

MIT ESP Splash 2022

Date: Saturday, November 19, 2022

Room: 1-150

Time: 7:05 pm - 7:55 pm

S15128 Crystal Field Theory: Why Copper Solutions are Blue

Teachers

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Year: Junior

Major: Course 5 (Chemistry)

Hometown: Stamford, CT

Group: Mircea Dincă Research Lab

Course description

Have you ever wondered what makes certain transition metal solutions have distinct colors, from copper's vivid blue color to nickel's green hue? The theory that addresses this phenomenon is crystal field theory.

This rigorous class will go over the chemistry concepts behind crystal field theory and discuss interesting properties/applications of some coordination complexes.

Note:

This handout is uploaded to the Splash page, along with contemporary research papers for those interested.

If you like this class, we recommend taking S15142 "Why is CO poisonous, but not O₂? Answers from Molecular Orbital Theory" taught by Vivian Hir and Melbourne Tang, tomorrow from 10:05 am - 10:55 am in room 1-135!

Periodic table

S-block

p-block

Number																													
Symbol																													
Name																													
Mass																													
1	2											13	14	15	16	17	18												
1 H Hydrogen 1.008												5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180												
3 Li Lithium 6.941	4 Be Beryllium 9.012											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948												
11 Na Sodium 22.990	12 Mg Magnesium 24.305											19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.414	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.293												
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.227	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [209]	85 At Astatine [209]	86 Rn Radon [222]												
87 Fr Francium [223]	88 Ra Radium [226]	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [265]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]												
Lanthanide Series		57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.243	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967													
Actinide Series		89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]													

d-block

f-block → beyond this class

Orbital: describes the wavefunction of an electron, or the probability of an electron existing in space

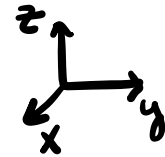
An orbital can only have 2 electrons existing together (with opposite spins), otherwise the electrostatic repulsion is too great and unstable.

⇒ possible: 1↓ impossible: 1↑ or ↓↓


↓ denotes an orbital

Orbitals and wavefunctions can be approximated by the blocks of the periodic table.

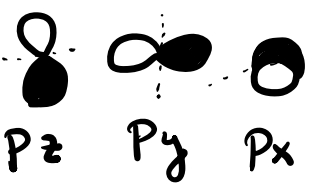
* background / supplementary info *



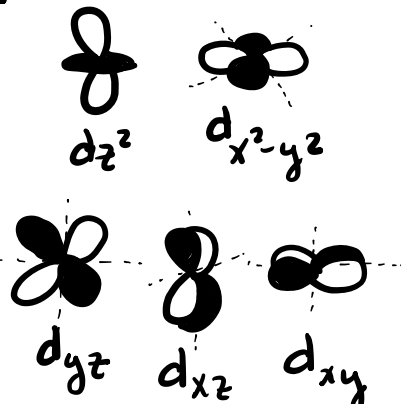
S-block

Shape:  electron can be located within this sphere around the nucleus

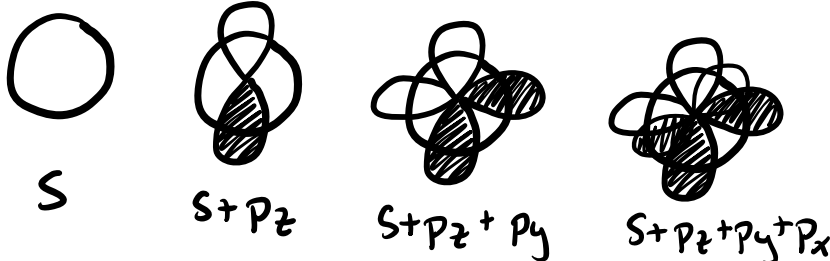
P-block

Shape:  electron can be located within this dumbbell around the nucleus
 This shape comes from adding a nodal plane to the s orbital

d-block

Shape:  electron can be located within these lobes.
 note: to arrive at these shapes, rigorous mathematical and quantum mechanical calculations are required.

Superimposed



(too complicated to depict with d)



"degenerate states" \equiv same energy but different orbitals, or wavefunctions

How do we get bonds?

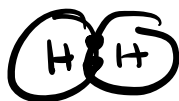
Answer: two of these orbitals will mix!

example: hydrogen binds with hydrogen to get H_2

Hydrogen has 1 electron in s block:



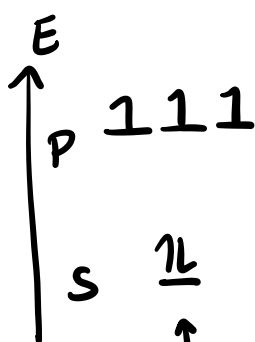
σ = sigma bonding



two electrons make a bond

what about N_2 ? triple bond!

π = pi bonding



these interact



lower in energy because

s orbitals are closer to

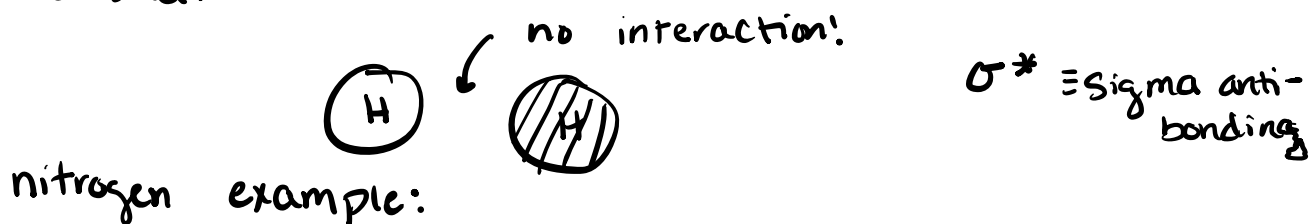
the nucleus and have most interaction. Lower energy = more stable

Hund's Rule: electrons will singly occupy all orbitals in a degenerate state before pairing up.

Anti-bonding

phases: notice in p and d orbitals a dark/shaded lobe. This represents different phases of the orbital when adding a node. The derivation of this is beyond this class.

If two hydrogens interacted with opposite phases, they would not bond. They would form an anti-bonding combination.



antibonding interaction!



$\pi^* \equiv$ pi antibonding

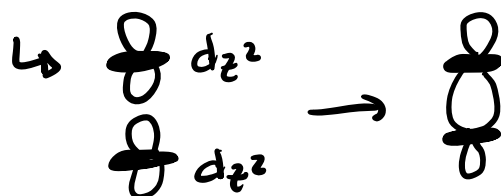
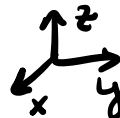
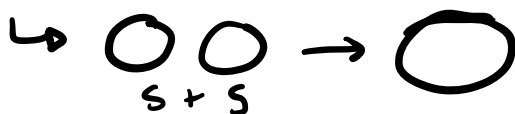


interactions cancel out.

- bonding rules:
- 1) must be same phase
 - 2) must have similar symmetry
i.e. S binds with S
Px with Px, etc.
 - 3) must be similar in energy
i.e. H s orbital will not interact with
Pb s orbital because their energies are too different.

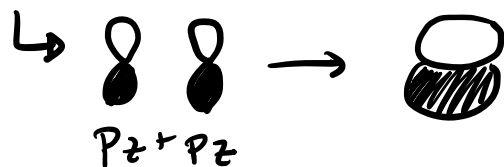
Types of bonds

Sigma: σ : Strongest bond type. Most orbital overlap.

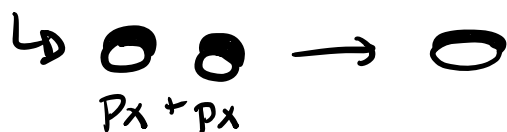


"head-on interaction"

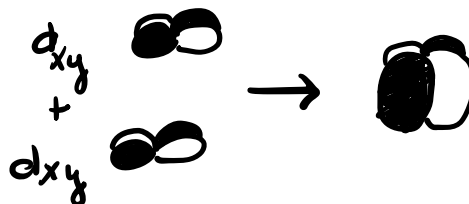
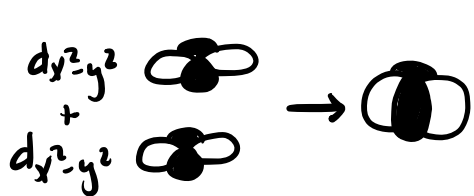
pi: π : Second strongest bond. Less overlap



"side-side interaction"



delta: δ : weakest bond. only seen in metal complexes which have d orbitals.



Transition metal complexes

Transition metal complexes are colorful!

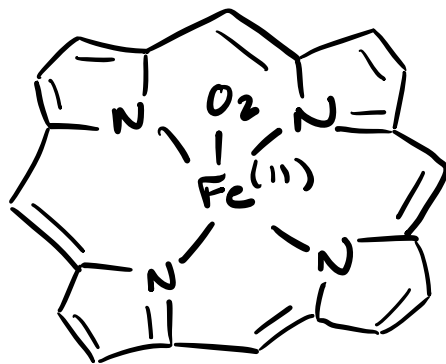
We love colors in the lab. Who wants brown solutions

We'll uncover why they're different colors.

Why do we care about transition metals?

1. These complexes are super important in biology!

Hemoglobin: Fe complexes carry oxygen to your cells



"square planar"

Vitamin B12: Cobalt complex

Cisplatin: Pt complex to treat cancer

2. Can be used in solar cells or as LEDs

↳ "perovskites"

3. Can create crystal lattice structures to selectively collect gases

↳ "metal-organic frameworks"

4. Many more!

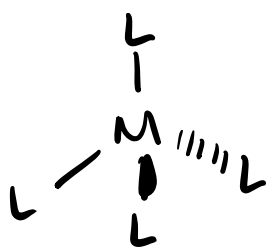
Coordination complexes

Metal complexes bond with their d orbitals.

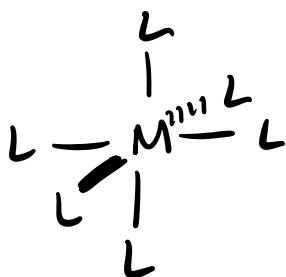
Because of their different orbital orientations, they can bind with different atoms or molecules (called "ligands") and create different geometries and topologies.

Examples:

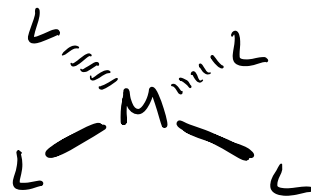
M \equiv metal, L \equiv ligand



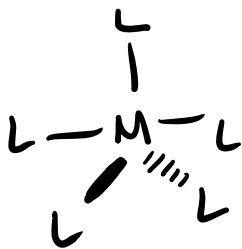
trigonal pyramid



Octahedral



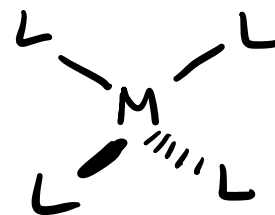
square planar



trigonal bipyramid



See-saw



tetrahedral

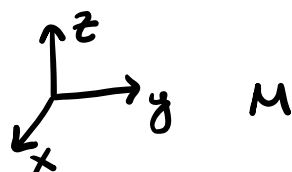
Each of these geometries have a different interaction with the metal d orbitals, causing a split in the degeneracy of the five d orbitals.

Crystal Field Theory (CFT)

CFT is the splitting of degenerate d or f orbitals due to the presence of an electric field caused by interacting ligands.

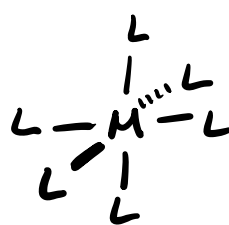
Different ligand fields, or metal complex geometries, will yield different splittings based on orbital interactions.

Free metal ion experiencing no field

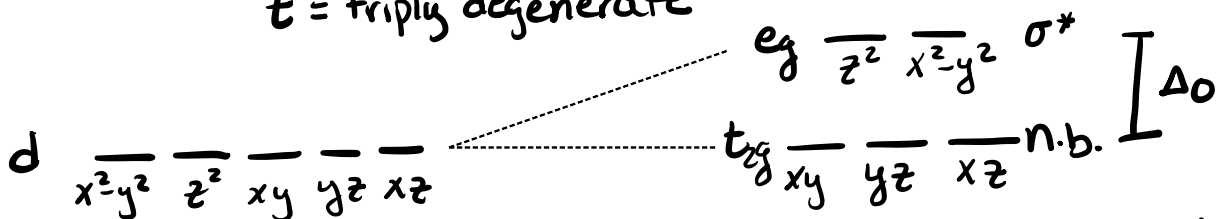


e ≡ doubly degenerate
t ≡ triply degenerate

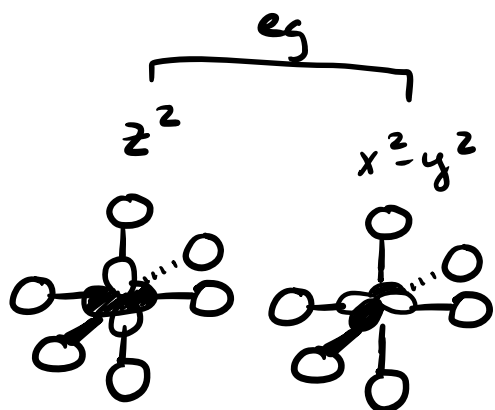
octahedral field



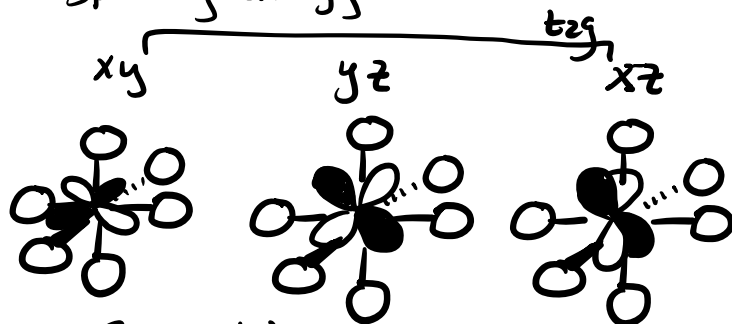
imagine L as s orbital point charges interacting with M



$\Delta_0 \equiv$ "delta octahedral" splitting energy for octahedral field

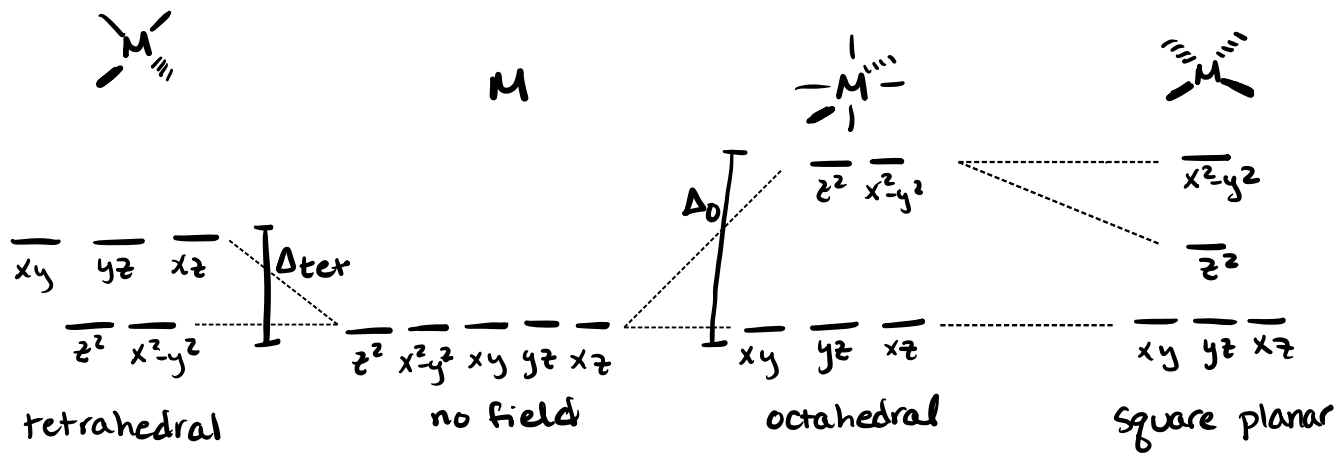
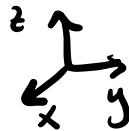


These lobes interact directly with the point charges \Rightarrow $e^- - e^-$ repulsion is destabilizing



These lobes lie in between point charges and do not interact \Rightarrow "non-bonding" (n.b.) orbitals

Other representations:



$\Delta_{tet} = \frac{4}{9} \Delta_o$ This is due to the number of interacting point charges.

The different interactions of the point charge positions with the d orbitals cause these shifts in splitting.

But, in reality, ligands are not point charges. They have different electronic properties and densities.

How do ligands effect the crystal field splitting?

Spectrochemical series:

$I^- < Br^- < SCN^- < Cl^- < S^{2-} < N_3^- < F^- < ONO^- < OH^-$
 $< SO_4^{2-} < NO_2^- < C_2O_4^{2-} < O^{2-} < H_2O \sim NCS^- < EDTA^{4-}$
 $< NH_3 \sim Py < en < bpy \sim phen < NO_2^- < PR_3 < CH_3 < CN^- \sim CO$

I^- to $H_2O \equiv$ weak field NCS^- to $CO \equiv$ strong field

Weak field ligands tend to have smaller splitting and therefore form high spin complexes

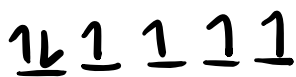
Strong field ligands tend to have larger splitting and therefore form low spin complexes.

We mentioned Hund's rule and pairing energy.

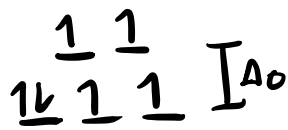
High spin occurs when the splitting energy is small comparable to the e^-e^- pairing energy. This means, instead of pairing electrons in the lowest energy state before adding to the next state, electrons will half-fill all states before pairing.

Low spin occurs when the splitting energy is large comparable to the pairing energy. Thus, electrons will pair before filling the next state.

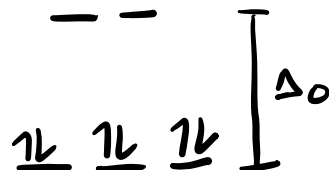
Example:



Fe^{2+}
group 8
 d^6



$[Fe(H_2O)_6]^{2+}$
weak field ligand
small Δ_0
high spin



$[Fe(CN)_6]^{4-}$
Strong field ligand
large Δ_0
low spin

Now we know how ligands influence CFT.

But how does the metal impact this?

Δ_o increases with:

1) larger metals \Rightarrow low spin

- These compounds have very large orbitals which interact more with the ligands creating a large Δ_o

- 5d metals are almost exclusively low spin

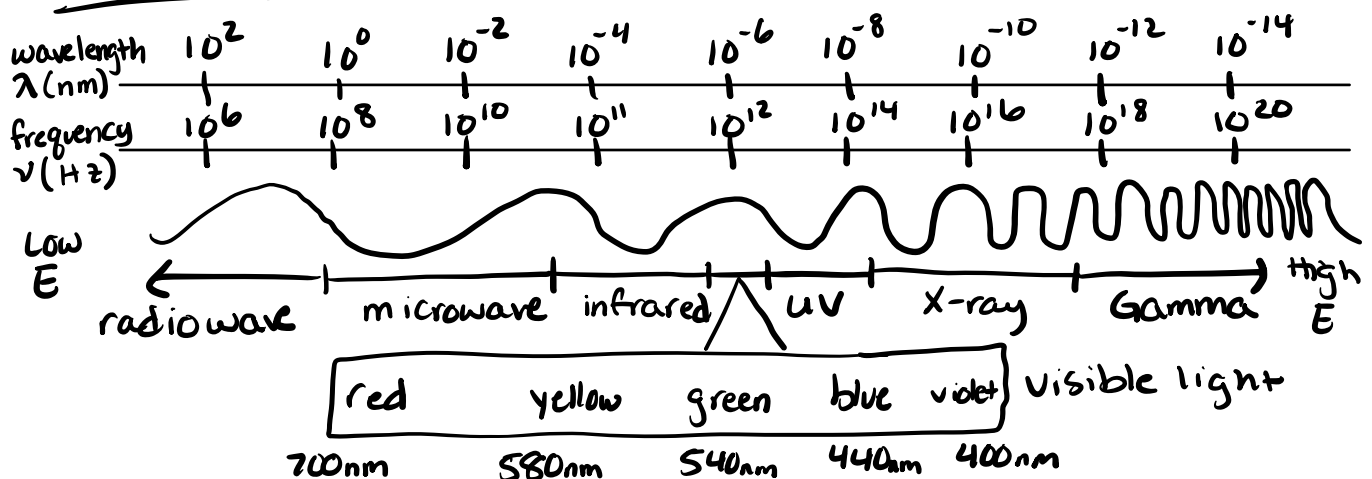
2) low oxidation state \Rightarrow low spin

- High oxidation states (+3, +4, +5 charges) mean the metal is electropositive, so it draws more electron density toward itself \Rightarrow small splitting \Rightarrow high spin

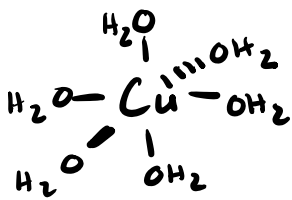
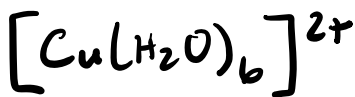
Considering metal and ligand effects, we can determine the crystal field splitting and electron filling. Once we know this, we can figure out the color of the complex.

C O L O R S !

Electromagnetic series



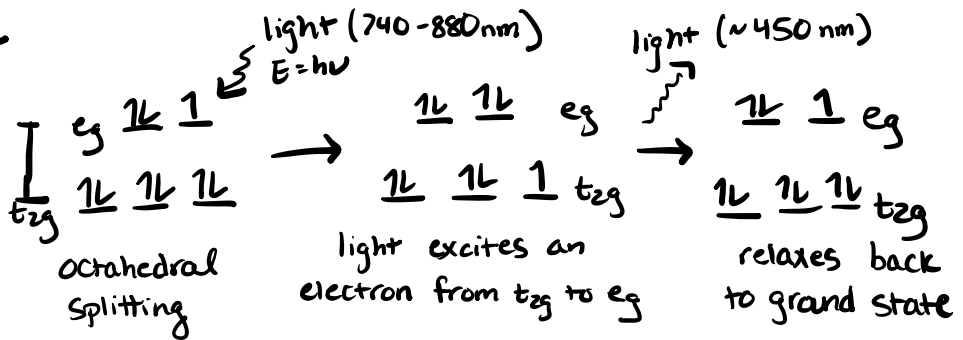
Case Studies:



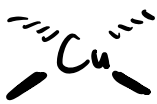
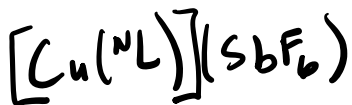
group II

Cu^{2+}

electron count: d^9



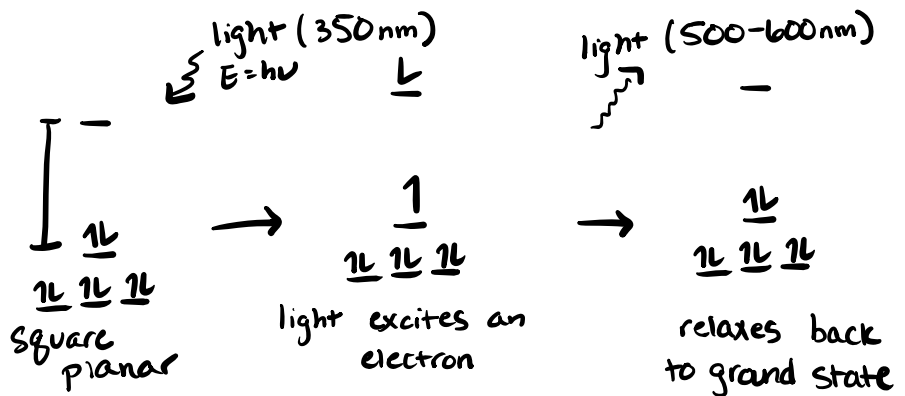
Due to the small splitting size, the light absorbed by this Cu complex is red. Therefore, the light emitted and observed is blue!



group II

Cu^{3+}

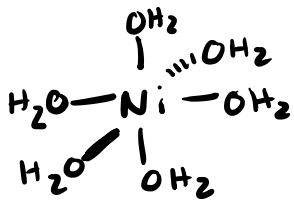
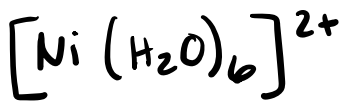
electron count: d^8



Larger crystal field splitting in Cu^{3+}

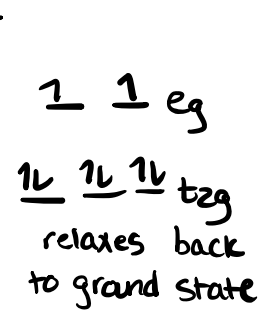
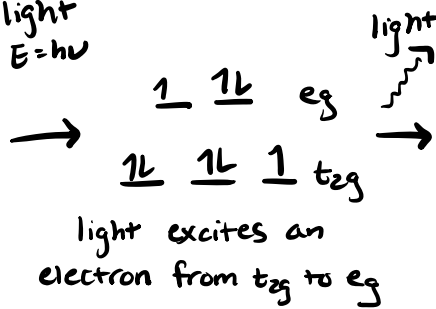
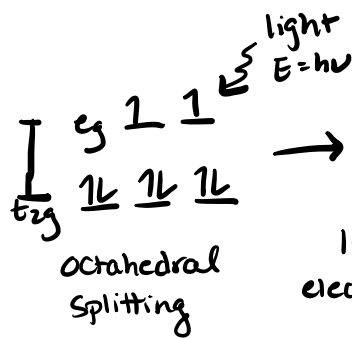
Light absorbed is violet and emitted is yellow

The reason why transition metal complexes have different visible colors is because of CFT. The d-d gap is generally within the visible light range, and depending on the molecule, different colors exist in light!

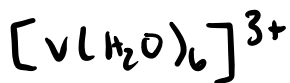


group 10
Ni²⁺

electron count: d⁸



Green!

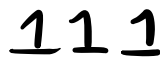


V(III) = d²

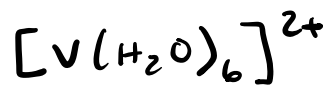
absorbs violet
emits yellow



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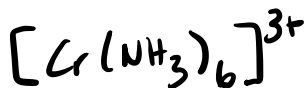


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V(II) = d³

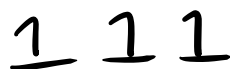
absorbs yellow
emits violet



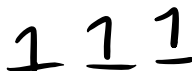
strong field

Cr(III) = d³

absorbs violet
emits yellow



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weak field ligand
lower energy
high spin

Cr(III) = d³

absorbs orange
emits green

d¹⁰ complexes like $[\text{Cu}(\text{PPh}_3)_4]^+$ and $[\text{Zn}(\text{H}_2\text{O})_6]^{2+}$ are usually colorless.