(31) **Today**

Section 10.5 The Jahn-Teller Effect

Chap 12

Next Class (32)

Chap 12

(33) **Second Class from Today**

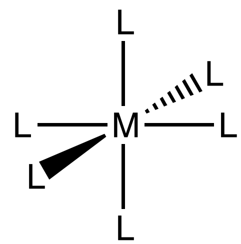
Chap 12

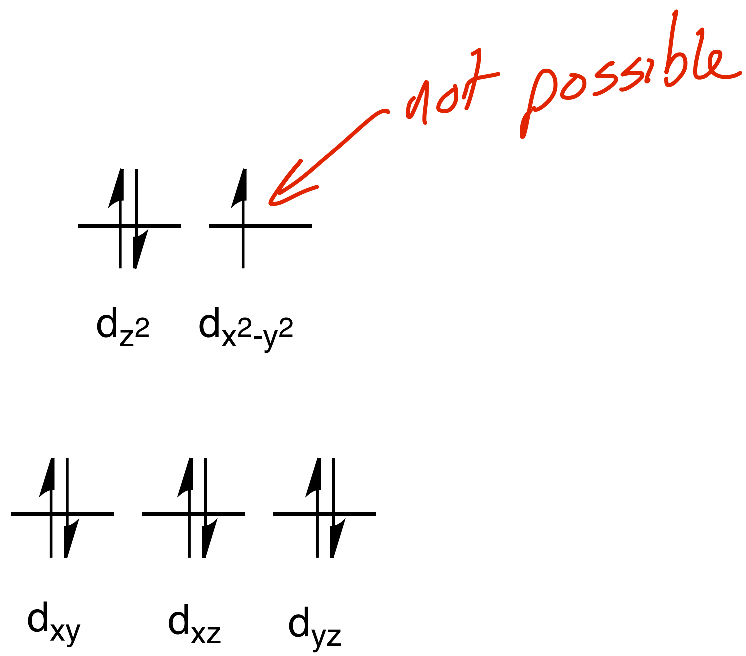
Third Class from Today (34)

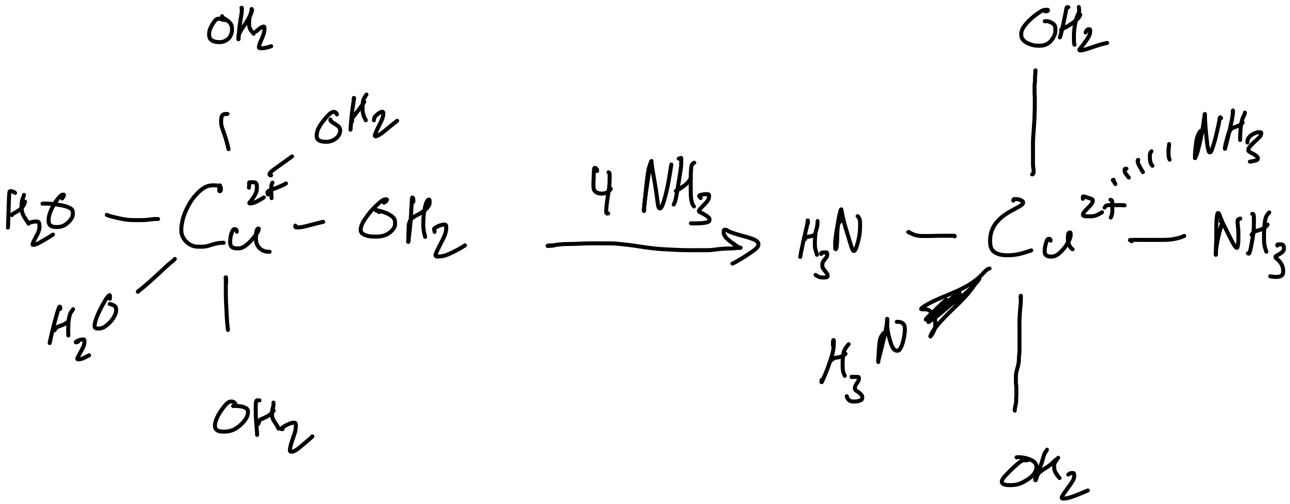
Chap 12?

Unevenly occupied degenerate orbitals are not possible.

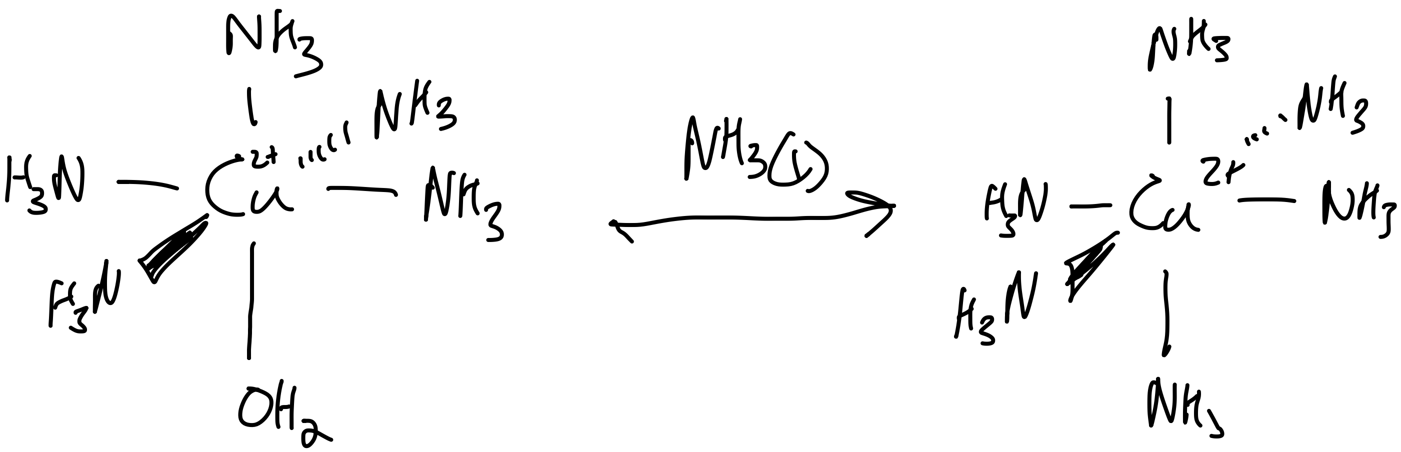
Molecules will distort to remove degeneracy.







K very favorable

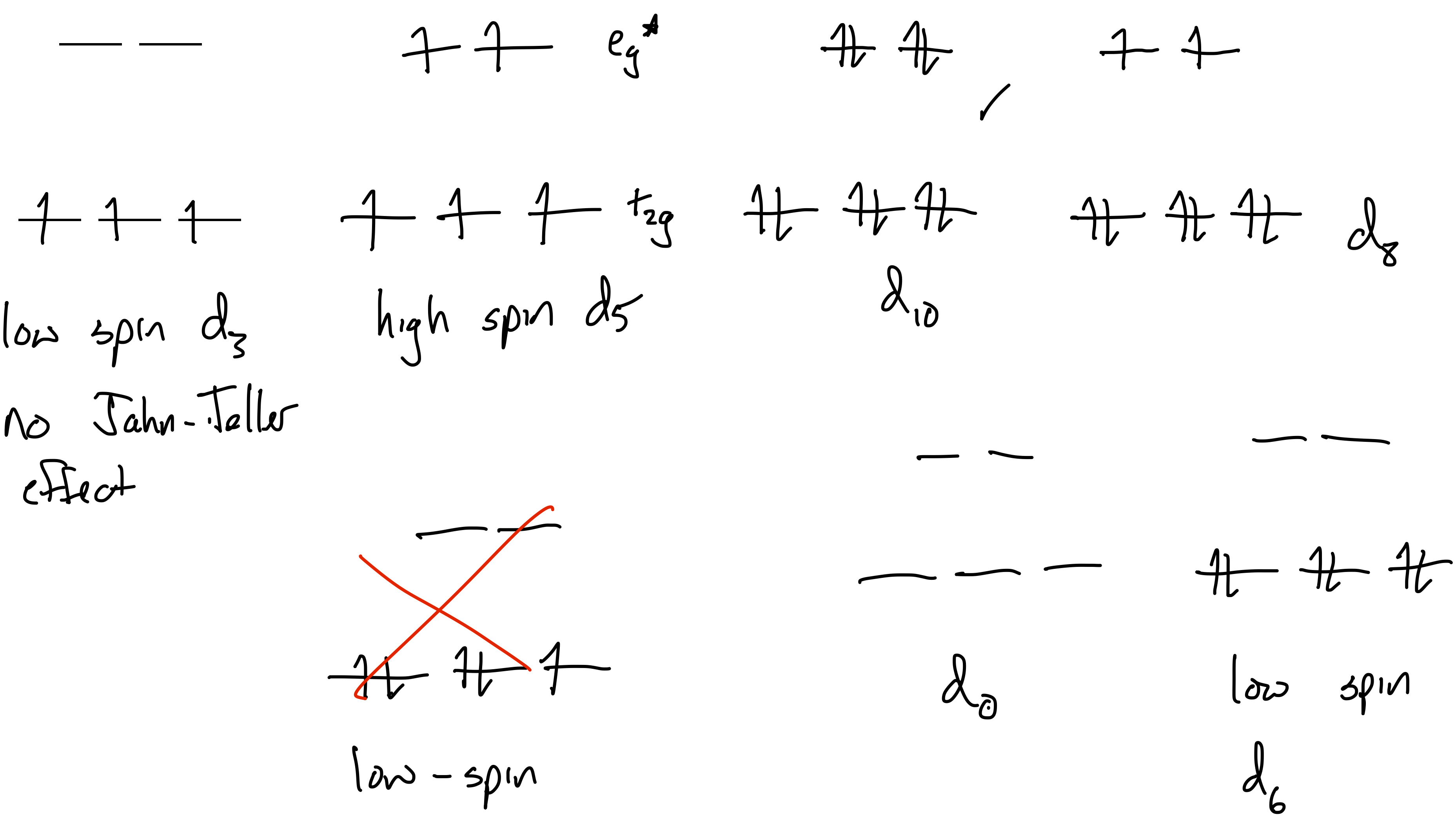


K not favorable

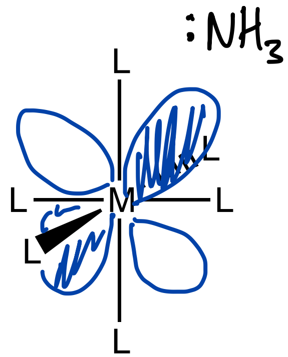
perhaps because the bonds are weaker as a result of Jahn-Teller Effect
so in aqueous solution ([H2O] >> [NH3]) H2O displaces the weakly held NH3

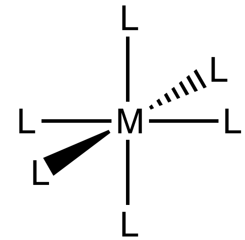
Which arrangements of electrons will not experience Jahn-Teller Effects?

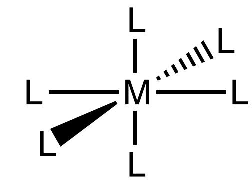
no uneven distribution of e^-'s

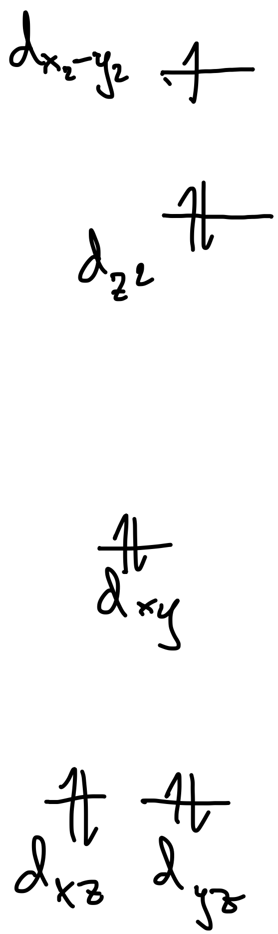


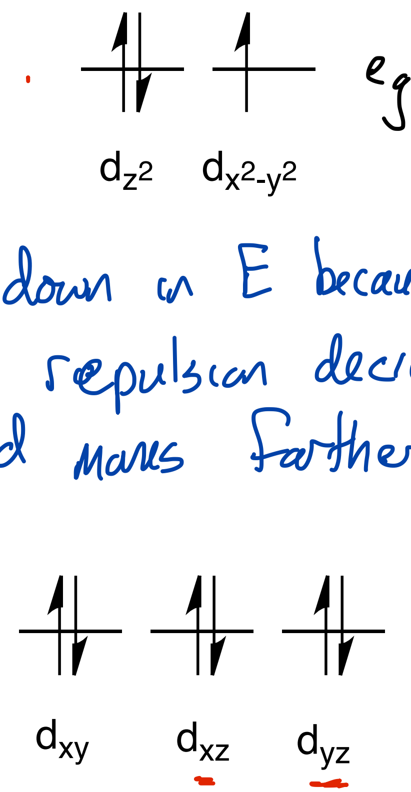
Jahn-Teller Effect Molecule distorts to remove the degeneracy Section 10.5



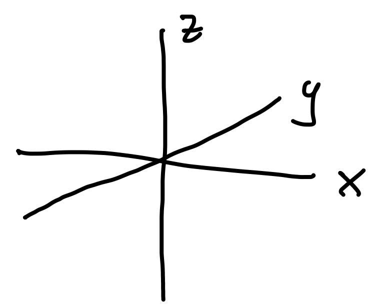


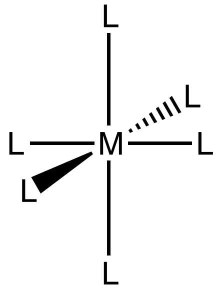


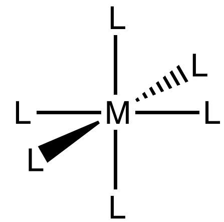


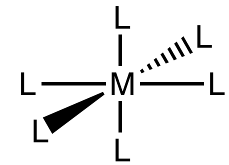


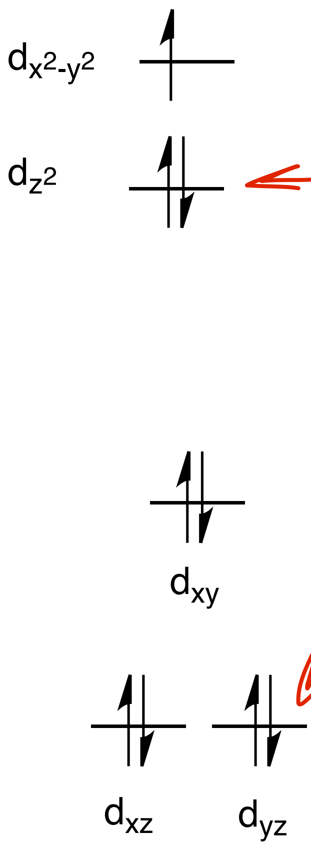
goes down in E because $e^- - e^-$ repulsion decreases as ligand moves farther away







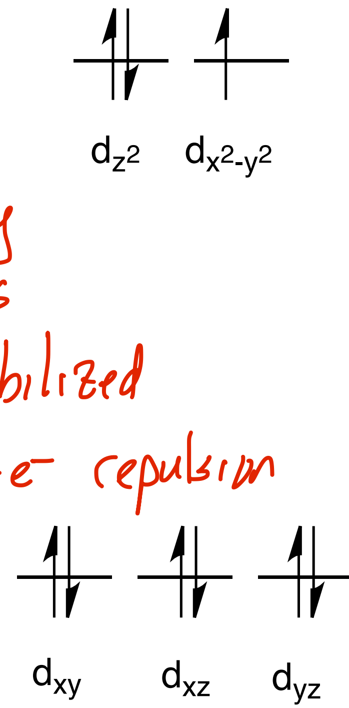




ligand Farther away on z axis

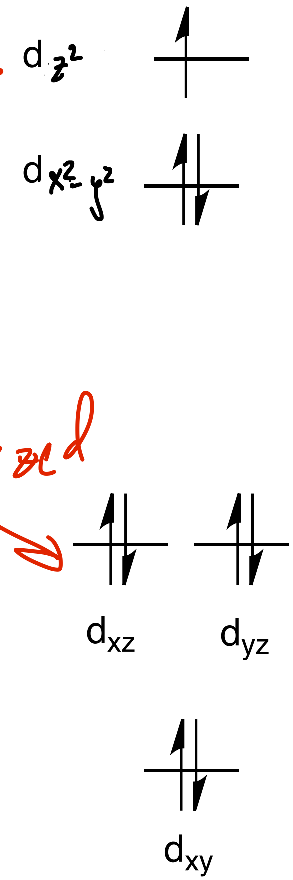
less destabilized

less e^- – e^- repulsion



ligand gets closer on the z axis....

more destabilized



Substitution one ligand is exchanged for another

$$[Ni(H_2O)_6]^{2+} + 6\ NH_3 \longrightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$$

oxidation-reduction e^-'s are being transfered to or from the metal

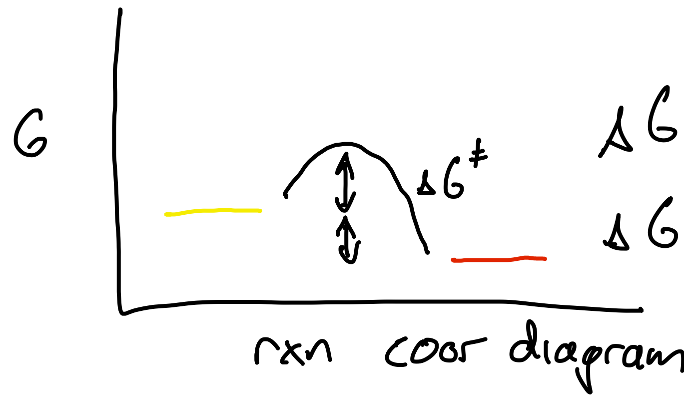
$$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+} + 2Ag$$

Cu loses $2e^-$ and 2 Ag^+ ions each gain 1 e^-

reactions on the ligands

react quickly

react slowly ... if at all

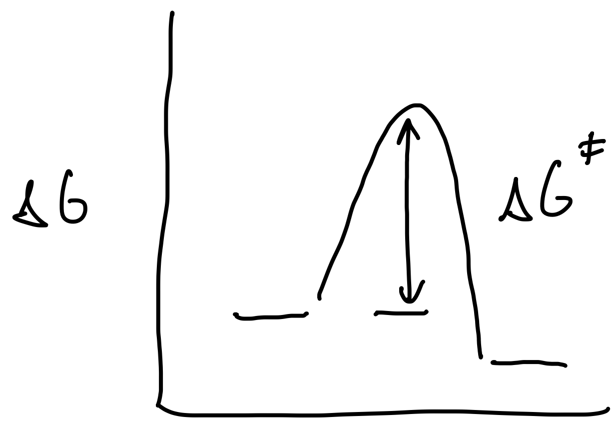


$\Delta G^{\ddagger}$ small = fast

$\Delta G < 0$ Favorable

will still react quickly with F^-

$[Fe(H_2O)_6]^{3+} + SCN^- \rightleftharpoons [Fe(H_2O)_5(SCN)]^{2+} + H_2O$



$\Delta G^{\ddagger}$ is large so $[Co(NH_3)_6]^{3+}$ is considered "inert"

$\Delta G < 0$

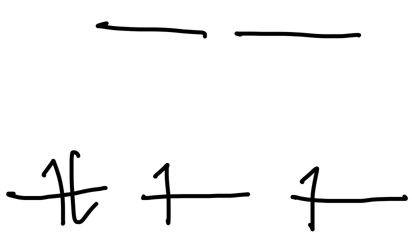
$[Co(NH_3)_6]^{3+} + 6\ H_3O^+ \rightleftharpoons [Co(H_2O)_6]^{3+} + 6\ NH_4^+$

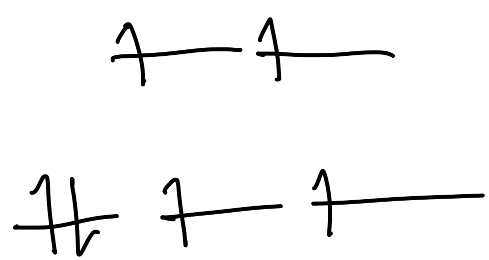
inert

Inert

Werner studied Co(III) Cr(III) Pt(II) Pt(IV)

"Inert" (Slow Reactions)		**Labile (Fast Reactions)**
d^3 low-spin d^4, d^5, and d^6 strong-field d^8	weak-field d^8	d^1, d^2 high-spin d^4, d^5, and d^6 d^7, d^9, d^{10}





more repulsion between d e^-'s & ligands

Mechanisms of Substitution $Y + ML_5X \rightarrow ML_5Y + X$ Section 12.2

Dissociation dissociative mechanism S_N1

$$[Fe(H_2O)_6]^{3+} + SCN^{\ominus} \rightarrow \underbrace{[Fe(H_2O)_5]^{3+}}_{\text{intermediate}} + H_2O + SCN^{-} \rightarrow [Fe(H_2O)_5SCN] + H_2O$$

Association associative mechanism

$$ML_5X + Y \rightarrow \underbrace{YML_5X}_{\text{intermediate}} \rightarrow YML_5 + X$$

Interchange

transition state cannot be seen or isolated

$$ML_5Y + X \rightarrow [Y \cdots ML_5 \cdots X]^{\ddagger} \rightarrow YML_5 + X \qquad S_N2$$

simultaneous bond breaking + making

I_d more bond breaking

I_a more bond making

$$ML_5X \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ML_5 + X$$

$$ML_5 + Y \xrightarrow{k_2} ML_5Y$$

assuming $k_2 \gg k_{-2}$

$$\frac{d[ML_5Y]}{dt} = k_2[ML_5][Y]$$

the rate at which ML_5 forms = rate at which it is consumed

rate formation

$$k_1[ML_5X] = k_{-1}[ML_5][X] + k_2[ML_5][Y]$$