1. **Solutions of $[Cr(H_2O)_6]^{3+}$ ions are pale green but the chromate ion $[CrO_4]^{2-}$ is an intense yellow. Characterize the origins of the transitions and explain their relative intensities.**

   $[Cr(H_2O)_6]^{3+}$ contains octahedrally coordinated Cr^{3+} (d^3). This ion shows three spin-allowed 'd-d' transitions. The energies of these bands, and hence the colour, depend on both Δ_{oct} and B. These ligand-field transitions are formally orbitally forbidden (as $\Delta l = 0$). Due to the octahedral symmetry, d-p mixing is not possible (Laporte's rule) and can only occur during vibrations which remove the centre of inversion. This gives rise to only small degrees of d-p mixing and so the intensity of the transitions is fairly low and the colour is pale.

   The chromate ion contains Cr^{6+}. This ion is highly oxidizing due to its high charge and this causes the oxygen to metal charge transfer transitions to occur in the visible region of the spectrum and give rise to the colour. In the $[Cr(H_2O)_6]^{3+}$ ion, the lower +3 charge on the metal means that the charge transfer bands occur in the ultraviolet and do not affect the colour. The charge transfer transitions involve excitation of an electron from an oxygen-based p-orbital (or lone pair orbital) into an empty metal d-orbital. They are fully orbitally allowed and hence the bands are intense and the colour is deep.

   (Note that Cr^{6+} is d^0 so there are no ligand-field transitions possible. However, the presence of the charge transfer bands in the visible region is due to the high charge on the metal rather than the absence of 'd-d' bands.)

2. **Common glass used for windows and many bottles is green because of Fe^{2+}. It is decolourized by addition of MnO_2 to form Fe^{3+} and Mn^{2+}. Why is the glass decolourized?**

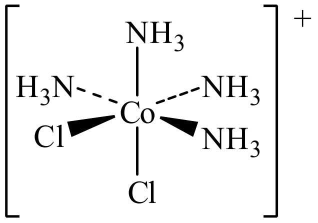
   Fe^{2+} is a d^6 ion can shows one spin-allowed transition in both octahedral and tetrahedral environments. Ligand-field transitions are formally orbitally forbidden (as $\Delta l = 0$). In tetrahedral environments, d-p mixing can occur via covalency with the ligands. This allows the transitions to occur but due to the small amount of covalency, the transitions have relatively low intensity. In octahedral environments, d-p mixing is not possible (Laporte's rule) and can only occur during vibrations which remove the centre of inversion. This gives rise to only small degrees of d-p mixing and so the intensity of the transitions is lower than in tetrahedral systems. In octahedral and tetrahedral environments, the single transition occurs at Δ_{oct} and Δ_{tet} respectively giving rise to the colour of the compound.

   However, both Fe^{3+} and Mn^{2+} are d^5 ions and exhibit no spin-allowed transitions in either octahedral or tetrahedral environments. Transitions only occur via weak spin-orbit coupling leading to very low intensity bands and very pale colours. Glass containing these ions is thus almost colourless.

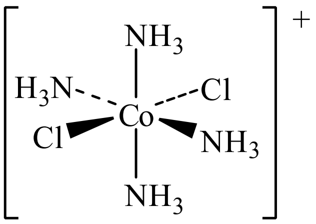
3. **$[Co(NH_3)_4Cl_2]^+$ exists in two isomeric forms.**

(i) **Draw the structures of these isomers**

Cis and *trans* geometrical isomers are possible:



cis



trans

(ii) **Predict which isomer will give rise to the more intense ‘d-d’ bands**

Both contain Co^{3+}. Ligand-field transitions are formally orbitally forbidden (as $\Delta l = 0$). In complexes, such as the *cis* isomer, without a centre of inversion d-p mixing can occur via covalency with the ligands. This allows the transitions to occur but due to the small amount of covalency, the transitions have relatively low intensity. In complexes, such as the *trans* isomer, with a centre of inversion, d-p mixing is not possible (Laporte’s rule) and can only occur during vibrations which remove the centre of inversion. This gives rise to only small degrees of d-p mixing and so the intensity of the transitions is lower.

The *cis* isomer gives rise to the more intense ‘d-d’ bands.