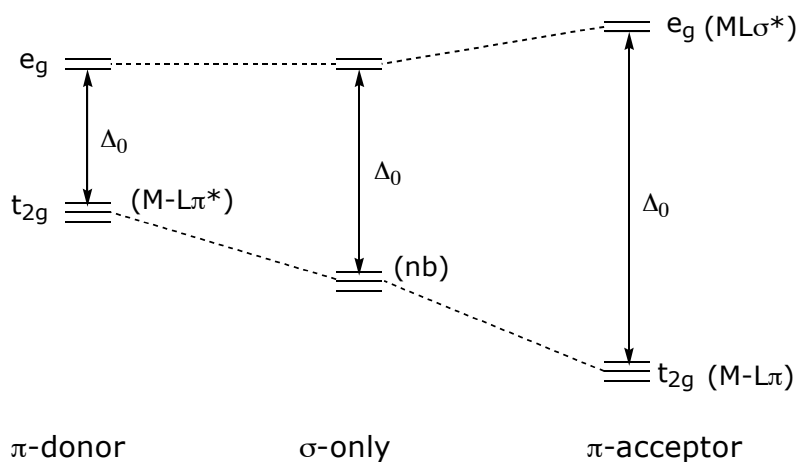


Lecture 18: Spectrochemical Series (O_h) / Descent in Symmetry

The AOM method has provided a quantitative measure of the d-splittings. The e_g/t_{2g} splitting (called the octahedral ligand field splitting $\Delta_0 = 10Dq$). Follows the general trend.



Point to consider about the Δ_0 splitting:

1) charge on the metal

As charge \uparrow , electrostatic attraction between M and L \uparrow , M-L bond distance \downarrow and S_{ML} \uparrow . Also as charge \uparrow , M becomes more electronegative, decreasing ΔE_{ML} . Both trends lead to a greater field strength for the more highly charged ion.

	$\Delta_0 / \text{cm}^{-1}$		$\Delta_0 / \text{cm}^{-1}$		$\Delta_0 / \text{cm}^{-1}$
$\text{Cr}(\text{H}_2\text{O})_6^{2+}$	14,100	$\text{V}(\text{H}_2\text{O})_6^{2+}$	12,300	$\text{Co}(\text{H}_2\text{O})_6^{2+}$	9,300
$\text{Cr}(\text{H}_2\text{O})_6^{3+}$	17,000	$\text{V}(\text{H}_2\text{O})_6^{3+}$	18,600	$\text{Co}(\text{H}_2\text{O})_6^{3+}$	18,200

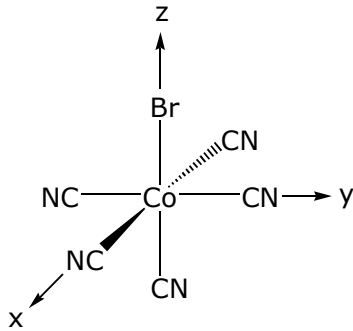
2) the nature of the metal ion

radial extension of 2nd and 3rd row TMs is greater... thus S_{ML} larger, leading to the following trend in Δ_0 : 1st row TM \ll 2nd row TM \sim 3rd row TM

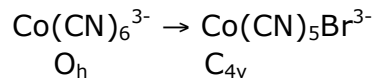
	$\Delta_0 / \text{cm}^{-1}$
$\text{Co}(\text{NH}_3)_6^{3+}$	22,870
$\text{Rh}(\text{NH}_3)_6^{3+}$	34,100
$\text{Ir}(\text{NH}_3)_6^{3+}$	41,200

Descent in Symmetry... O_h Ligand Field \rightarrow ...

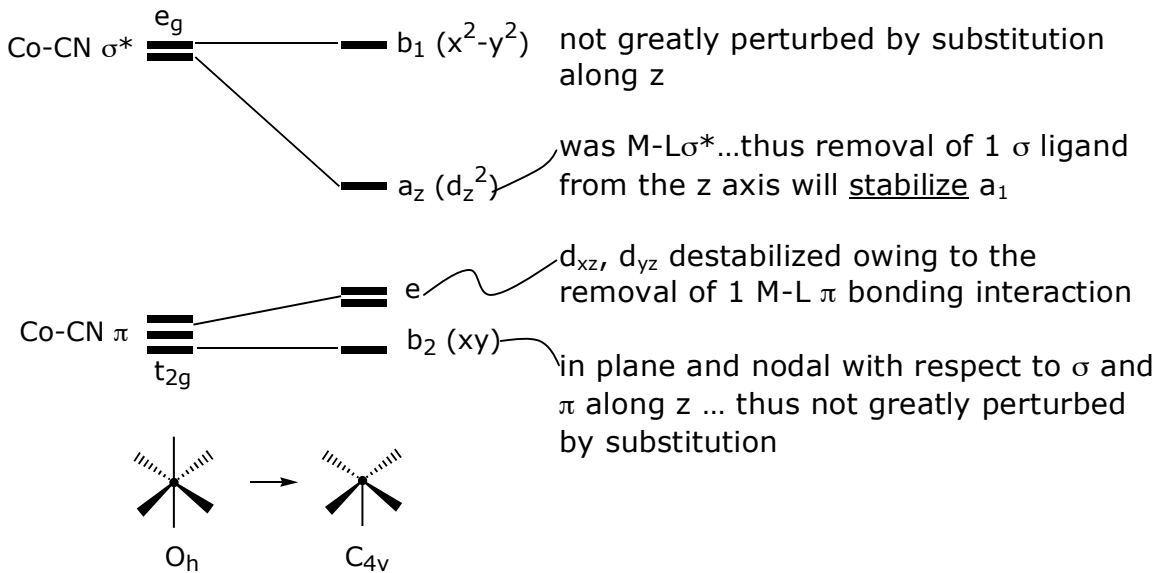
The MO diagram for O_h complexes proves to be a convenient starting point for deducing the electronic structure of many lower symmetry metal complexes. For example, consider $\text{Co}(\text{CN})_5\text{Br}^{3-}$



Could build MO from first principles... alternatively, may correlate electronic structure of this C_{4v} complex to its O_h parent Complex, $\text{Co}(\text{CN})_6^{3-}$



Consider perturbations to σ and π interactions upon substituting π -accepting CN^- with π -donating Br^- . First let's simply remove the CN^- ligand,



Addition of Br^- to C_{4v} fragment will give rise to the new interactions:

σ : Br (p_z) will interact with d_{z^2} , s , and p_z of metal. All of these will be $\text{M-L } \sigma^*$ with regard to M orbitals, $\text{M-L } \sigma$ with regard to ligand

π : Br (p_x, p_y) will interact with d_{xz} and d_{yz} ($\text{M-L}\pi^*$)

