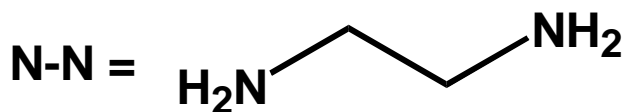
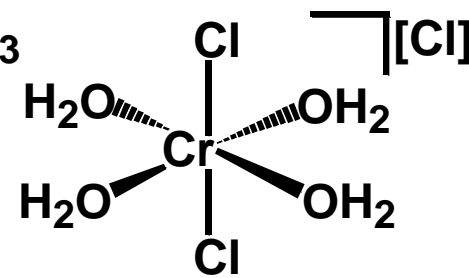
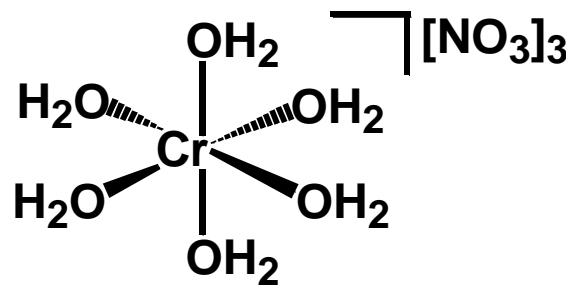
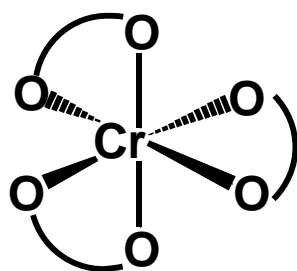
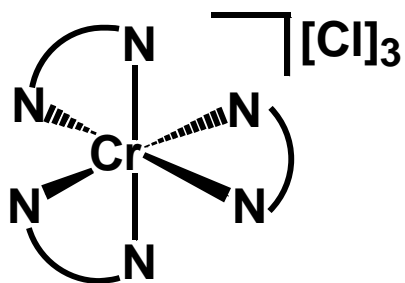


## ESPERIENZA 4

Determinazione del  $\Delta_o$  di una serie di complessi di  $\text{Cr}^{3+}$   
e verifica della serie spettrochimica

I complessi studiati:



## Analisi spettroscopica

La legge di Lambert e Beer:  $A = \epsilon b c$

Preparare una soluzione per ogni complesso tale per cui  $A \leq 1$ ,  
tenendo presente che  $\epsilon$  è compreso tra  $10$  e  $100 \text{ cm}^{-1} \text{ M}^{-1}$ .

Gli ioni  $d^3$  danno **3 bande di assorbimento**:



**Nel Visibile**



**Nell'U. V.**

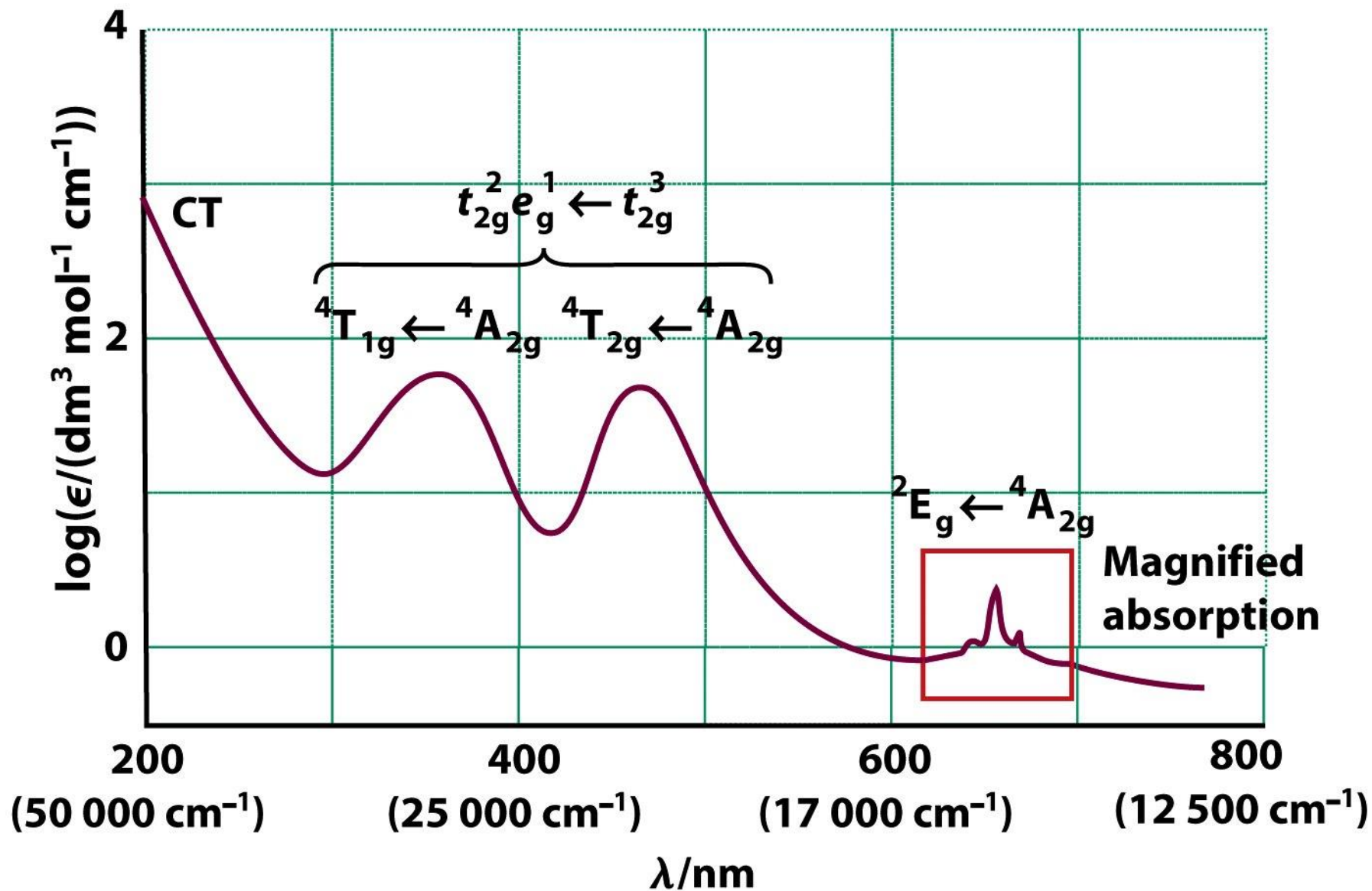


Figure 19-19  
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# Analisi spettroscopica

Metodo 1:

Si considera solo la banda, nel **Visibile**, a più bassa energia



Relazioni utili:

$$\Delta E = h \nu = h c / \lambda$$

$$\Delta E = \frac{(6.623 \cdot 10^{-34} \text{ J s})(3.00 \cdot 10^8 \text{ m s}^{-1})}{\lambda \text{ m}} \times (6.022 \cdot 10^{23} \text{ mol}^{-1}) = \Delta o \text{ (kJ mol}^{-1}\text{)}$$

$$1 \text{ cm}^{-1} = 0.01196 \text{ k J mol}^{-1} \implies \Delta o \text{ (cm}^{-1}\text{)}$$

# Analisi spettroscopica

Metodo 2:

Si considerano entrambe le bande nel **Visibile**



Si utilizza il diagramma di **Tanabe - Sugano**

$$\frac{\lambda_2}{\lambda_1} = n \quad \lambda_1 \text{ e } \lambda_2 \text{ si esprimono in cm}^{-1}$$

Con il righello si cerca sul diagramma l'ascissa corrispondente ad **n**, che è il valore di  $\Delta o/B$ .

Sull'ordinata si legge il valore di **E/B** corrispondente alla banda a minore energia  $\lambda_1$ : es. **m**.

Conosco **E (cm<sup>-1</sup>)**, è il valore sperimentale di  $\lambda_1$ , per cui posso ricavare **B = E/m**.


$$\Delta o / B = n \implies n B = \Delta o \text{ (cm}^{-1}\text{)}$$

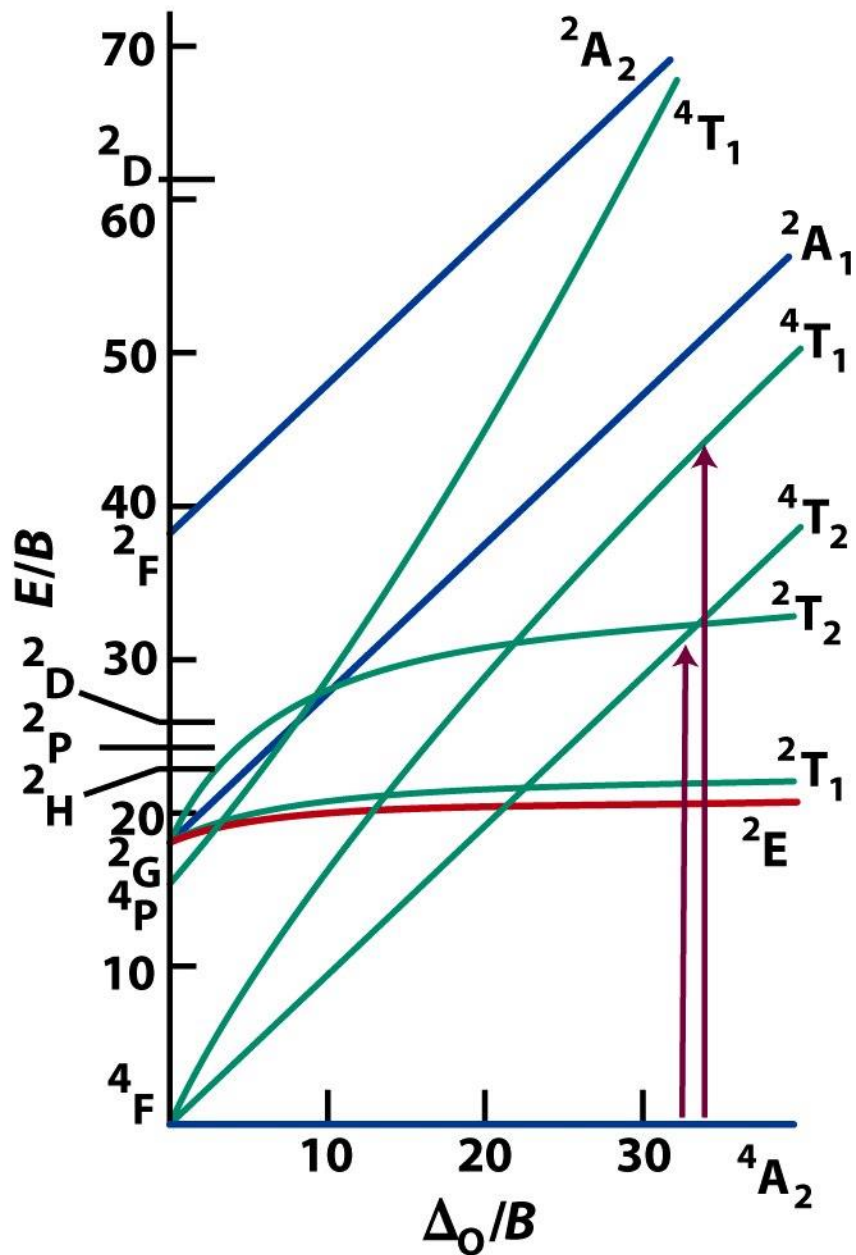


Figure 19-27

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# Analisi spettroscopica

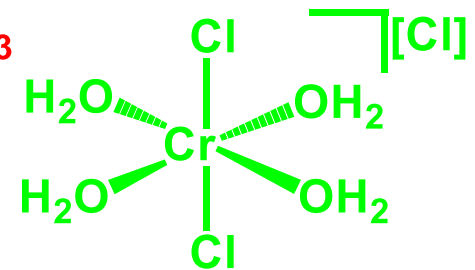
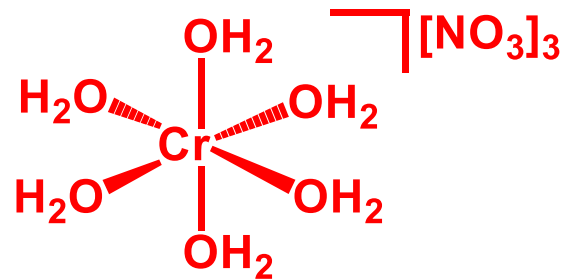
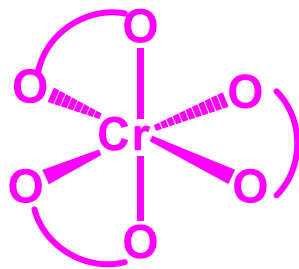
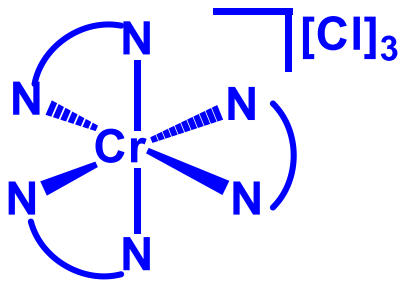
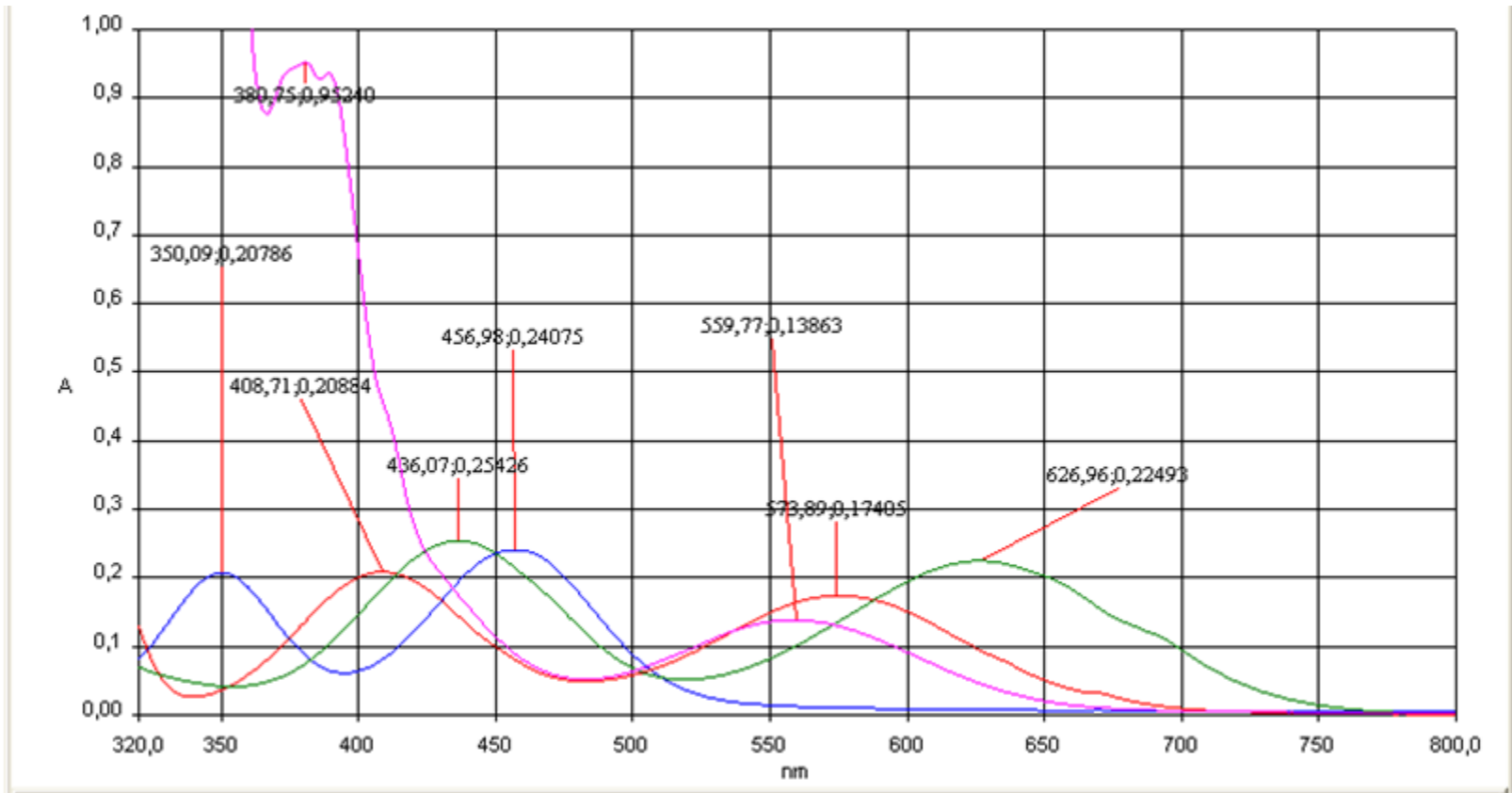
## Tabella 1

Complesso	MM (g/mol)	V <sub>sol</sub> (mL)	M (mol/L)
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## Tabella 2

Complesso	$\lambda_1$ (cm <sup>-1</sup> )	A <sub><math>\lambda_1</math></sub>	$\epsilon_{\lambda_1}$ (cm <sup>-1</sup> M <sup>-1</sup> )	$\lambda_2$ (cm <sup>-1</sup> )	A <sub><math>\lambda_2</math></sub>	$\epsilon_{\lambda_2}$ (cm <sup>-1</sup> M <sup>-1</sup> )
[Cr(H <sub>2</sub> O) <sub>6</sub> ][NO <sub>3</sub> ] <sub>3</sub>	17421.60	0.412	13.42	24509.80	0.496	16.16
[Cr(H <sub>2</sub> O) <sub>4</sub> Cl <sub>2</sub> ][Cl]	17182.13	0.414	13.57	24154.59	0.526	17.25
[Cr(acac) <sub>3</sub> ]	17937.22	0.133	66.50	26281.21	0.912	456.00
[Cr(en) <sub>3</sub> ][Cl] <sub>3</sub>	21881.84	0.407	52.93	28571.43	0.361	46.94

# Spettri UV-Visibile



$\text{Cl}^- < \text{H}_2\text{O} < \text{acac} < \text{en}$



## Analisi spettroscopica

**Tabella 3**

Complesso	$\Delta o$ (k J mol <sup>-1</sup> )	$\Delta o$ (cm <sup>-1</sup> )	$\Delta o$ (cm <sup>-1</sup> ) <sub>TS</sub>
[Cr(H <sub>2</sub> O) <sub>6</sub> ][NO <sub>3</sub> ] <sub>3</sub>	208.451	17421.60	
[Cr(H <sub>2</sub> O) <sub>4</sub> Cl <sub>2</sub> ][Cl]	205.586	17182.13	
[Cr(acac) <sub>3</sub> ]	214.621	17937.22	
[Cr(en) <sub>3</sub> ][Cl] <sub>3</sub>	261.818	21881.84	

