

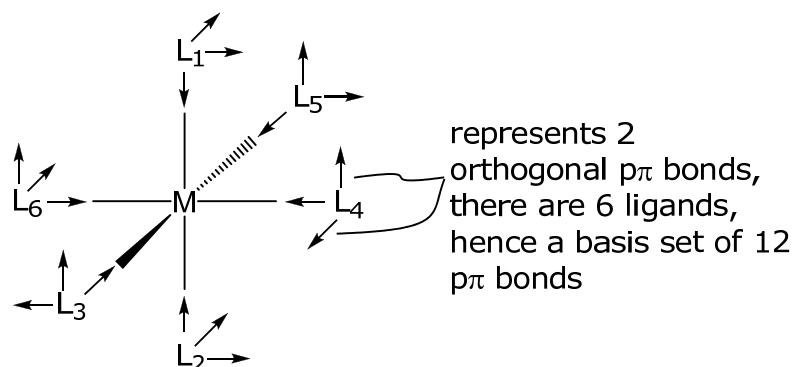
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5.04 Principles of Inorganic Chemistry II
Fall 2008

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5.04, Principles of Inorganic Chemistry II
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Lecture 13: Octahedral ML_6 π Complexes

The basis set needs to be expanded for metal complexes with ligands containing π -orbitals. An appropriate basis for ligands with two orthogonal π orbitals, e.g. CO, CN^- , O^{2-} , X^- , to the σ bond is shown below,



The arrow is indicative of the directional phase of the $p\pi$ orbitals. Owing to their ungerade symmetry, in constructing the $p\pi$ representation

- ❖ a p orbital, i.e. arrow, that transforms into itself contributes +1
- ❖ a p orbital that transforms into minus itself contributes -1
- ❖ a p orbital that moves, contributes 0

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	
Γ_σ	6	0	0	2	2	0	0	0	4	2	$\rightarrow a_{1g} + t_{1u} + e_g$
Γ_π	12	0	0	0	-4	0	0	0	0	0	$\rightarrow t_{1g} + t_{1u} + t_{2g} + t_{2u}$

There is a second method to derive the $p\pi$ basis. The Cartesian coordinate systems on each ligand contains the σ and π basis sets. Thus the $\Gamma_{x,y,z}$ irreducible representation (which is the sum of $\Gamma_x + \Gamma_y + \Gamma_z$ or $\Gamma_z + \Gamma_{x,y}$ for irreducible representations for which x,y,z are not triply degenerate) defines the 1σ and $2p\pi$ bonds of each ligand. Since the bond is coincident with the ligand, an unmoved atom is approximated by Γ_σ . On the basis of geometrical considerations, the following is true,

$$\Gamma_{\text{unmoved atoms}} = \Gamma_\sigma$$

$$\Gamma_{\sigma+\pi} = \Gamma_{x,y,z} \cdot \Gamma_\sigma$$

$$\Gamma_\pi = \Gamma_{\sigma+\pi} - \Gamma_\sigma$$

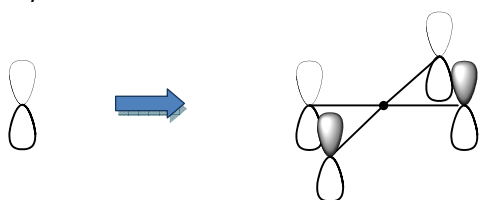
O _h	E	8C ₃	6C ₂	6C ₄	3C ₂	i	6S ₄	8S ₆	3σ _h	6σ _d	
Γ _σ	6	0	0	2	2	0	0	0	4	2	→ a _{1g} + t _{1u} + e _g
T _{1u} = Γ _{x,y,z}	3	0	-1	1	-1	-3	-1	0	1	1	
Γ _{σ+π}	18	0	0	2	-2	0	0	0	4	2	→ a _{1g} + e _g + t _{1g} + 2t _{1u} + t _{2g} + t _{2u}

$$\Gamma_{\sigma+\pi} = a_{1g} + e_g + t_{1g} + 2t_{1u} + t_{2g} + t_{2u}$$

$$\Gamma_{\sigma} = a_{1g} + t_{1u} + e_g$$

$$\Gamma_{\pi} = \Gamma_{\sigma+\pi} - \Gamma_{\sigma} = t_{1g} + t_{1u} + t_{2g} + t_{2u}$$

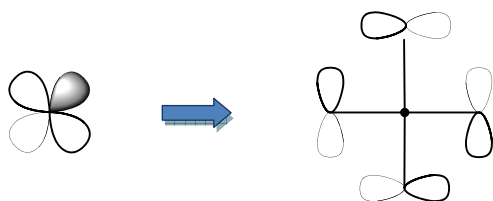
The σ SALCs have already been derived in Lecture 12. Methods 1-3 of Lecture 12 can be employed to determine the pπ SALCs. For the orbitals that transform as t_{1u} and t_{2g}, Method 3 (mirror the metal atomic orbital symmetry) is convenient. For the t_{1u} SALC,



and 2 others (in the xz and yz planes as defined by the symmetries of the p_y and p_x orbitals)

$$p_z \quad \psi_{t_{1u}}^{(1)} = \frac{1}{2} (L\pi_3 + L\pi_4 + L\pi_5 + L\pi_6)$$

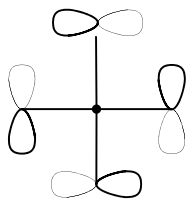
The t_{2g} SALCs have the mirrored symmetry of the (d_{xy}, d_{xz}, d_{yz}) orbital set,



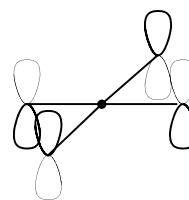
and 2 others (in the xy and xz planes as defined by the symmetries of the d_{xy} and d_{xz} orbitals)

$$d_{yz} \quad \psi_{t_{2g}}^{(1)} = \frac{1}{2} (L\pi_1 - L\pi_2 - L\pi_4 + L\pi_6)$$

Non-bonding SALCs must be ascertained from projection operators and Schmidt orthogonalization methods.

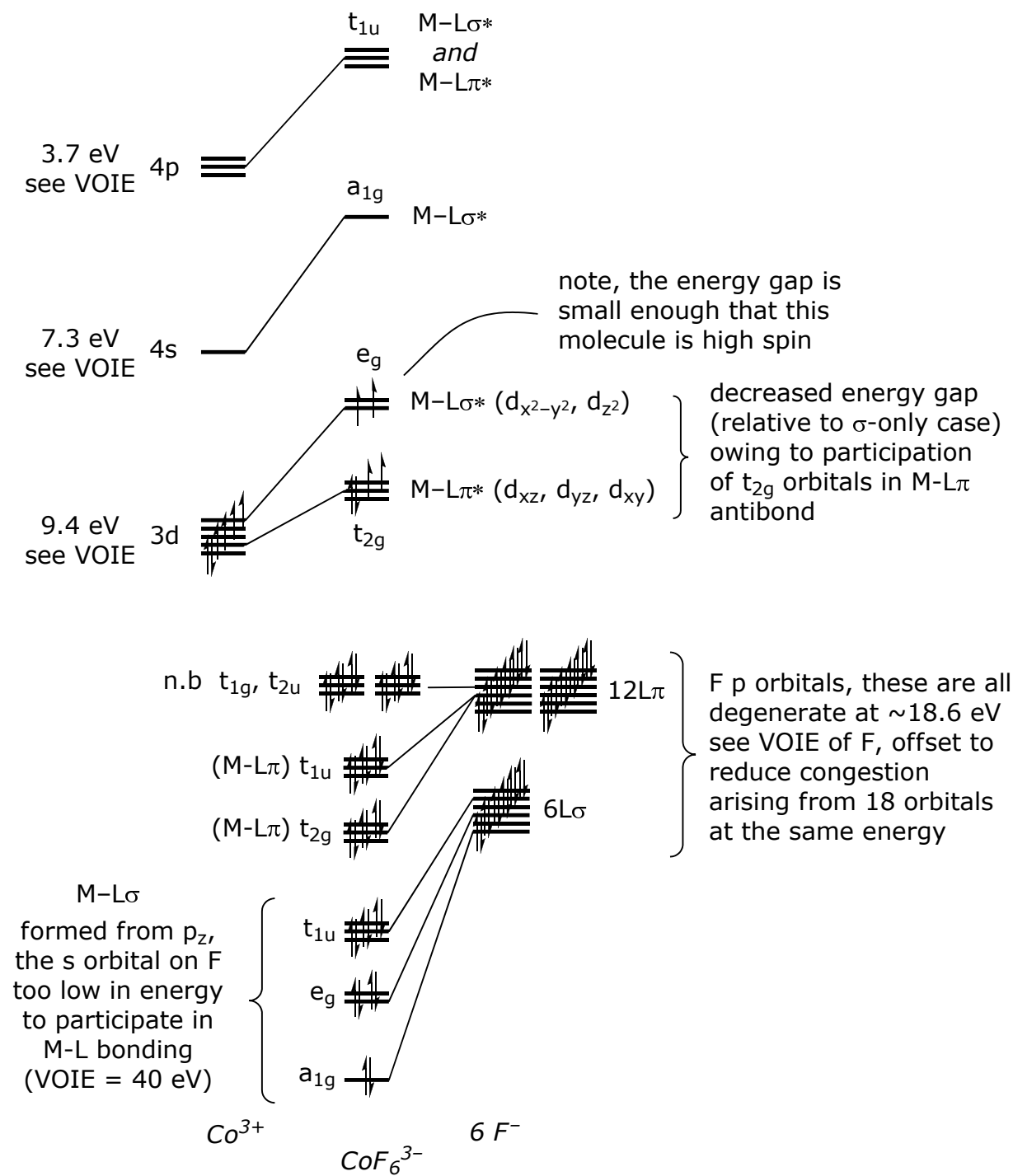


t_{1g} (and 2 others in the xz and xy planes)

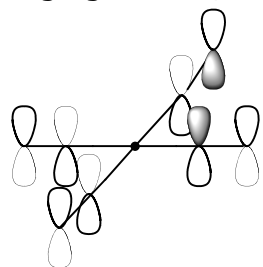


t_{2u} (and 2 others in the xz and yz planes)

For a π donor complex such as CoF_6^{3-} ,

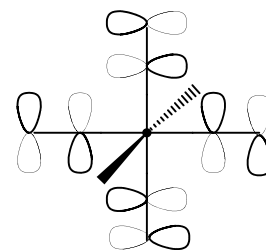


For a π -accepting ligand set, orbitals have the same form (or symmetry) as π donors,



t_{1u}

$$\psi_{t_{1u}}^{(1)} = \frac{1}{2} \left(L\pi_3^* + L\pi_4^* + L\pi_5^* + L\pi_6^* \right)$$



t_{2g}

$$\psi_{t_{2g}}^{(1)} = \frac{1}{2} \left(L\pi_1^* - L\pi_2^* - L\pi_4^* + L\pi_6^* \right)$$

The only difference between the π -donor and π -acceptor MO diagrams is the relative placement of the π^* orbitals relative to the metal atomic orbitals; for $\text{Co}(\text{CN})_6^{3-}$,

