Ligand Field Theory

The electrostatic crystal field theory and the molecular orbital theory were combined into a more complete theory called ligand field theory. This theory was given by Griffith and Orgel.

According to CFT, the splitting of metal d-orbitals is a result solely of electrostatic effects and the bonding between metal and ligand is ionic with no covalent character. The physical measurements such as electron spin resonance (ESR) or electro paramagnetic resonance (EPR), give evidences in favour of covalent bonding in coordination complexes.

CFT treats ligands as point charges or dipoles and does not take into account the overlap of ligand and metal orbitals.

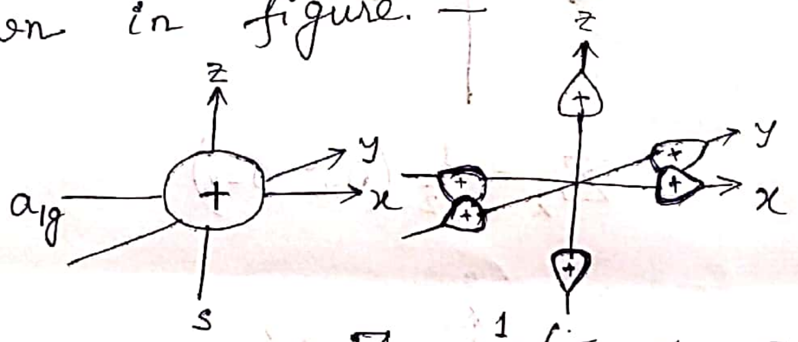
Ligand Field Theory for Octahedral Complexes

Molecular orbitals are formed by the linear combinations of metal and ligand atomic orbitals having the same symmetry.

The linear combinations of ligand orbitals or ligand group orbitals (LGOs) with the metal orbitals occours along the octahedral axes, i.e., ligand orbitals overlap with those metal orbitals which lie on the axes. The ligand orbital must match the symmetries of metal orbitals available for bonding. The central metal cation Contains ns, np and (n-1) d orbitals. This orbitals are devided by Oh symmetry into four sets.

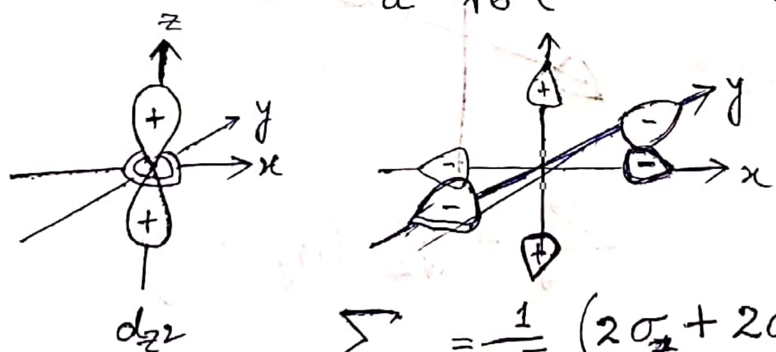
Metal Orbital	Symmetry	Degeneracy.
s	a_{1g}	1
P_x, P_y, P_z	t_{1u}	3
d_{xy} d_{yz} d_{zx}	t_{2g}	3
$d_{x^2-y^2}$, d_{z^2}	e_g	2

In order to formation of σ-bonds within the Complex, there must be positive overlap of metal orbitals with the ligand orbitals directed along the bonding axes. The metal and ligand orbitals must also have same sign. a_{1g} orbital is spherical and it overlaps with ligand orbitals on all axes. The t_{1u} and e_g orbitals have lobes which lie on the axes and thus are capable of σ-bond formation. The lobes of t_{2g} orbitals lie in between the axes so these orbitals donot overlap with the ligand orbitals. Thus t_{2g} orbitals are nonbonding. The LGOs must have the a_{1g}, t_{1u}, and e_g symmetry. So it is concluded that the metal orbitals that participate in bond formation are a_{1g}, t_{1u} and e_g. Bonding interaction b/w metal orbital and ligand orbital is shown in figure. –

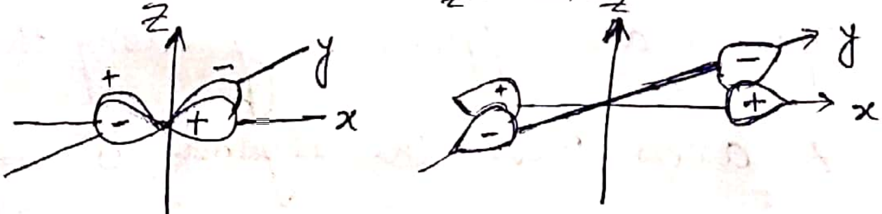


$$\Sigma_a = \frac{1}{\sqrt{6}}\left(\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y} - \sigma_z - \sigma_{-z}\right)$$

e_g

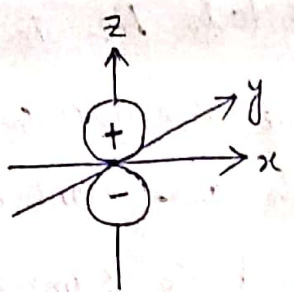


$$\Sigma_{z^2} = \frac{1}{2\sqrt{3}}\left(2\sigma_z + 2\sigma_{-z} - \sigma_x - \sigma_{-x} - \sigma_y - \sigma_{-y}\right)$$

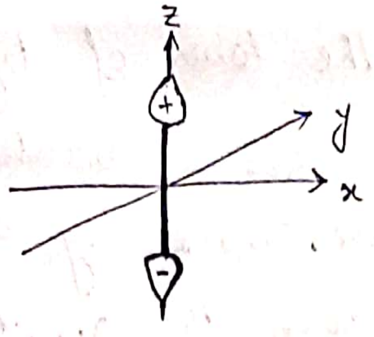


$$\Sigma_{x^2-y^2} = \frac{1}{2}\left(\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y}\right)$$

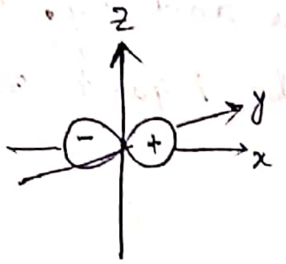
t_{1u}



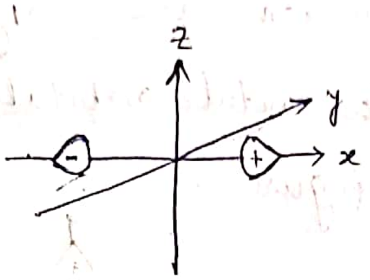
P_z



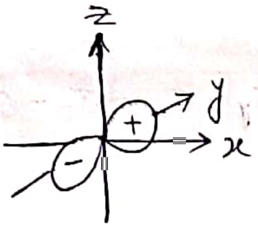
$$\Sigma_z = \frac{1}{\sqrt{2}}(\sigma_z - \sigma_{-z})$$



P_x

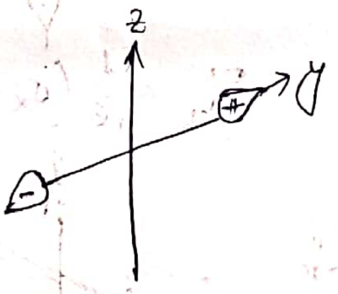


$$\Sigma_x = \frac{1}{\sqrt{2}}(\sigma_x - \sigma_{-x})$$



P_y

y.



$$\Sigma_y = \frac{1}{\sqrt{2}}(\sigma_y - \sigma_{-y})$$

Since, the six ligands are approaching along the $+x, -x, +y, -y, +z$, and $-z$ axes thus the ligand σ-orbitals are represented as $\sigma_x, \sigma_{-x}, \sigma_y, \sigma_{-y}, \sigma_z$, and σ_{-z} respectively.

Since, the sign of the wave function for the metal a_{1g} (4S) orbital everywhere the same which is taken to be

Positive. The six ligands can interacts equally with this orbitals. The linear Combination of ligand σ-orbital which can overlap with the a_{1g} orbital is —

$$\Sigma_{a_{1g}} = \frac{1}{\sqrt{6}}\left(\sigma_x + \sigma_{-x} + \sigma_y + \sigma_{-y} + \sigma_z + \sigma_{-z}\right)$$

where, $\frac{1}{\sqrt{6}}$ = Normalisation Constant.

Since, one

Σ_a = Wave function of LGO

σ = Wave function of Contributing orbital.

Since one lobe of P_x orbital has +ve sign and the others has -ve sign. Thus the linear Combination of ligand σ orbitals that can overlap with P_x orbital is —

$$\Sigma_x = \frac{1}{\sqrt{2}}\left(\sigma_x - \sigma_{-x}\right)$$

Similarly, for P_y and P_z orbitals, the linear Combination of ligand σ-orbital that can overlap with P_y and P_z. orbitals is

$$\Sigma_y = \frac{1}{\sqrt{2}}\left(\sigma_y - \sigma_{-y}\right); \quad \Sigma_z = \frac{1}{\sqrt{2}}\left(\sigma_z - \sigma_{-z}\right)$$

The ligand σ-orbitals (LGOs) that can interact $d_{x^2-y^2}$ orbital of metal will have Components only along the x and y axes.

$$\Sigma_{x^2-y^2} = \frac{1}{2}\left(\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y}\right)$$

The ligand σ-orbital (or LGO) that matches the d_{z^2}, metal orbital is

$$\Sigma_{z^2} = \frac{1}{\sqrt{12}}\left(2\sigma_z + 2\sigma_{-z} - \sigma_x - \sigma_{-x} - \sigma_y - \sigma_{-y}\right)$$

Since, the LGOs (Ligand σ-orbitals) have no symmetry with t_{2g}, The t_{2g} orbitals will not participate in σ bond formation and hence t_{2g} orbitals are non-bonding where there is no possibility of π-bonding. If the ligands orbitals have appropriate symmetry, the t_{2g} orbitals can participate in π-bonding. In this case t_{2g} orbitals are represented by $\pi_{xy} = \pi_{yz} = \pi_{zx}$.

The metal and ligand a_{1g} orbitals overlap to give two molecular orbitals (One bonding and One antibonding), the doubly degenerate metal and ligand e_g orbitals overlap to give four molecular orbitals (two degenerate bonding and two degenerate antibonding), the triply degenerate metal and ligand t_{1u} (orbitals overlap to give six molecular orbitals (three degenerate bonding t_{1u} and three degenerate antibonding t_{1u}^*). There are therefore six bonding combinations in all and six antibonding combinations. The triply degenerate metal t_{2g} orbitals remain non-bonding and fully localized on the central metal cation/atom.

The greatest contribution to the molecular orbital of lowest energy is from atomic orbitals of lowest energy. For ligands, the ligand σ-orbitals (LGOs) are derived from atomic orbitals with energies that lie below those of the metal d-orbitals. Thus the six-bonding molecular orbitals of the complex are mainly ligand orbitals in character. These six bonding molecular orbitals can accomodate the 12 electrons provided by the six ligand lone pairs. Therefore the electrons provided by the ligands are largely confined to the ligands in complese just as assumed by the crystal field theory. However the contribution of d-orbitals is not zero so some amount of ligand electrons leak on to the central metal cation. The d-electrons of metal atom or cation occupy the non-bonding (t_{2g} orbitals) and the antibonding molecular orbitals.

Since the overlap of metal 4s and 4P orbitals with ligand orbitals is considerably better than that of the 3d orbitals since d-orbitals are large and diffuse and as a result overlap of d-orbitals with other is poor. Consequently the a_{1g} and t_{1u} molecular orbitals are the lowest in energy and the corresponding antibonding molecular orbitals a_{1g}^*.

and t_{1u}* the highest in energy. The e_g and e_g* orbitals arising from $3d$ orbitals are displaced less from their barycentre because of poorer overlap. The t_{2g} orbitals being non bonding in a σ-only system, are not displaced at all from their original energy.

The octahedral ligand field splitting parameter Δ_0 is the t_{2g} and e_g* separation.

Eelctrons may now be entered to the molecular orbitals of the complex.* In case of strong ligand field complexes (LS complexes) Δ_0 is high so the pairing of electrons takes place in t_{2g} orbitals. In case of weak ligand complexes Δ_0 is small i.e., t_{2g} and e_g* orbitals are of comparable energy. Thus the pairing of electrons in t_{2g} orbitals takes place after half filling of e_g* orbitals.

When the Ligands are Strong(er)

Example: $[Co(NH_3)_6]^{3+}$ $Co^{3+} \rightarrow 1s^2 \cdot 2s^2 \cdot 2p^6 \cdot 3s^2 \cdot 3p^6 \cdot 3d^6$

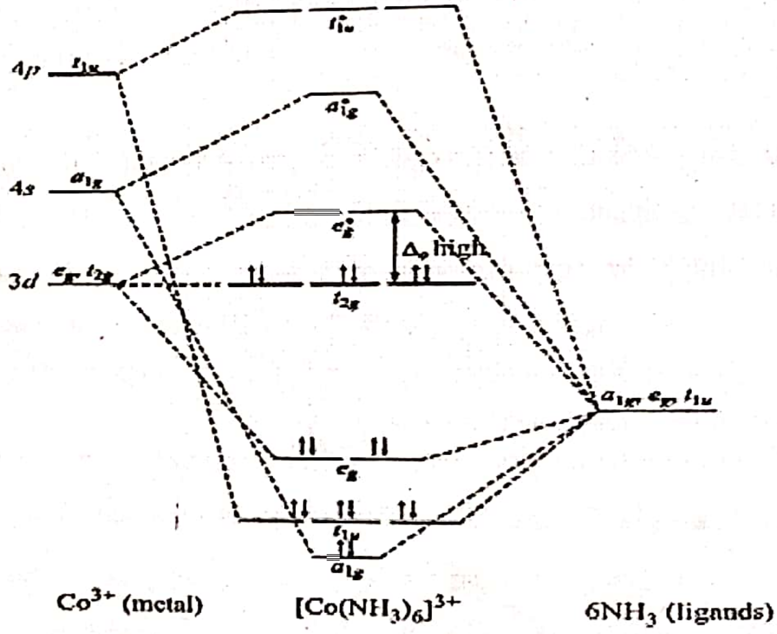
There are total of 18 valence electrons, twelve from six ligands and six from the $3d^6$ configuration of Co^{3+} ion. Since NH_3 is a strong ligand. The electronic configuration in molecular orbitals is $a_{1g}^2, t_{1u}^6, e_g^4, t_{2g}^6$. (Pairing of electrons occurs due to the presence of strong ligand, Δ_0 high $[Co(NH_3)_6]^{3+}$ is diamagnetic because all electrons are paired.

* the six bonding orbitals accomodate 12 electrons supplied by ligands. The remaining n electrons of d^n orbitals of metal atom/ion are accommodated in the nonbonding t_{2g} orbitals and the antibonding e_g* orbitals.

Energy Level Diagram for L.S. Complexes

Example : $[Co(NH_3)_6]^{3+}$, $Co^{3+} \longrightarrow 3d^6$

Ligand electron in bonding orbital
Metal " in nonbonding "



When the Ligands are Weak(er)

Example: $[CoF_6]^{3-}$ $Co^{3+} \rightarrow 1s^2 \cdot 2s^2 \cdot 2p^6 \cdot 3s^2 \cdot 3p^6 \cdot 3d^6$

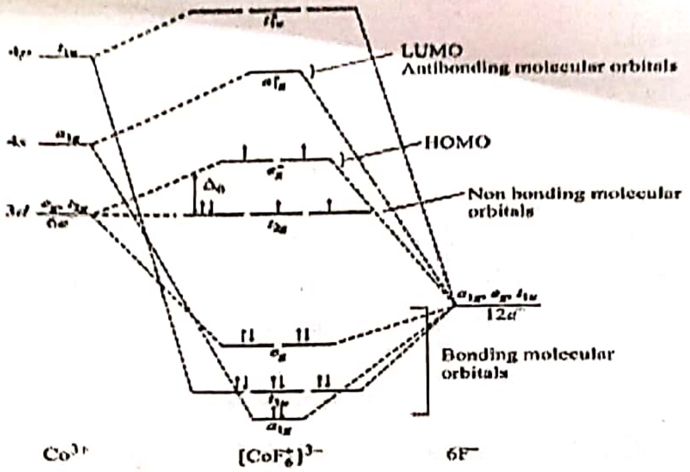
There are total of 18 valence electrons, twelve from F^- (ligands) and six from the $3d^6$ configuration of Co^{3+} ion. Since F^- is a weak ligand, the electronic configuration in molecular orbitals in $[CoF_6]^{3-}$ is $a_{1g}^2\ t_{1u}^6\ e_g^4\ t_{2g}^4\ e_g^{*2}$ because F^- is a weak ligand. The complex $[CoF_6]^{3-}$ is paramagnetic because there are unpaired electrons in t_{2g} and e_g* orbitals.

Thus both ligand field theory and crystal field theory explain magnetic and spectral properties of octahedral complexes on the two sets of orbitals (t_{2g} and e_g*)separated by energy gap Δ_0.

If this energy gap is greater than the pairing energy (P) low spin complex will be formed but if the energy gap Δ_0 is smaller than pairing enegy, high spin complex will be formed.

Energy Level Diagram for High Spin Complex

Example: $[CoF_6]^{3-}$ $Co^{3+} \rightarrow 3d^6$



π-Bonding

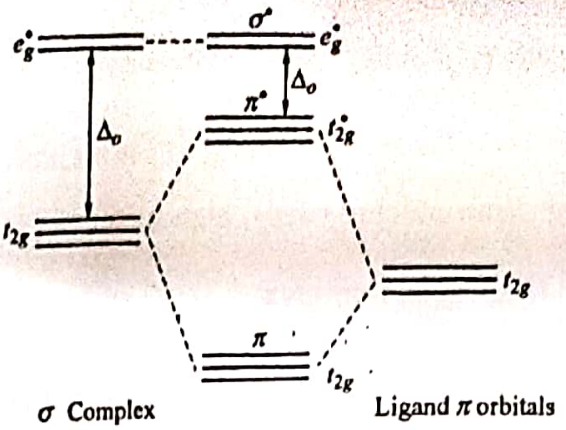
We have considered only metal-ligands σ-interactions. If the ligands in a complex have orbitals with local π symmetry with respect to the M-L axis (as two of the *p*-orbitals of halide ligand have), they may form bonding and antibonding π-molecular orbitals with the metal orbitals. When ligand π-orbitals are taken into account, the combinations that can be formed from them include **SALCS** of t_{2g} symmetry. These combinations have net overlap with the metal t_{2g} orbitals, which are therefore no longer purely non bonding on the metal atom. Depending on the relative energies of the ligand and metal orbitals, the energies of the t_{2g} molecular orbitals lie above or below the energies they had as nonbonding atomic orbitals so the value of Δ_0 decreased or increased respectively.

π-Donors

π-donor ligand is a ligand that, before any bonding is considered, has filled orbitals of π-symmetry around the M-L axis. The energies of these full π-orbitals are usually close to but some what lower than those of the metal *d*-orbitals. The ligands of this kind have no low energy vacant π-orbitals. So we consider only the full orbitals when considering the effects of π-bonding in the complex. Such ligands include Cl⁻, Br⁻ and H_2O. Because the ~~full~~ filled π-orbitals of π-donor ligands lie lower in energy than the partially filled *d*-orbitals of metal. When they form molecular orbitals with the metal t_{2g} orbitals, the bonding molecular orbitals lie lower than the ligand orbitals and antibonding molecular orbitals lie above the energy of *d*-orbitals of the free metal ion. Since the ligand π-orbitals are lower in energy than that of the metal *d*-orbitals, so the electrons supply by the ligands occupy the bonding molecular orbitals and the electrons from metal *d* (t_{2g}) orbitals occupy the antibonding molecular orbitals. Since the level of e_g* orbitals is unaffected by π-interaction,

Δ_0 is reduced as a result of π-bonding.

* difference between t_{2g}* and e_g*



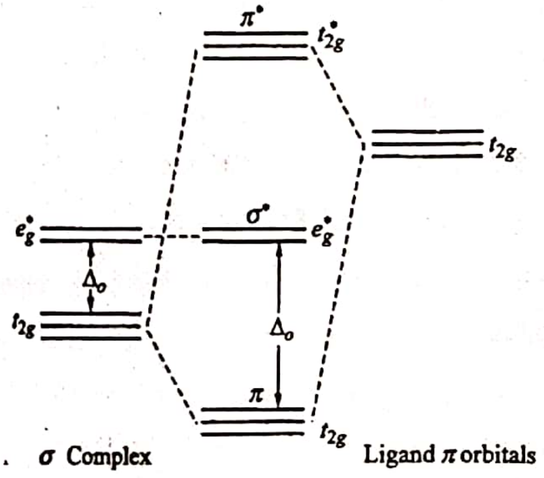
π-Bonded complex

Example: $[CoF_6]^{3-}$

The t_{2g} orbitals of the metal can interact with t_{2g} LGOs constructed from the fluorine 2*p*-orbitals to form π-bonding and antibonding molecular orbitals. Since fluorine is more electronegative than cobalt, the fluorine 2*p*-orbitals lie at a lower energy than the corresponding metal *d*-orbitals. Since the 2*p*-orbitals on the fluoride ligands are filled, these electrons will fill the resultant π-bonding (t_{2g} π) molecular orbitals. The electrons from the 3*d* (t_{2g}) orbitals of the cobalt are therefore in π-antibonding molecular orbitals (π*) at a higher energy than they would be if π-bonding had not taken place.

π-Acceptor

A π-acceptor ligand (like CO, CN^-, R_3P etc.) is a ligand that has ~~filled~~ vacant π-orbitals at (usually) or ~~lower~~ higher energies than metal t_{2g} orbitals. It also has the empty π-orbitals with the correct symmetry to overlap with the metal t_{2g} orbitals forming π-bonds. This often described as back bonding. Because the π-acceptor orbitals on most ligands are higher in energy than the metal t_{2g} orbitals, they form molecular orbitals in which the bonding t_{2g} orbitals are largely of metal *d*-character. These bonding molecular orbitals lie slightly lower in energy than the metal *d* (t_{2g}) orbital themselves. The net result is that Δ_0 increased by the π-acceptor interaction. This account for the position of these ligands as strong field ligands at the right of spectrochemical series.



beta

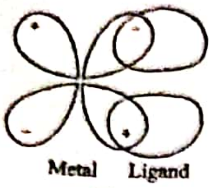
$\Delta_0 = e_g^a \xrightarrow[\Delta_0]{} t_{2g}$

Example : The π* orbital of CO has its largest amplitude on the C atom and has the correct symmetry for overlap with the t_{2g} orbitals of the metal cation. In contrast, the full bonding π-orbital of CO is low in energy and is largely localised on the O atom (becuase that is the more electronegative atom). As a result, the π-donor character of CO is very low and in most (if not all) *d*-metal carbonyls complexes CO is a net π-acceptor.

Types of π-bonds :

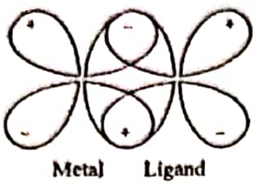
(1) *d*π–*p*π (2) *d*π–*d*π (3) *d*π–π* (4) *d*π–σ*

Representation of π-bonding



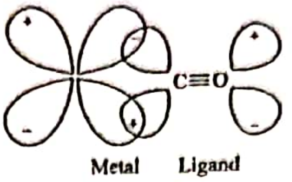
(a)

dπ-pπ



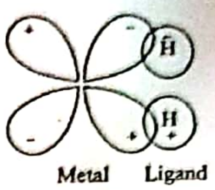
(b)

dπ-dπ



(c)

dπ-π*



(d)

dπ-σ*

Type	Description	Ligand Examples
dπ–pπ	Donation of electrons from filled *p*-orbitals of ligand to empty *d*-orbitals of metal.	RO^-, RS^-, O^{2-}, F^-, Cl^-, Br^-, I^-, R_2N^-
dπ–dπ	Donation of electrons from filled *d*-orbitals of metal to the empty *d*-orbitals of ligand.	R_3P, R_3As, R_2S
dπ–π*	Donation of electrons from filled *d*-orbitals of metal to empty π-antibonding orbitals of ligand.	CO, CN^-, N_2, C_2H_4, RNC, C_5H_5N
dπ–σ*	Donation of electrons from filled *d*-orbitals of metal to empty σ* orbitals of ligand.	H_2, R_3P, alkanes

Effect on Δ_0: It has been concluded that value of Δ_0 increasing in order of π-donar < weak π-donar < neither π-donar nor π-acceptor < weak π-acceptor < strong π-acceptors. Hence, $I^- < Br^- < Cl^- < F^- < OH^- < O^{--} < H_2O < Py, NH_3 < en < bpy, phen < NO_2^- < PPh_3 < CH_3^-, H^- < CN^-, CO$