

Predicting Spectra: $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$

- Hexammine chromium(III) chloride was synthesised via the reaction of anhydrous CrCl_3 with liquid ammonia (activated by the addition of $\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$) to produce $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$. $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$ forms orange/yellow crystals on cooling. Yellow to orange wavelengths cover the range 565-625 nm.
- What is the ground state term symbol for $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$? How many transitions can be expected for the Cr ion? What are the possible transitions? Sketch a possible UV-vis spectrum. Would you expect all of the primary transitions to be visible in a UV-vis spectrum? What is the electronic configuration of each state for the stronger transitions? Use the transition dipole moment to show why the charge transfer excitation from the ligand t_{1u} level is allowed. Show that vibronic coupling allows the two lowest energy major transitions to gain intensity.
- What is the ground state term symbol for $[\text{Cr}(\text{NH}_3)_6]\text{Cl}_3$?
 - Cl are -1 each so the complex must be $[\text{Cr}(\text{NH}_3)_6]^{3+}$. Cr is in group 6, d^6 in zero oxidation state, ammonia ligands are neutral, and the +3 charge means removing 3e gives $(6-3)=3$ the Cr is d^3 . Oxidation state is Cr(III)
 - using the d^3 Tanabe-Sugano diagram, Error! Reference source not found., the ground state term symbol of the *free ion* is 4F and in the *strong ligand field* is $^4A_{2g}$
- How many transitions can be expected for the Cr ion?
 - we can associate transitions with specific electronic configurations, assuming spin conservation, the allowed excitations are to the $^4T_{2g}$, $^4T_{1g}$ and $^4T_{1g}(\text{P})$ levels
 - none of these levels cross so the order of the excitations will not change with the ligand field
 - using the the Tanabe-Sugano diagram we might also expect to see very weak spin-forbidden transitions to the 2E_g , $^2T_{1g}$, $^2T_{2g}$, $^2A_{1g}$ and $^2A_{2g}$ levels
 - Thus, we can expect to find 3 stronger transitions and up to 5 weaker transitions

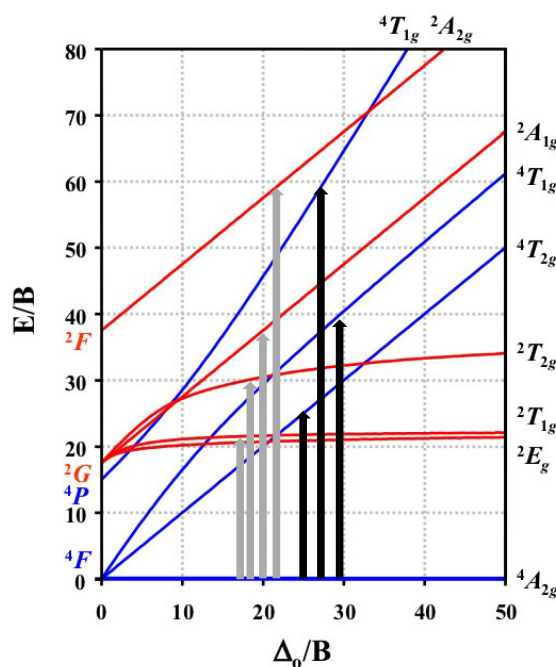


Figure 1 Tanabe-Sugano diagram for d^3 .

- Sketch a possible UV-vis spectrum.
 - $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is yellow/orange we are told the yellow to orange wavelengths cover the range 565-625 nm, therefore the absorbance must be in all other areas of the spectrum
 - in sketching a spectrum we are making an educated guess, it does not have to be exactly the same as the actual spectrum!
 - we can assume that NH_3 is a medium to high field ligand (guess) estimate a Δ_{oct}/B of perhaps ≈ 25 -30, this gives the rough spacing and ordering of peaks
 - we assume strong absorption in the blue-violet region due to the primary transitions ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$
 - the last transition ${}^4A_{2g} \rightarrow {}^4T_{1g}(\text{P})$ is very high in energy and likely in the uv-vis part of the spectrum
 - since the colour is yellow/orange we can assume the formally forbidden transitions ${}^4A_{2g} \rightarrow {}^2E_g, {}^2T_{1g}$, have a small intensity leading to absorption of red light
 - in-fact from the measured uv-vis spectra the primary absorptions occur at 460 and 350nm.

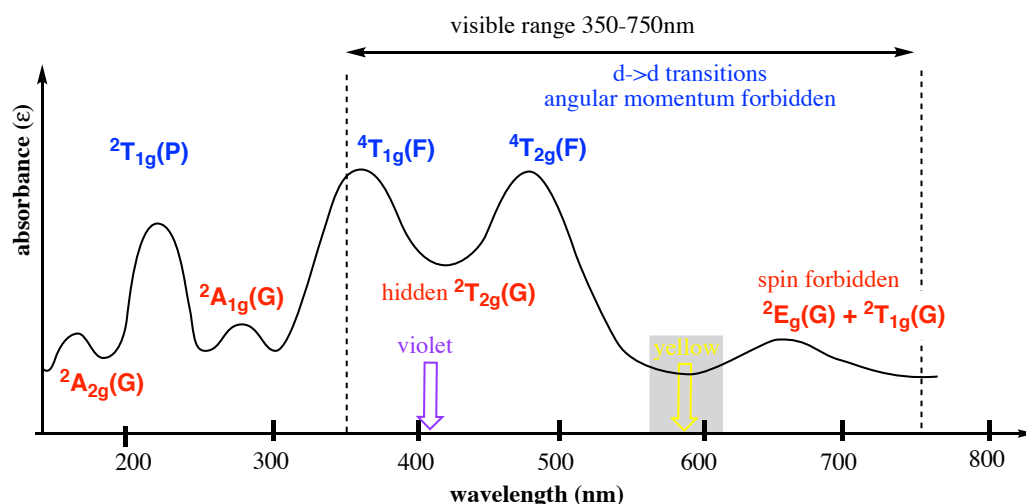


Figure 4 Sketch of the spectrum for $[\text{Cr}(\text{NH}_3)_6]^{3+}$

- Would you expect all of the primary to be visible in a UV-vis spectrum?
 - the last transition ${}^4A_{2g} \rightarrow {}^4T_{1g}(\text{P})$ is very high in energy and likely in the UV-vis part of the spectrum or perhaps hidden by higher energy transitions such as charge transfer
- What is the electronic configuration of each state for the stronger transitions?
 - the ground state is $(t_{2g})^3$, there 3 unpaired electrons, the complex is high spin $S=1/2+1/2+1/2=3/2$ and the multiplicity is 4
 - the term symbols for d^3 cannot be determined from the direct product, we must use information from **L7 Table 1** in the notes:
$$(t_{2g})^3 = {}^4A_{2g} + {}^2E_g + {}^2T_{1g} + {}^2T_{2g}$$
 - this result is consistent with the Tanabe-Sugano diagram, the ground state must be ${}^4A_{2g}$ as this is the only symbol with a multiplicity of 4

- excitations should go into the e_g level so options are (maintaining multiplicity) $(t_{2g})^2(e_g)^1$ and $(t_{2g})^1(e_g)^2$

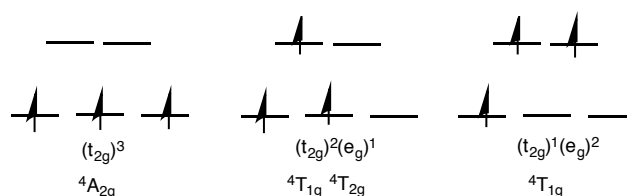


Figure 2 Possible distributions of electrons for d^3

- the transition to $(t_{2g})^0(e_g)^3$ would require a spin change and thus this transition is spin forbidden
- we could try to determine the state term symbols from taking the direct product of the occupied orbitals, however I've just taken information for the basic configurations (ie $(t_{2g})^2$ etc) from **L7 Table 1** in the notes

$$(t_{2g})^2(e_g)^1 = (A_{1g} + E_g + T_{1g} + T_{2g}) \otimes E_g = E_g + (A_{1g} + A_{2g} + E_g) + (T_{1g} + T_{2g}) + (T_{1g} + T_{2g})$$

$$(t_{2g})^1(e_g)^2 = T_{2g} \otimes (A_{1g} + A_{2g} + E_g) = T_{2g} + T_{1g} + (T_{1g} + T_{2g})$$

- it is clear the lowest energy states cannot be determined just from the direct product alone, however looking at the Orgel diagrams **L7 Figure 8** in the notes the excitations are:

$$(t_{2g})^2(e_g)^1 \Rightarrow {}^4T_{1g} + {}^4T_{2g}$$

$$(t_{2g})^1(e_g)^2 \Rightarrow {}^4T_{1g}$$

- thus the transitions to the ${}^4T_{2g}$ and ${}^4T_{1g}$ states are single excitations $(t_{2g})^2(e_g)^1$
- the transition to the ${}^4T_{2g}(P)$ state (the P is known from the Tanabe-Sugano diagram) is a double excitation $(t_{2g})^1(e_g)^2$ This information is consistent with the transition being much higher in energy in the Tanabe-Sugano diagram
- the spin forbidden transition without excitation into the e_g levels $(t_{2g})^3(e_g)^0$ generates a 2E_g state, now with two electrons paired.
- Use the transition dipole moment to show why the charge transfer excitation from the ligand t_{1u} level is allowed.
 - to a first approximation we consider NH_3 a sigma donor ligand, we use the standard octahedral energy diagram for ML_6 for L =sigma ligand shown below in Error! Reference source not found..
 - possible relevant transitions are shown as filled arrows, these include the metal based transitions in grey and a charge transfer transition shown in blue
 - note that the ligand based e_g level is not the originating CT level because this would be parity forbidden and thus would not give rise to an intense transition, the transition must be from the t_{1u} .

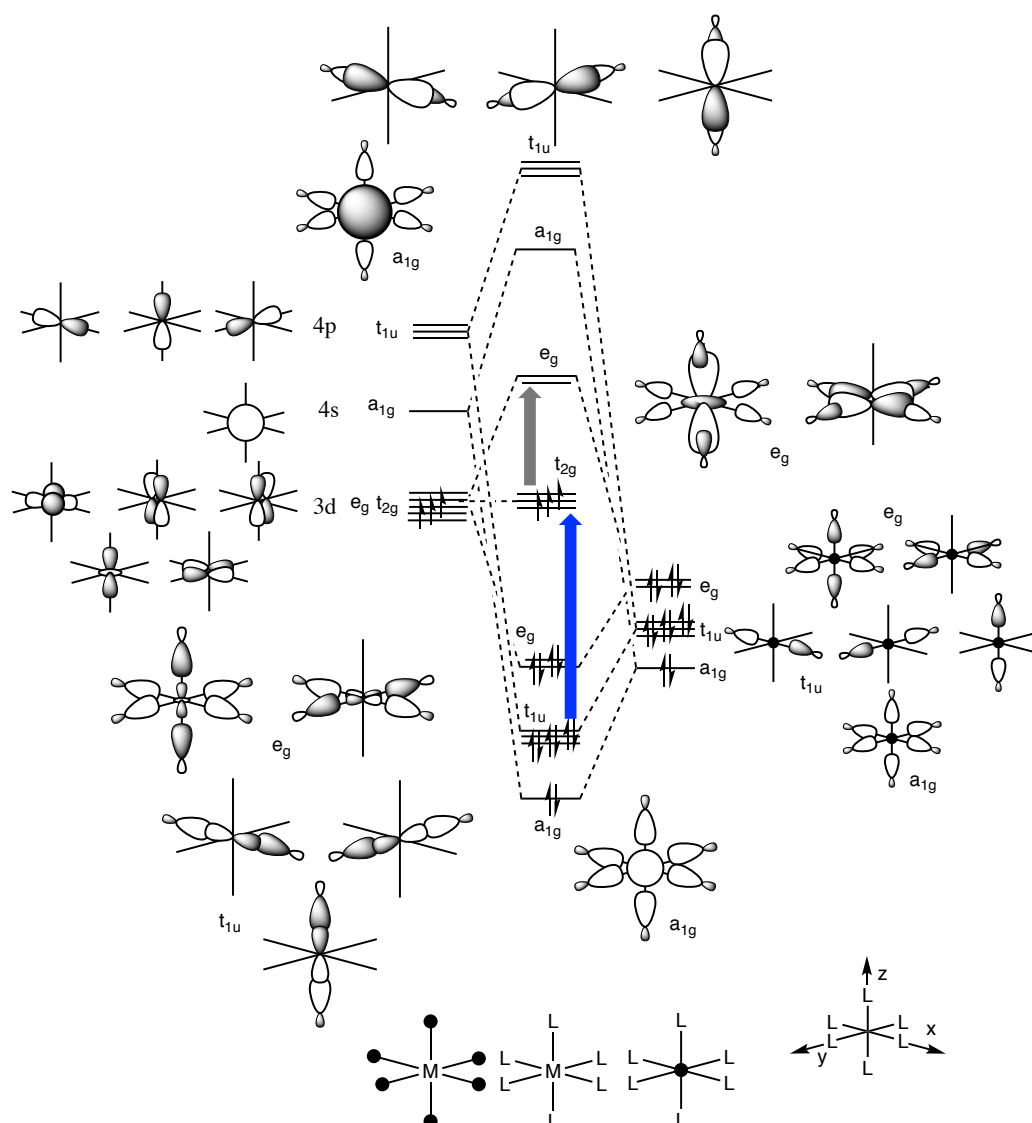


Figure 6 Energy diagram for ML_6 for $L=\text{sigma ligand}$: $[\text{Cr}(\text{NH}_3)_6]^{3+}$

- we need to evaluate the components of the transition dipole moment, for a transition to be allowed we know that there must be a totally symmetric component

$$\Gamma^A \in \{ \Gamma^{(f)} \otimes \Gamma^\mu \otimes \Gamma^{(i)} \}$$

- the initial state will be high-spin and from the d^3 Tanabe-Sugano diagram we know the ground state symmetry is ${}^4A_{2g}$
- the final state would take an electron from a ligand t_{1u} orbital and go into the a metal t_{2g} orbital, we are maintaining a multiplicity of 4 to be spin-allowed
- the final state symmetry is evaluated through the partially occupied levels t_{1u} and t_{2g} . All the other electrons will be spin paired and thus not change the symmetry of the final state.
- the t_{1u} level has a configuration $(t_{1u})^5$ and has one hole so the symmetry of this state must be T_{1u}
- the t_{2g} level has a configuration of $(t_{2g})^4$ and has 2 unpaired electrons $S=1/2+1/2=1$ and thus must have a multiplicity of $(2S+1)=2*1+1=3$. Using our notes from **L7 Table 1** tells us that the only symmetry with a multiplicity of 3 is T_{1g}

- thus the term symbol for the final electronic state is $T_{1u} \otimes T_{1g}$ and we use the multiplication tables provided to evaluate this as shown below

$$\Gamma^{(f)} = T_{1u} \otimes T_{1g} = A_{2u} + E_u + T_{1u} + T_{2u}$$

- the symmetry of the dipole moment is t_{1u} from the O_h character table
- the transition dipole moment is evaluated below, it is easiest to evaluate the last two terms first $T_{1u} \otimes A_{2g}$ from the multiplication tables provided (ie $T \otimes A = T$ and $1 \otimes 2 = 2$ and $u \otimes g = u$ giving T_{2u})
- we don't need to work out the rest of the expression! We have T_{2u} on both "sides" which means we will have an A_{1g} component, and so this integral will be non-zero and the transition will be allowed.

$$\begin{aligned}\Gamma^A &\in \left\{ \Gamma^{(f)} \otimes \Gamma^\mu \otimes \Gamma^{(i)} \right\} \\ &= (A_{2u} + E_u + T_{1u} + T_{2u}) \otimes T_{1u} \otimes A_{2g} \\ &= (A_{2u} + E_u + T_{1u} + T_{2u}) \otimes (T_{2u})\end{aligned}$$

- Show that vibronic coupling allows the two lowest energy major transitions to gain intensity.
 - the primary transitions are ${}^4A_{2g} \rightarrow {}^4T_{2g}$ and ${}^4A_{2g} \rightarrow {}^4T_{1g}$

$$\Gamma^A \in \left\{ \Gamma_{elec}^{(f)} \Gamma_{vib}^{(f)} \otimes \Gamma^\mu \otimes \Gamma_{elec}^{(i)} \Gamma_{vib}^{(i)} \right\}$$

$$\Gamma^A \in \left\{ \Gamma_{elec}^{(f)} \Gamma_{vib}^{(f)} \otimes \Gamma^\mu \otimes \Gamma_{elec}^{(i)} \Gamma_{vib}^{(i)} \right\}$$

$$\Gamma_{elec}^{(f)} = T_{2g} \text{ or } T_{1g} \text{ and } \Gamma_{vib}^{(f)} = (A_{1g}, E_g, T_{1u}, T_{2g}, T_{2u})$$

$$\Gamma^\mu = T_{1u} \text{ and } \Gamma_{elec}^{(i)} = A_{2g} \text{ and } \Gamma_{vib}^{(i)} = A_{1g}$$

$$\Gamma_{elec}^{(i)} \Gamma_{vib}^{(i)} = A_{2g} \otimes A_{1g} = A_{2g}$$

$$\Gamma_{elec}^{(f)} \otimes \Gamma^\mu = \{T_{2g}, T_{1g}\} \otimes T_{1u} = \{A_{2u} + E_u + T_{1u} + T_{2u}, A_{1u} + E_u + T_{1u} + T_{2u}\}$$

$$\begin{aligned}\left\{ \Gamma_{elec}^{(f)} \otimes \Gamma^\mu \otimes \Gamma_{elec}^{(i)} \Gamma_{vib}^{(i)} \right\} &= A_{2g} \otimes \{A_{2u} + E_u + T_{1u} + T_{2u}, A_{1u} + E_u + T_{1u} + T_{2u}\} \\ &= \{A_{1u} + E_u + T_{2u} + T_{1u}, A_{2u} + E_u + T_{2u} + T_{1u}\}\end{aligned}$$

$$\Gamma_{vib}^{(f)} = A_{1g} + E_g + 2T_{1u} + T_{2g} + T_{2u}$$

$$A_{1g} \in \left\{ A_{1g}, E_g, \boxed{2T_{1u}}, T_{2g}, \boxed{T_{2u}} \right\} \otimes \left\{ A_{1u}, A_{2u}, E_u, \boxed{T_{1u}}, \boxed{T_{2u}} \right\}$$

- thus since both sides contain the same IR, vibronic coupling will allow these transitions