

Admin:

1) Return test 2

Last time:

(1) Crystal field theory-ML₆

(2) student survey

Today:

(1) Crystal field theory-ML₄

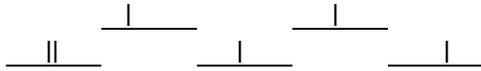
(2) Valence bond theory

(0) ML₆ case (L=monodentate ligand) Consider octahedral complexes:

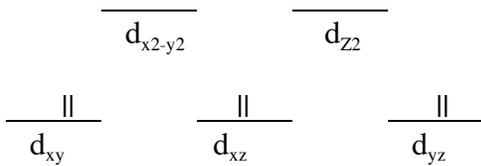
Consider ${}_{26}\text{Fe}^{2+}$ in weak field and strong field:

(Another: ${}_{27}\text{Co}^{3+}$) $[\text{Ar}]3d^6:4s^2$

so if weak: spin=4 (*high spin*)



and if strong: spin=0 (*low spin*)



So weak field gives higher spin and so on.

Another example: potassium hexachlorochromate(II):

$\text{K}_4[\text{Cr}(\text{Cl})_6]$;

complex is $[\text{Cr}(\text{Cl})_6]$.

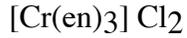
Remember halides => weak ligand; weak field,

${}_{24}\text{Cr}^{2+}$, $[\text{Ar}]3d^4$



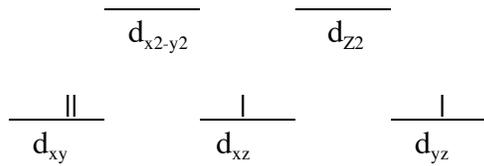
and spin=4.

compare with
potassium tris(ethylenediammine)chromate(II):



still 24Cr^{2+} , $[\text{Ar}]3d^4$

Remember en => strong ligand; strong field,



spin=2. (less spin than weak field)

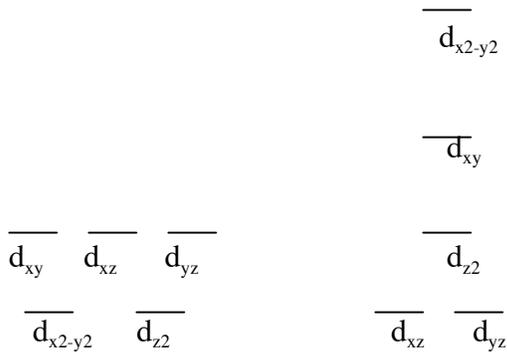
color is different.

Now, consider square planar complexes:

Metals that tend to have square planar:

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

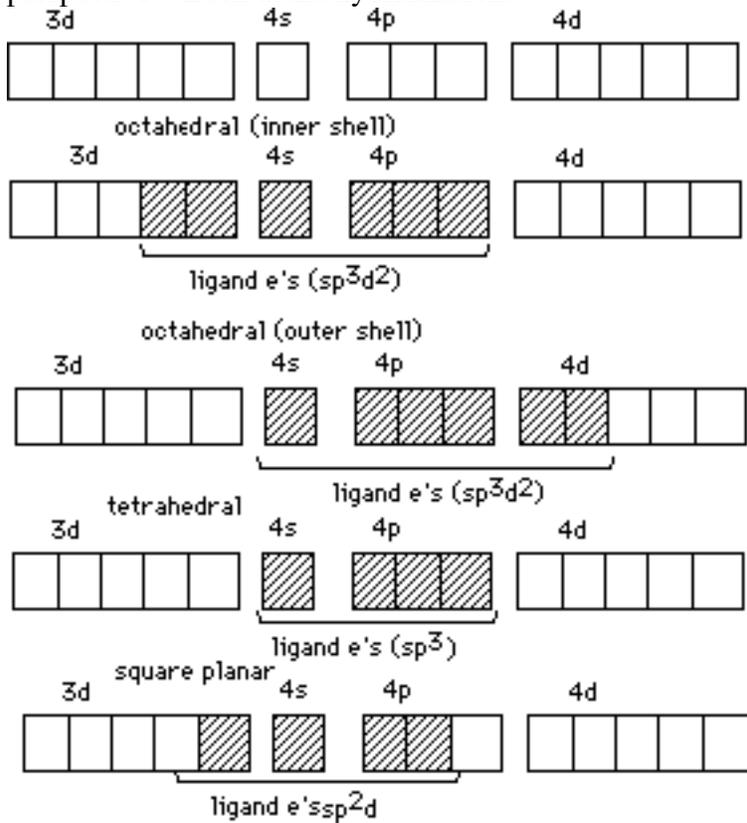
But Ni can have both sq pl & tetrah(F-)



Tetrahedral
(weak)
 d^{10} and others

Square Planar
(strong)
 d^8

How to view this from Valence bond theory perspective? Look at the hybridization:

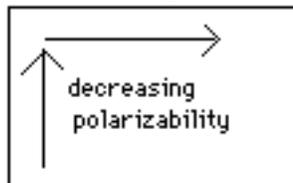


Hardness or softness of a Lewis acid or base:

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



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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.

Hard Lewis acids tend to combine with hard Lewis bases &

Soft Lewis acids tend to combine with soft Lewis bases.

HSAB principle

e.g.

(e.g. hard acids = lithophiles :
combine with oxides;or halides,carbonates)

soft acids = siderophiles

chalcophiles = found in nature as sulfides