Chem 241

Lecture 12

Reminder

- We have an exam on the 19th (Friday).
  - → You may bring a model kit
  - → Pencil and calculator

Recap

- Coordination Compounds
- Isomers
- CFT

Square-planar complexes (spl)

- the CFT diagram for spl geometry can be derived from the O_h CFT diagram by removing two trans ligands, and shortening the remaining 4.
- $\eta\Delta_{sp} = 1.3\ \Delta_o$
- Spl geometry is most favorable for d8 complexes
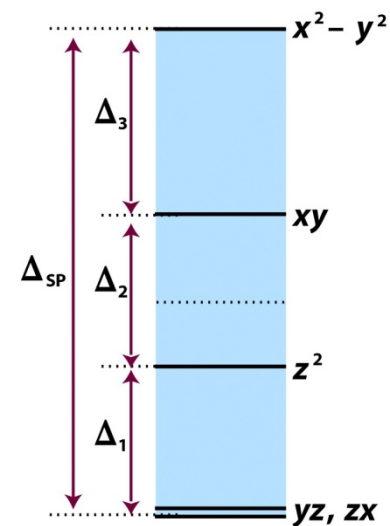- Particularly for 2nd and 3rd row metals, which have larger values of Δ_o

Figure 19-9
Shriver & Atkins Inorganic Chemistry, Fourth Edition
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Jahn-Teller distortion

- Theorem: when an electronic degeneracy exists, the complex will distort so as to remove the degeneracy and minimize the energy.
- Most important for complexes with degeneracies in the orbitals pointed at the ligands (higher energy orbitals.
- e.g., 6 coordinate d^9
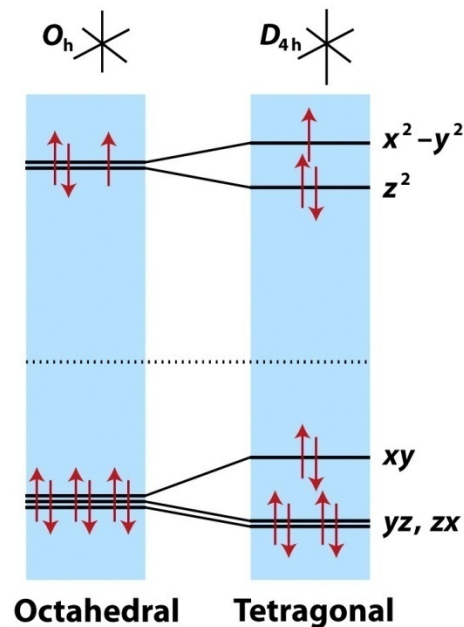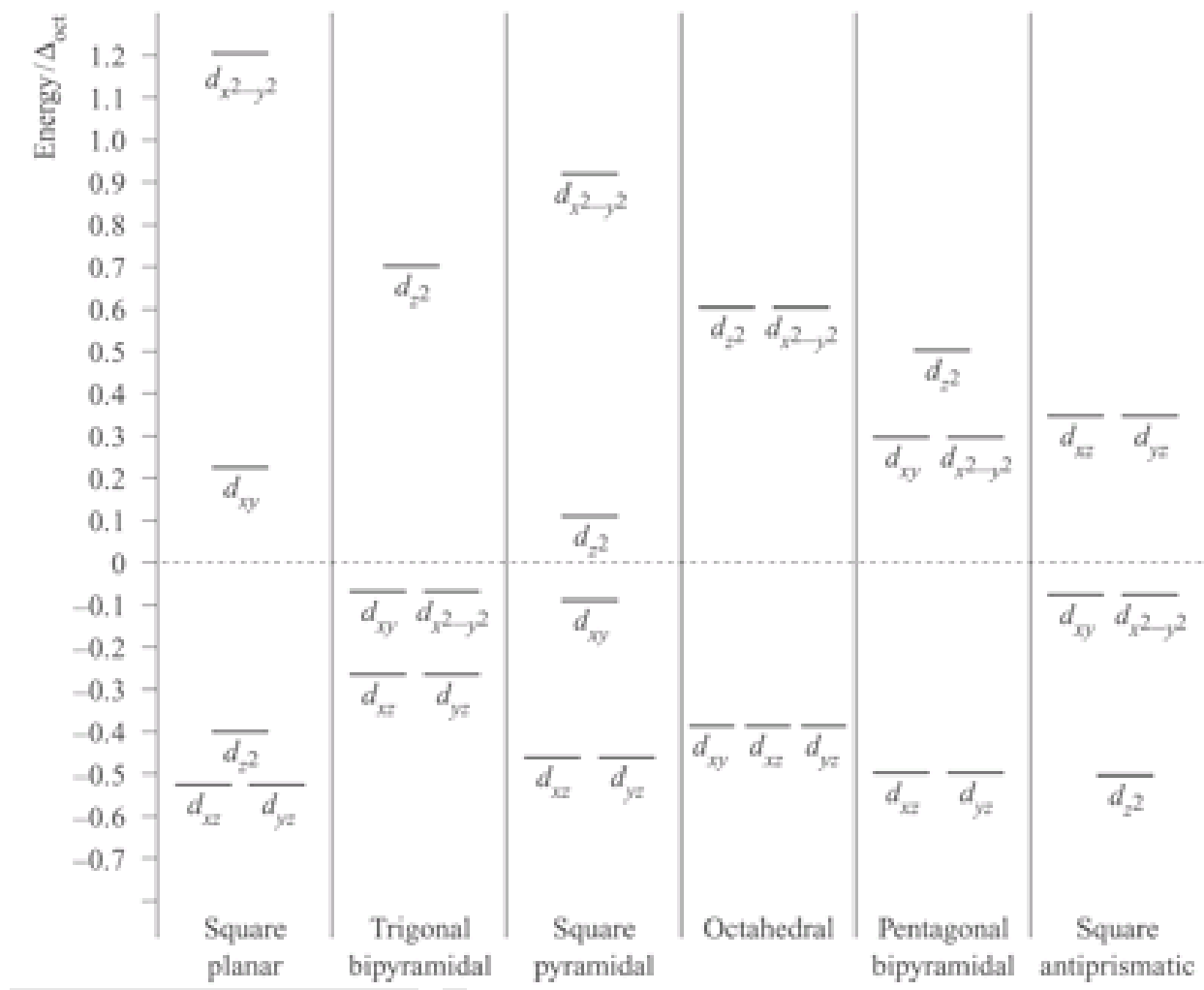- Does not predict the nature of the distortion.

Figure 19-10
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Splitting

Ligand Field Theory

- MOT for O_h symmetry
- Metal valence orbitals for a 1st row case:

O_h $(m3m)$	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	$h=48$
A_{1g}	1	1	1	1	1	1	1	1	1	1	$x^2+y^2+z^2$
A_{2g}	1	1	-1	-1	1	1	-1	1	1	-1	
E_g	2	-1	0	0	2	2	0	-1	2	0	$(2z^2-x^2-y^2, x^2-y^2)$
T_{1g}	3	0	-1	1	-1	3	1	0	-1	-1	(R_x, R_y, R_z)
T_{2g}	3	0	1	-1	-1	3	-1	0	-1	1	(xy, yz, zx)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1	
A_{2u}	1	1	-1	-1	1	-1	1	-1	-1	1	
E_u	2	-1	0	0	2	-2	0	1	-2	0	
T_{1u}	3	0	-1	1	-1	-3	-1	0	1	1	(x, y, z)
T_{2u}	3	0	1	-1	-1	-3	1	0	1	-1	

$$3d \ - \ t_{2g} + e_g$$
$$4s \ - \ a_{1g}$$
$$4p \ - \ t_{1u}$$

Ligand Field Theory

- Ligands with only valence orbital
- 6 Ligand s-donor orbitals lead to 6 SALCS:

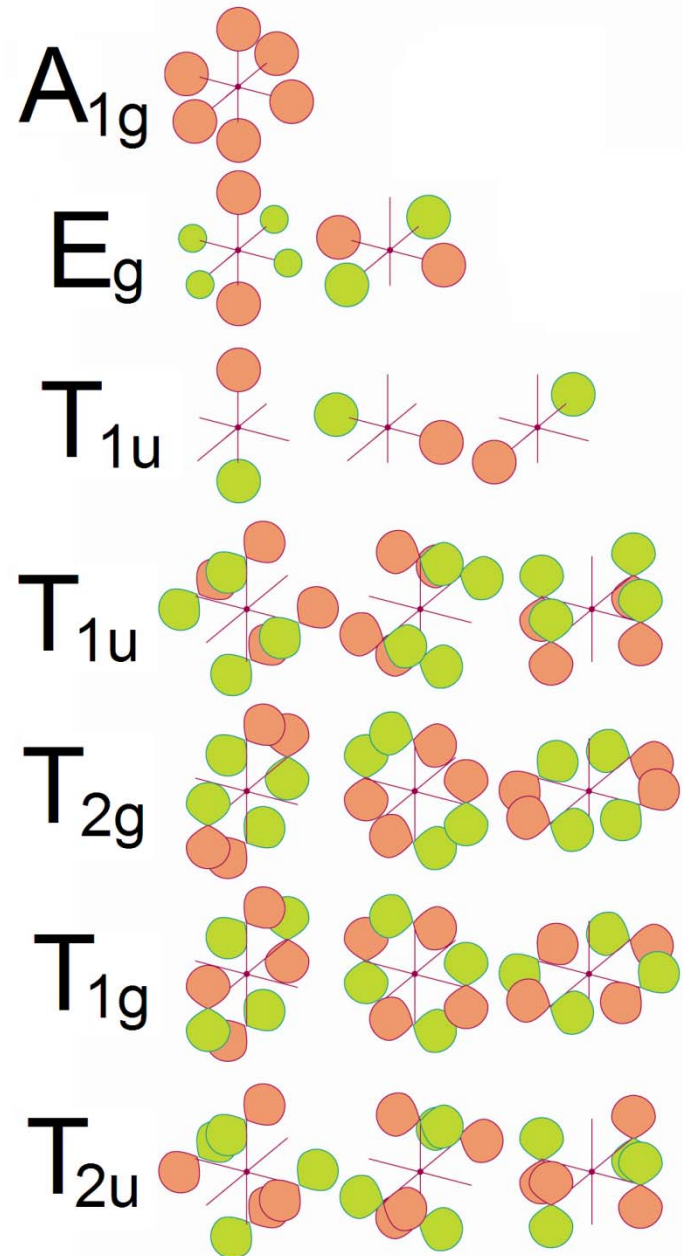- $\sigma_1 + \sigma_2 + \sigma_3 + \sigma_4 + \sigma_5 + \sigma_6$ (a_{1g})
- $\sigma_1 - \sigma_2 + \sigma_3 - \sigma_4$ (e_g)

  $2\sigma_6 + 2\sigma_5 - \sigma_1 - \sigma_2 - \sigma_3 - \sigma_4$
- $\sigma_1 - \sigma_3$ (t_{1u})

  $\sigma_2 - \sigma_4$

  $\sigma_5 - \sigma_6$

A_{1g}

E_g

T_{1u}

T_{1u}

T_{2g}

T_{1g}

T_{2u}

Ligand Field Theory

A good σ-donor should result in a strong metal-ligand overlap, hence a more strongly anti-bonding e_g set and a larger value of Δ_o.
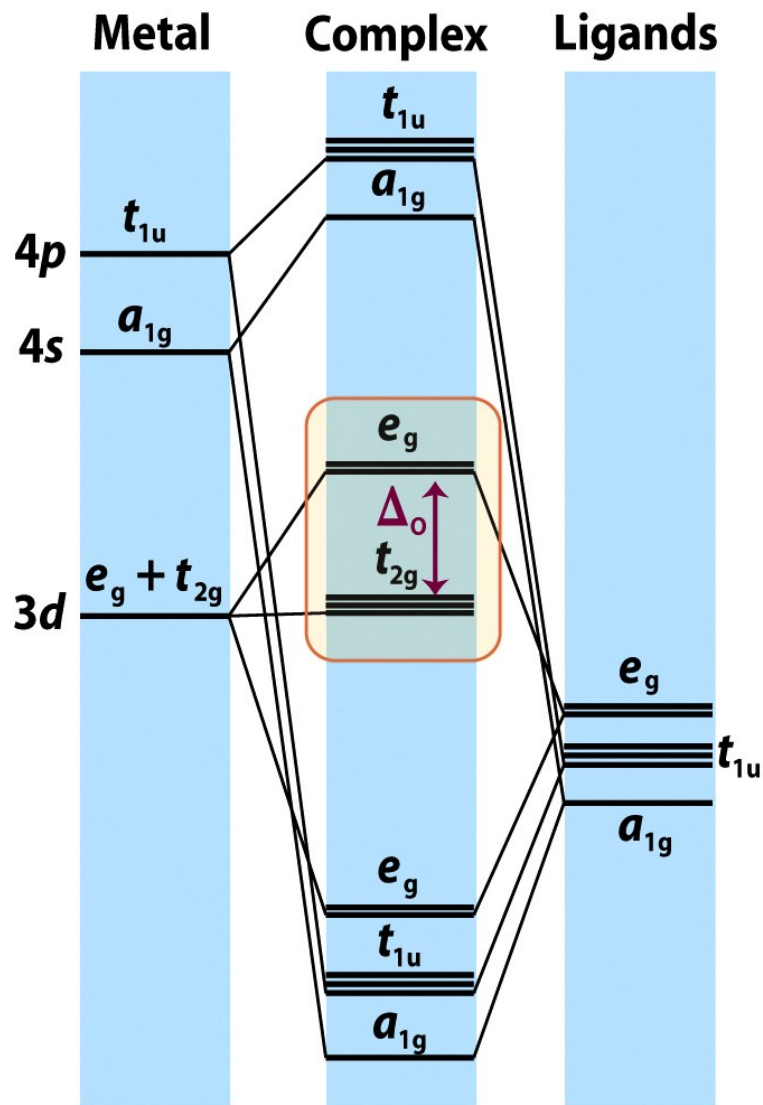

Figure 19-13
Shriver & Atkins Inorganic Chemistry, Fourth Edition
kins, T. L. Overton, J. P. Rourke, M. T. Weller, and F. A. Armstrong

Consider π-orbitals

Metal **Complex** **Ligands**

t_{1u}

a_{1g}

$4p$ t_{1u}

$4s$ a_{1g}

e_g

Δ_o

t_{2g}

$3d$ $e_g + t_{2g}$

e_g

t_{1u}

a_{1g}

e_g

t_{1u}

a_{1g}

A_{1g}
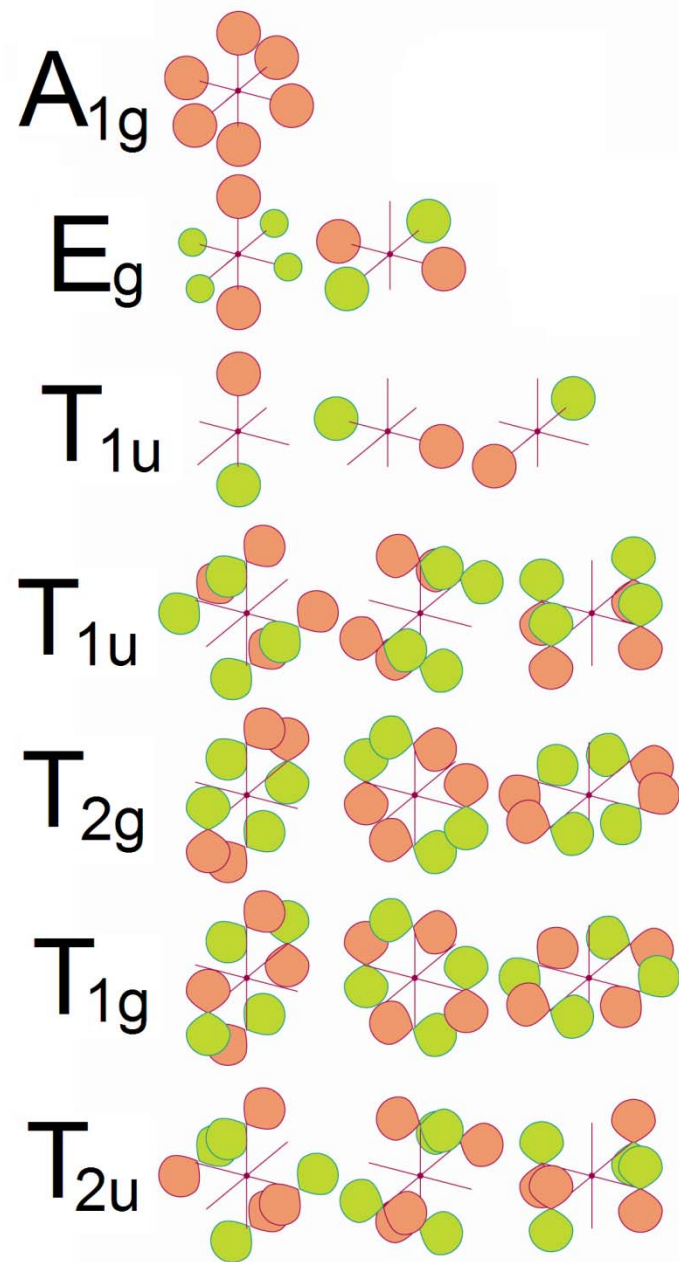
E_g

T_{1u}

T_{1u}

T_{2g}

T_{1g}

T_{2u}

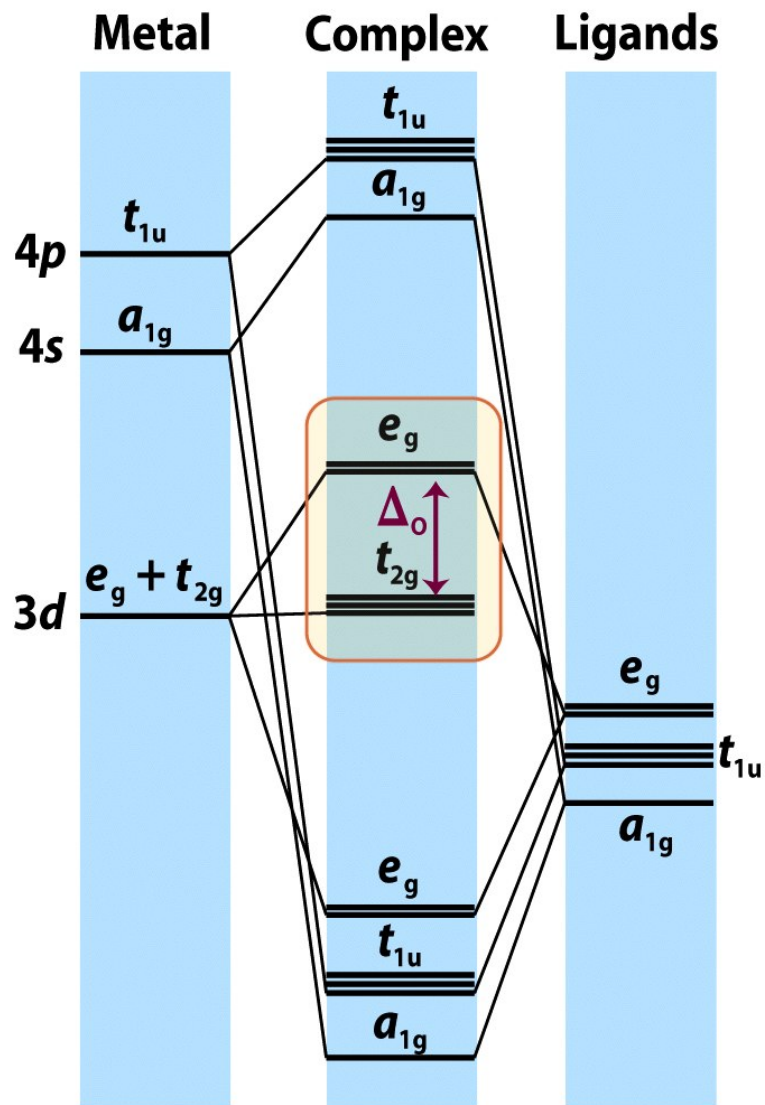Figure 19-13
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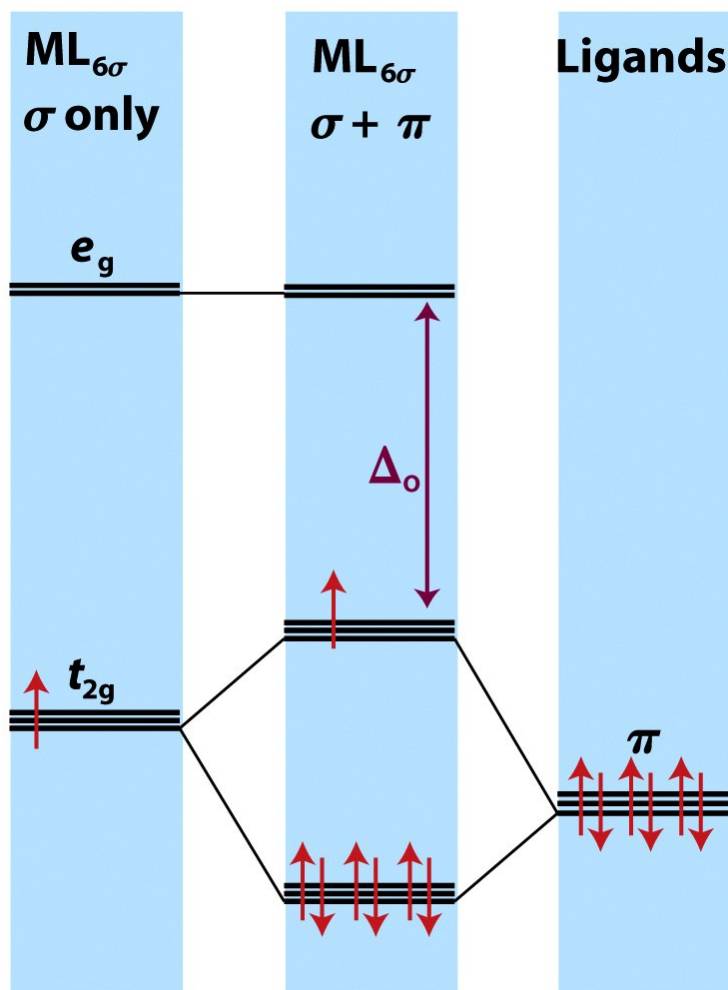
Consider π-orbitals

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Figure 19-18
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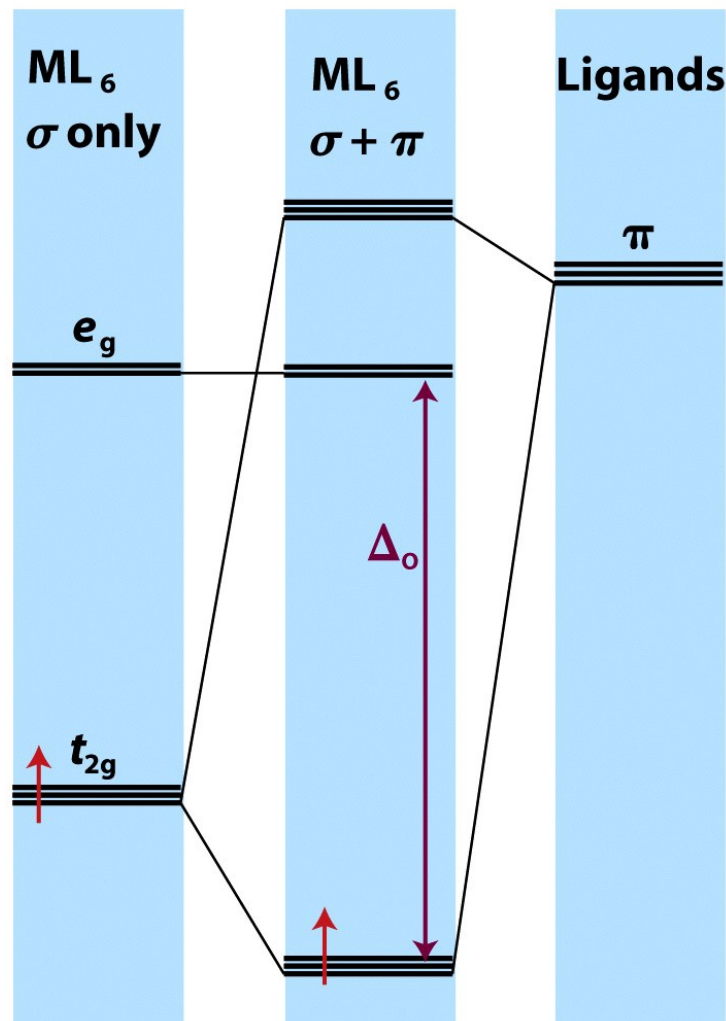
Coordination compounds

We are now in a position to understand the spectrochemical series.

- Δ_o: I^- < Br^- < S^{2-} < $-SCN^-$ < Cl^- < $-O_2N^-$ < N_3^- < F^- < OH^- < ox^{2-} < H_2O < $-NCS^-$ < CH_3CN < py < NH_3 < en < bipy < phen < $-NO_2^-$ < PPh_3 < CN^- < CO

Δ_o: σ + π-donors < σ-donors < σ-donors + π-acceptors

Absorption

Figure 19-19
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Charge Transfer

Figure 19-28
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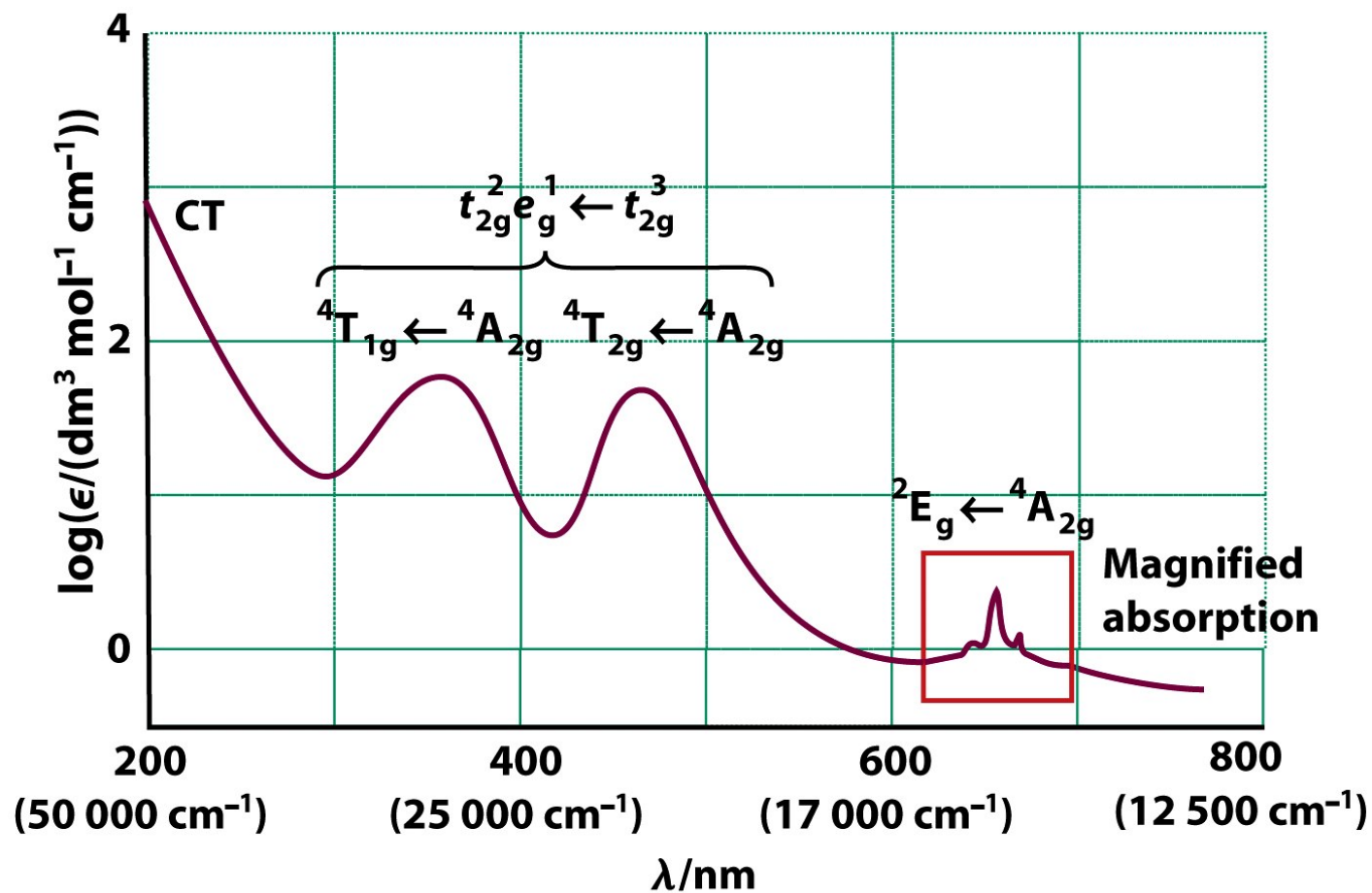© 2006 by D. F. Shriver, P. W. Atkins, T. L. Overton, J. P. Rourke, M. T. Weller and F. A. Armstrong
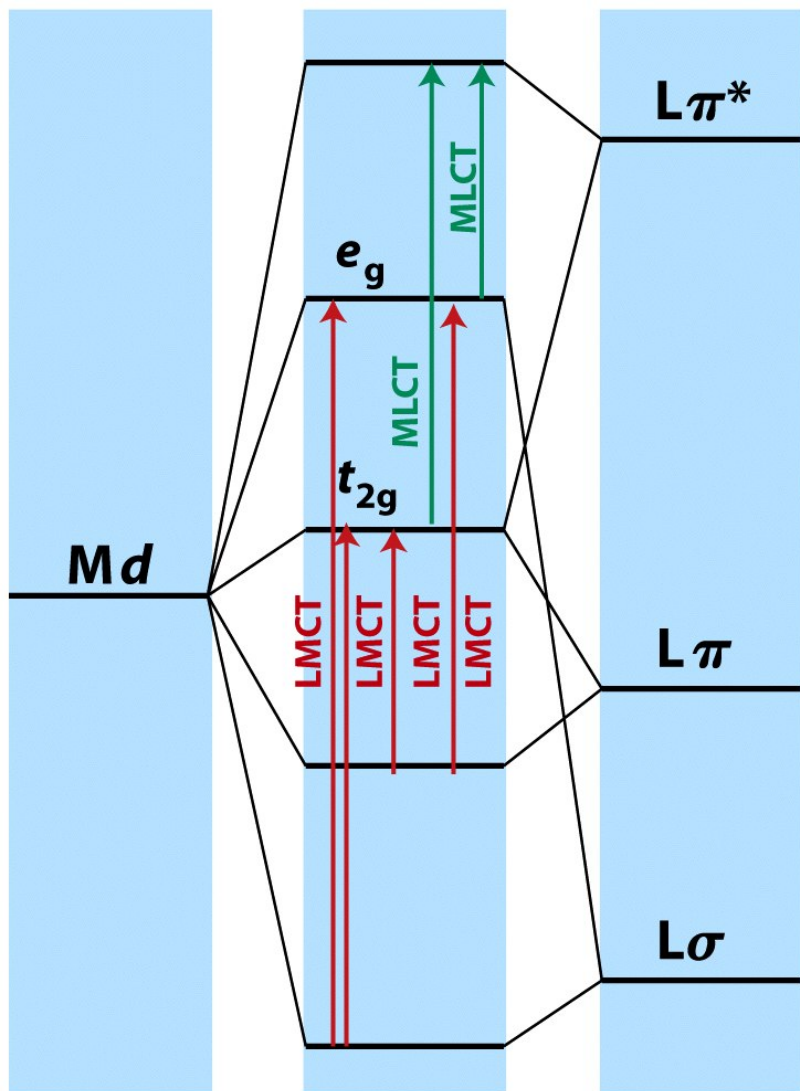

Figure 19-29
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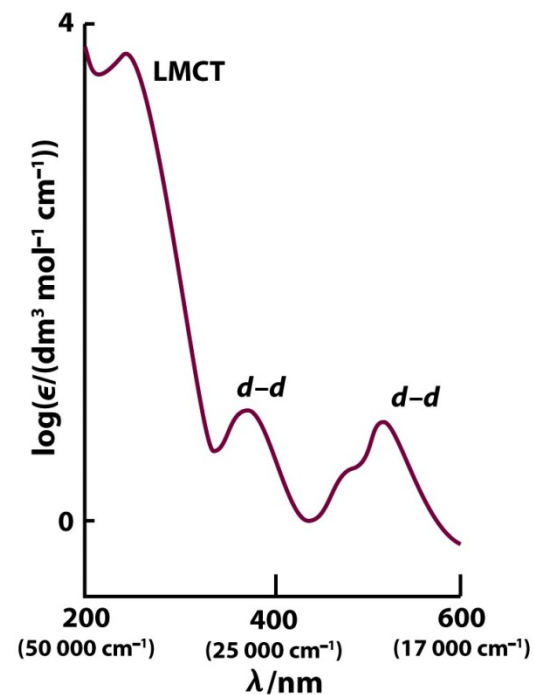
Solvatochromism

- Negative solvatochromism corresponds to <u>hypsochromic shift</u>,
- Positive solvatochromism corresponds to <u>bathochromic shift</u> with increasing solvent polarity.

$n - \pi^*$ transition

non-polar
ES ———

$h\nu_{np}$

$h\nu_{np} < h\nu_p$ $h\nu_p$ increase in transition energy (shift to lower wavelength)

non-polar solvent $\Rightarrow$ polar solvent

GS ———
polar

(2)

GS = ground state, ES = excited state   ↜ specific stabilization of the ground state

$\pi - \pi^*$ transition

polar
ES ———

$h\nu_{np}$

specific stabilization of the excited state

$h\nu_{np} > h\nu_p$ $h\nu_p$ decrease in transition energy (shift to higher wavelength)

non-polar solvent $\Rightarrow$ polar solvent

(2)

GS ———
non-polar

GS = ground state, ES = excited state