

MO Concept of M-L Bonding: Crystal Field Theory- III

Coordination Chemistry-II

Inorganic Chemistry-4

Semester IV

CEMA-CC-4-10-TH



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References:

1. Inorganic Chemistry by R. P. Sarkar (Vol II)
2. Inorganic Chemistry by J. E. Huheey (4th Ed)
3. Inorganic Chemistry by G. E. Rodgers (3rd Ed)
4. Inorganic Chemistry by R. L. Dutta (Vol I)
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MO Concept of M-L Bonding

Although the crystal field theory adequately accounts for a surprisingly large quantity of data on transition metal complexes, the theory has serious limitations. There are several experimental and semi-theoretical arguments that can be presented against the assumption that metal d orbitals is a result solely of electrostatic effects and that the bonding between metal and ligand is ionic with no covalent character. Nonetheless, the molecular orbital approach to coordination compounds starts with the idea of symmetry permitted overlap between atomic orbitals on metals and appropriate ligand group orbitals. Molecular orbitals are formed by the LCAO approach and electrons from metal ion and ligands are assigned to these MOs filling lowest energy level first.

A. Complexes involving only Sigma (σ) Bonding

First consider an octahedral complex ML_6 involving metal-ligand σ -bonding only. We first pick out the valence shell atomic orbitals of the metal suitable for bonding. If M is a metal of the first transition series, the metal orbitals are:

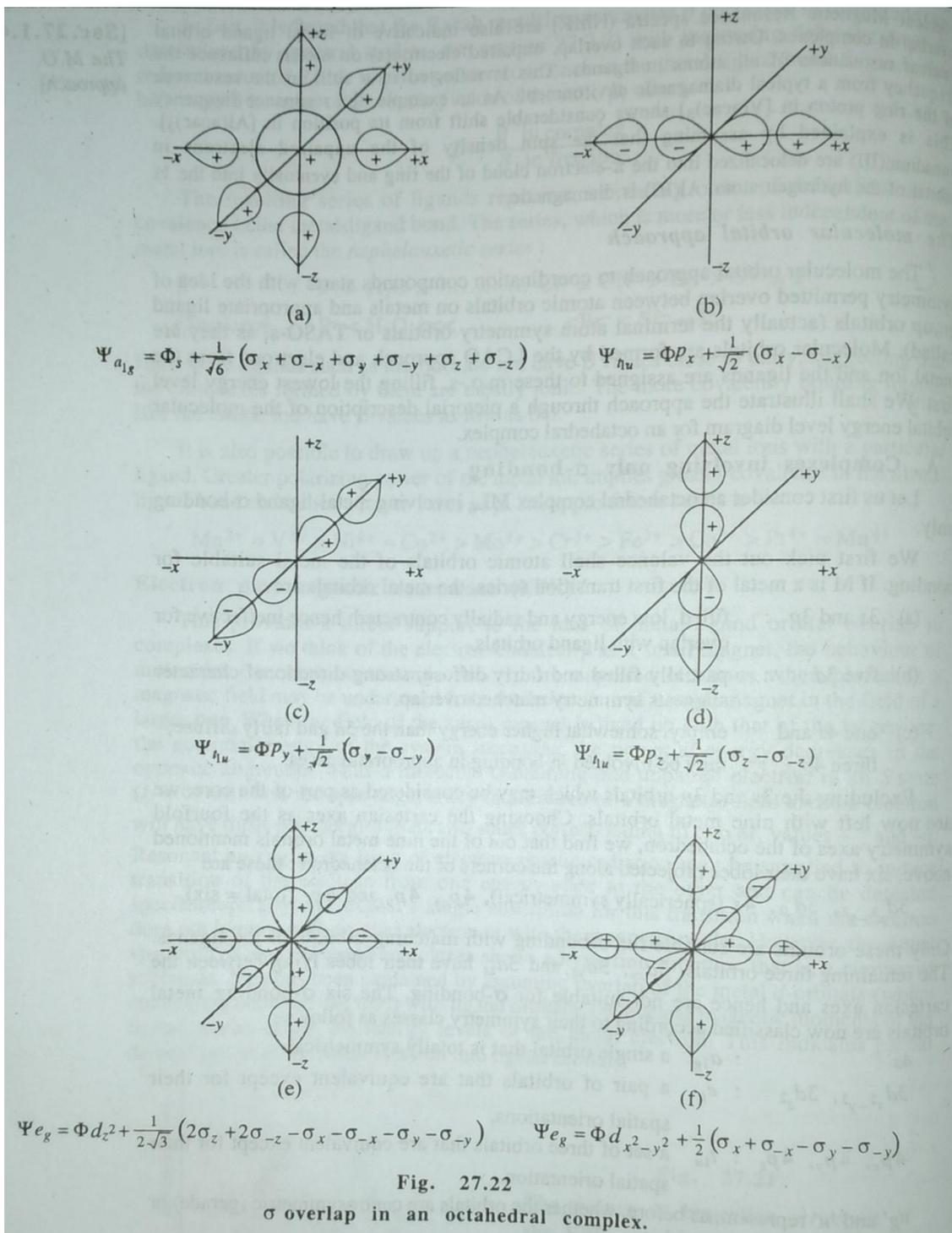
- a. **3S and 3p** : Filled, low energy and radially contracted; hence ineffective for overlap with ligand orbitals.
- b. **Five 3d** : Partially filled and fairly diffuse; strong directional character suggests symmetry matched overlap.
- c. **One 4s and three 4p** : Empty, somewhat Higher energy than the 3d and fairly diffuse; may be involved in bonding in appropriate cases.

Excluding the 3s and 3p orbitals which may be considered as part of the core, we are now left with nine metal orbitals. Out of the nine, six have their lobes projected along the corners of the octahedron: these are $3d_{x^2-y^2}$, $3d_{z^2}$, $4s$, $4p_x$, $4p_y$, $4p_z$ (total six). Only these orbitals are suitable for σ -bonding with matching orbitals of the ligands. The remaining 3 orbitals $3d_{xy}$, $3d_{yz}$, and $3d_{zx}$ have the lobes in between the axes and hence are not suitable for σ -bonding. The Six σ -bonding metal orbitals are now classified according to their symmetry classes as follows:

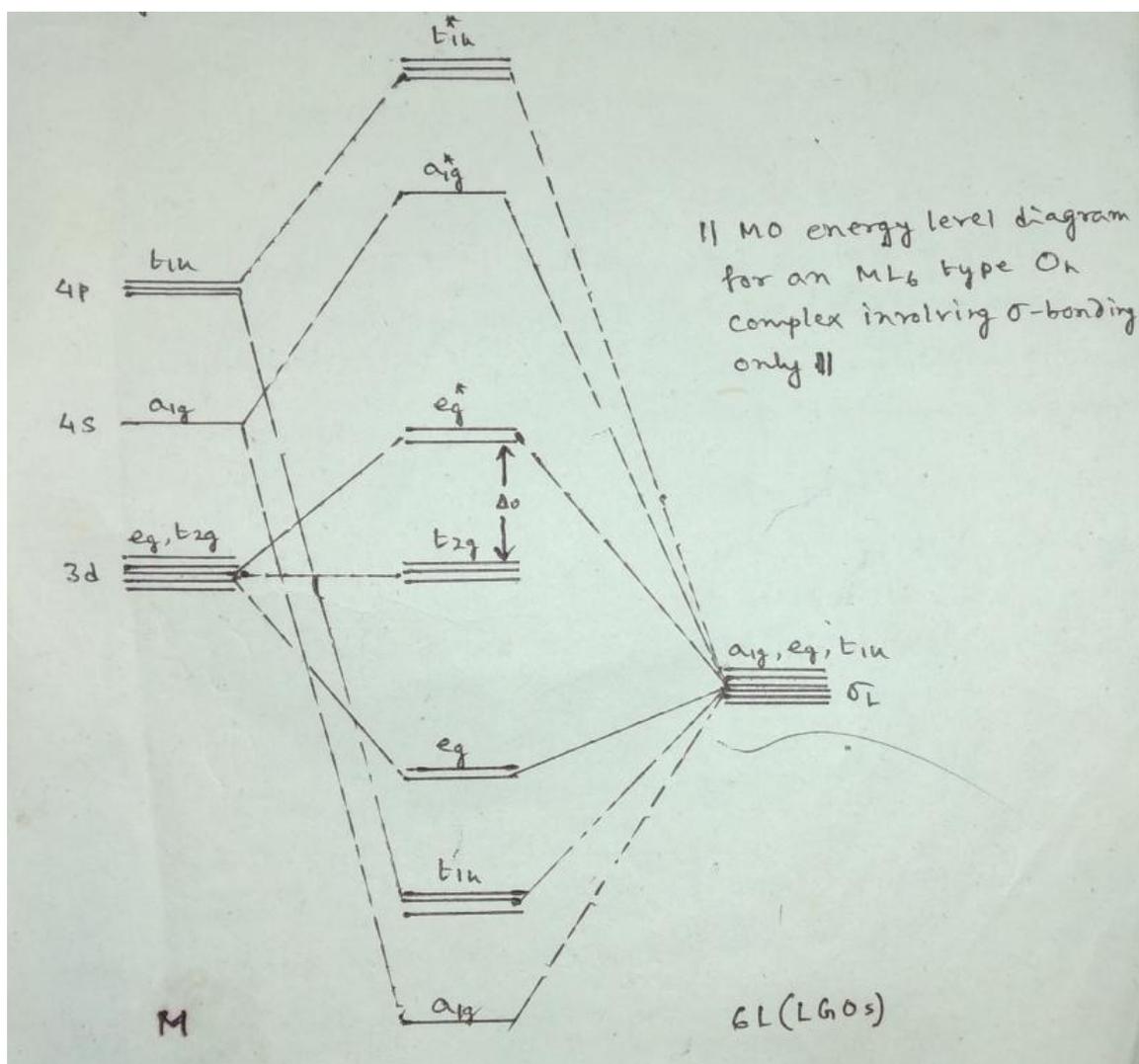
4s : **a_{1g}** , a single orbital that is totally symmetrical
 $3d_{x^2-y^2}$, $3d_{z^2}$: **e_g** , a pair of orbitals those are equivalent except for their spatial orientations.
 $4p_x$, $4p_y$, $4p_z$: **t_{1u}** , a set of three orbitals those are equivalent except for their spatial orientation.
'g' and 'u' represent whether the orbitals are centrosymmetric (gerade) or noncentrosymmetric (ungerade).

Now consider the σ -bonding orbitals from ligands. Since the molecular orbitals we are seeking will be linear combination of metal and ligand atomic orbitals having the same symmetry, it is appropriate to begin by constructing linear combinations of the ligand orbitals, or ligand group orbitals (LGOs), that will overlap with metal orbitals along the octahedral bonding axes. In most cases they will be composed of s and p atomic orbitals; they can be represented by lobes as in the following figures. The linear

combinations of ligand σ -orbitals suitable for bonding with the three symmetry classes of metal orbital (denoted by Φ) are expressed algebraically as normalised linear combination of individual ligand σ -orbitals. Thus the linear combination of ligand σ -orbitals that has the same symmetry as the metal $d_{x^2-y^2}$ orbital (e_g) has a plus sign in the $+x$ and $-x$ directions and minus sign in the $+y$ and $-y$ directions. This gives us the ligand group orbital (LGO) having the combination $(\sigma_x + \sigma_{-x} - \sigma_y - \sigma_{-y})$. The combination of other matching LGOs are found similarly and shown in following figure with respective normalising constants. In order to actually participate in a σ -bond within the complex; a metal orbital must be capable of positive overlap with a ligand group orbital directed along the bonding axes. For the moment, let us merely consider the directional requirement and ignore the fact that for positive overlap, the metal and ligand orbitals must also have the same sign.



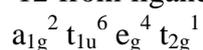
We are now in the final step to construct and a MO energy level diagram for the complex ML_6 . For the transition metals the most usual order of energies of metal orbitals is $3d < 4s < 4p$ for the first row transition metals. For most ligands the ligand σ -orbitals are lower in energy than metal valence orbitals. Again, for each combination of metal and ligand orbitals, there will be a lower energy bonding molecular orbital and a higher energy antibonding molecular orbital. The t_{2g} orbitals on the metal (d_{xy}, d_{yz}, d_{zx}) remain unchanged in energy as they are nonbonding in a σ -only bonding description. The resulting molecular orbital energy level diagram is shown in the following figure.



We may make the following observations on it.

1. The six bonding molecular orbitals (three t_{1u} , two e_g , and one a_{1g}) are closer in energy to the low energy ligand orbitals; hence these molecular orbitals are expected to have greater ligand character.
2. The antibonding molecular orbitals are expected to resemble the metal orbitals more to which they are close in energy.
3. Any electron in the nonbonding t_{2g} orbital will have only metal character in absence of π -bonding.
4. The central part of the diagram consisting of the t_{2g} and e_g^* molecular orbitals corresponds to the t_{2g} and e_g level in the crystal field theory where they were considered as pure metal orbitals. Here also the orbitals have greater metal character.

Let us now see how simple magnetic and spectroscopic properties of complexes may be explained by using this MO diagram. If we consider a d^1 metal ion, $[Ti(H_2O)_6]^{3+}$, we have to place a total of 13 electrons; one from metal and $6 \times 2 = 12$ from ligands into the MO energy levels. The occupancy will be



The single unpaired electron in the t_{2g} level accounts for the paramagnetism of the complex ($\mu \sim 1.7$ BM). For complexes of the metal ions with two or three d electrons the highest occupied MO will have the configuration t_{2g}^2 (two unpaired electrons) and t_{2g}^3 (three unpaired electrons), respectively. A d^4 metal ion gives rise to a choice between the two alternative electronic configuration



The energy gap thus corresponds to the crystal field splitting or $10 Dq$ in an octahedral field in the crystal field theory.

The electronic spectra of complexes maybe similarly explained from the molecular orbital energy level diagram. For a d^1 metal complex like $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$, the ground state electron configuration is t_{2g}^1 and the first excited states corresponds to $t_{2g}^0 e_g^{*1}$. Hence the complex is expected to absorb radiation of frequency of ν where $\Delta = h\nu$, Δ being the separation between t_{2g} and e_g levels.

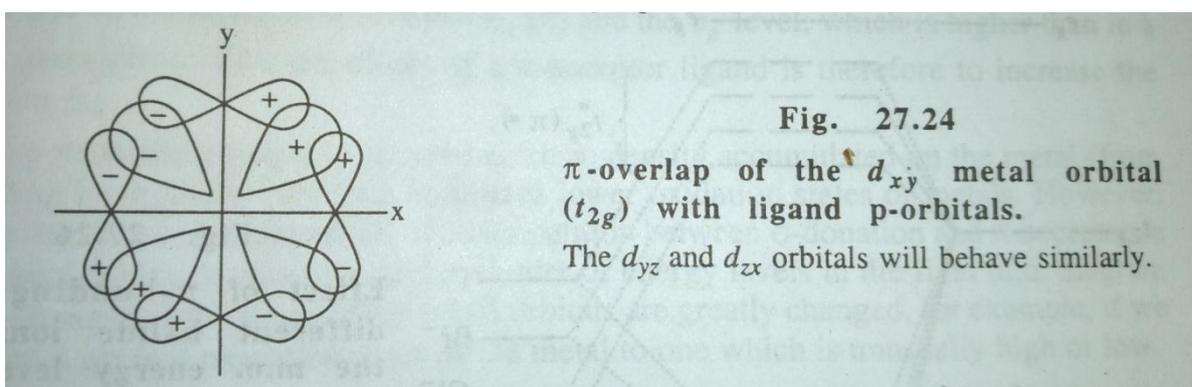
B. Effect of Pi (π) Bonding

So far we have considered the metal ligand bond as a pure σ -Sigma interaction. However, in many complexes, also involves π -interaction; the extent of this is determined by the symmetry of the orbitals as well as the matching size and energy of the orbitals.

In π -bonds, a nodal surface plane passes through the internuclear axis and the electron clouds are distributed symmetrically on the two sides of this plane. Hence that metal and ligand orbitals which are perpendicular to the internuclear axis can take part in π -bond formation (subject to match in size and energy). Such π -bonding may involve π -donor effects as well as π -acceptor effects.

In octahedral complex of the transition metals the t_{2g} and t_{1u} metal orbitals (d_{xy} , d_{yz} , d_{zx} ; p_x , p_y , p_z) are capable of π -bond formation; the p-orbitals naturally prefer to form stronger σ -bonds. The t_{2g} metal orbitals (nonbonding in a σ -description) form π -bonds with LGOs of matching symmetry. These ligand π -orbitals maybe simple p- π orbitals as in R_3P and arsines, or MOs of a polyatomic ligand like CO, CN^- etc. We begin with simple p-orbitals. The effect of such π -interaction on energy level diagram depends mainly upon two factors:

- i. The relative energies of ligand π -orbitals and the metal t_{2g} orbitals and
- ii. Whether the ligand π -orbitals are filled or empty.

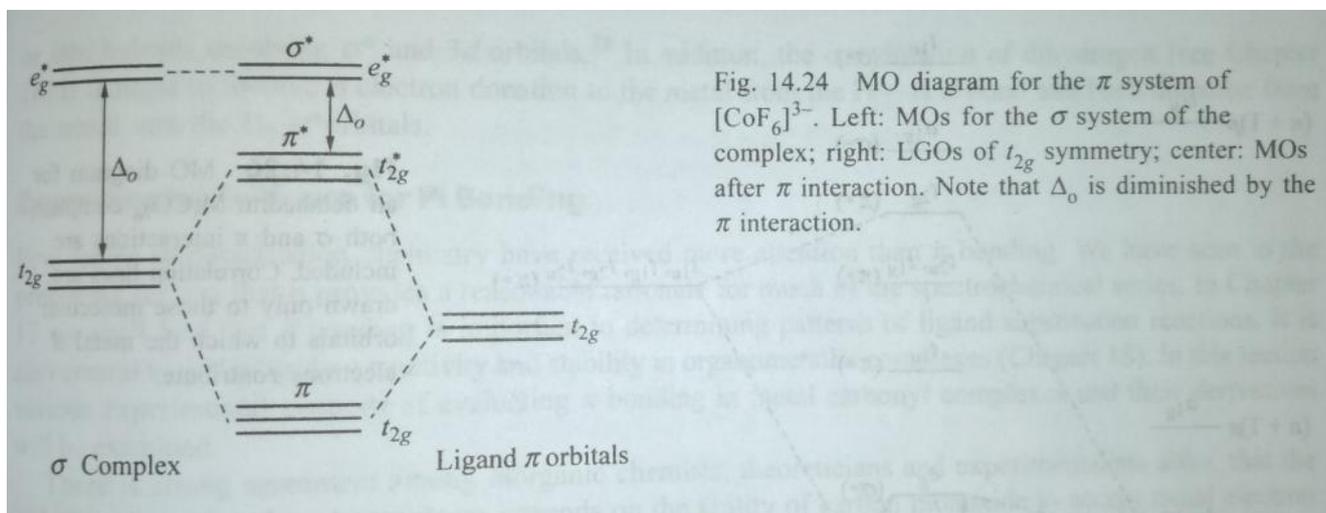


Two distinct cases may be considered:

I. Ligands possess filled Pi (π) orbitals of lower energy:

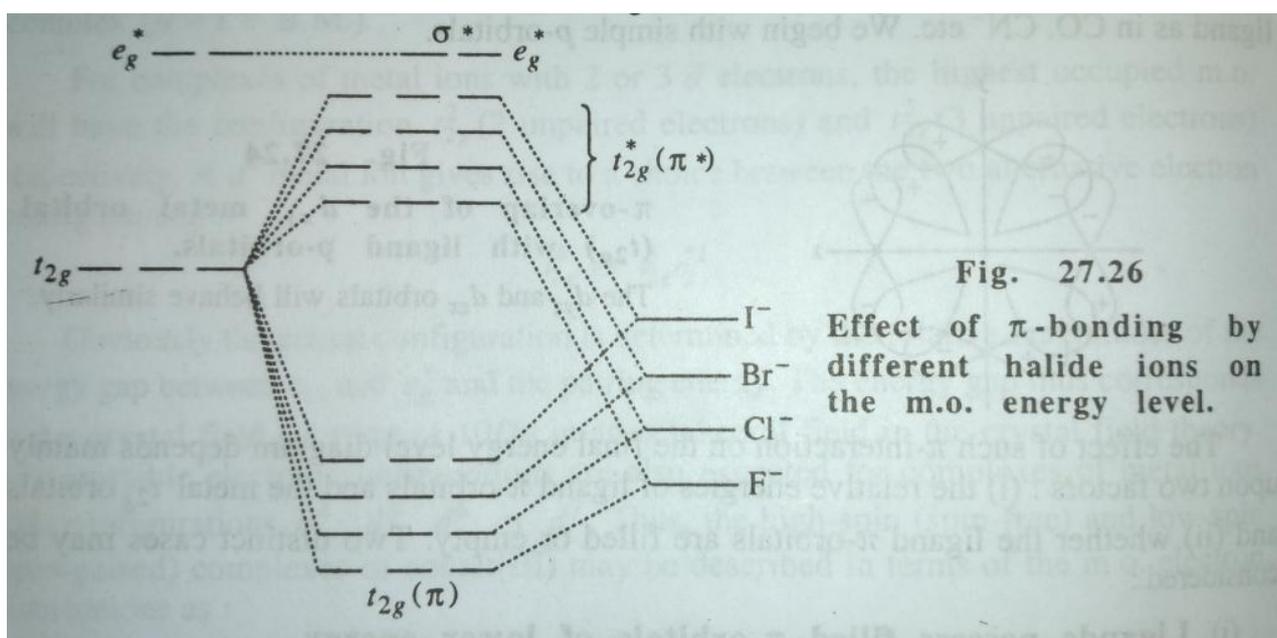
The complex $[\text{CoF}_6]^{3-}$ is an example of this category. It is convenient to regard a halide ligand (X^-) to use its sp hybrid orbitals in bonding. One hybrid sp orbital is used in the M-X σ -donor bond. The other hybrid, located on the other side of M-X interaction plays further effective part in bonding. The lone pairs of electrons on the halogen atoms occupy p_x and p_y orbitals (if internuclear axis lies along z). The filled p_x

& p_y orbitals are of the correct symmetry to interact with the metal t_{2g} orbitals. Since the halogens are more electronegative, the filled p-orbitals will be at a lower energy than the corresponding metal 3d orbitals. A bonding and an antibonding combination of the π -type will result (figure below). The bonding π -MOs will more closely resemble the halide p-orbitals. Conversely the antibonding orbitals are closer in energy to the metal t_{2g} orbitals and so are largely metal based. Effectively the metal t_{2g} orbitals are slightly pushed up in energy.



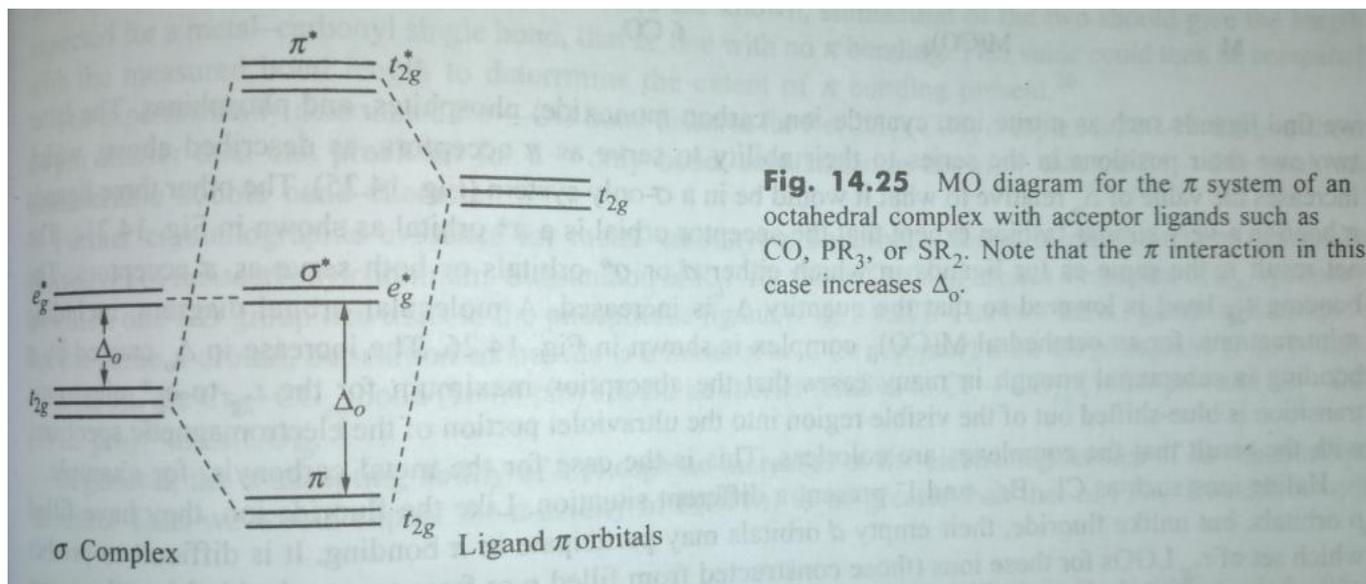
The electrons in the p-orbitals of the ligands occupy the lower bonding set of molecular orbitals and the highest occupied molecular orbital is located in the t_{2g}^* and e_g^* molecular orbitals, depending upon the number of metal electrons. Δ_o now corresponds to the new separation between t_{2g}^* and e_g^* level, which is lower than that in the σ -only description (\Rightarrow weak field ligands). The interaction of the two sets of orbitals corresponds to a partial transfer of electron density from ligand p-orbitals to the metal; hence the ligands are called π -donor ligands.

Such π -bonding interactions help us to analyse the relative positions of certain ligands in the spectrochemical series. The greater the π -donor capacity of the ligand, the more will be destabilization of the t_{2g}^* orbital level and lesser will be the magnitude of Δ . The effect is shown for the halide ion in figure.



II. Ligands possess empty orbitals of higher energy than metal t_{2g} orbitals:

Phosphines, arsines, carbon monoxide etc. belong to this category. These ligands possess vacant orbitals with correct symmetry to enter π -interaction with the metal t_{2g} orbitals. These are therefore called π -acceptor ligands or π -acid ligands (Lewis acid). In fact, these are σ -Lewis base and π -Lewis acid ligands. Carbon monoxide is an excellent example of π -acceptor ligands. In forming a metal carbonyl, the HOMO of CO, localised near the carbon atomic orbitals in energy, will first form a $C \rightarrow M$ σ -donor bond. The LUMO of CO, the π^* -MOs are fully vacant and possess the correct symmetry for π -interaction with metal t_{2g} orbitals forming π and π^* t_{2g} orbitals.



The bonding t_{2g} π -orbitals are now closer in energy to the metal t_{2g} orbitals. Since the ligand π^* MO level is vacant, the electrons in the metal t_{2g} orbital are now assigned to t_{2g} (π) MO, whereby they get somewhat stabilized. Δ_o now corresponds to the separation between t_{2g} (π) and e_g^* level, which is higher than in a σ -only description. The net effect of a π -acceptor ligand is therefore to increase the separation Δ_o (hence strong ligand). Such π -bonding helps to remove electron density accumulated on the metal (from σ -donation by ligands) and thus stabilizes lower oxidation states of metals which cannot be further lowered. However the net effect is always the result of a competition between σ -donation and π -acceptance in the metal-ligand interaction and the order of energy levels in the final MO diagram may be changed if the energies of metal orbitals are greatly changed, for example, if we pass from in normal oxidation state of the metal to one which is unusually high or low.

σ^* -orbitals on ligands may also serve as π -acceptors. Phosphines, for example, were supposed to use empty pure d-orbitals as π -acceptor. But they may also accept π -electron density into low-lying σ^* -orbitals or into some hybrid involving σ^* and 3d orbitals. Complexes of dihydrogen (H_2) are supposed to involve donation from σ -MO of H_2 and back donation from metal into the σ^* -MO of H_2 .

We can now put the role of π -bonding in perspective. The order of ligands in the spectrochemical series is partly that of the strengths with which they can participate in M-L σ -bonding. For example, both CH_3^- and H^- are very high in spectrochemical series because they are very strong σ -donors. However, when π -bonding is significant, it has a strong influence on Δ_o : π -donor ligands decrease Δ_o and π -acceptor ligands increase Δ_o . This effect is responsible for CO (a strong π -acceptor being high on the spectrochemical series) and for OH^- (a strong π -donor) being low in the series. The overall order of the spectrochemical series may be interpreted in broad terms as dominated by π -effects (with a few important exceptions), and in general the series can be interpreted as follows:

– Increasing $\Delta_o \rightarrow$

π -donor < weak π -donor < no π effects < π -acceptor

Representative ligands that match these classes are

π -donor	weak π -donor	no π effects	π -acceptor
I ⁻ , Br ⁻ , Cl ⁻ , F ⁻	H ₂ O	NH ₃	PR ₃ , CO

Notable examples of where the effect of σ -bonding dominates include amines (NR₃), CH₃⁻, and H⁻, none of which has orbitals of π -symmetry of an appropriate energy and thus are neither π -donor nor π -acceptor ligands. It is important to note that the classification of a ligand as strong-field or weak-field does not give any guide as to the strength of the M-L bond.

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