COORDINATION CHEMISTRY AND COLORED COMPLEXES. YR2 DP Chemistry HL

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Coordination chemistry is the same concept as complex ions. In these chemical species there is a positively charged metal cation that is surrounded by ligands. Ligands are formed via **coordinate covalent bonds**, otherwise known as **dative bonds**. These bonds exist when the external species contributes both electrons in the ligand. In reality, some of these may not be actual chemical bonds, but ligands forming due to ion/dipoles. We studied this when we demonstrated hydration shells forming around a metal cation.

Typically, the number of positive charges on the metal cation correlates with the number of ligands that will form. Two ligands per charge. Remember, all of these ligands can also be seen as Lewis acid/Base interactions. Lewis bases donate electrons (free electrons on outer species) and Lewis acids accept electrons (cation).

$$Cu^{2+} + 4H_2O \rightarrow Cu(H_2O)_4^{2+}$$
$$Fe^{3+} + 6H_2O \rightarrow Fe(H_2O)_6^{3+}$$

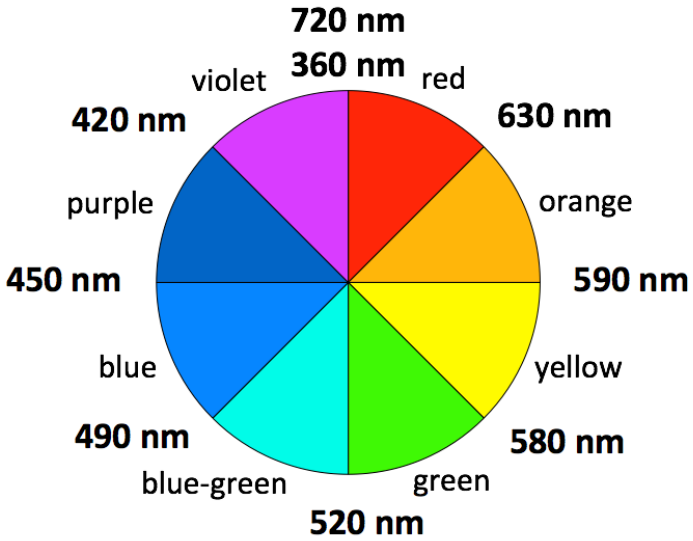
Coordinated complexes are generally very soluble, have high K_f values and they are frequently brightly colored when they have partially filled d-orbitals. Note, Sc^{3+} and Zn^{2+} are colorless as they have no unpaired d-orbital electrons.

Ion	Ion configuration	Color
Sc^{3+}	[Ar]	Colorless
Ti^{3+}	[Ar] $3d^1$	Violet
V^{3+}	[Ar] $3d^2$	Green
Cr^{3+}	[Ar] $3d^3$	Violet
Mn^{2+}	[Ar] $3d^5$	Pink
Fe^{3+}	[Ar] $3d^5$	Yellow
Fe^{2+}	[Ar] $3d^6$	Green
Co^{2+}	[Ar] $3d^7$	Pink
Ni^{2+}	[Ar] $3d^8$	Green
Cu^{2+}	[Ar] $3d^9$	Blue
Zn^{2+}	[Ar] $3d^{10}$	Colorless

When these coordinated complexes are exposed to visible light they will absorb one wavelength and transmit, or reflect, complementary wavelengths. If the transmitted wavelengths are in the visible region the observed colors will be:

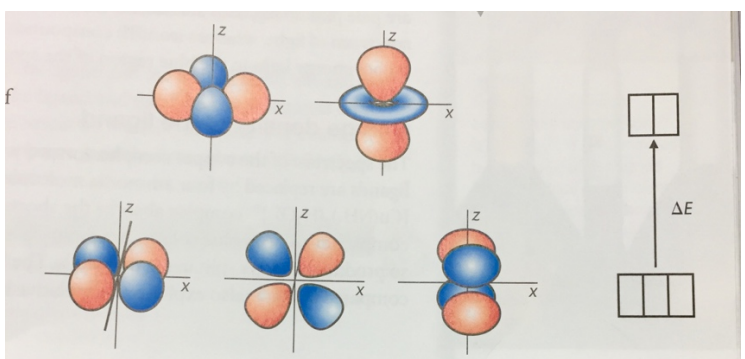
Color	Wavelength Range /nm
Red	630 - 700
Orange	590 - 630
Yellow	560 – 590
Green	490 - 560
Blue	450 - 490
Violet	400 - 450

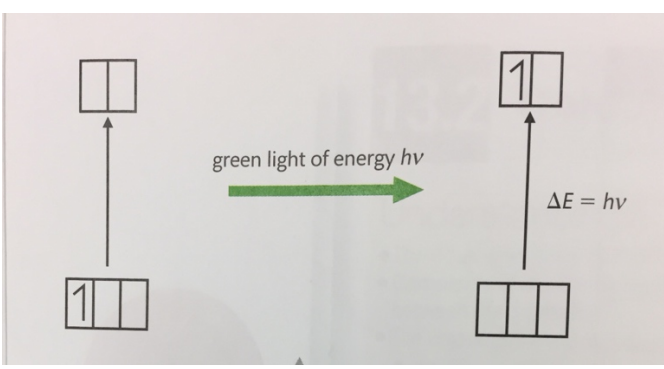
An example: Copper (II) Sulfate appears blue because it absorbs orange light. Orange and turquoise are complementary colors, in that they are opposite each other in the color wheel.



White light is composed of all of the colors of the visible spectrum. Ions of transition metals display colors because their ions absorb certain colored wavelengths. $[Fe(H_2O)_6]^{3+}$, for example appears yellow because it absorbed light in the blue region of the spectrum.

Transition metals absorb light because the d-orbitals split into two different sublevels. When transition metals are isolated (not involved in bonding) their d-orbital electrons are said to be **degenerate** (all having the same energy). When the ligands form, the electrical field produced by the free electrons will split these d-orbital electrons into two sub-levels. The octahedral complex of $[Ti(H_2O)_6]^{3+}$ has six water molecules oriented in the x,y, and z axes. When light passes through this complex, one 3-d electron is excited from the lower to the higher energy sublevel. A photon of green light is absorbed and the complimentary color (purple) is transmitted. This accounts for the purple colored complex of $[Ti(H_2O)_6]^{3+}$.





The energy separation between the orbitals is ΔE and the color of the complex depends on:

1. The nuclear charge and the identity of the central atom (remember high charge densities are required)
2. The geometry of the complex ion will determine the electrical field created by the ligand's lone pair.
3. The number of d electrons present and the oxidation number of the central atom.

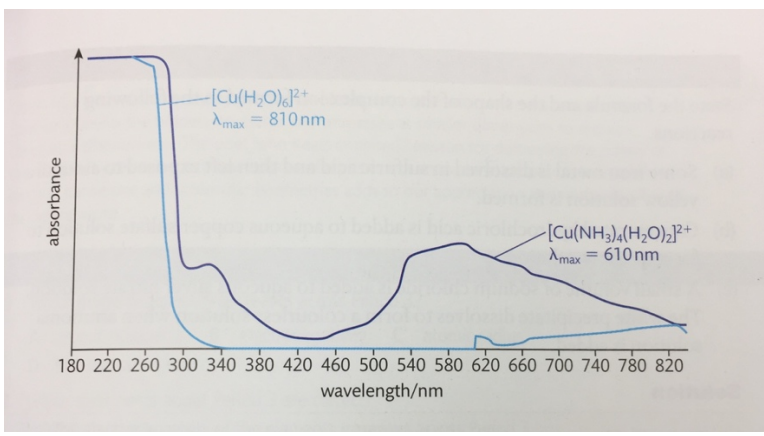
<u>Charge Density of the Cation:</u>
The strength of the coordinate/dative bond between the ligand and the central atom depends on the Coulombic forces between the lone pair and the charge density of the cation. The higher the charge density, the more energetic the photon absorbed will be.
Example:

$[Mn(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ both have the same electron configuration, but iron has the higher nuclear charge and will resultantly form stronger ligands.

- Manganese II compounds will appear to transmit pink colors (as they absorb in the green region, 550 nm).
- Iron III compounds will appear to transmit yellow colors (as they absorb in the blue region, 490 nm).

Remember, $E = \frac{hc}{\lambda}$ the longer the wavelength, the lower energy absorbed.

<u>Charge Density of the Ligand:</u>
Certain ligands, like ammonia (NH_3) have higher charge densities than do water. If a hydrated copper II ion, $[Cu(H_2O)_6]^{2+}$ has some of its water molecules replaced with ammonia molecules, $[Cu(NH_3)_4(H_2O)_6]^{2+}$, the complex will absorb shorter, more energetic wavelengths. This will result in a deeper blue color than it transmits as $[Cu(H_2O)_6]^{2+}$. The following graph will demonstrate this:



The following table will highlight ligand types and the ΔE of the splitting:

LIGAND	I^-	Br^-	S^{2-}	Cl^-	H_2O	OH^-	NH_3	CN^-	CO
λ MAX	Longest Wavelength	Wavelength increasing ←----------							Shortest wavelength
ΔE	Weakest Field	ΔE increasing ----------→							Strongest Field

Geometry of the Complex:

In the classic Cobalt (II) chloride equilibrium:

$$\text{Heat} + \underset{\text{Pink}}{[Co(H_2O)_6]^{2+}} + 4Cl^- \rightleftharpoons \underset{\text{Purple}}{} + 6H_2O + \underset{\text{Blue}}{[Co(Cl)_4]^{2-}}$$

On the left side of the equation, the cobalt/water complex takes on an octahedral geometry. On the right, the cobalt/chloride takes on a tetrahedral geometry. The splitting of d-orbital energy depends on the relative orientation of the ligand and the d-orbitals.

The Number of d-Electrons and the Oxidation State of the Central Atom:

The strength of the interactions between the ligand and the central metal cation and the amount of electron repulsion between the ligand and the d-electrons depends on the number of d-electrons and hence the oxidation number of the metal. For example, $[Fe(H_2O)_6]^{2+}$ absorbs violet light and so appears green, whereas $[Fe(H_2O)_6]^{3+}$ absorbs blue light and appears orange. The higher charge creates an absorption of higher energy wavelengths, and the transmittance of lower energy wavelengths.