5.03, Inorganic Chemistry
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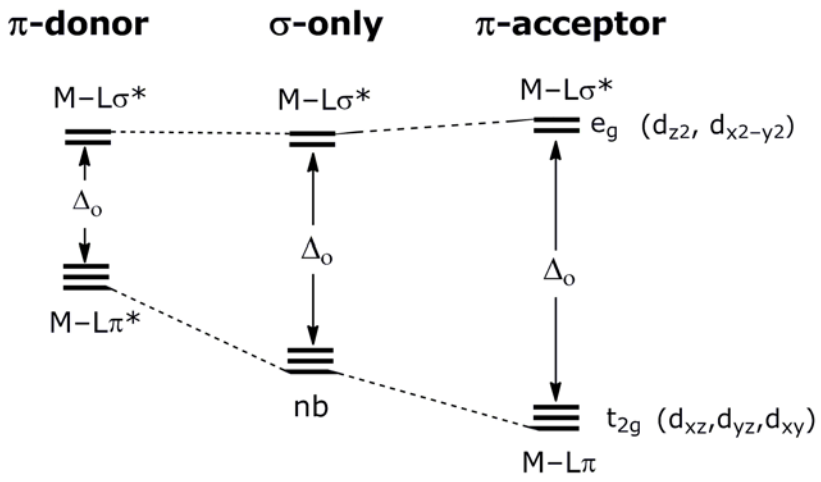
Lecture 27 April 11: Spectrochemical Series

The AOM and MO methods arrive at the same result for metal complexes in an octahedral field. The octahedral crystal field splitting, Δ_O, increases for a ML_6 (O_h) complex along the series L = π-donor < σ-only < π*-acceptor.



the Δ_O splitting will be affected by:

(1) *charge on the metal*

Why? As the charge on the metal increases, the electrostatic attraction between the positively charged metal and electron pair on the ligand increases and hence the metal-ligand bond distance thus decreases, causing a greater S_{ML}. The greater overlap leads to a larger crystal field splitting.

…for M^{n+} ↑ ↓ ↑ ↑

n+ d(M–L) S_{ML} ∴ Δ_O

Also, as the charge the metal ion increases, the metal becomes more electronegative, and hence the electronegativity difference between the metal and ligand atomic orbitals decreases owing to stabilization of E_M relative to E_L. Because ΔE_{ML} decreases, the interaction energy based on the Wolfsberg–Helmholz model is increased. Both trends increase the ligand field strength for the more highly charged metal ion.

These trends can be seen by considering the same ligand set about a metal ion in differently charged states:

Complex	Δ_O /cm^{-1}
$Cr(H_2O)_6^{2+}$	14,100
$Cr(H_2O)_6^{3+}$	17,000
$V(H_2O)_6^{2+}$	12,300
$V(H_2O)_6^{3+}$	18,600
$Co(H_2O)_6^{2+}$	9,300
$Co(H_2O)_6^{3+}$	18,200

(2) *nature of the metal ion*

Why? The radial extension of the wavefunctions of 2nd and 3rd row transition metal ions is much greater than their first row relatives. Thus S_{ML} is larger, leading to the following trend in Δ_O for a given ligand field and metal of a given charge,

$$1^{st} \text{ row TM} \ll 2^{nd} \text{ row TM} \sim 3^{rd} \text{ row TM}$$

Data supporting this trend are

Complex	Δ_O /cm^{-1}
$Co(NH_3)_6^{3+}$	22,870
$Rh(NH_3)_6^{3+}$	34,100
$Ir(NH_3)_6^{3+}$	41,200

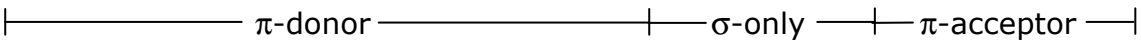
(3) *nature of the ligand field*

Why? As we have now shown with AOM and MO methods, different ligands engender different values of Δ_O. The field strength of various ligands may be assessed by measuring Δ_O for different ligands about a given metal ion of given charge,

Complex	Δ_O /cm^{-1}	Complex	Δ_O /cm^{-1}
$V(H_2O)_6^{3+}$	18,560	$Rh(H_2O)_6^{3+}$	27,000
VF_6^{3-}	16,100	$Rh(NH_3)_6^{3+}$	34,000
VCl_6^{3-}	12,200	$RhCl_6^{3-}$	20,300
$V(CN)_6^{3-}$	23,850	$Rh(CN)_6^{3-}$	~50,000

From these types of experiments, one may deduce a general ranking of ligands in terms of ligand field strength. This ranking is called the **spectrochemical series**:

$$I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < O^{2-} < OH^- < H_2O < NH_3 < CN^- < CO < NO^+$$



In the above ranking, the ligand type has been overlayed onto the spectrochemical series. As is readily apparent from the position of the ligands in the series, π-donors give weak ligand fields (i.e. small Δ_O), σ-only give intermediate ligand fields and π-acceptors give strong ligand fields.

(4) *number and geometry of ligands*

For example, a tetrahedral complex has a smaller ligand field than an octahedral complex. As we have derived from AOM,

$$\Delta_t = -4/9\Delta_O$$