Colour of the complexes

Spectrochemical Series (strength of ligand interaction)

Increasing Δ

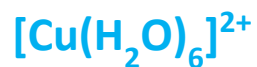I⁻ < Br⁻ < SCN⁻ (S-bonded) < Cl⁻ < F⁻ < OH⁻ < $C_2O_4^{2-}$ < O^{2-} < H_2O < NCS⁻ (N-bonded) < py < NH_3 < en < 1,10-phenanthroline < NO_2^- < PPh_3 < CN⁻ < CO

- Weak field ligands: H_2O, F⁻, Cl⁻, OH⁻
- Strong field ligands: CO, CN⁻, NH_3, PPh_3

Increasing Δ

Energy

$[CrF_6]^{3-}$
Green

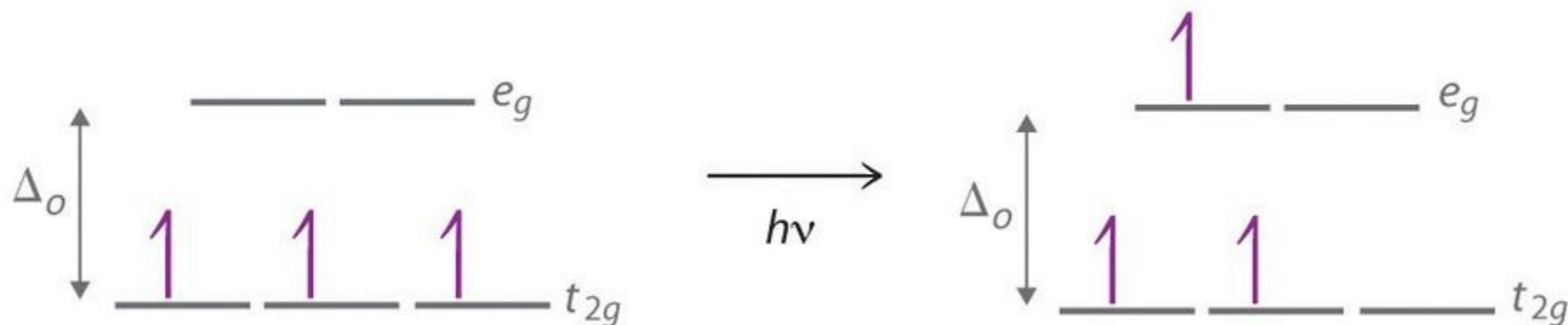$[Cr(H_6O)_6]^{3+}$
Violet

$[Cr(NH_3)_6]^{3+}$
Yellow

$[Cr(CN)_6]^{3-}$
Yellow
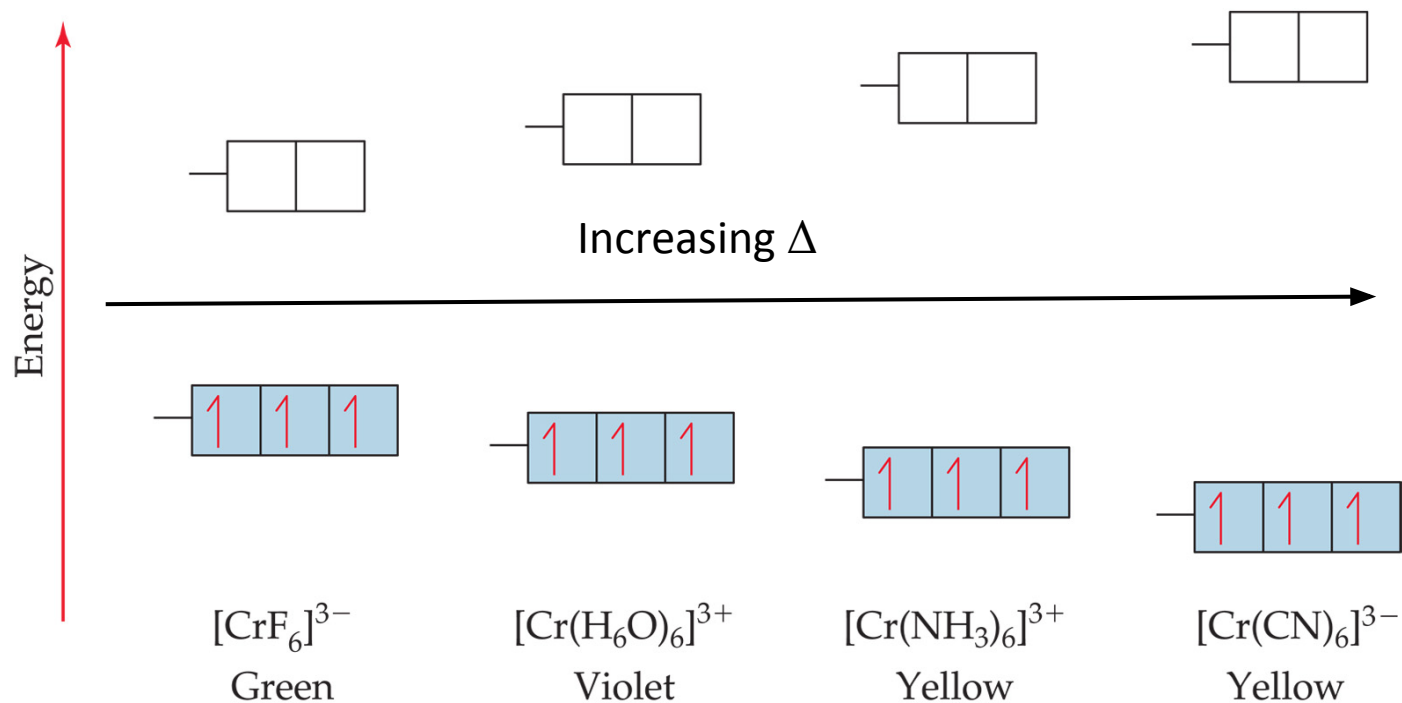
Different ligands on same metal give different colors

Addition of NH$_3$ ligand to [Cu(H$_2$O)$_6$]$^{2+}$ changes its color

[Cu(H$_2$O)$_6$]$^{2+}$ [Cu(NH$_3$)$_6$]$^{2+}$

The striking colors exhibited by transition-metal complexes are caused by excitation of an electron from a lower-energy d orbital to a higher-energy d orbital, which is called a **d–d transition**


$E = h\nu = hc\lambda = \Delta o$

For a photon to effect such a transition, its energy must be equal to the difference in energy between the two d orbitals, which depends on the magnitude of Δ_o. In a d–d transition of an octahedral complex, an electron in one of the t_{2g} orbitals of an octahedral complex such as the $[Cr(H_2O)_6]^{3+}$ ion absorbs a photon of light with energy equal to Δ_o, which causes the electron to move to an empty or singly occupied e_g orbital.

The human eye perceives a mixture of all the colors, in the proportions present in sunlight, as white light. Complementary colors, those located across from each other on a color wheel, are also used in color vision.

The eye perceives a mixture of two complementary colors, in the proper proportions, as white light.

Likewise, when a color is missing from white light, the eye sees its complement. For example, when red photons are absorbed from white light, the eyes see the color green.
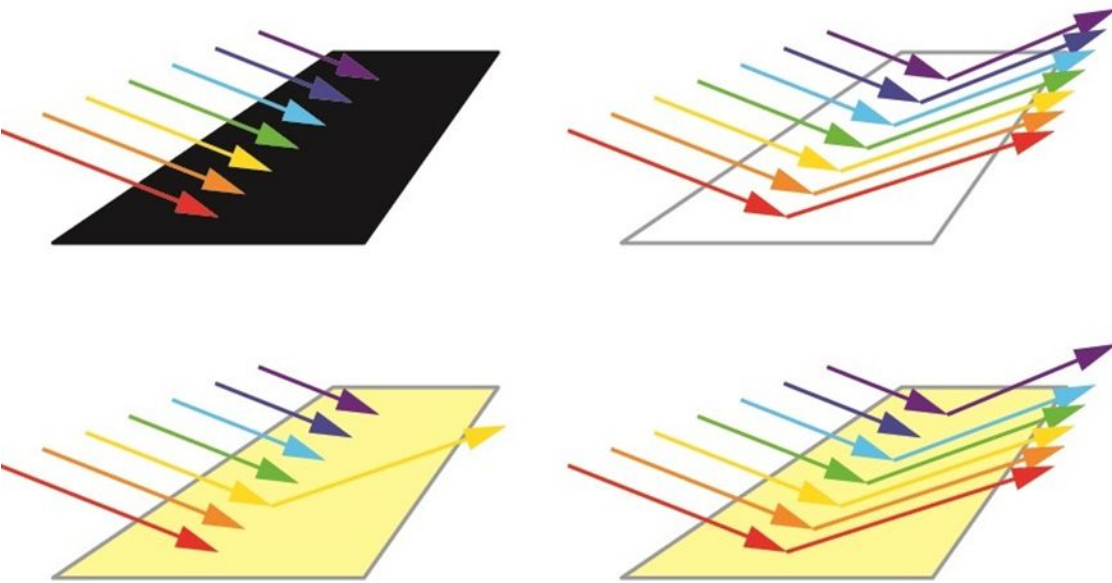

(a)
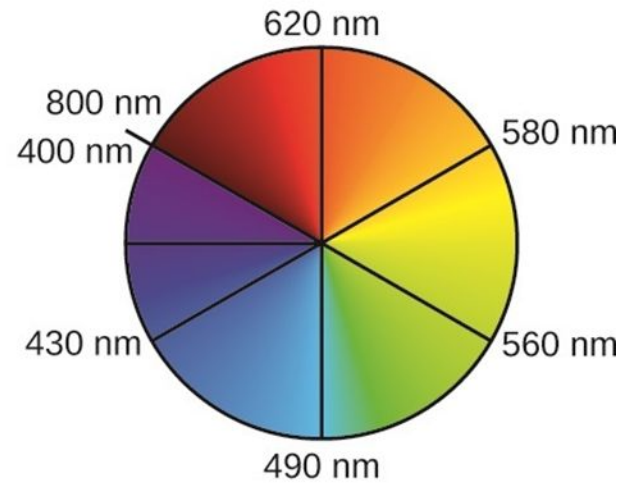
(b)

When violet photons are removed from white light, the eyes see lemon yellow.

The blue color of the [Cu(NH3)4]2+[ion results because this ion absorbs orange and red light, leaving the complementary colors of blue and green If white light (ordinary sunlight, for example) passes

through [Cu(NH3)4]SO4[solution, some wavelengths in the light are absorbed by the solution. The [Cu(NH3)4]2+[ions in solution absorb light in the red region of the spectrum. The light which passes through the solution and out the other side will have all the colors in it except for the red. We see this mixture of wavelengths as pale blue (cyan).

The diagram gives an impression of what happens if you pass white light through a [Cu(NH3)4]SO4solution

White light   Blue-appearing light
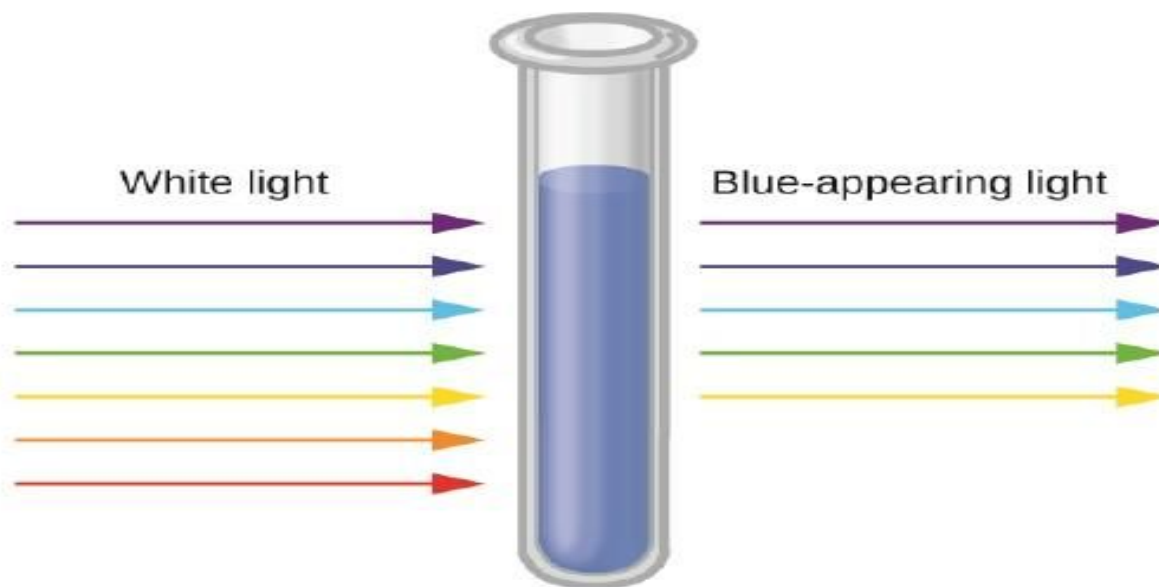
Problem 1.0

The octahedral complex $[Ti(H_2O)_6]^{3+}$ has a single d electron. To excite this electron from the ground state t_{2g} orbital to the e_g orbital, this complex absorbs light from 450 to 600 nm. The maximum absorbance corresponds to Δ_o and occurs at 499 nm. Calculate the value of Δ_o in Joules and predict what color the solution will appear.

Convert wavelength into frequency

$v = c/\lambda$

=3.00×10to the power of 8m/s(

499nm)×(1m/10 to the power of 9)m)=

=   6.01×10 to the power of 14 s−1= convert into HZ =6.01×10 to the power of 14Hz

E= hv

(6.63×10 to the power of −34J · s)×(6.01×10to the power of 14Hz)

=3.99×10to the power of −19 in terms of J

Because the complex absorbs 600 nm (orange) through 450 (blue), the indigo, violet, and red wavelengths will be transmitted, and the complex will appear purple.

Color Depends on Ligand Field

The specific ligands coordinated to the metal center also influence the color of coordination complexes. Because the energy of a photon of light is inversely proportional to its wavelength, the color of a complex depends on the magnitude of Δ_o, which depends on the structure of the complex.

For example, the complex $[Cr(NH_3)_6]^{3+}$ has strong-field ligands and a relatively large Δ_o. Consequently, it absorbs relatively high-energy photons, corresponding to blue-violet light, which gives it a yellow color.

A related complex with weak-field ligands, the $[Cr(H_2O)_6]^{3+}$ ion, absorbs lower-energy photons corresponding to the yellow-green portion of the visible spectrum, giving it a deep violet color.

dentify the color (either blue, green, yellow, or orange) for the following complex ions formed with Co3+:
1.[Co(CN)6]−2
2.[Co(NH3)6]3+
3.[CoF6]−4
4.[Co(H2O)6]3+

Solution
Each of these complex ions has the same metal with the same oxidation state, so the ligand field is the relevant factors. Each of the complex ions also has an octahedral ligand field, so we only need to compare the strength of the ligands in determining Δo
 which is determined by the spectrochemical series.
The ligands for each complex ions are: (a) CN− (b) NH3 (c) F− and (d) H2O which are ranked in increasing Δo magnitude:
The relationship between the Δo and the energy of the photons are absorbed in the d-d transition of Co3+ is given by equating Planck's equation to the crystal field splitting parameter:
$E=h\nu=hc\lambda=\Delta o$
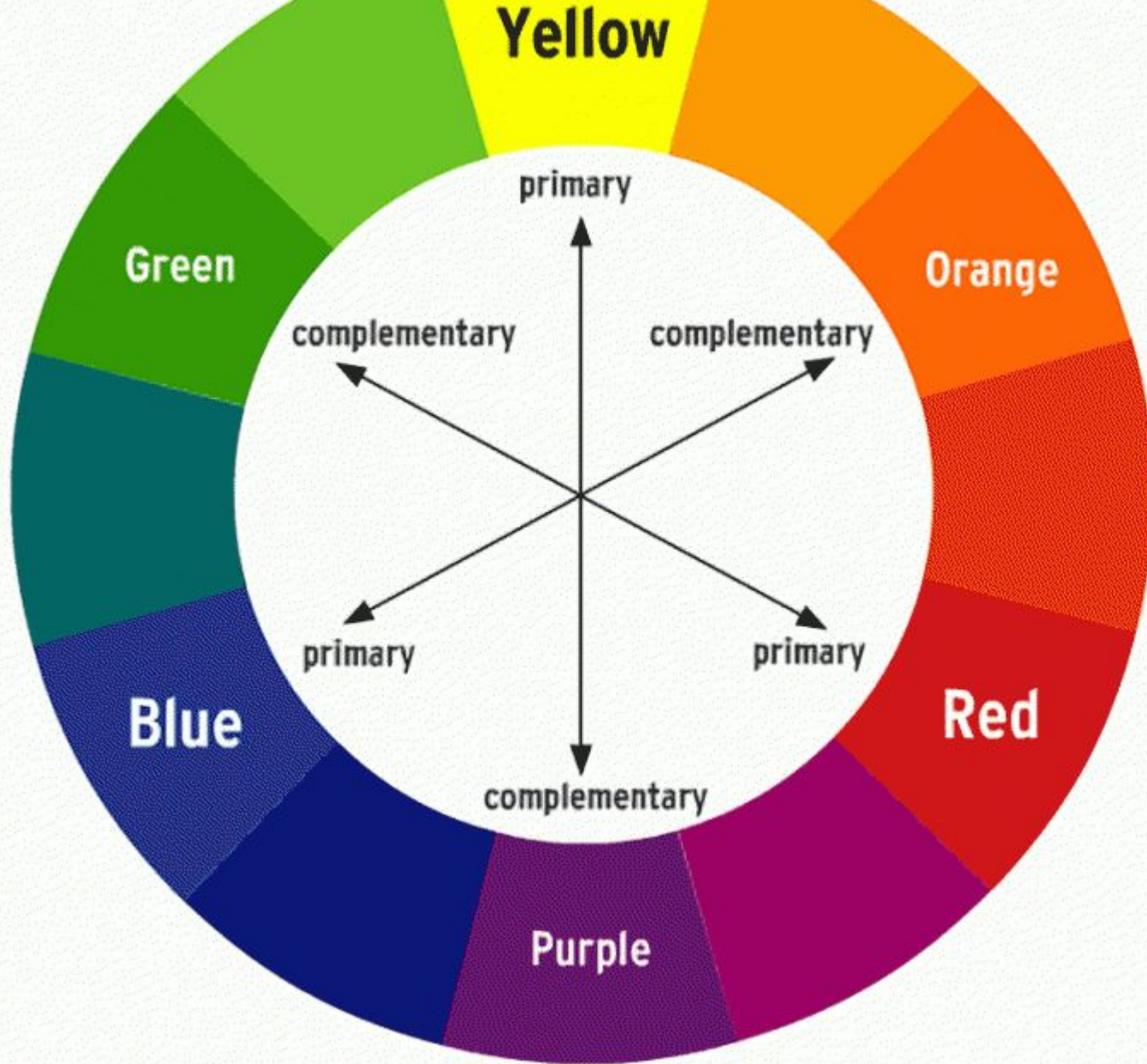
we need to get a relative correlation between observed color (to the eye) and the wavelength of the light that is absorbed.

From the complementary color wheel

we get the following relationships (arranged from highest energy absorbed to lowest):

- 400-nm Violet light absorbed → Green-yellow observed
- 430-nm Blue light absorbed → Orange observed
- 450-nm Blue light absorbed → Yellow observed
- 490-nm Blue-green light absorbed → Red observed
- 570-nm Yellow-green light absorbed → Violet observed
- 580-nm Yellow light absorbed → Dark blue observed
- 600-nm Orange light absorbed → Blue observed
- 650-nm Red light absorbed → Green observed

Of the four possible colors given in the problem (blue, green, yellow, and orange),

the corresponding colors that are absorbed are (600 nm, 650 nm, 450 nm, and 430, respectively).

absorbed light corresponds to the higher energy photons,

so we would correlate the four wavelengths of absorbing photons in terms of increasing energy to observed color:

F− is green<H2O is blue<NH3 is yellow<CN−is orange

Therefore
 $[CoF6]3^{-4-}$ is green<$[Co(H2O)6]3+$ is blue<$[Co(NH3)6]3^{+3}$ is yellow<$[Co(CN)6]3^{-2}$ is orange