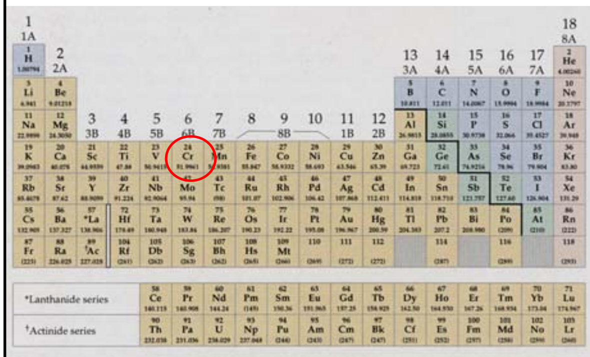
Consider the octahedral complex $Cr[(en)_3]^{2+}$

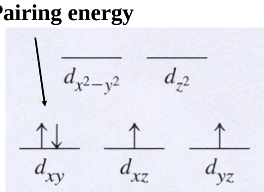
Cr(II) or Cr^{2+}

Cr [Ar] $4s^1 3d^5$ Cr^{2+} [Ar] $3d^4$



Octahedral complex with 4 *d* electrons

Pairing energy

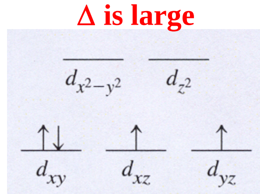


Δ is large

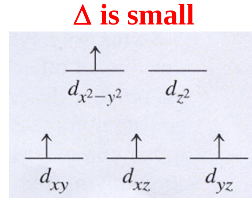
Typically, lower energy attained by pairing e- before populating higher E.

Octahedral complex with 4 *d* electrons

Δ is large

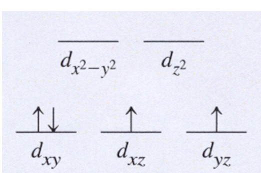


Δ is small

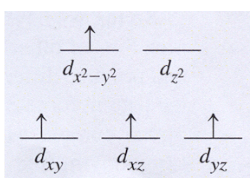


$Cr[(en)_3]^{2+}$

Octahedral complex with 4 *d* electrons



Low Spin

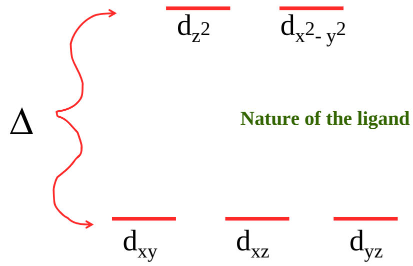


High Spin

Which one?

Crystal field splitting can result in high spin or low spin complexes, <u>depending on the ligands</u>

Crystal Field Splitting Energy



Nature of the ligand determines Δ

Spectrochemical Series

Strong Field
Large Δ

Ligands arranged in order of decreasing magnitude of the splitting of energies of d orbitals in coordination compounds

Weak Field
Small Δ

Spectrochemical Series

Strong Field
Large Δ

Strong field
(large Δ)

$CN^- > \underline{N}O_2^- > en > py \approx NH_3 > EDTA^{4-} > SC\underline{N}^- > H_2O > ON\underline{O}^- > ox^{2-} > OH^- > F^- > \underline{S}CN^- > Cl^- > Br^- > I^-$

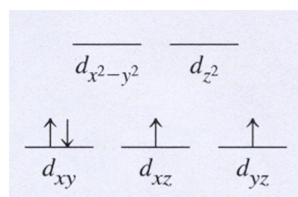
(small Δ)

Underlining indicates the donor atom.

Weak field

Weak Field
Small Δ

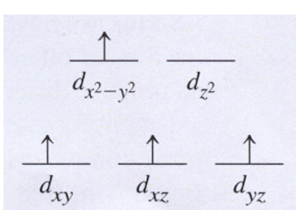
Strong-field ligands produce a Large Crystal Field Splitting, resulting in Low Spin complexes



Δ is Large

2 unpaired electrons

Weak-field ligands produce a Small Crystal Field splitting, resulting in High Spin complexes



Δ is Small

4 unpaired electrons

$Cr[(en)_3]^{2+}$

Spectrochemical Series

Strong Field

Strong field
(large Δ)

$CN^- > \underline{N}O_2^- > en > py \approx NH_3 > EDTA^{4-} > SC\underline{N}^- > H_2O > ON\underline{O}^- > ox^{2-} > OH^- > F^- > \underline{S}CN^- > Cl^- > Br^- > I^-$

(small Δ)

Underlining indicates the donor atom.

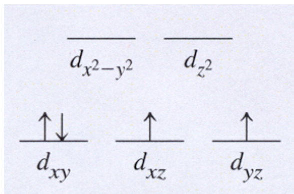
Weak field

Weak Field

en is a Strong Field ligand

Strong-field ligands produce a large crystal field splitting, resulting in low spin complexes

$Cr(en)_3^{2+}$



Low Spin

2 unpaired electrons

Distinction between high-spin and low-spin octahedral complexes can only be made for d^4 to d^7 Electron Configurations

d^0-d^3 and d^8-d^{10} configurations have only one way of filling in e-.

---

d^0-d^3 configurations have only one way of filling in electrons

d^3

____ ____

| ___ | ___ | ___

Distinction between high-spin and low-spin octahedral complexes can only be made for d^4 to d^7 Electron Configurations

d^7

High spin: | ___ | ___ / || ___ || ___ | ___

Low spin: | ___ ____ / || ___ || ___ || ___

High spin
$\Delta < P$

Low spin
$\Delta > P$

---

d^8-d^{10} configurations have only one way of filling in electrons

d^9

|| ___ | ___

|| ___ || ___ || ___

How many unpaired electrons does $[Re(H_2O)_6]Cl_2$ have?

Is it a Low Spin or High Spin Complex?

Coordination Compounds

Determine the Shape

Determine Oxidation State of the metal

Determine Number of of d electrons

Determine if Ligand is Weak field or Strong field

Draw energy level diagram

How many unpaired electrons does $[Re(H_2O)_6]Cl_2$ have?

$[Re(H_2O)_6]Cl_2$

Octahedral Complex

How many unpaired electrons does $[Re(H_2O)_6]Cl_2$ have?

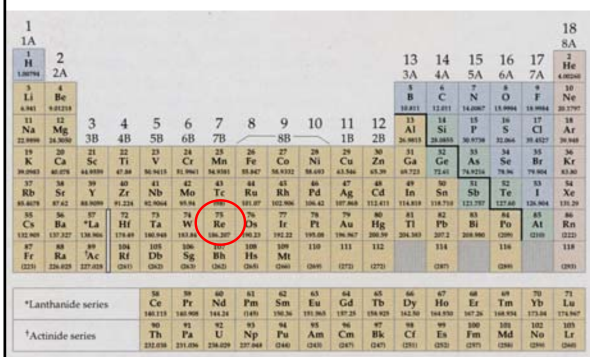
$[Re(H_2O)_6]^{2+}\ 2Cl^-$

Oxidation State?

Oxidation State = 2 – (6 x 0) = 2+

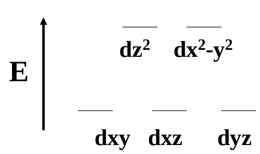
Re^{2+} or Rhenium(II)

Re [Xe] $6s^2 5d^5$ Re^{2+} [Xe] $5d^5$



How many unpaired electrons does $[Re(H_2O)_6]Cl_2$ have?

$[Re(H_2O)_6]^{2+}\ 2Cl^-$ d^5



d-orbital splitting in an octahedral crystal field

Spectrochemical Series

Strong field (large Δ)

$CN^- > \underline{N}O_2^- > en > py \approx NH_3 > EDTA^{4-} > SC\underline{N}^- > H_2\underline{O} > \underline{O}NO^- > ox^{2-} > OH^- > F^- > \underline{S}CN^- > Cl^- > Br^- > I^-$

(small Δ) *Weak field*

Underlining indicates the donor atom.

H_2O is a weak field ligand

How many unpaired electrons does $[Re(H_2O)_6]Cl_2$ have?

$[Re(H_2O)_6]^{2+}$ $2Cl^-$

d^5

↑ ↑
d_{z^2} $d_{x^2-y^2}$

↑ ↑ ↑
dxy dxz dyz

Δ is small

How many unpaired electrons does $[Re(H_2O)_6]Cl_2$ have?

$[Re(H_2O)_6]^{2+}$ $2Cl^-$

d^5

↑ ↑
d_{z^2} $d_{x^2-y^2}$

↑ ↑ ↑
dxy dxz dyz

5 unpaired e-

High-spin complex

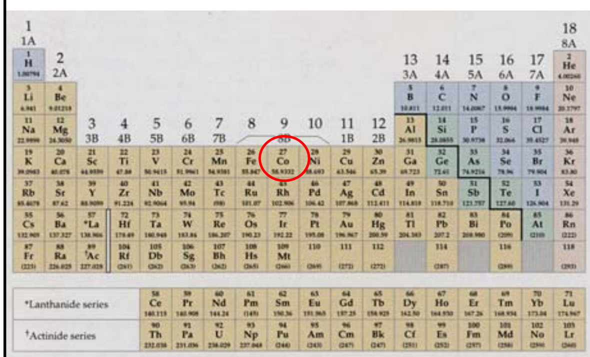
MAGNETIC PROPERTIES

Why $[CoF_6]^{-3}$ is paramagnetic

and $[Co(NH_3)_6]^{+3}$ is diamagnetic

Octahedral
Co^{3+}

Co [Ar] $4s^2 3d^7$ Co^{3+} [Ar] $3d^6$



Spectrochemical Series

Strong Field

Strong field
(large Δ)

$CN^- > NO_2^- > en > py \approx NH_3 > EDTA^{4-} > SCN^- > H_2O > ONO^- > ox^{2-} > OH^- > F^- > SCN^- > Cl^- > Br^- > I^-$
(small Δ)

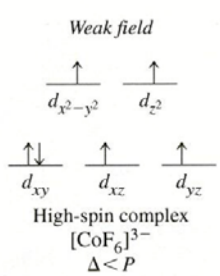
Underlining indicates the donor atom. *Weak field*

Weak Field

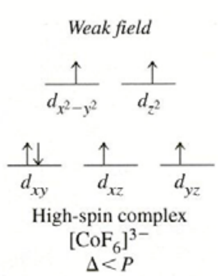
F^- is a Weak Field ligand

d-orbital splitting in a
<u>Weak</u> octahedral crystal field

Δ is small



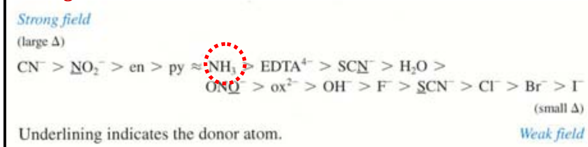
High-Spin complex



Paramagnetic

Spectrochemical Series

Strong Field

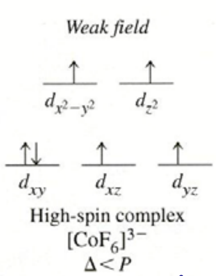


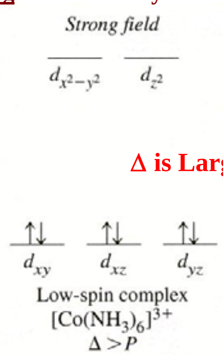
Weak Field

NH_3 is a Strong Field ligand

d-orbital splitting in a
Strong octahedral crystal field

High-Spin complex



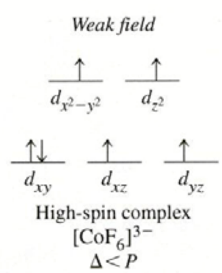


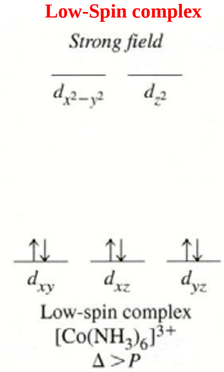
Δ is Large

Paramagnetic

Low-Spin complex

High-Spin complex





Paramagnetic **Diamagnetic**

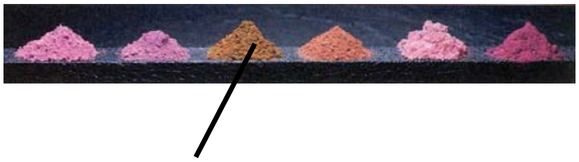
The effects of ligands on the colors of coordination compounds

$[CoCl(NH_3)_5](NO_3)_2$

The effects of ligands on the colors of coordination compounds

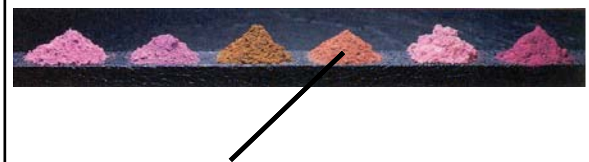
$[CoBr(NH_3)_5](NO_3)_2$

The effects of ligands on the colors of coordination compounds



$[CoI(NH_3)_5](NO_3)_2$

The effects of ligands on the colors of coordination compounds

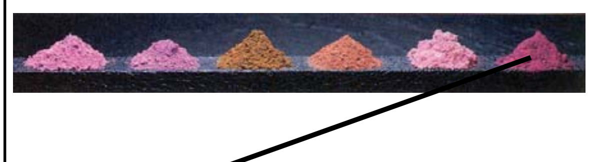


$[CoNO_2(NH_3)_5](NO_3)_2$

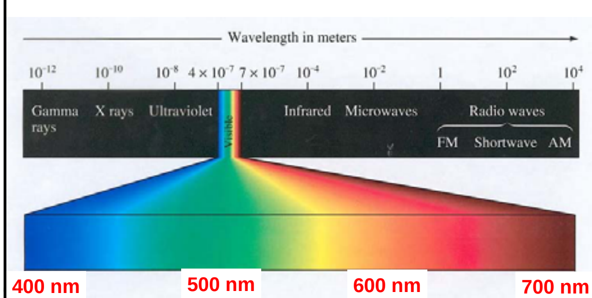
The effects of ligands on the colors of coordination compounds

$[CoSO_4(NH_3)_5]NO_3$

The effects of ligands on the colors of coordination compounds



$[CoCO_3(NH_3)_5]NO_3$



Eye can detect photons from 400-700nm

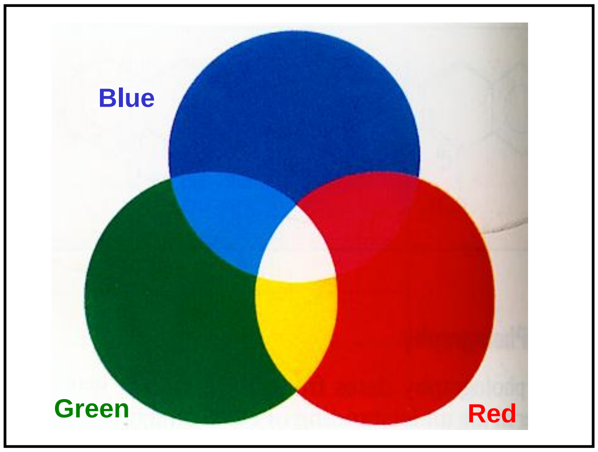
Visible Spectrum

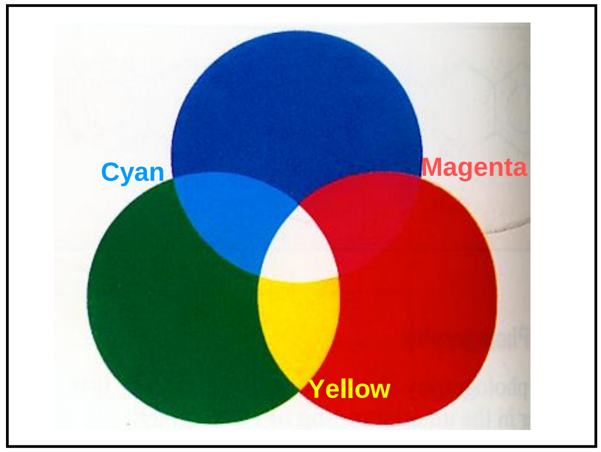
(Each wavelength corresponds to a different color)

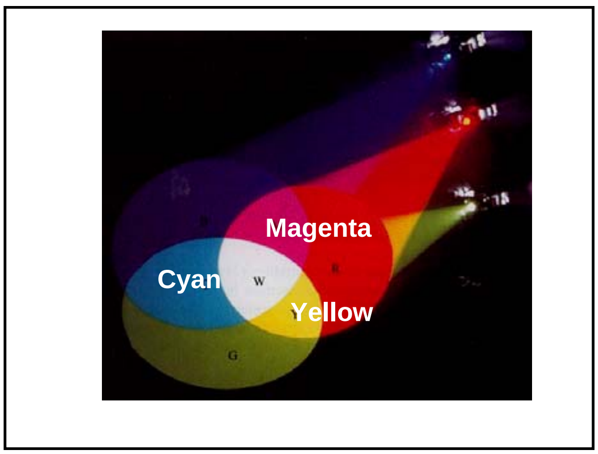
400 nm ← Higher energy, Shorter Wavelength

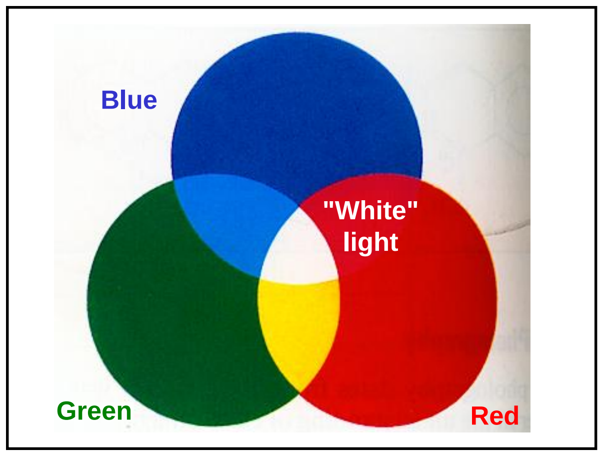
700 nm → Lower energy, Longer Wavelength

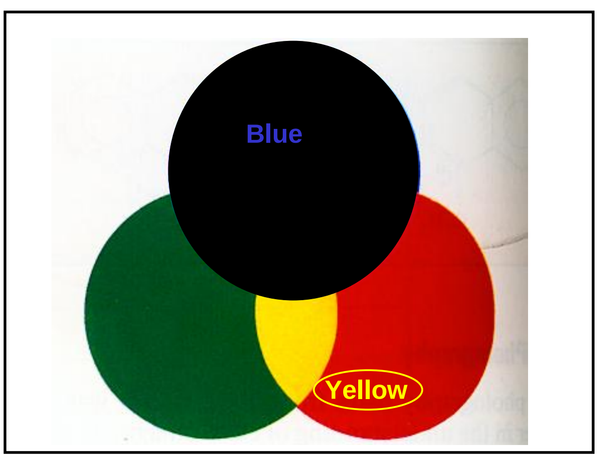
White = all the colors (wavelengths)

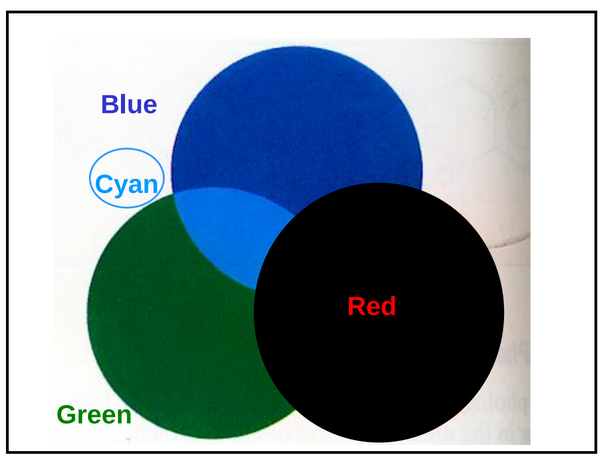

Blue
Green
Red

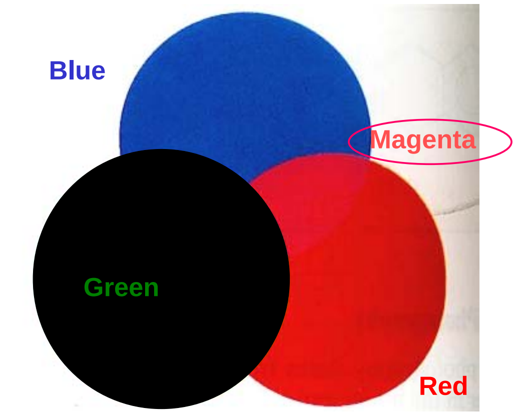

Cyan
Magenta
Yellow

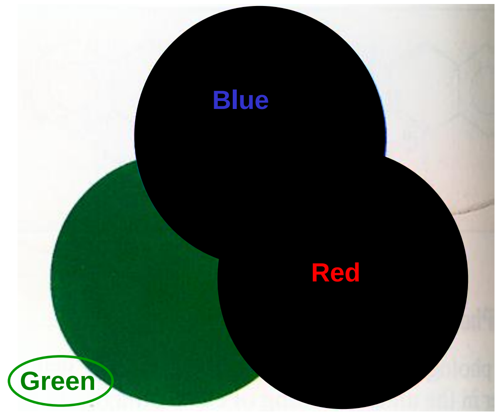

Magenta
Cyan
Yellow

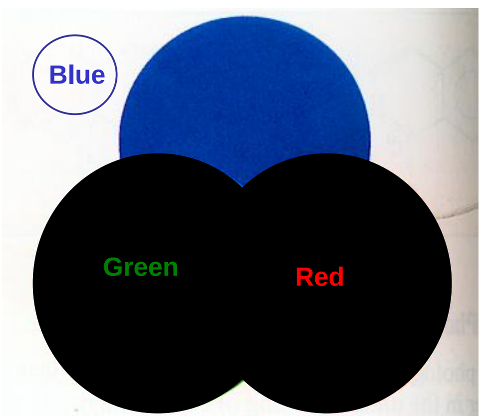

Blue
"White"
light
Green
Red

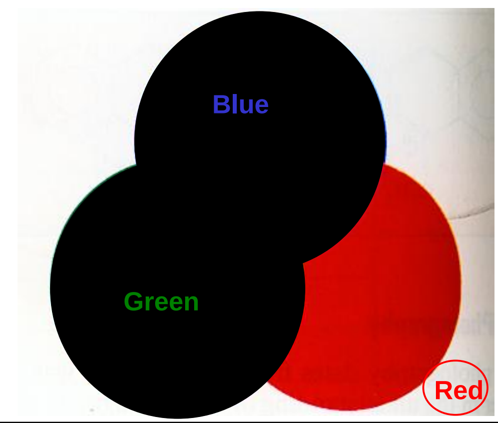

Blue
Yellow

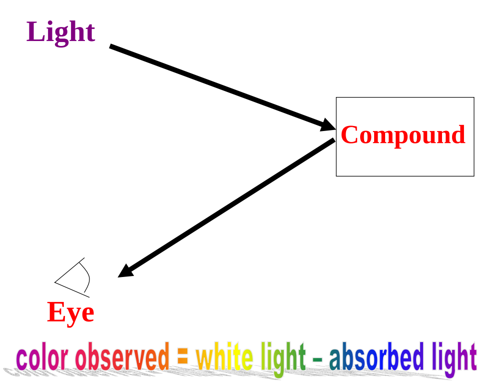

Blue
Cyan
Red
Green





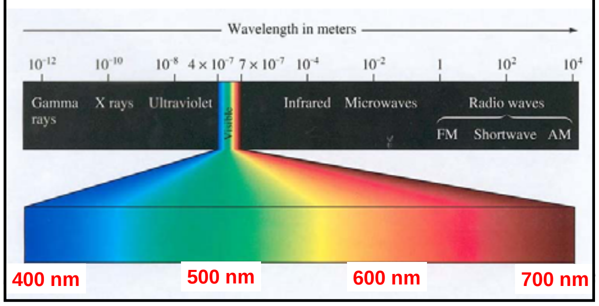


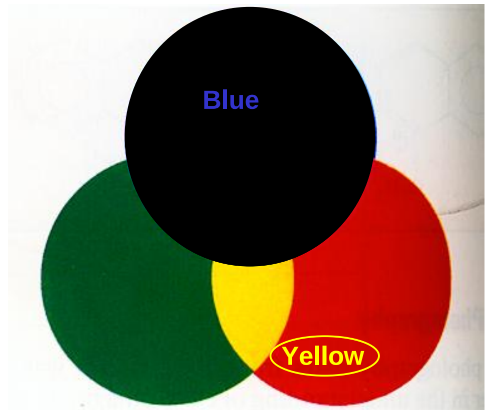


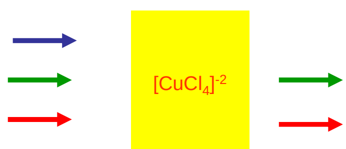


Coordination compounds are highly colored because they can absorb photons in the visible region of the electromagnetic spectrum to produce the complementary color.

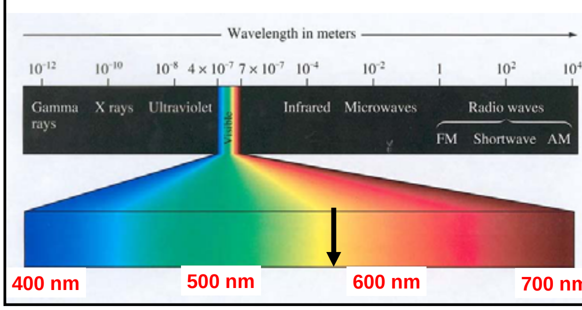
A solution of $[CuCl_4]^{-2}$ is yellow. In what region of the electromagnetic spectrum does it absorb light?

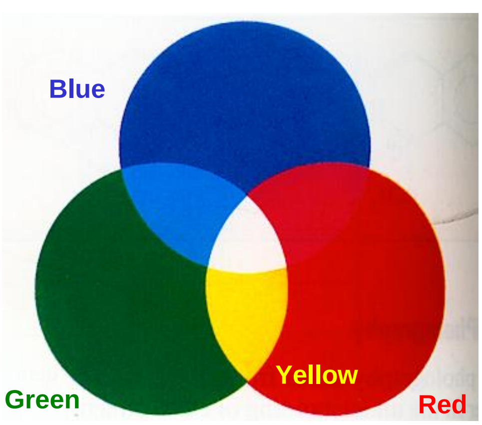


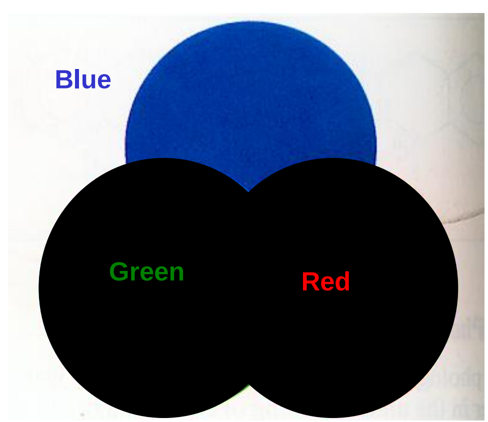


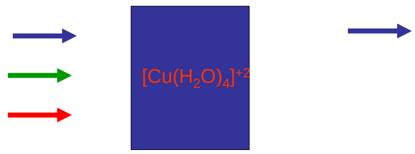


A solution of $[Cu(H_2O)_4]^{+2}$ absorbs mostly at 580 nm. What should be its color?

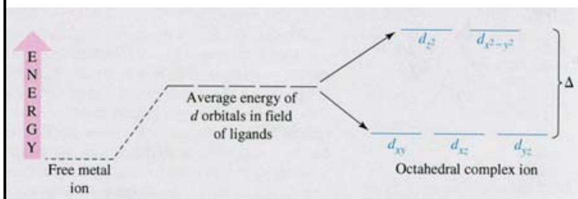








Coordination compounds are highly colored because they can absorb photons in the visible region of the electromagnetic spectrum to produce the complementary color.

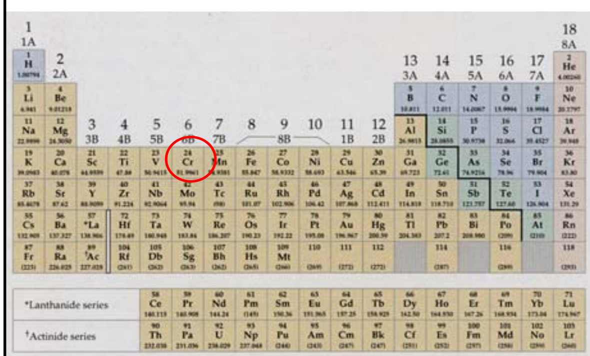


Explain the colors of:

$[Cr(NH_3)_6]Cl_3$ **$[Cr(H_2O)_6]Cl_3$**

Oxidation State: Cr^{3+}

Cr [Ar] $4s^13d^5$ **Cr^{3+} [Ar] $3d^3$**



Spectrochemical Series

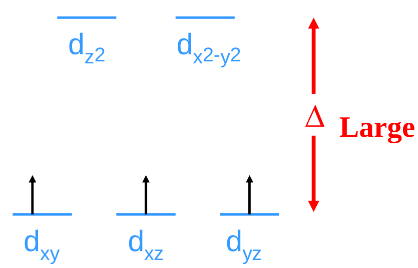
Strong field
(large Δ)

$CN^- > NO_2^- > en > py \approx NH_3 > EDTA^{4-} > SCN^- > H_2O >$
$ONO^- > ox^{2-} > OH^- > F^- > SCN^- > Cl^- > Br^- > I^-$
(small Δ)

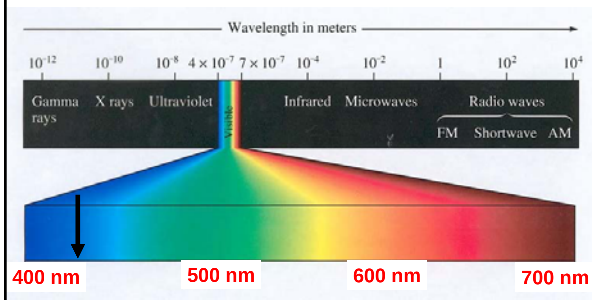
Underlining indicates the donor atom. *Weak field*

NH_3 is a stronger field ligand

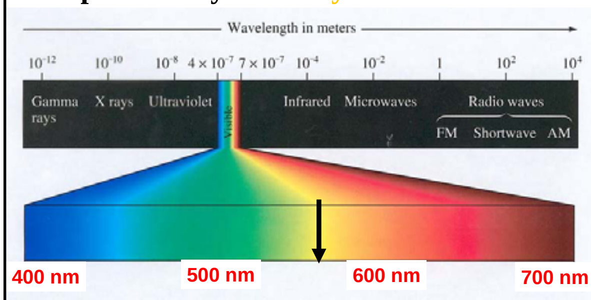
$[Cr(NH_3)_6]Cl_3$



$[Cr(NH_3)_6]Cl_3$ **absorbs at higher frequency (lower wavelength) i.e. in the blue.**

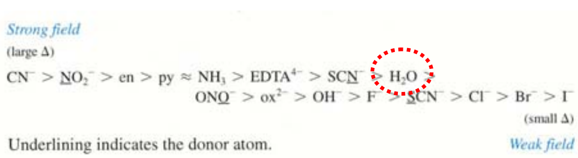


$[Cr(NH_3)_6]Cl_3$ **absorbs at higher frequency (lower wavelength) i.e. in the blue. The complementary color is yellow**

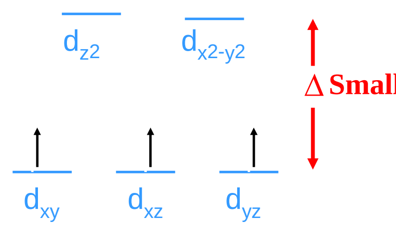


$[Cr(H_2O)_6]Cl_3$

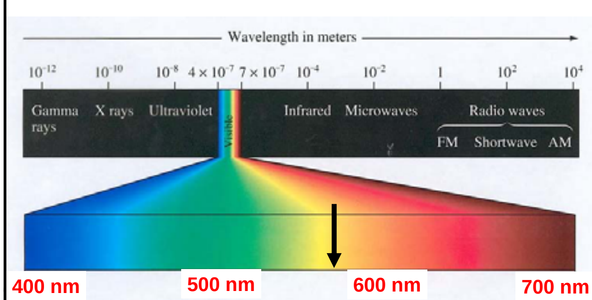
Spectrochemical Series



H_2O is a weaker field ligand



$[Cr(H_2O)_6]Cl_3$ **absorbs at lower frequency (higher wavelength) i.e. in the yellow.**



$[Cr(H_2O)_6]Cl_3$ **absorbs at lower frequency (higher wavelength) i.e. in the yellow. The complementary color is violet.**