LECTURE 27/36 NOV/11/02

CRYSTAL FIELD THEORY

READ GRAY CH 5

TODAY'S LEC 148 - 158
NEXT LEC 158 - 170

Transition Metals: partially filled d-orbitals

Table 15.5
Electron Configurations and Other Properties of the First-Row Transition Metals

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
Electron configurations									
M	$4s^2 3d^1$	$4s^2 3d^2$	$4s^2 3d^3$	$4s^1 3d^5$	$4s^2 3d^5$	$4s^2 3d^6$	$4s^2 3d^7$	$4s^2 3d^8$	$4s^1 3d^{10}$
M^{2+}	—	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	$3d^7$	$3d^8$	$3d^9$
M^{3+}	[Ne]	$3d^1$	$3d^2$	$3d^3$	$3d^4$	$3d^5$	$3d^6$	...	...
Ionization energy/kJ · mol^{-1}									
First	631	658	650	652	717	759	760	736	745
Second	1235	1309	1414	1591	1509	1561	1645	1751	1958
Third	2388	2650	2828	2986	3251	2956	3231	3393	3578
Radius/Å									
M	1.44	1.36	1.22	1.17	1.17	1.16	1.16	1.15	1.17
M^{2+}	—	0.90	0.88	0.85	0.80	0.77	0.75	0.72	0.72
M^{3+}	0.81	0.77	0.74	0.68	0.66	0.63	0.64	—	—

Common Geometries of Transition Metal Complexes

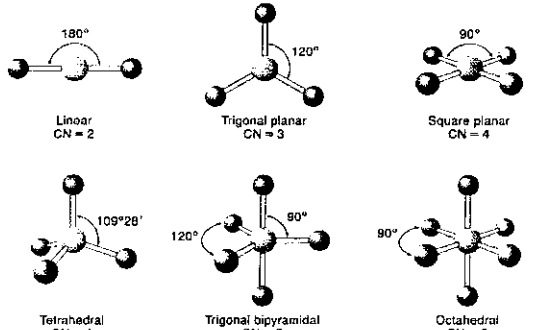
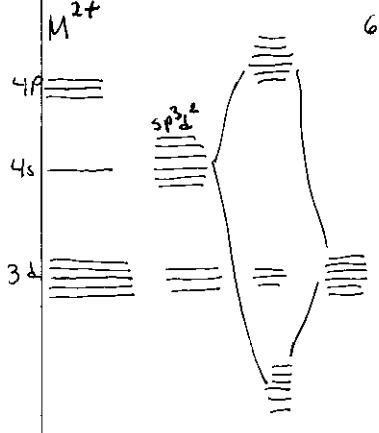


Figure 15.23

ML_n		Hybridization
ML_2	linear	sp
ML_3	Trig planar	sp^2
ML_4	sq. planar	sp^2d
	tetrahedral	sp^3
ML_5	sq. pyramidal	sp^3d^2
	trig bipyramidal	sp^3d
ML_6	octahedral	sp^3d^2



d^8 $12e^-$ $= 20e^-$

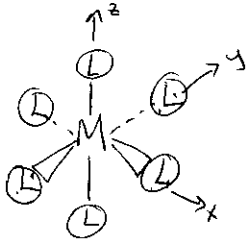
$Ni(NH_3)_6^{2+}$

$\Rightarrow$ PARAMAGNETIC

WRONG

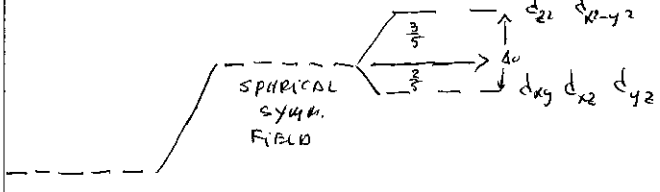
NO COLOR EXPLANATION

CRYSTAL FIELD THEORY



NOTICE THAT THE d_{z^2} AND $d_{x^2-y^2}$ ORBITALS POINT IN THE DIRECTION OF THE LIGANDS. IN CONTRAST d_{xy}, d_{yz} AND d_{xz} ORBITALS DO NOT POINT IN THE DIRECTION OF THE LIGANDS. WE CAN THINK THAT THE d ORBITALS ARE SURROUNDED BY THE LIGANDS. THE ELECTRON CLOUD DUE TO THE LIGANDS HAS AN OCTAHEDRAL SYMMETRY, THIS CLOUD HAS A WET EFFECT PRODUCING A FIELD AROUND THE METAL. TO FIRST APPROXIMATION WE CAN CONSIDER AN ION (M^{2+}) IN

A FIELD W/ SPHERICAL SYMMETRY, BUT THIS FIELD AFFECTS EQUALLY ALL d ORBITALS. IF WE CONSIDER THE ACTUAL OCTAHEDRAL SYMMETRY, THE EXTERNAL, TO THE M^{+4}, FIELD INTERACTS STRONGLY WITH THE d_{z^2} AND $d_{x^2-y^2}$ ORBITALS. THUS THE 5 d ORBITAL SPLIT UNDER AN OCTAHEDRAL FIELD. THIS FIELD IS CALLED THE "CRYSTAL FIELD"



$\Delta_o \equiv$ OCTAHEDRAL CRYSTAL FIELD SPLITTING ENERGY

e_g ORBITALS d_{z^2} $d_{x^2-y^2}$ — POINT AT LIGANDS GREAT REPULSION ↑ ENERGY

t_{2g} ORBITALS d_{xy} d_{xz} d_{yz} — POINT AWAY LESS REPULSION ↓ E

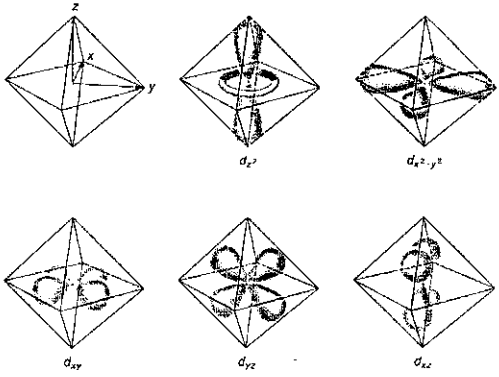


Figure 15.24

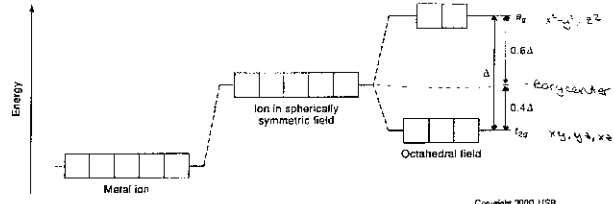


Figure 15.25

COLOR → ABSORPTION OF PHOTON $h\nu = \Delta_o$

$Ni(H_2O)_6^{2+}$	SEE GREEN	ABS RED
$Ni(NH_3)_6^{2+}$	SEE BLUE	ABS ORANGE
$Ni(en)_3^{2+}$	SEE VIOLET	ABS YELLOW
$Ni(dmgh)_2(H_2O)_2^{2+}$	SEE RED	ABS GREEN

ACCORDING TO CFT

λ_{ABS} DECREASES

E INCREASES

Δ_o INCREASES

Δ_o INCREASES SPECTROCHEMICAL SERIES

$$F^- < H_2O < NH_3 < en < dmgh < o\text{-}phen < NO_2^- < CN^-$$

↑ WEAK FIELD LIGAND

↑ STRONG FIELD LIGAND

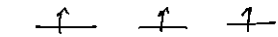
$$I^- < Br^- < Cl^- < SCN^- < F^- < OH^- < H_2O < NH_3 < NO_2^- < CN^-, CO$$

d^0 Sr^{2+} t_{2g}^0

d^1 Ti^{3+} t_{2g}^1

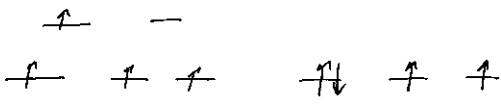
d^2 Ti^{2+} t_{2g}^2

d^3 V^{2+} t_{2g}^3



P ≡ PAIRING ENERGY COST OF ↑↓ vs ↑ ↑

d^4 t_{2g}^4 $t_{2g}^3 e_g^1$



HIGH SPIN

$\Delta_o < P$

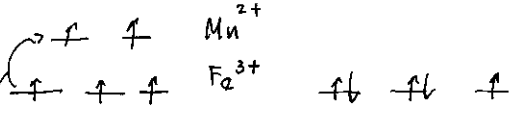
HS

LOW SPIN

$\Delta_o > P$

LS

d^5 t_{2g}^5 $t_{2g}^3 e_g^2$



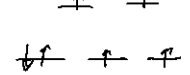
Mn^{2+}

Fe^{3+}

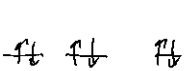
→ TRANSITION SPIN FORBIDDEN => RARE PROCESS WEAKLY COLORED

d^6 t_{2g}^6

$t_{2g}^4 e_g^2$



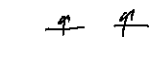
High spin



low spin

d^7 $t_{2g}^6 e_g^1$

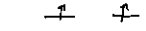
$t_{2g}^5 e_g^2$



d^8 $t_{2g}^6 e_g^2$

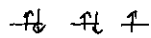
d^9 $t_{2g}^6 e_g^3$

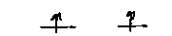
d^{10} $t_{2g}^6 e_g^4$

$Fe(H_2O)_6^{+3}$  WEAK / COLOR - PALE ORANGE

Fe^{3+} $\downarrow NO_2^-$

$Fe(NO_2)_6^{-3}$ STRONG / DEEP RED

 MORE TRANS. ALLOWED

$Co(F)_6^{-3}$ WEAK  PARA MAGNETIC

Co^{3+}

 DIA MAGNETIC

$Co(CN)_6^{3-}$ STRONG