

**B.Sc. Semester-IV
Core Course-VIII (CC-VIII)
Inorganic Chemistry**



I. Coordination Chemistry

17. The Origin of Colour in Coordination Compounds



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Coordination Chemistry: 20 Lectures

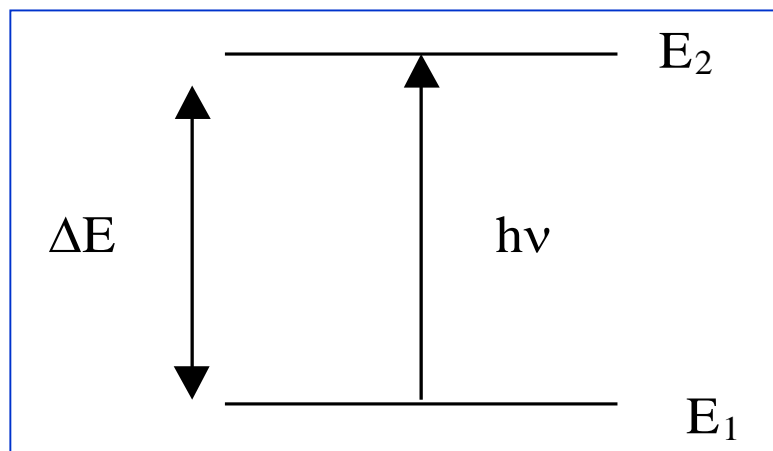
Werner's theory, valence bond theory (inner and outer orbital complexes), electroneutrality principle and back bonding. Crystal field theory, measurement of $10 Dq$ (Δ_o), CFSE in weak and strong fields, pairing energies, factors affecting the magnitude of $10 Dq$ (Δ_o , Δ_t). Octahedral vs. tetrahedral coordination, tetragonal distortions from octahedral geometry Jahn-Teller theorem, square planar geometry. Qualitative aspect of Ligand field and MO Theory.

IUPAC nomenclature of coordination compounds, isomerism in coordination compounds. Stereochemistry of complexes with 4 and 6 coordination numbers. Chelate effect, polynuclear complexes, Labile and inert complexes.

Coverage:

1 The Origin of Colour in Coordination Compounds

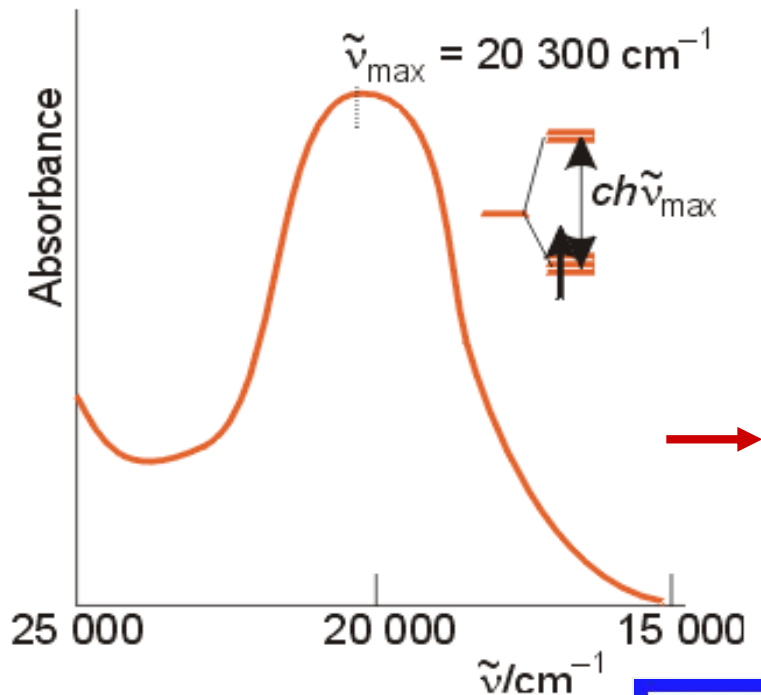
The Origin of Colour in Coordination Compounds



$$\Delta E = E_2 - E_1 = h\nu$$

Ligands influence Δ_o , therefore the colour

The Optical Absorption Spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$



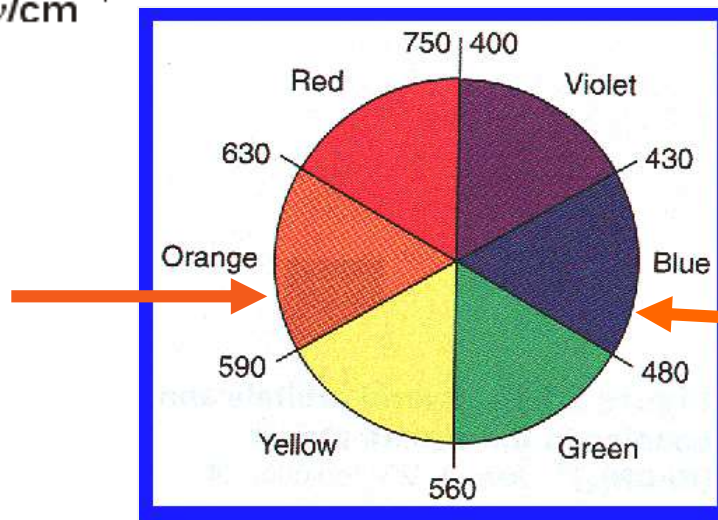
Assigned transition: $e_g \rightarrow t_{2g}$

This corresponds to the energy gap

$$\Delta_o = 243\text{ kJ mol}^{-1}$$

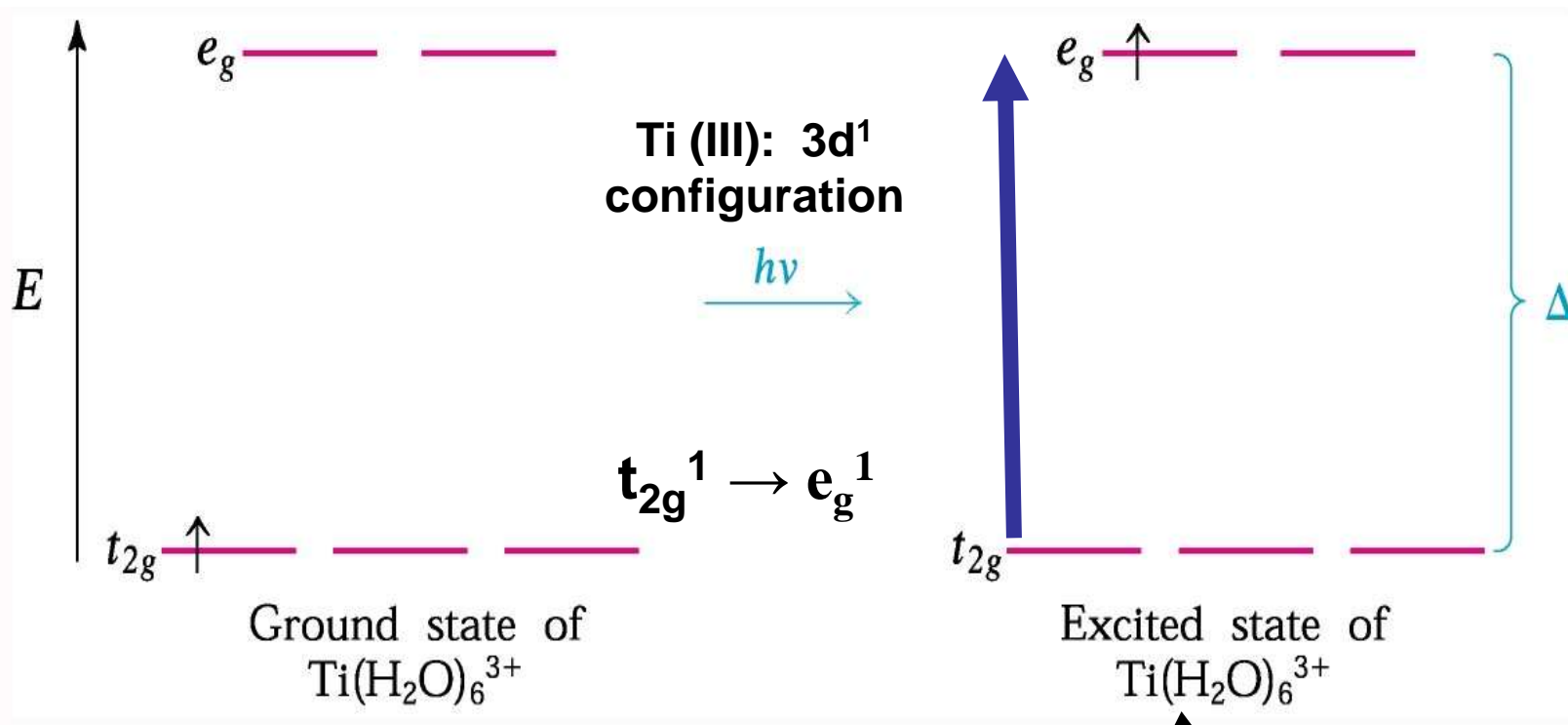


absorbed colour

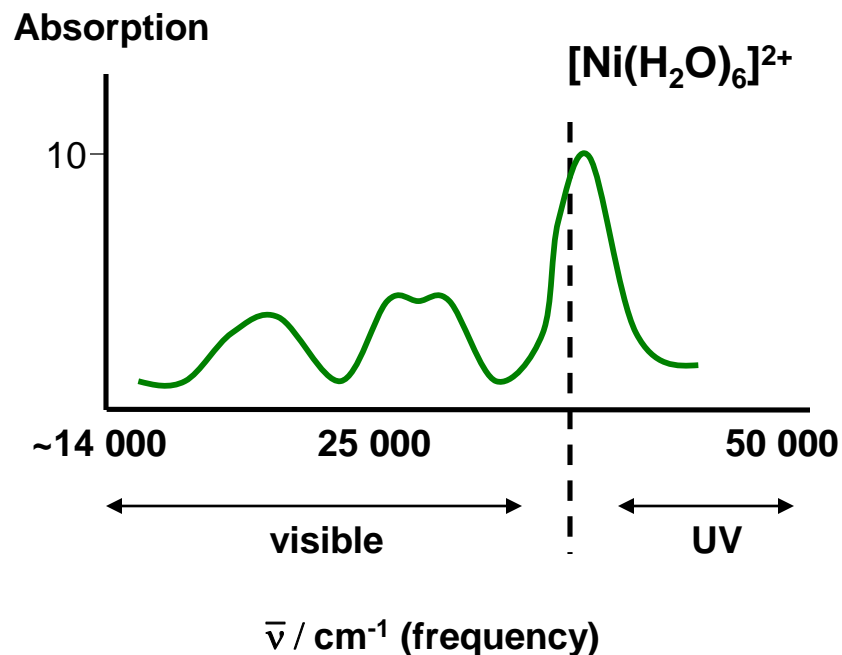
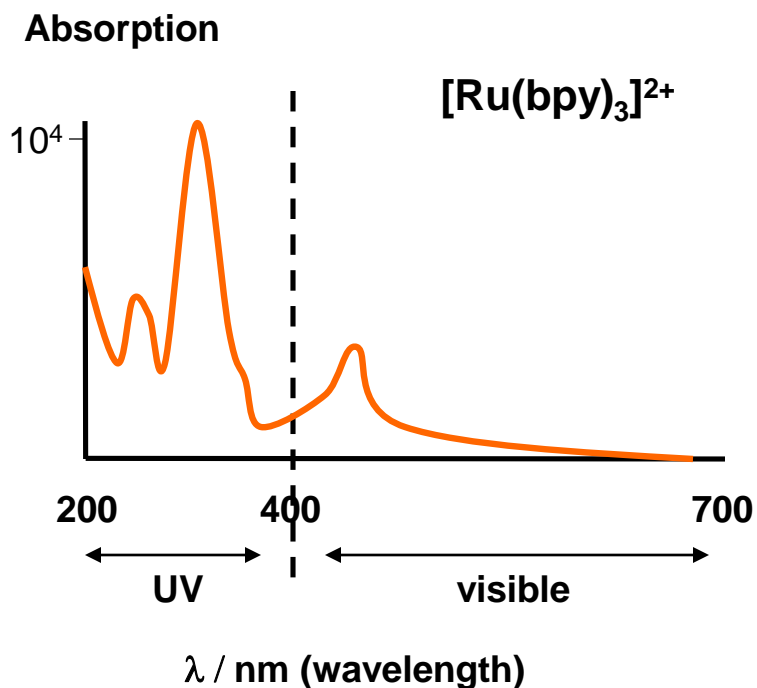


observed colour

Ti(H₂O)₆³⁺ Absorbs Light Due to an Electron Transition from a t_{2g} d-orbital to an e_g d-orbital



Absorption of radiation leading to electronic transitions within a molecule or complex



- UV** = higher energy transitions - between ligand orbitals
- visible** = lower energy transitions - between d-orbitals of transition metals
- between metal and ligand orbitals

Absorption maxima in a visible spectrum have three important characteristics:

1. **Number** (how many there are)

This depends on the **electron configuration** of the metal centre

2. **Position** (what wavelength/energy)

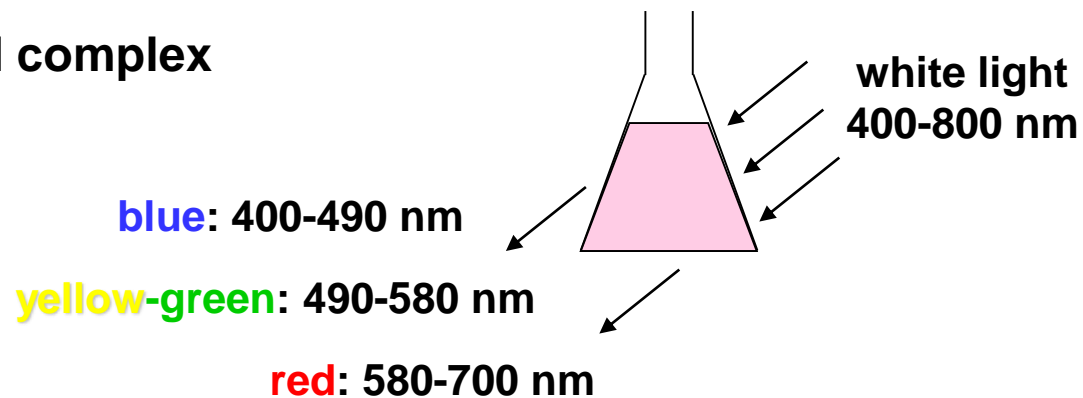
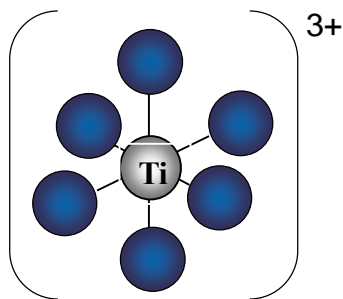
This depends on the **ligand field splitting** parameter, Δ_{oct} or Δ_{tet} and on the degree of inter-electron repulsion

3. **Intensity**

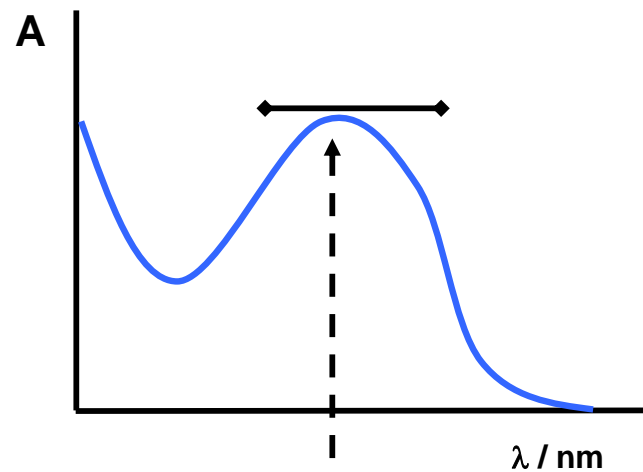
This depends on the "**allowedness**" of the transitions which is described by two selection rules

Absorption of light

$[\text{Ti}(\text{OH}_2)_6]^{3+}$ = d^1 ion, octahedral complex

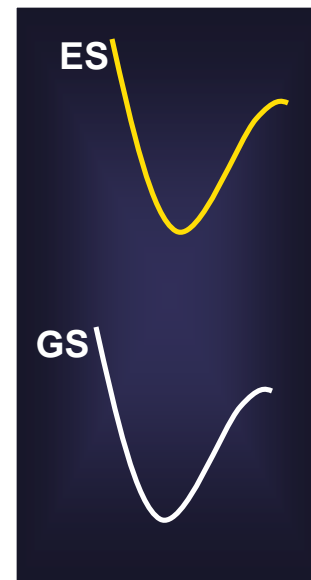
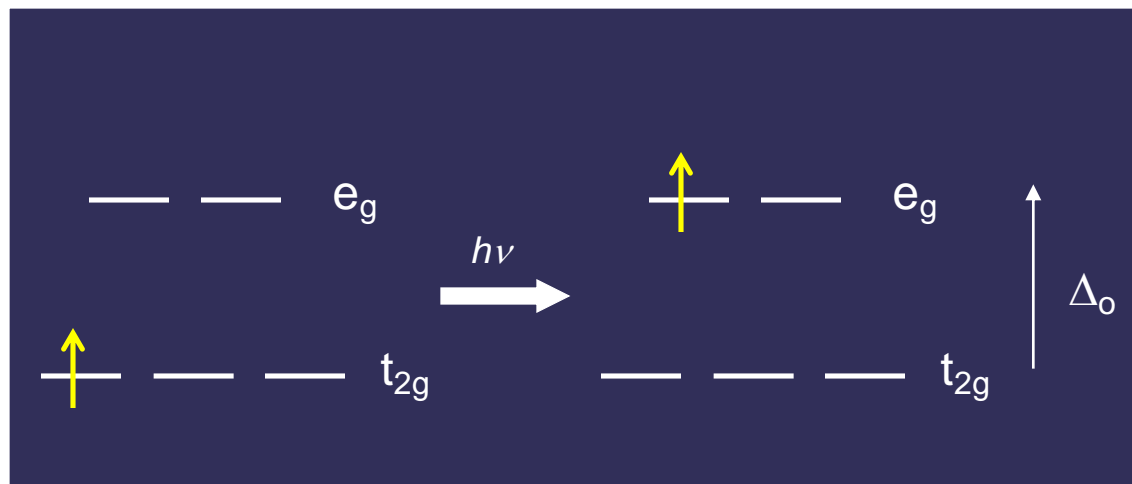
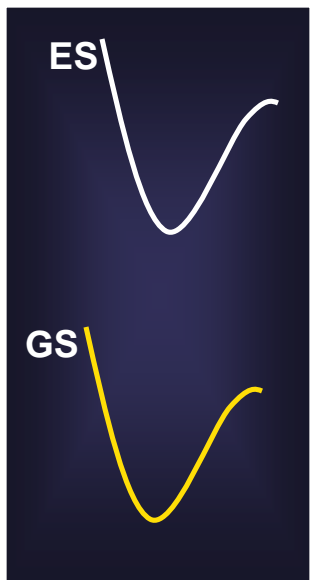


This complex is has a light purple colour in solution because it absorbs green light



$\lambda_{\text{max}} = 510 \text{ nm}$

The energy of the absorption by $[\text{Ti}(\text{OH}_2)_6]^{3+}$ is the ligand-field splitting, Δ_o



complex in electronic Ground State (GS) \longrightarrow d-d transition \longrightarrow complex in electronic excited state (ES)



$$\lambda_{\text{max}} = 510 \text{ nm}$$

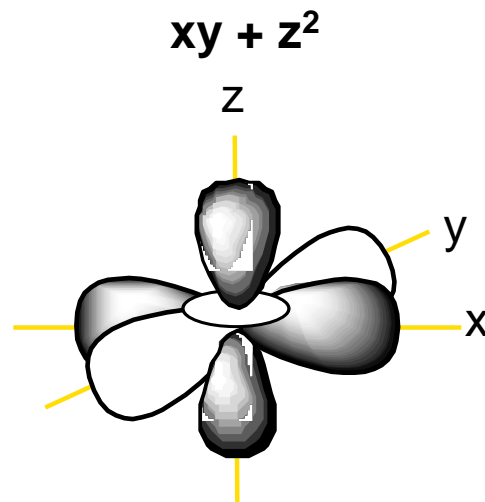
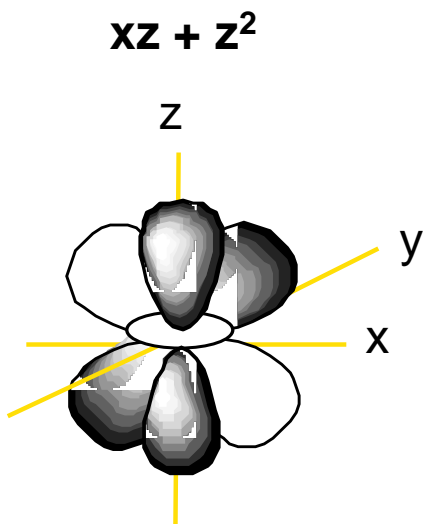
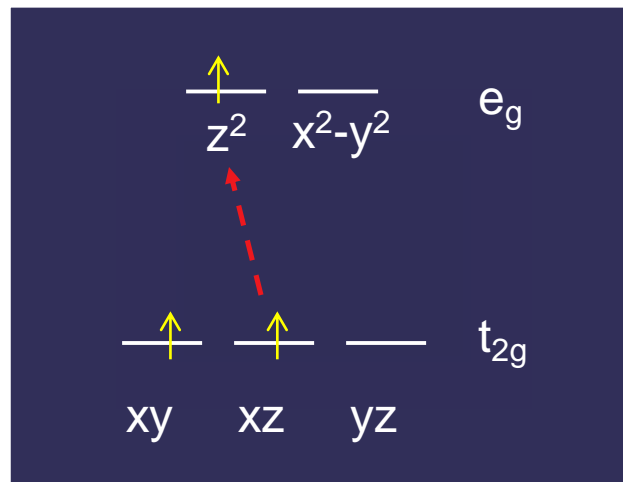
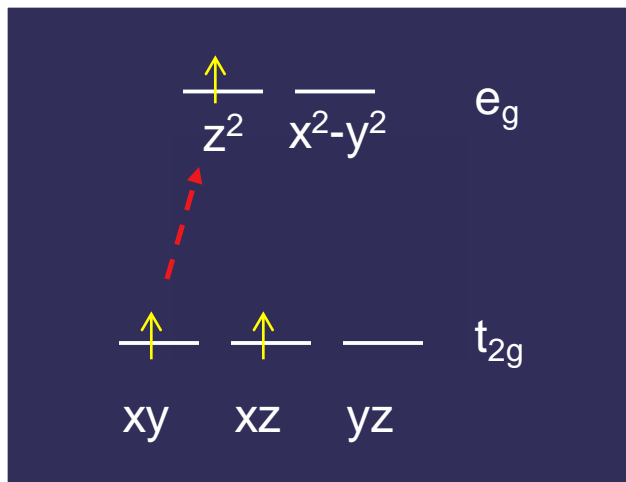
$$\Delta_o \text{ is } \therefore 243 \text{ kJ mol}^{-1}$$

$$20\,300 \text{ cm}^{-1}$$

An electron changes orbital; the ion changes energy state

Electron-Electron Repulsion

d^2 ion



lobes overlap, large electron repulsion lobes far apart, small electron repulsion

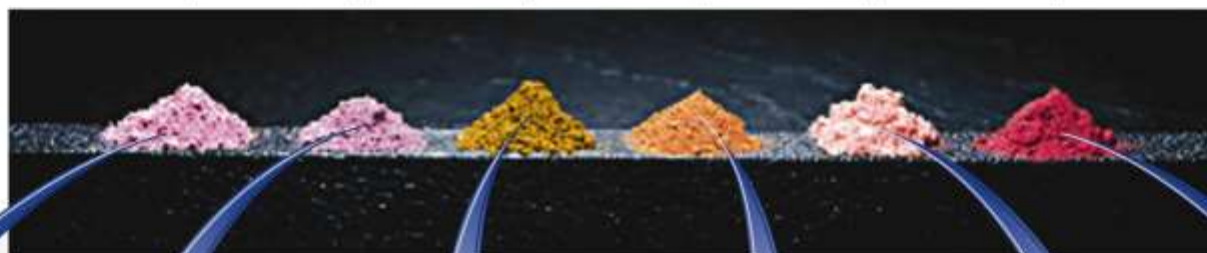
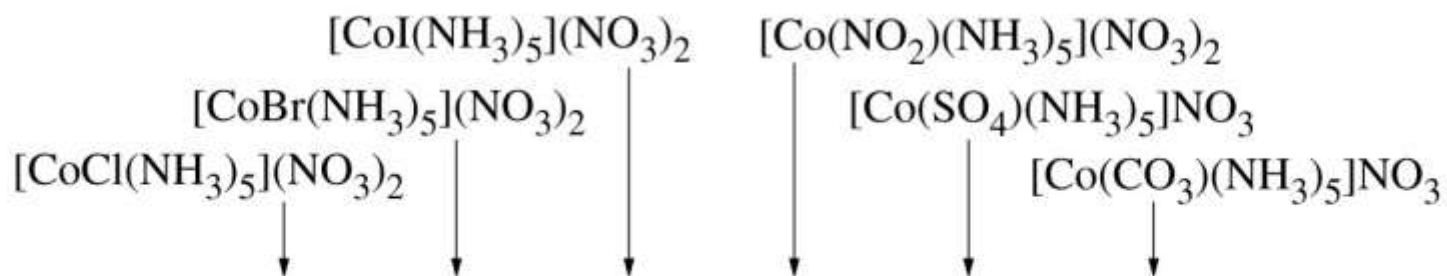
These two electron configurations do not have the same energy

Selection Rules

Transition	ϵ	complexes
Spin forbidden Laporte forbidden	$10^{-3} - 1$	Many $d^5 O_h$ complexes [Mn(OH₂)₆]²⁺
Spin allowed Laporte forbidden	$1 - 10$	Many O_h complexes [Ni(OH₂)₆]²⁺
	$10 - 100$	Some square planar complexes [PdCl₄]²⁻
	$100 - 1000$	6-coordinate complexes of low symmetry, many square planar complexes particularly with organic ligands
Spin allowed ligands Laporte allowed	$10^2 - 10^3$	Some MLCT bands in cxs with unsaturated
or	$10^2 - 10^4$	Acentric complexes with ligands such as acac, with P donor atoms
	$10^3 - 10^6$	Many CT bands, transitions in organic species

The colour can change depending on a number of factors e.g.

1. Metal charge
2. Ligand strength, e.t.c.



THANK YOU