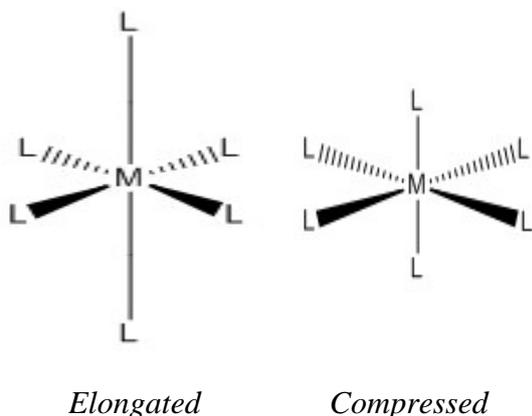


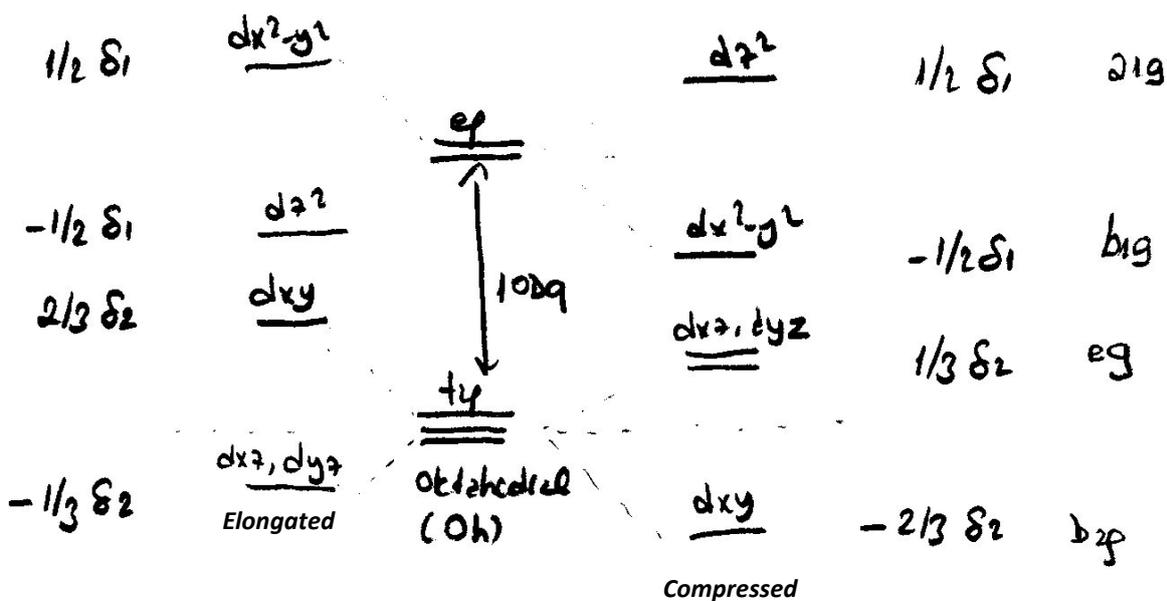
CRYSTAL FIELD THEORY (CFT)

JAHN-TELLER EFFECT (TETRAGONAL DISTORTION)

The approach of the trans two ligands to the central atom or far away the trans two ligands from the central atom is called tetragonal distortion. This distortion is typically observed among octahedral complexes where the two axial bonds can be shorter or longer than those of the equatorial bonds.



Jahn-Teller Distortion for an Octahedral Complex



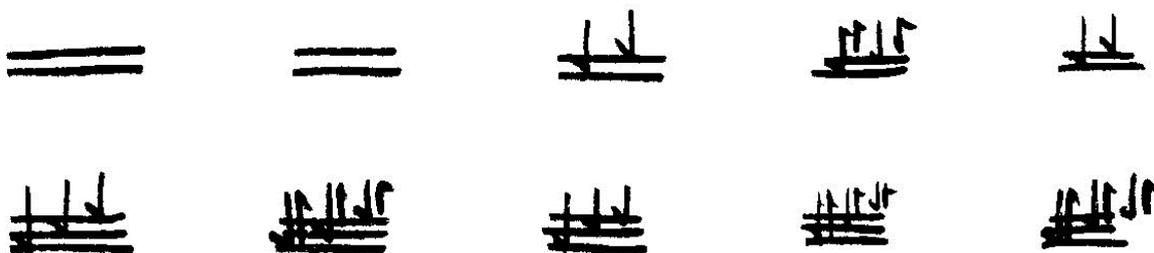
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$$\begin{aligned}
 \text{CFSE } (d^9) &= 4(-1/3\delta_2) + 2(+2/3\delta_2) + 2(-1/2\delta_1) + 1(+1/2\delta_1) = -1/2\delta_1 \quad \text{Elongated} \\
 &= 2(-2/3\delta_2) + 4(+1/3\delta_2) + 2(-1/2\delta_1) + 1(+1/2\delta_1) = -1/2\delta_1 \quad \text{Compressed} \\
 \text{CFSE } (d^4) &= 2(-1/3\delta_2) + 1(+2/3\delta_2) + 1(-1/2\delta_1) = -1/2\delta_1 \quad \text{Elongated} \\
 &= 1(-2/3\delta_2) + 2(+1/3\delta_2) + 1(-1/2\delta_1) = -1/2\delta_1 \quad \text{Compressed} \\
 \text{CFSE } (d^3) &= 4(-1/3\delta_2) + 2(+2/3\delta_2) + 1(-1/2\delta_1) = -1/2\delta_1 \quad \text{Elongated} \\
 &= 2(-2/3\delta_2) + 4(+1/3\delta_2) + 1(-1/2\delta_1) = -1/2\delta_1 \quad \text{Compressed}
 \end{aligned}$$

$\delta_1 < \delta_2 < 10Dq$

				The energy saved by distortion
d^1		t_{2g}^1	Compressed octahedral	$2/3\delta_2$
d^2		t_{2g}^2	Compressed octahedral	$2/3\delta_2$
d^3		t_{2g}^3	There is no John-Teller	0
d^4	high spin	$t_{2g}^3 e_g^1$	Compressed or elongated octahedral	$1/2\delta_1$
	low spin	t_{2g}^4	Elongated octahedral	$4/3\delta_2$
d^5	high spin	$t_{2g}^3 e_g^2$	There is no John-Teller	0
	low spin	t_{2g}^5	Elongated octahedral	$2/3\delta_2$
d^6	high spin	$t_{2g}^4 e_g^2$	Compressed octahedral	$2/3\delta_2$
	low spin	t_{2g}^6	There is no John-Teller	0
d^7	high spin	$t_{2g}^5 e_g^2$	Elongated octahedral	$2/3\delta_2$
	low spin	$t_{2g}^6 e_g^1$	Compressed or elongated octahedral	$1/2\delta_1$
d^8		$t_{2g}^6 e_g^2$	There is no John-Teller	0
d^9		$t_{2g}^6 e_g^3$	Compressed or elongated octahedral	$1/2\delta_1$
d^{10}		$t_{2g}^6 e_g^4$	There is no John-Teller	0

If there is a global symmetric charge density, there is no John-Teller. For this, we have to look at both t_{2g} and e_g .

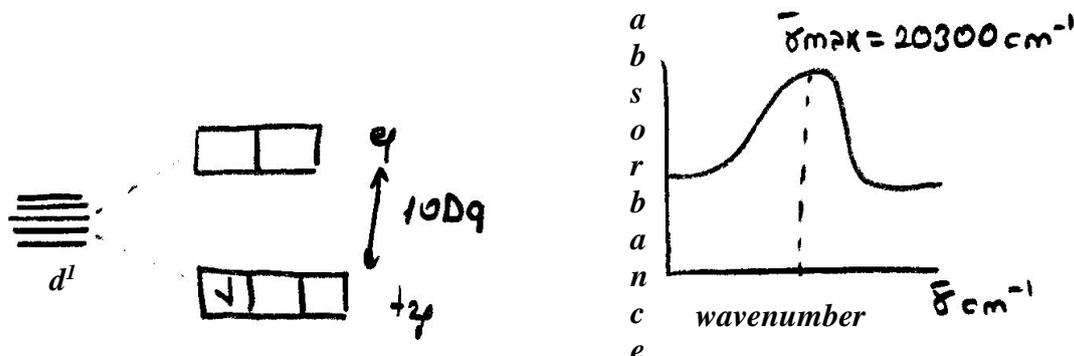


John-Teller effect is not observed

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10Dq PARAMETER AND ELECTRONIC SPECTRA

Example: UV spectrum of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex ion in aqueous solution



When the UV visible light is passed from the aqueous solution of the complex, the electron in t_{2g} absorbs $\Delta_o(10Dq)$ energy and it jumps to a higher e_g orbital. So, $t_{2g} \rightarrow e_g$ transition takes place. The energy of light that causes this transition ($h\nu$) is equal to $10Dq$. Maximum molar absorption is at 20300 cm^{-1} . Since $1\text{kJ}\cdot\text{mol}^{-1} = 83.6 \text{ cm}^{-1}$, the absorbed energy is $243 \text{ kJ}\cdot\text{mol}^{-1}$ ($\text{CFSE} = \Delta_o = 10Dq = 243 \text{ kJ}\cdot\text{mol}^{-1}$). The absorbed $243 \text{ kJ}\cdot\text{mol}^{-1}$ energy falls into the greenish-yellow zone of the electromagnetic spectrum. So, an aqueous solution of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ absorbs greenish-yellow component of white light, and that's why $d-d$ transition takes place and as a result aqueous solution appears purple, because purple is the complementary colour of greenish-yellow.

$$10Dq = h\nu = h \cdot \frac{c}{\lambda} = h \cdot c \cdot \bar{\nu}_{\text{max}}$$

$$10Dq = (6,626 \cdot 10^{-34} \text{ J}\cdot\text{s}) \cdot \frac{3 \cdot 10^8 \text{ m}\cdot\text{s}^{-1}}{4,926 \cdot 10^{-7} \text{ m}} = 4,03 \cdot 10^{-19} \text{ J} = 243 \text{ kJ}\cdot\text{mol}^{-1}$$

$$243 \text{ kJ}\cdot\text{mol}^{-1} \cdot \frac{1 \text{ kcal}}{4,18 \text{ kJ}} = 57,60 \text{ kcal}\cdot\text{mol}^{-1} \quad 10Dq = 5,76 \text{ kcal}\cdot\text{mol}^{-1}$$

$$\text{CFS} = -4Dq = -4 \cdot 5,76 = -23,04 \text{ kcal}\cdot\text{mol}^{-1}$$

In most books, $10Dq$ is given in cm^{-1} .

$$\bar{\nu} = 1/\lambda = 1/4,926 \cdot 10^{-5} = 20300 \text{ cm}^{-1}$$

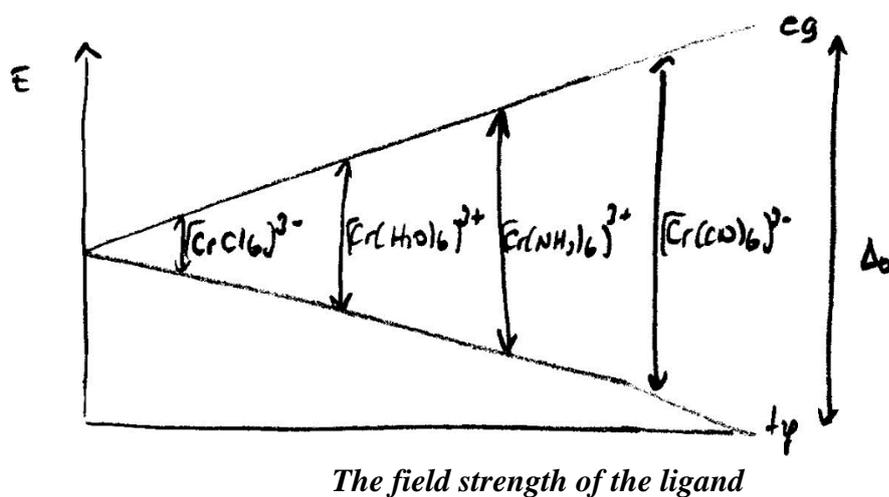
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SPECTROCHEMICAL SERIES

The energy difference, Δ_o determines the color of the coordination complex. According to the spectrochemical series, the high spin ligands are considered "weak field," and absorb longer wavelengths of light (weak Δ_o), while complexes with low spin ligands absorb light of greater frequency (high Δ_o). The color seen is the complementary color of that of the wavelength absorbed. To predict which possible colors and their corresponding wavelengths are absorbed, the spectrochemical series can be used:

(Strong field/large Δ_o /low spin) $\text{CO} > \text{CN}^- > \text{PPh}_3 > \text{:CH}_3^- > \text{H}^- > \text{NO}_2^- > o\text{-phenantroline} \sim \text{dipyridine} > \text{SO}_3^{2-} > \text{en} > \text{NH}_3 \sim \text{pyridine} > \text{NH}_2\text{-CO-O}^- > \text{CN}^- > \text{NCS}^- > \text{H}_2\text{O} > \text{C}_2\text{O}_4^{2-} > \text{C}_2\text{H}_5\text{OH} > \text{OH}^- > (\text{NH}_2)_2\text{-CO(urea)} > \text{F}^- > \text{N}_3^- \sim \text{NO}_3^- > \text{Cl}^- > \text{SCN}^- > \text{S}_2^{2-} > \text{Br}^- > \text{I}^-$
 (weak field/ small Δ_o /high spin)

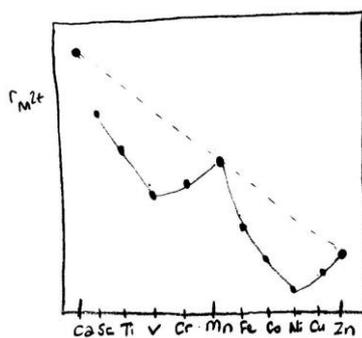


FACTORS AFFECTING CFSE

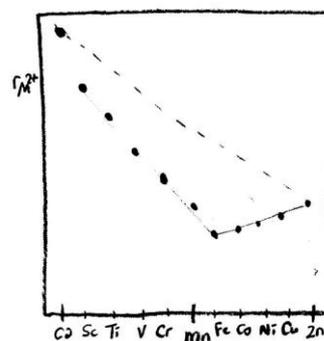
1. Charge of the central atom
2. The radius of the central atom
3. Coordination number
4. Geometry
5. Type of ligand

EFFECTS OF CRYSTAL FIELD SPLITTING

Crystal field splitting affects the lattice energy, hydration energy, ion radii, stability constants and reduction potentials of complexes. The change in the radii of the M^{2+} metal cations over the period results from the splitting of the d orbitals. Since the CFSE of the d^0 , d^5 and d^{10} configurations in the weak octahedral field are 0, the radii of the Ca^{2+} , Mn^{2+} and Zn^{2+} metal cations having these configurations is above the curve indicating the reduction in the radii over the period. It is expected that the radius decreases over the period. The radius value of other ions except Ca^{2+} , Mn^{2+} and Zn^{2+} ions is below this curve. This is because the d orbitals split into two groups (t_{2g} and e_g). The single d electron enters t_{2g} orbital in Sc^{3+} ion. Since the interaction of t_{2g} orbitals with the ligand orbitals is small, the ligands are closer to the central atom and therefore the radius decreases. This decreasing continues until the d^3 configuration (V^{3+}) in the weak octahedral field. The fourth d electron in Cr^{2+} also enters e_g orbital. The interaction of e_g orbitals with the ligand orbitals are high, so the ligands move away from the central atom and therefore the radius increases. The increasing in the radius continues until the d^5 configuration (Mn^{2+}). Since the sixth electron enters t_{2g} orbitals in Fe^{2+} , the radius decreases again. As the ninth electron in Zn^{2+} and the tenth electron in Cu^{2+} enters e_g orbitals, the radius increases.



Weak-field octahedral



Strong-field octahedral