

Admin: reminder Final Exam is Monday 8-10:30am

**Last time:**

- 1) Crystal field theory (22-7)
  - spectrochemical series
  - color wheel
- 2) nomenclature of coordination compounds
- 3) student survey

Today:

- 1) go over energy diagrams for 4 ligands
- 2) isomerism in coordination complexes

**Lecture:**

In the case of 4 ligands, we can have either:

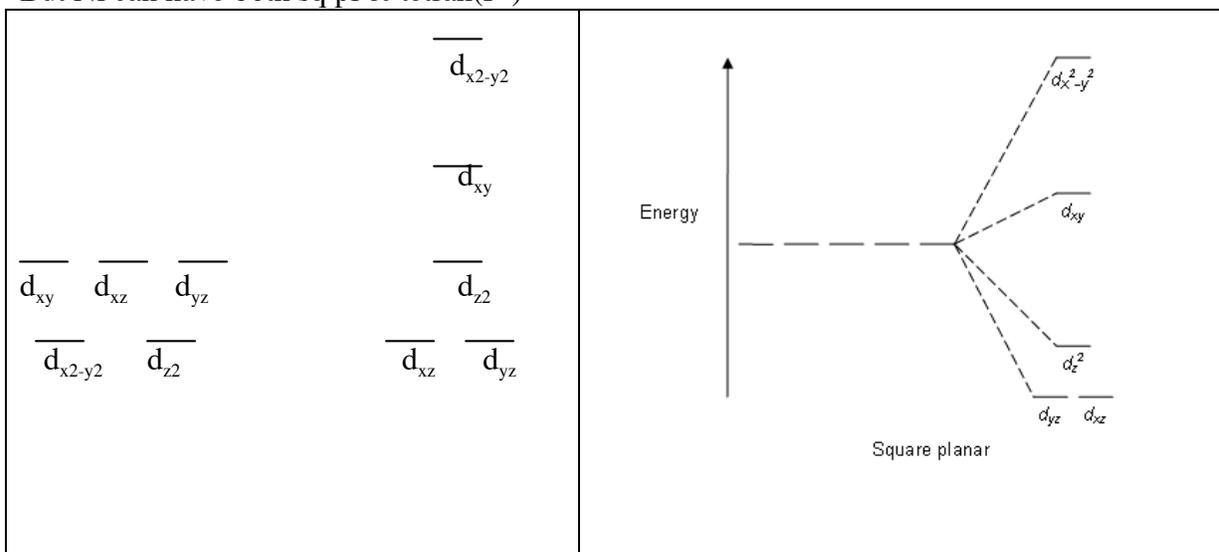
- a) tetrahedral or,
- b) square planar

Now, consider **square planar** complexes:

Metals that tend to have square planar:

$\text{Ni}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{Pt}^{2+}$  ( $d^8$  orbitals)

But Ni can have both sq pl & tetrah(F-)



**Isomers** are sometimes observed with coordination complexes:

*Linkage* isomers:  $\text{SCN}^-$  (thiocyanate ion) can bond with either S or N atoms:  $:\underline{\text{S}}=\text{C}=\underline{\text{N}}:$

$\text{M}-\text{S}=\text{C}=\text{N}$  is “thiocyanato”

$\text{M}-\text{N}=\text{C}=\text{S}$  is “isothiocyanato”

*Geometric* isomers: (cis vs trans)

Possible for square planar:  $\text{Ma}_2\text{b}_2$  type of complexes



Possible also for octahedral:  $\text{Ma}_2\text{b}_4$

*Enantiomers* or *optical isomers*

$\text{Mabcd}$  type of tetrahedral complexes.

You are responsible to the extent covered – look at the examples .

stereoisomers: have same formula but different spatial arrangements: structural isomers, linkage isomers, In addition,

2 kinds: optical and geometric isomers

geometrical isomers: e.g.  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$

(sq planar: cis & trans configs)

Possibilities for tetrahedral complexes

$\text{MA}_4, \text{MA}_3\text{B}, \text{MA}_2\text{B}_2, \text{MA}_2\text{BC}$  one isomer

$\text{MABCD}$  2 isomers; mirror images (optical isomers)

$\text{MA}_2\text{B}_2$  sq planar: 2 geo isomers: cis and trans

Octahedral: many possibilities:

This is optional

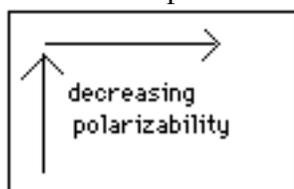
**Hardness or softness of a Lewis acid or base:**

Phenomenon is that specific metals tend to form salts with specific anions:

<u>metal</u>	<u>anion</u>
Ca, Mg	carbonate
Cu, Pb, Hg	sulfide
Na, K	Chloride
Al, Ti and Fe	Oxide

Underlying principle: how tightly bound the metal electrons are:

tightly bound = low polarizability



As effective  $z$  increases, the lower the polarizability.

Hard = low polarizability; Soft = high polarizability

Hard acid: acceptor of  $e^-$  pair is of low polarizability. eg. most metal ions and atoms. (the smaller the ionic radius and the higher the oxidation state, the harder the Lewis acid).

Hard base:  $e^-$  pairs are of low polarizability ; due to high electronegativity of the atom to which the lone pair is assigned.

Soft base: opposite of above. Say the  $e^-$  pair is far from the nucleus: eg iodide., then it is polarizable and hence soft. (eg

Soft acids: like Au and Pt. Not affected by oxygen.

**HSAB principle**

HSAB stands for 'hard and soft acids and bases. HSAB is widely used for explaining stability of compounds and reaction mechanisms and pathways. The theory is used in contexts where a qualitative, rather than quantitative description would help in understanding the predominant factors which drive chemical properties and reactions. This is especially so in transition metal chemistry where numerous experiments have been done to determine the relative ordering of ligands and transition metal ions in terms of their hardness and softness.

Remember: Hard Lewis acids tend to combine with hard Lewis bases & Soft Lewis acids tend to combine with soft Lewis bases. e.g. (e.g. hard acids = lithophiles : combine with oxides;or halides,carbonates)  
soft acids = siderophiles  
chalcophiles = found in nature as sulfides