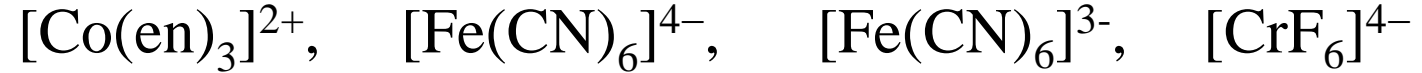


Lecture 4

Crystal Field Theory

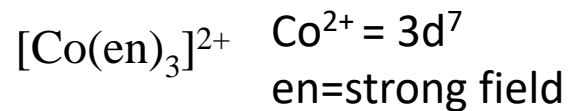
Two problems are also added with solution for your understanding

Problem solving! (Home work)

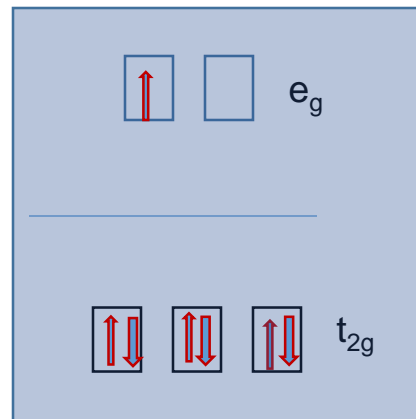


Classify the above given octahedral complexes and write in the boxes below as those

Having no tetragonal distortion	Having slight tetragonal distortion which is seen from UV Visible spectral studies	Having significant tetragonal distortion indicated as varying bond distances in their structure
$[\text{Fe(CN)}_6]^{4-}$	$[\text{Fe(CN)}_6]^{3-}$	$[\text{CrF}_6]^{4-}$ $[\text{Co(en)}_3]^{2+}$



Electronic degeneracy in the e_g orbital =
Significant Jahn Teller distortion



Fe^{II} (LS): No distortion
 Fe^{III} (LS): have slight distortion
 Cr(II) (HS): will have significant distortion

Problem Solving

Arrange the given metal complexes in the increasing order of intensity of color (ϵ) shown by them. Justify your order by writing below each the status of the selection rules for these complexes (no partial marks)



Least intense		Most intense
$[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	$[\text{CoBr}_4]^{2-}$
Spin Forbidden Laporte Forbidden	Spin Allowed Laporte Forbidden	Spin Allowed Laporte Allowed (Tetrahedral)

Problem solving !!

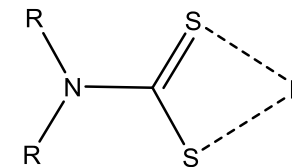
Cobalt form three octahedral complexes, $[\text{MCl}_6]^{4-}$, $[\text{M}(\text{R}_2\text{NCS}_2)_3]$ and $[\text{M}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$. These have magnetic moments 0, 1.73 and 3.9 BM (not in the order). Assign the magnetic moments to the complexes and predict the relative strength of the dithiocarbamate ligand.

Solution:

$[\text{CoCl}_6]^{4-}$ Co^{2+} , $3d^7$, Cl^- weak ligand, HS, 3 unpaired e's ~ 3.9 BM

$[\text{Co}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$. Co^{2+} , CN^- strong ligand, LS 1 unpaired e 1.73 BM

$[\text{Co}(\text{R}_2\text{NCS}_2)_3]$, Co^{3+} , $3d^6$, 0 BM means ligand is strong field and low spin complex



Magnetic properties of metal complexes

Magnetism is caused by moving charged electrical particles (Faraday, 1830s). These particles can be the current of electrons through an electric wire, or the movement of charged particles (protons and electrons) within an atom. These charged particles move much like planets in a solar system:

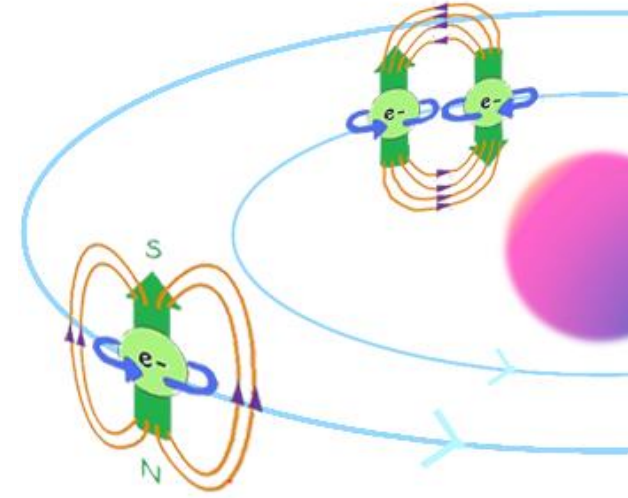
nucleus spin around its own axis, causing a **very weak** magnetic field.

electrons orbit around the nucleus, causing a **weak** magnetic field.

electrons spin around their own axis, causing a **significant** magnetic field.

Spinning electrons generate the bulk of the magnetism in an atom.

Within each orbit, electrons with opposite spins pair together, resulting in no net magnetic field. Therefore **only unpaired electrons** lead to magnetic moment



The **spin-only** formula (μ_s)

$$\mu_s = \sqrt{n(n+2)}$$

SUPER STRONG NEODYMIUM MAGNETS



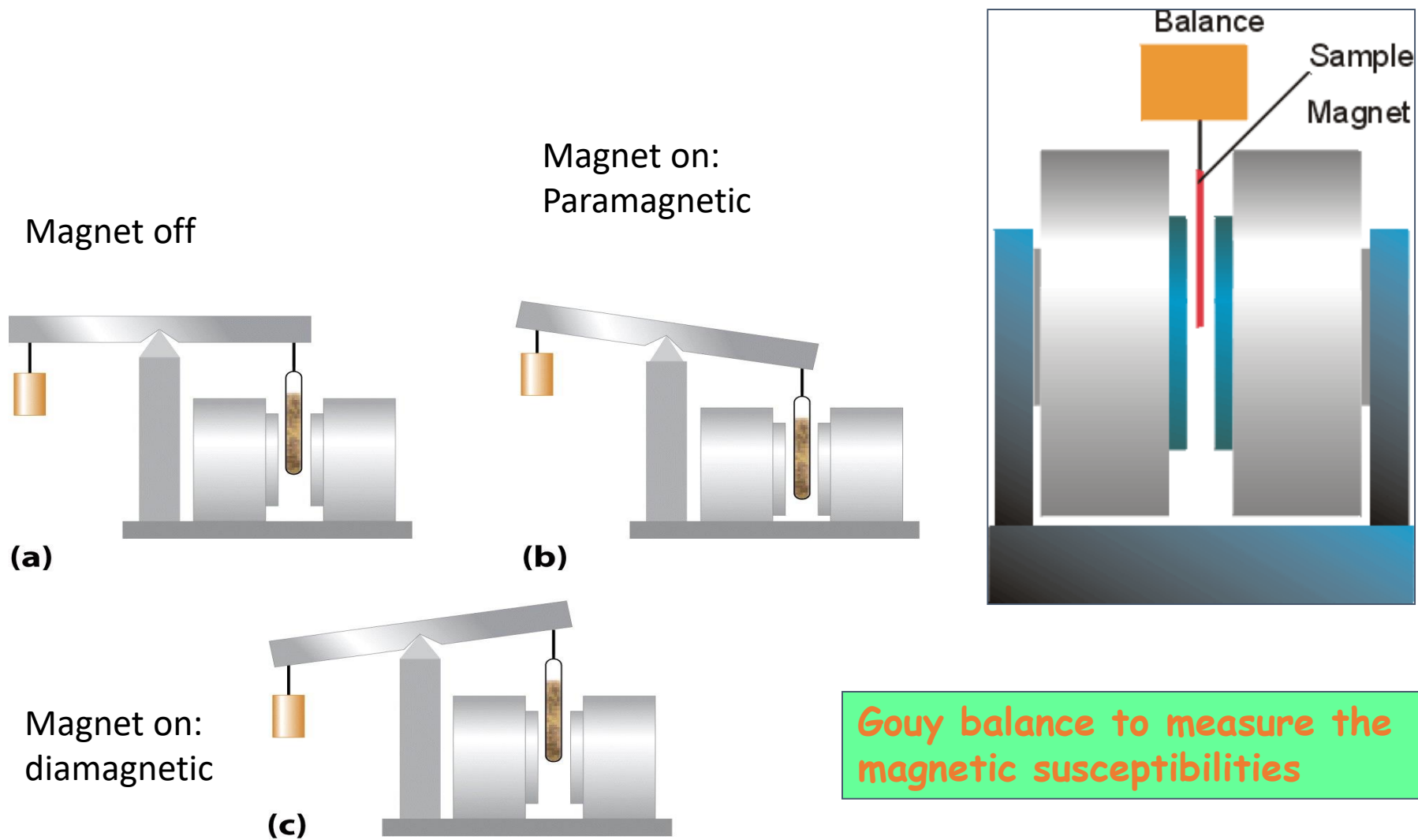
CRUSHING HAND

18

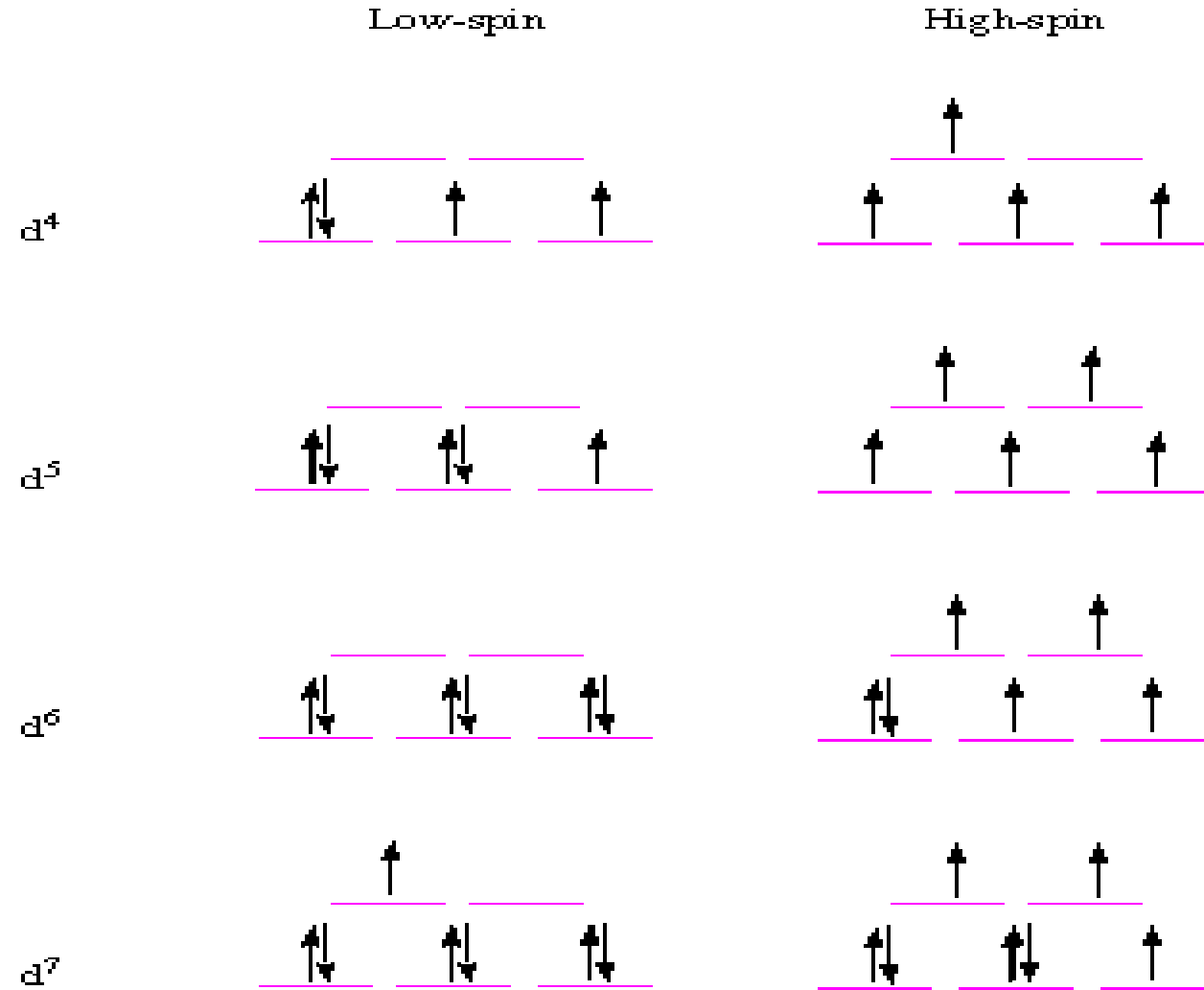
THIS CONTENT IS RECOMMENDED
FOR VIEWERS OVER 18 YEARS OLD

https://www.youtube.com/watch?v=0t8yDnyOaQ8&ab_channel=MagnetExpert

Magnetic properties of transition metal complexes



How Crystal Field theory explains magnetic moments of TM complexes to a decent extent?



Strength of the ligand, type of complex , size of the metal and its oxidation state affects crystal field splitting

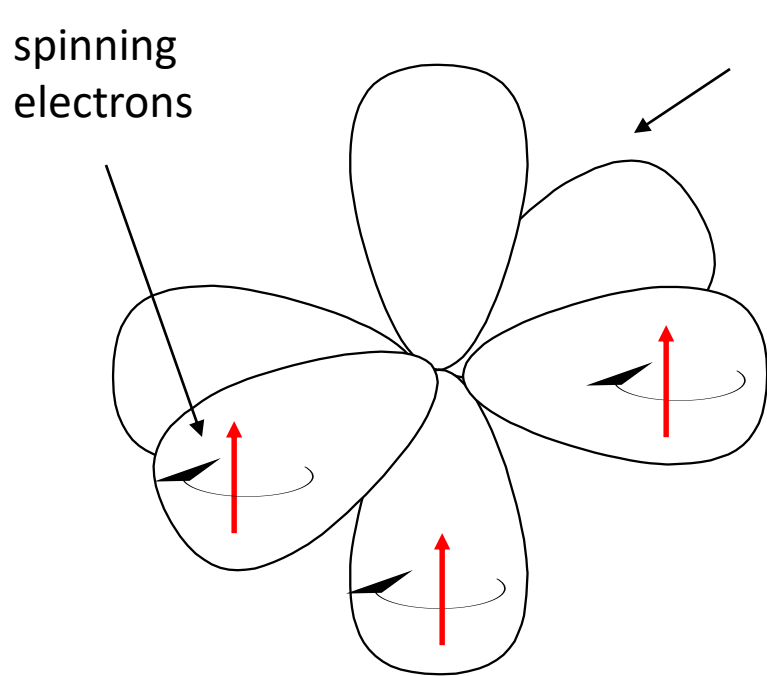
Magnetic properties: Spin only and effective

The **spin-only** formula (μ_s) applies reasonably well to metal ions from the first row of transition metals: (units = μ_B , Bohr-magnetons); magnetic moments value of high-spin complexes of first row d-block ions are given below.

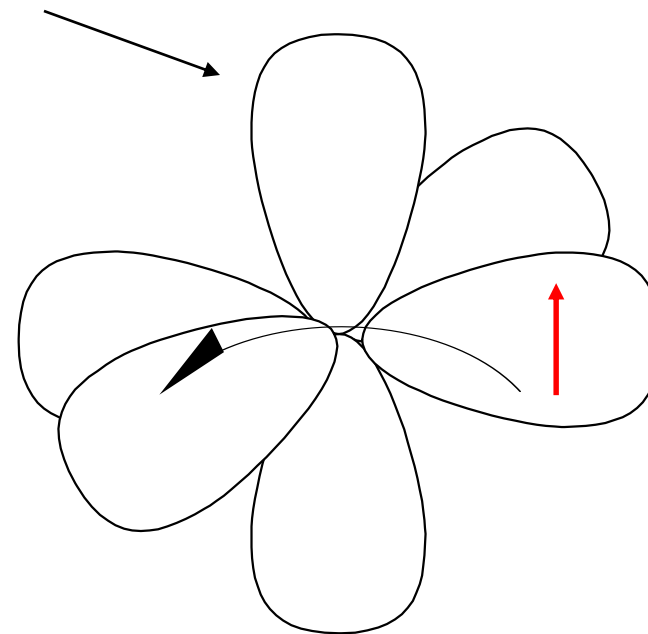
Metal ion	d ⁿ configuration	μ_s (calculated)	μ_{eff} (observed)
Ca ²⁺ , Sc ³⁺	d ⁰	0	0
Ti ³⁺	d ¹	1.73	1.7-1.8
V ³⁺	d ²	2.83	2.8-3.1
V ²⁺ , Cr ³⁺	d ³	3.87	3.7-3.9
Cr ²⁺ , Mn ³⁺	d ⁴	4.90	4.8-4.9
Mn ²⁺ , Fe ³⁺	d ⁵	5.92	5.7-6.0
Fe ²⁺ , Co ³⁺	d ⁶	4.90	5.0-5.6
Co ²⁺	d ⁷	3.87	4.3-5.2
Ni ²⁺	d ⁸	2.83	2.9-3.9
Cu ²⁺	d ⁹	1.73	1.9-2.1
Zn ²⁺ , Ga ³⁺	d ¹⁰	0	0

Spin and orbital contributions to μ_{eff}

For the first-row d-block metal ions the main contribution to magnetic susceptibility is from electron spin. However, there is also an orbital contribution (especially for the second and third row TM) from the motion of unpaired electrons from one d-orbital to another. This motion constitutes an electric current, and so creates a magnetic field.

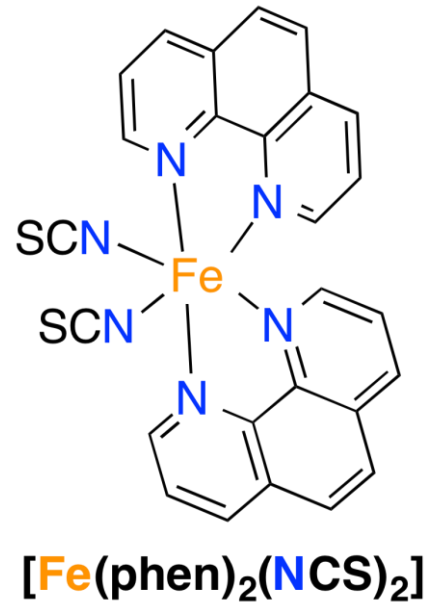
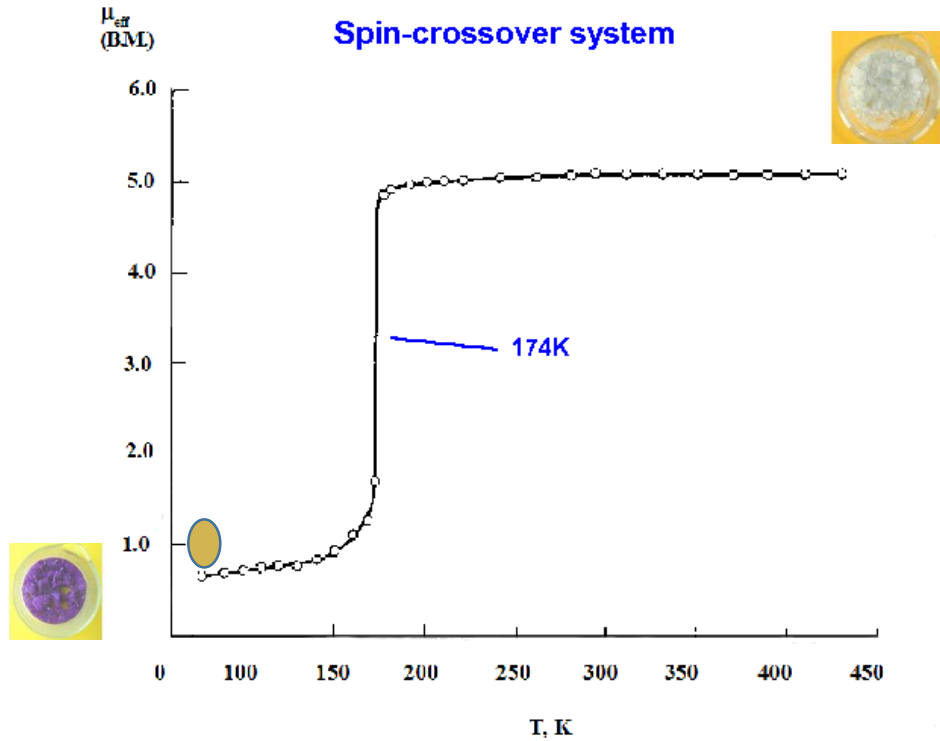


spin contribution – electrons are spinning creating an electric current and hence a magnetic field



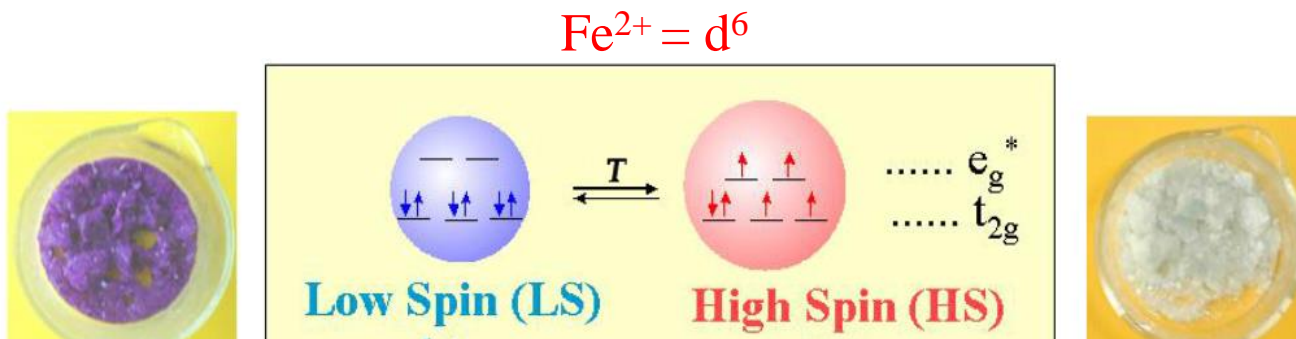
orbital contribution - electrons move from one orbital to another creating a current and hence a magnetic field

Temperature dependence of magnetic moments



Octahedral metal complexes with a d^4 – d^7 electronic configuration can, in principle, exist in the high spin (HS) or low spin (LS) states. Such systems can be switched between the two spin states by using external perturbations such as temperature; this is a phenomenon that is known as spin crossover (SCO).

How crystal field theory explains temperature dependence of μ_{eff}

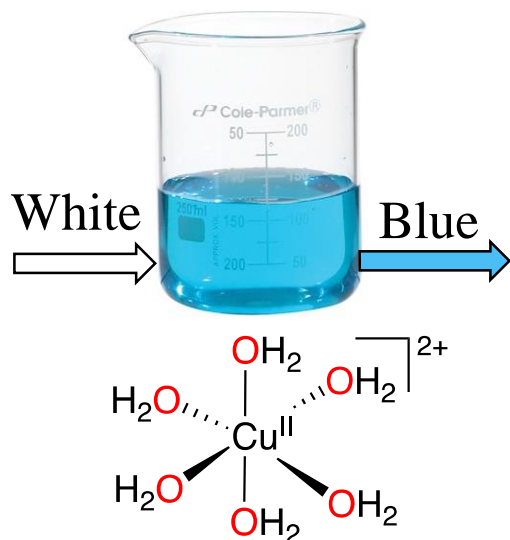
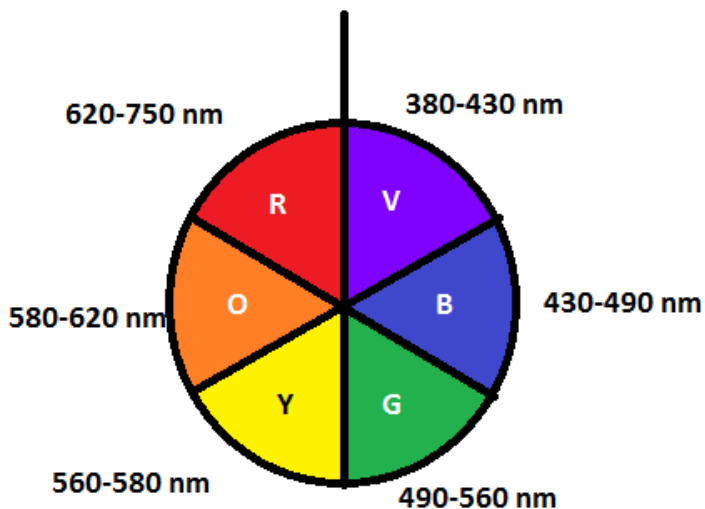


$T_{1/2}$ is the temperature for which there is coexistence of 50% of LS and 50% of HS molecules.

Colors of transition metal complexes

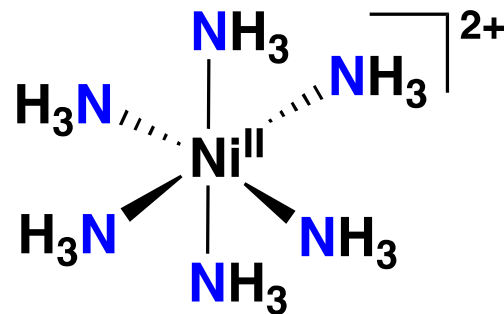
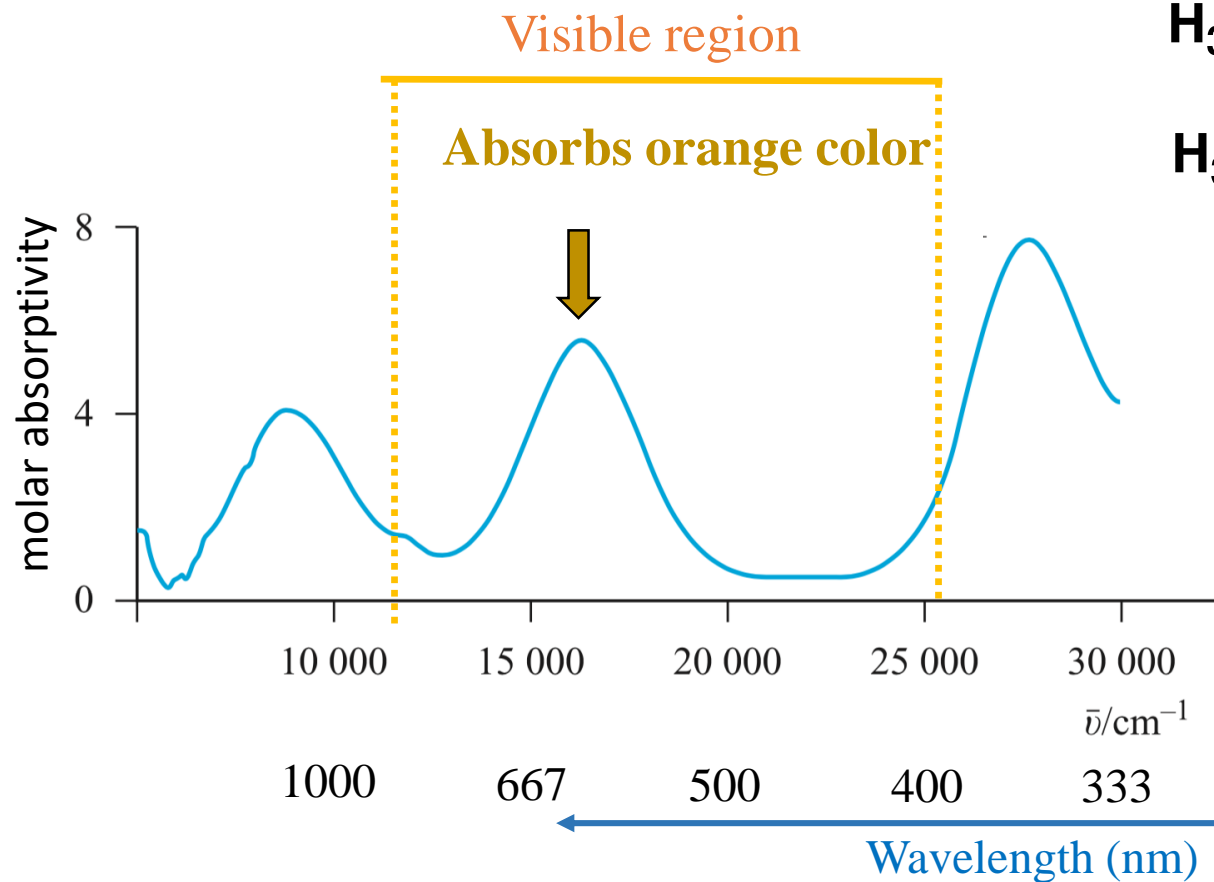
Why we observe color?

Colored solutions contain species that can absorb photons of visible light and use the energy of those photons to promote electrons in the species to higher energy levels. Because the energies of photons are related to the frequencies (and wavelengths) of light (Planck's equation, $E = h\nu$), only certain wavelength components are absorbed as white light passes through the solution. The emerging light, because it is lacking some wavelength components, is no longer white; it is colored.



Color of light absorbed	Approximate wavelength ranges / nm	Color of light transmitted
Red	700–620	Green
Orange	620–580	Blue
Yellow	580–560	Violet
Green	560–490	Red
Blue	490–430	Orange
Violet	430–380	Yellow

Electronic spectrum of Ni(II) complex



The **frequency**, **wavelength** or **energy** of a transition relates to the energy required to excite an electron:

- depends on Δ_{oct} and ligand-field strength of the molecule.
- decides **colour of molecule**

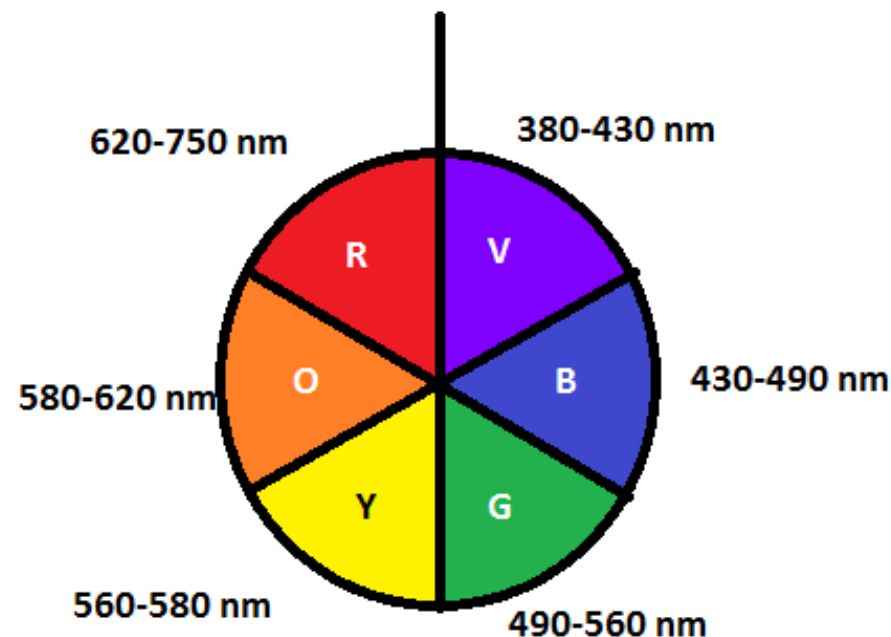
Problem solving!

$[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic and orange yellow. $[\text{CoF}_6]^{3-}$ on the other hand is paramagnetic and blue. Why?

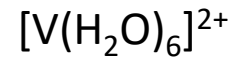
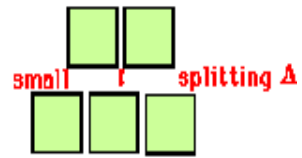
$[\text{Co}(\text{NH}_3)_6]^{3+}$: t_{2g}^6 diamagnetic = no unpaired electrons
Orange yellow means absorption in the Violet-blue region (higher frequency, larger Δ_o)
 d^6 LS

$[\text{CoF}_6]^{3-}$ paramagnetic $t_{2g}^4 e_g^2$
Blue means absorption in the orange region (lower frequency, smaller Δ_o) therefore d^6 HS

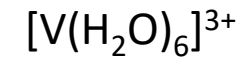
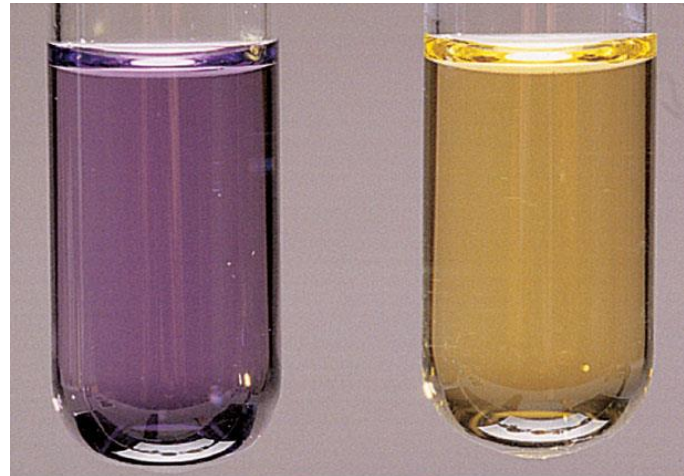
Δ_o splitting magnitude is higher for $[\text{Co}(\text{NH}_3)_6]^{3+}$ due to stronger ligand.



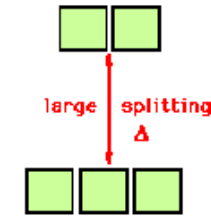
Effects of the metal oxidation state and of ligand strength on color.



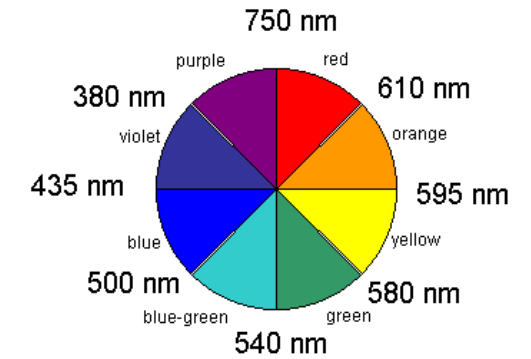
560 nm
17900 cm^{-1}



460 nm
21700 cm^{-1}



Wavelength Ranges for Colors
"Color Wheel"



Intensity of color in a transition metal complex

The absorbance is related to the concentration of the solution by the Beer–Lambert law:

$$A = \epsilon \times c \times l$$

The **molar absorption coefficient**, **molar extinction coefficient**, or **molar absorptivity** (ϵ), is a measurement of how strongly a chemical species absorbs light at a given wavelength. It is an intrinsic property of the species; the actual absorbance A , of a sample is dependent on the pathlength, ℓ , and the concentration, c , of the species via the **Beer–Lambert law**,

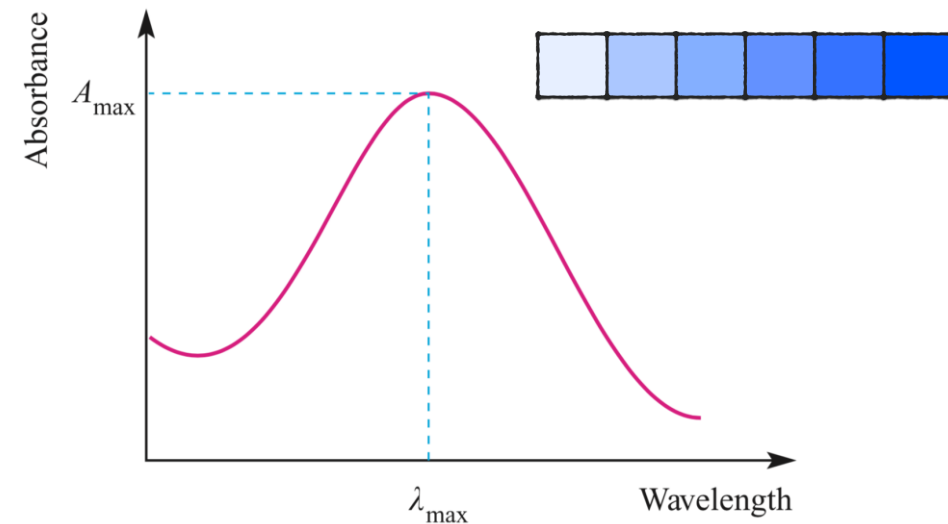
Selection rules:

Electronic transitions in a complex are governed by Selection rules

A selection rule is a quantum mechanical rule that describes the types of quantum mechanical **transitions that are permitted**.

They reflect the restrictions imposed on the state changes for an atom or molecule during an electronic transition.

Transitions **not** permitted by selection rules are said **forbidden**, which means that theoretically they must not occur (but in practice may occur with very low probabilities).



Electronic absorption spectra may be presented as plots of absorbance against wavenumber or wavelength, or as plots of ϵ_{\max} against wavenumber or wavelength.

Laporte Selection Rule

Statement : Only allowed transitions are those occurring with a change in parity (flip in the sign of *one* spatial coordinate.) OR During an electronic transition the azimuthal quantum number can change only by ± 1 ($\Delta l = \pm 1$)

Practical meaning of the Laporte rule

Allowed transitions are those which occur between **gerade** to **ungerade** or **ungerade** to **gerade** orbitals

Allowed

$g \rightarrow u$ & $u \rightarrow g$

Not allowed (FORBIDDEN)

$g \rightarrow g$ & $u \rightarrow u$

Laporte allowed transitions

$s \leftrightarrow p, p \leftrightarrow d, d \leftrightarrow f$ ($\Delta l = \pm 1$)

Laporte forbidden transitions

$s \leftrightarrow s, p \leftrightarrow p, d \leftrightarrow d, \text{ and } f \leftrightarrow f$ ($\Delta l = 0$)



Otto Laporte

German American
Physicist

Gerade = symmetric w r t centre of inversion

Ungerade = antisymmetric w r t centre of inversion

This rule affects Octahedral and Square planar complexes as they have center of symmetry

Tetrahedral complexes do not have center of symmetry: therefore this rule does not apply

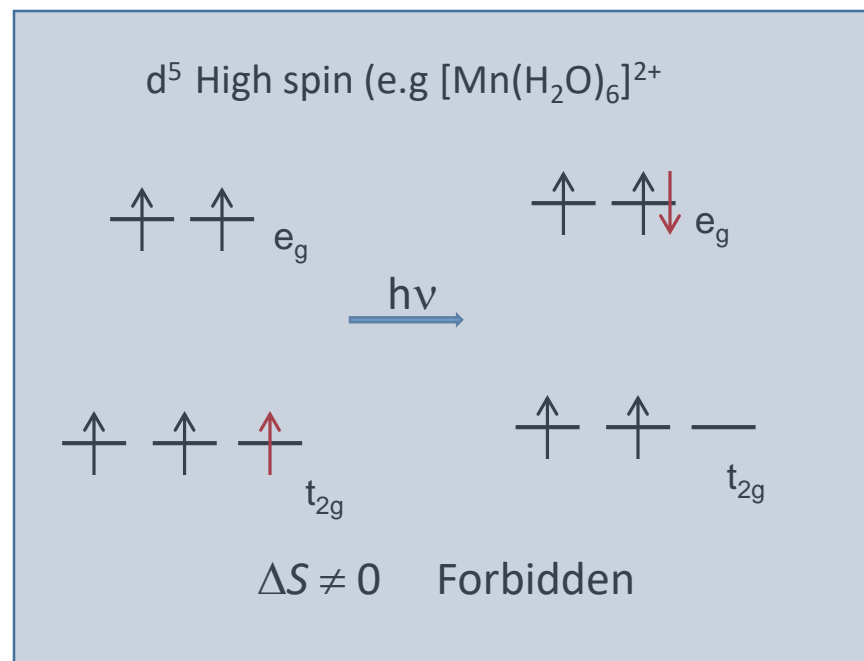
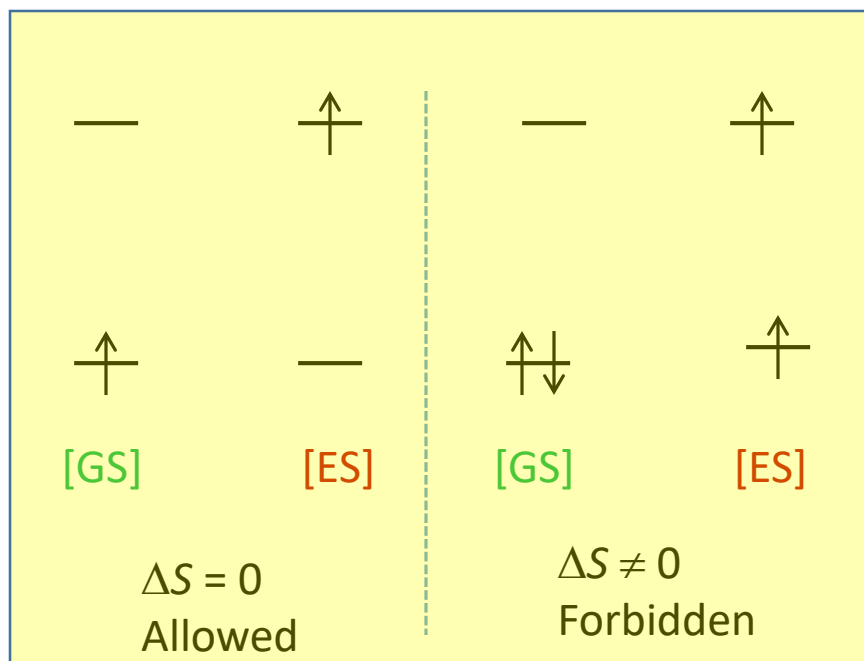
$t_{2g} \rightarrow e_g$ is forbidden or according to Laporte selection rule $d \rightarrow d$ transitions are not allowed !

Spin Selection Rule

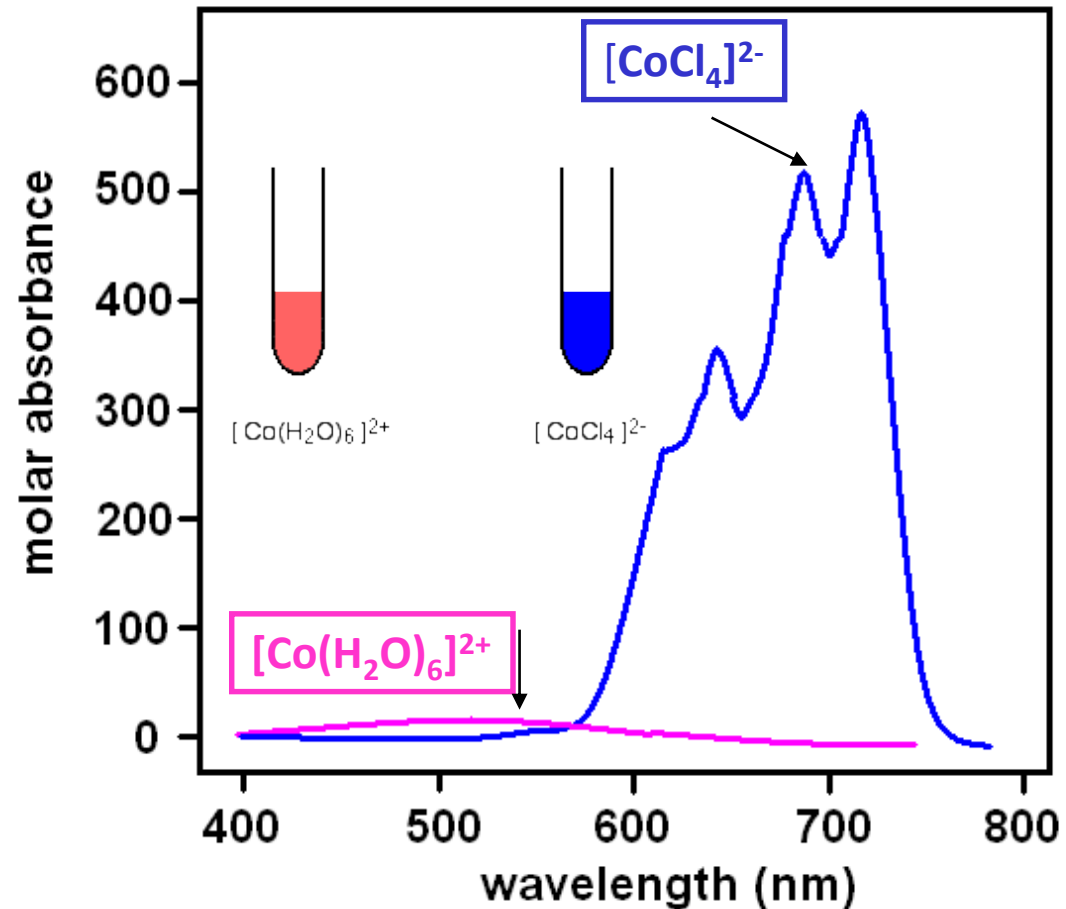
Statement : This rule states that transitions that involve a change in spin multiplicity are forbidden. According to this rule, any transition for which $\Delta S = 0$ is allowed and $\Delta S \neq 0$ is forbidden

Practical significance of the Spin Selection rule

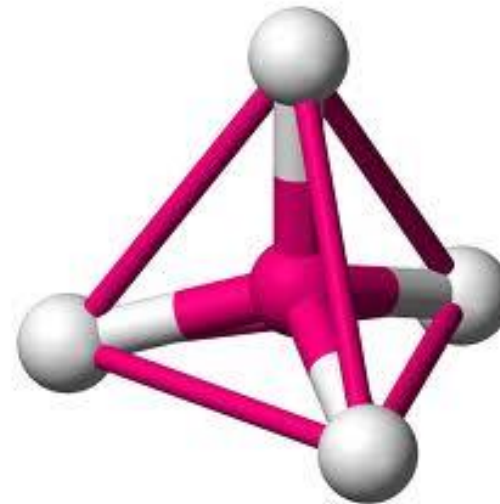
During an electronic transition, the electron should not change its spin ((An initially antiparallel pair of electrons cannot be converted to a parallel pair, so a singlet ($S=0$) cannot undergo a transition to a triplet ($S=1$) and vice versa.



The spectra of octahedral $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ and tetrahedral $[\text{CoCl}_4]^{2-}$ ions:



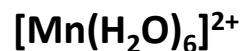
Intense d-d bands in the blue tetrahedral complex $[\text{CoCl}_4]^{2-}$, as compared with the much weaker band in the pink octahedral complex $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. This difference arises because the T_d complex has no center of symmetry, helping to overcome the $g \rightarrow g$ Laporte selection rule.



Classification of intensities of electronic transitions

Transition type	Example	Typical values of ϵ /m ² mol ⁻¹
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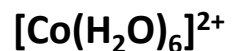
Spin forbidden,
Laporte forbidden
(partly allowed by **spin-orbit coupling**)



0.1



Spin allowed (octahedral complex),
Laporte forbidden
(partly allowed by **vibronic coupling and d-p mixing**)



1 - 10



Spin allowed (tetrahedral complex),
Laporte allowed (but still retain some original character)



50 - 150



Spin allowed,
Laporte allowed
e.g. **charge transfer** bands



1000 - 10⁶

