A bonds per anion**
**CC; Average number of C-C bonds per cations and/or electrons used for inert-electron pairs on cations**

# Polyanionic valence compound (1)

**$K_6Pd^{2+}Se_{20}$ : $VEC_A$= 128/20, AA=8/5**

**$K_6Pd[Se_5]_4$**



**AA = 1**

**AA = 4/3**

**AA = 6/4**

**AA = 8/5**

**$N'_{A/M} = 2/(2 - AA)$**

$N'_{A/M}$ : Average number of atoms in a non-cyclic charged anion molecule

---

# Polyanionic valence compounds (2)

- **$LaAs_2$** : $VEC_A$= 6.5; AA = 3/2; $N_{A/M}$ = 4
- $La_2{}^\wedge[As_4]$ LT, $La_4{}^\wedge[As_3]\,{}^\wedge[As_5]$ HT
- **$CsTe_4$** : $VEC_A$= 6.25; AA = 7/4; $N_{A/M}$ = 8
- $Cs_2{}^\wedge[Te_8]$
- **$Th_2S_5$** : $VEC_A$= 7.6; AA = 2/5
- $Th_2{}^\wedge[S_2][S]_3$
- **$Sr_5Si_3$** : $VEC_A$= 7.33; AA = 2/3
- $Sr_5{}^\wedge[S_2][S]$

# Polycationic valence compounds

- **HgCl** : VEC$_A$= 9; CC = 1
- [Hg-Hg]Cl$_2$
- **CCl$_3$** : VEC$_A$= 8.33; CC = 1
- [C-C]Cl$_6$
- **SiAs** : VEC$_A$= 9; CC = 1
- [Si-Si]As$_2$

---

## 6.4 Transition-metal cluster compounds

### 6.4.1 Metal-metal bond

$L_nM\text{-}ML_n$, $L_nM{=}ML_n$, $L_nM{\equiv}ML_n$,… so called cluster

Re, $d^5s^2$

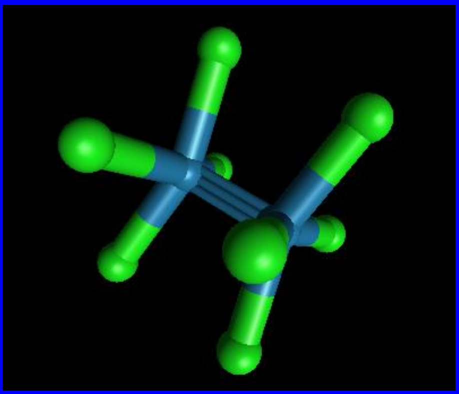
$Re_2Cl_8^{2-}$

Re-Re 2.24Å (2.76 Å in Re crystal) Cl…Cl 3.32 Å

$Re^{3+}$, $d^4$, $dsp^2$ hybridization( σ bond), remain four d and one p orbital

$$\sigma(d_{z2}-d_{z2})$$
$$\pi(d_{xz}-d_{xz})$$
$$\pi(d_{yz}-d_{yz})$$
$$\delta(d_{xy}-d_{xy})$$

Quadruple Bond



$[Re_2Cl_8]^{2-}$

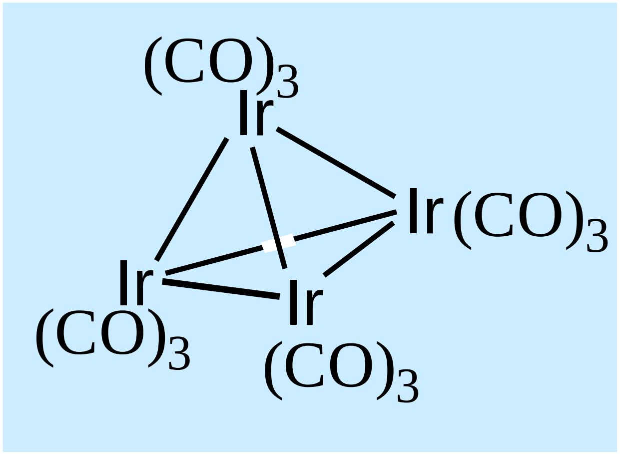
$$\sigma^2\pi^4\delta^2$$

Analog: $Mo_2(O_2CR)_4$ and $Cr_2(O_2CR)_4$

## 6.4 Transition-metal cluster compounds

### 6.4.1 Metal-metal bond

$L_nM\text{-}ML_n$, $L_nM{=}ML_n$, $L_nM{\equiv}ML_n$,… so called cluster

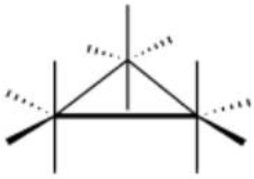


$Ir_4(CO)_{12}$

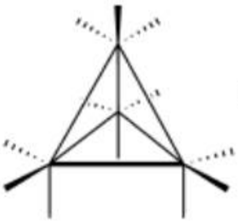
---

### 6.4.2 Cluster geometry

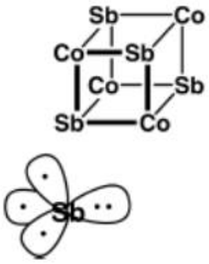
i. Structural polyhedron



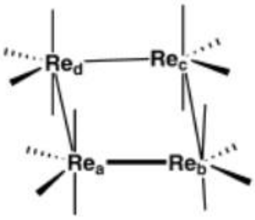
$Os_3(CO)_{12}$



$Ir_4(CO)_{12}$



$Co_4(CO)_{12}Sb_4$

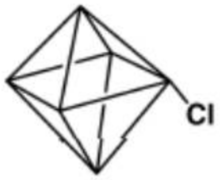


$Re_4(CO)_{16}^{2-}$

$Re_a\text{-}Re_b = 3.01Å$
$Re_b\text{-}Re_d = 2.96Å$
$Re_a\text{-}Re_c = 5.23Å$

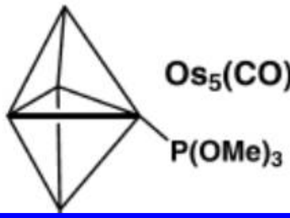
$Co_6(CO)_{14}^{4-}$

$Ir_6(CO)_{15}^{2-}$

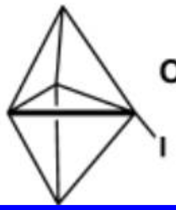


$Ir_6(CO)_{15}Cl^-$

$Ir_6(CO)_{15}PPh_3$



$Os_5(CO)_{15}[P(OMe)_3]$



$Os_5(CO)_{15}I^+$

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## ii. Electron counting

$$b = \frac{1}{2}(18n - g)$$

b: bond valence (total number of metal-metal bonds)

n: number of metal atoms

g: total electrons in valence shell, including all

In the case that main group atoms are included:

$$b = \frac{1}{2}(18n_1 + 8n_2 - g)$$

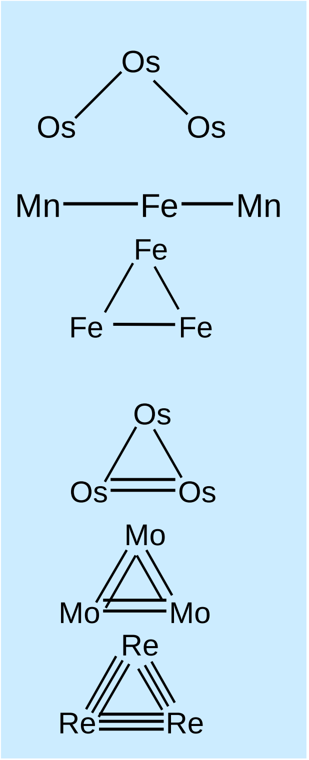
## iii. Bond valence and the cluster geometry

$$b = \frac{1}{2}(18n - g)$$

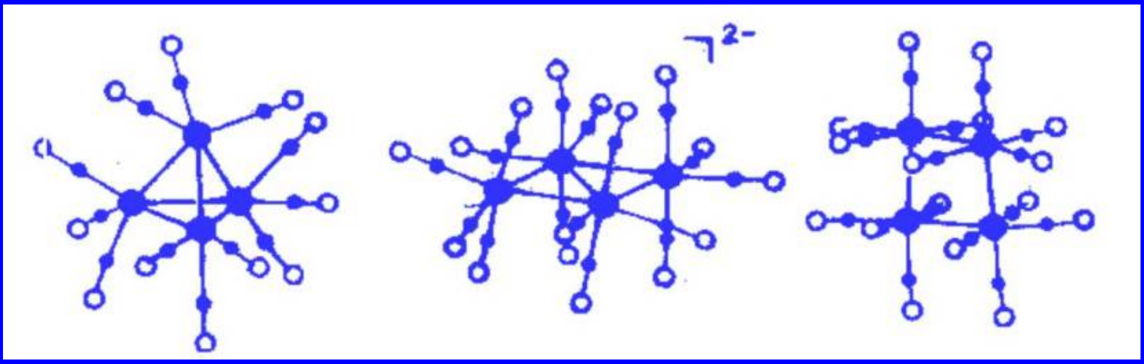
---

## Tri-nuclear compounds

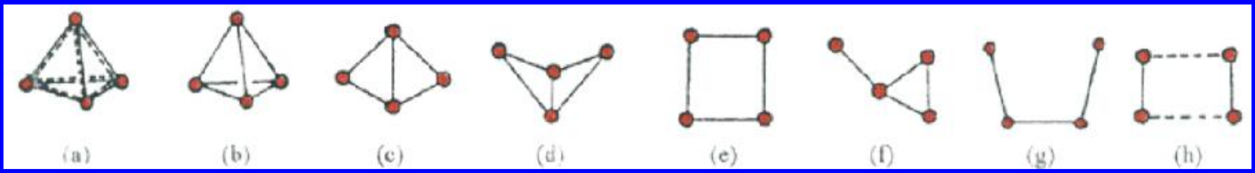
| **Metal cluster compounds** | **g** | **b** | **M-M / pm** |
|---|---|---|---|
| **$Os_3(CO)_9(\mu_3\text{-}S)_2$** | **50** | **2** | **Os-Os, 281.3** |
| **$Mn_2Fe(CO)_{14}$** | **50** | **2** | **Mn-Fe, 281.5** |
| **$Fe_3(CO)_{12}$** | **48** | **3** | **Fe-Fe, 281.5** |
| **$Os_3H_2(CO)_{10}$** | **46** | **4** | **2Os-Os, 281.5**<br>**Os=Os, 268.0** |
| **$[Mo_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3F_9)]^{5-}$** | **42** | **6** | **Mo=Mo, 250.2** |
| **$Re_3(\mu_2\text{-}Cl)_3(CH2SiMe_3)_6$** | **36** | **9** | **Re≡Re, 238.7** |



# Tetranuclear compounds



| $Ir_4(CO)_{12}$ | $Re_4(CO)_{16}^{2-}$ | $Os_4(CO)_{16}$ |
|---|---|---|
| g=4*9+12*2=60 | g=4*7+16*2+2=62 | g=4*9+16*2=64 |
| b=1/2(18*4-60)=6 | b=1/2(18*4-62)=5 | b=1/2(18*4-64)=4 |



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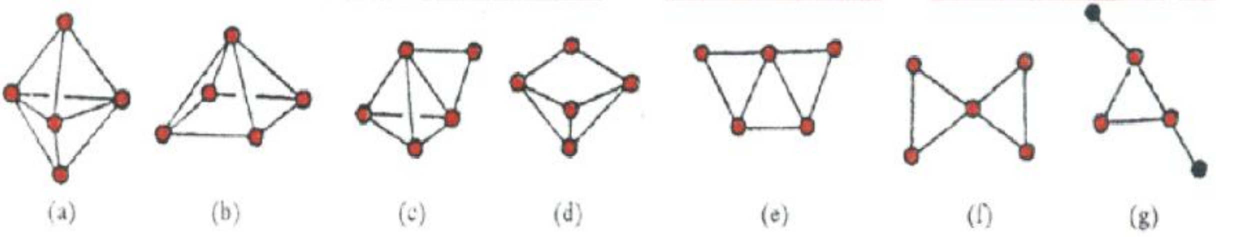
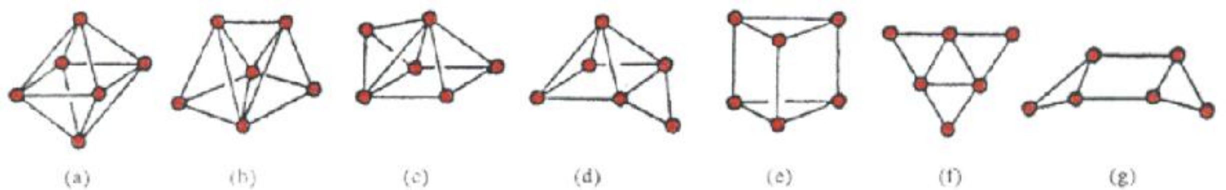
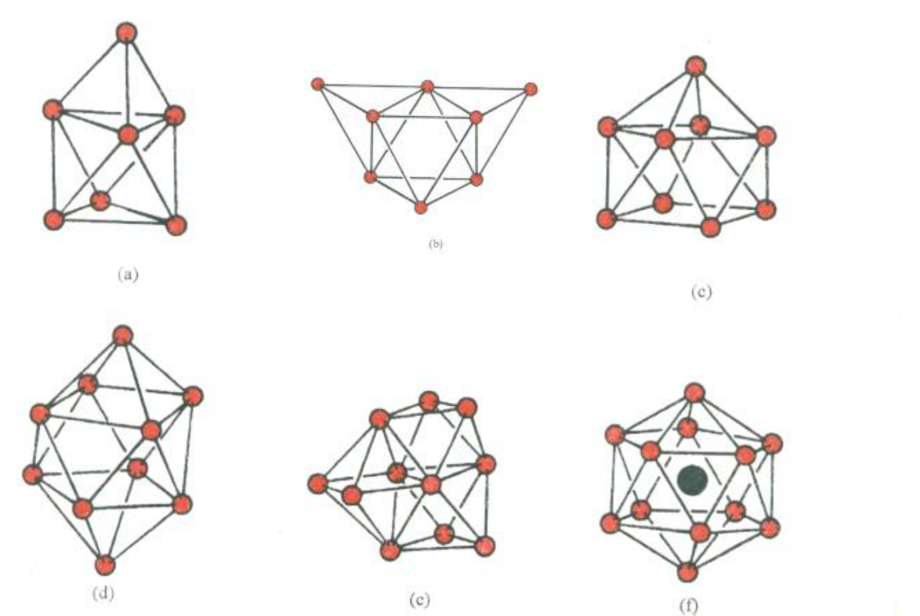
# Pentanuclear compounds



# Hexanuclear compounds



# Multi-nuclear (N>6) compounds



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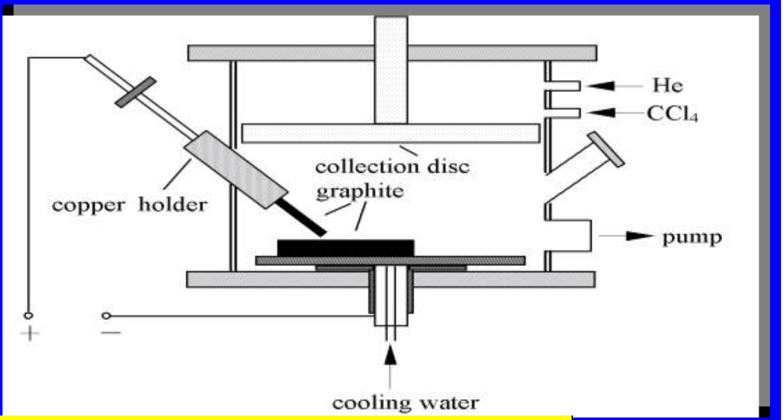
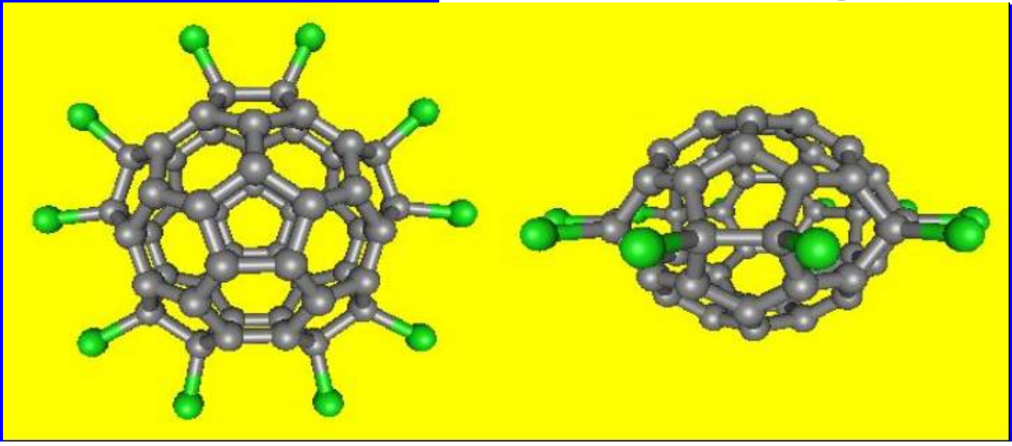
# 6.5 Carbon clusters and nanotubes

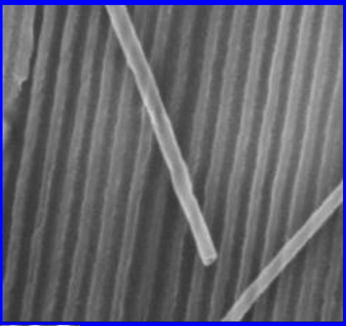
1. Fullerences

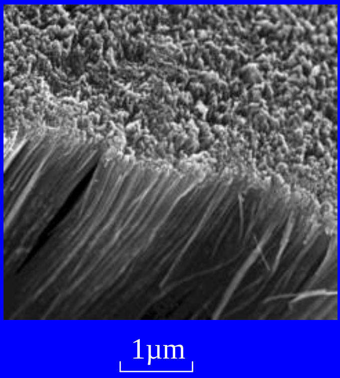


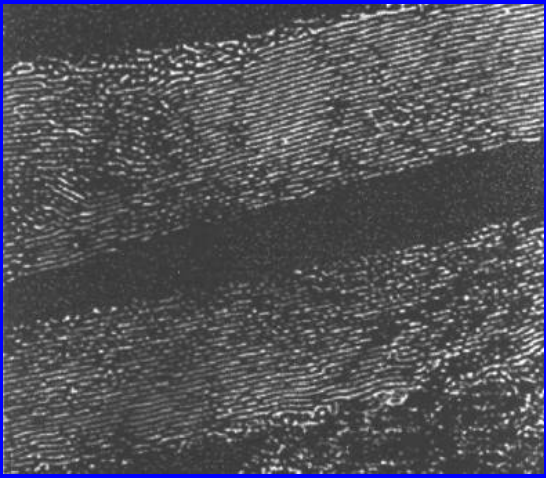
$C_{50}Cl_{10}$



## 2. Carbon nanotubes







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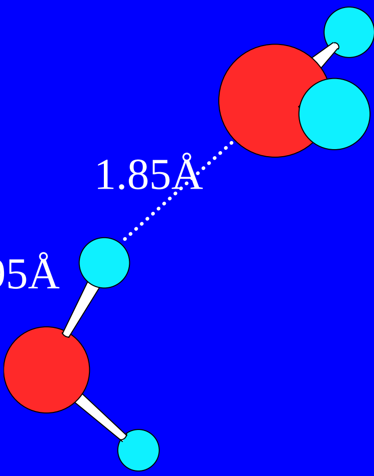
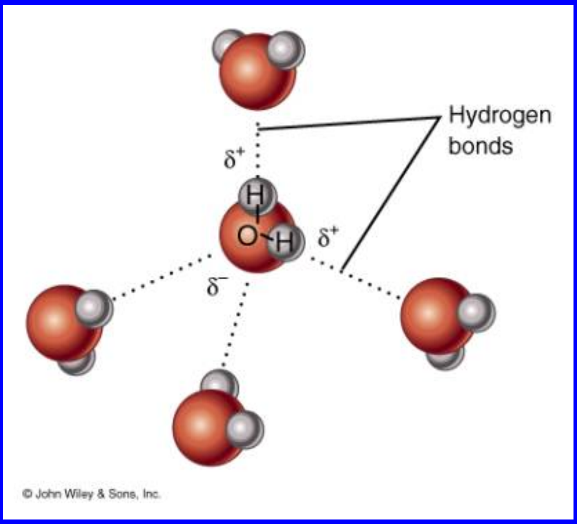
# 6.6 Hydrogen Bonding





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* Hydrogen bonding in DNA