CH 611 Advanced Inorganic Chemistry – Synthesis and Analysis

Quiz # 2 : Ligand Field Theory 10/05/2009

Print Name:_________________________

1.

In a transition metal complex of O_h symmetry (relative to a spherical ligand field);
The e_g orbitals have lobes that point at the ligands and so will increase in energy.
The t_{2g} orbitals have lobes that lie between ligands and so will decrease in energy.
The energy of the e_g set rises by +3/5 Δ_o
The energy of the t_{2g} set falls by -2/5 Δ_o
This results in zero energy change for the system.

2.

The magnitude of Δ_o depends upon which 3 of the following components

i) the metal ion
ii) the attaching ligands
iii) the counterion
iv) the solvent
v) the metal oxidation state

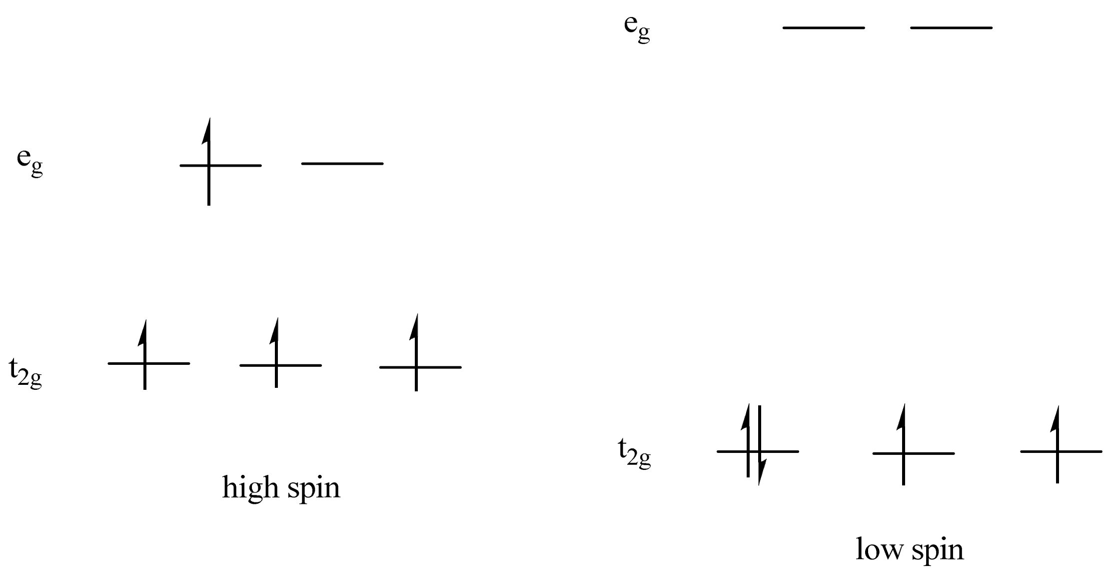
3.

The electrons fill the d orbitals starting with the t_{2g} set in accordance with

i) the aufbau principle
ii) Heisenberg uncertainty principle
iii) the Pauli exclusion principle
iv) Hund's rule of maximum multiplicity
v) Franck-Condon principle

4.

In 1st row metals complexes, low-field ligands (strong π - donors) favor high spin configurations whereas high field ligands (π-acceptors/ strong σ donors) favor low spin. The majority of 2nd and 3rd row metal complexes are low-spin irrespective of their ligands (*greater M-L overlap; decreased* Π_e *due to larger volume of d orbitals*). If the mean pairing energy (P) is greater than Δ_o, a lower energy state will result by putting the electron in the higher e_g level.
Draw both the "high spin" and "low spin" configurations for a first row d^4 transition metal complex.



5.

MO theory is a method for determining molecular structure in which electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule. Ligand field theory (LFT) represents an application of molecular orbital (MO) theory to transition metal complexes.
For effective overlap to occur between metal atom orbitals and the SALC's there are two important requisites. Please select these requisites from the following list:

i) Shape
ii) Energy
iii) Symmetry
iv) Size
v) Occupancy

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6.

Using the character table below determine the irreducible representations of the metal and ligand (σ only) orbitals for the O_h point group.

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		
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, xz, yz)
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		
Γ	6	0	0	2	2	0	0	0	4	2		$x^2+y^2+z^2$
A_{1g}	1	1	1	1	1	1	1	1	1	1		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2-x^2-y^2, x^2-y^2)$

Metal

A_{1g} : s

T_{1u} : p_x , p_y , p_z

E_g : dz^2 , dx^2-dy^2

T_{2g} : dxy, dxz, dyz

Ligand

Γ_σ : $A_{1g} + T_{1u} + E_g$

7.

Using the character table below determine the irreducible representations of the metal and ligand <u>(σ and π irreducible representations)</u> orbitals for the T_d point group.

TABLE 10-10
Representations of Tetrahedral Orbitals

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1			$x^2 + y^2 + z^2$
A_2	1	−1	1	−1			
E	2	−1	2	0			$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	−1	1		(R_x, R_y, R_z)	
T_2	3	0	−1	−1		(x, y, z)	(xy, yz, xz)
Γ_σ	4	1	0	0		$A_1 + T_2$	
Γ_π	8	−1	0	0		$E + T_1 + T_2$	

Metal

A_1 : s

T_2 : p_x , p_y , p_z

E : dz^2 , dx^2-dy^2

T_2 : dxy, dxz, dyz

Ligand

Γ_σ : $A_1 + T$

Γ_π : $E_g + T_1 + T_2$

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8.

Using the character table below determine the irreducible representations of the metal and ligand orbitals for the D_{4h} (square planar) point group in a σ only bonding system.

TABLE 10-9
Representations and Orbital Symmetry for Square-Planar Complexes

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
A_{1g}	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	R_z	
B_{1g}	1	−1	1	1		1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1		1	−1	1	−1	1		xy
E_g	2	0	−2	0		2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1		−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1		−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1		−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1		−1	1	−1	1	−1		
E_u	2	0	−2	0		−2	0	2	0	0	(x, y)	

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
Γ_{p_x}	4	0	0	−2		0	0	4	−2	0	$p_\parallel$
Γ_{p_y}	4	0	0	2		0	0	4	2	0	p_σ
Γ_{p_z}	4	0	0	−2		0	0	−4	2	0	$p_\perp$

$\Gamma_{p_y} = A_{1g} + B_{1g} + E_u$ (σ) Matching orbitals on the central atom: $s, d_{z^2}, d_{x^2-y^2}, (p_x, p_y)$

$\Gamma_{p_x} = A_{2g} + B_{2g} + E_u$ (∥) Matching orbitals on the central atom: $d_{xy}, (p_x, p_y)$

$\Gamma_{p_z} = A_{2u} + B_{2u} + E_g$ (⊥) Matching orbitals on the central atom: $p_z, (d_{xz}, d_{yz})$

Metal

A_{1g} : s

E_u : p_x , p_y

A_{2u} : p_z

A_{1g}: dz^2

B_{1g} : dx^2-dy^2

B_{2g} : dxy

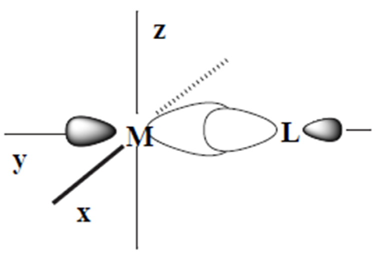
E_g : dxz, dyz

Ligand

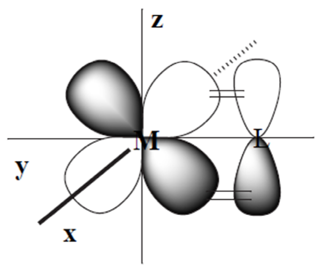
Γ_σ : $A_{1g} + B_{1g} + E_u$

9.

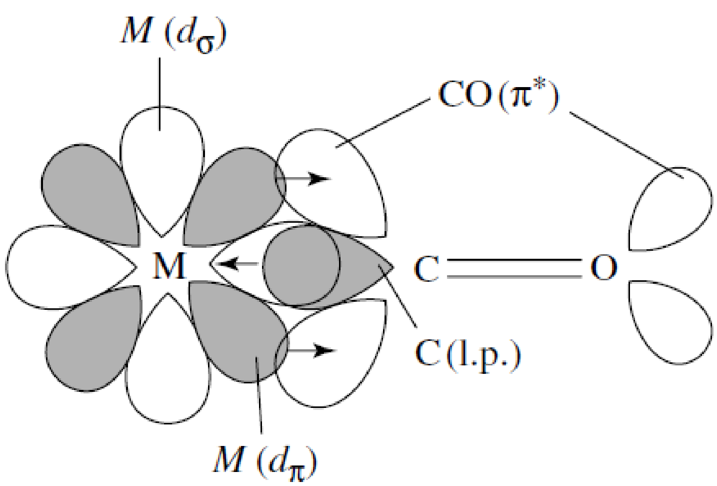
Draw the σ and π bonding interactions for a metal carbonyl bond. Very briefly explain why this interaction weakens the CO bond strength.



L → M σ-bonding



M → L π-bonding



Back donation from the metal to the carbonyl ligand populates the π^* anti-bonding orbital of the CO ligand thus reducing its bond order.

10.

In the following diagram label each of the three bonding schemes as either σ-only bonding, σ-donor/π-acceptor or σ-donor/π-donor bonding interactions.