❖ Structural Evidence from Electronic Spectrum

The electronic spectrum of transition metal complexes in the near-infrared, visible and ultraviolet region is quite useful in providing the information regarding their structural prototypes. The number of bands, their positions and molar absorptivity values must be considered for any conclusive remarks. Moreover, the spectra in the solution phase should also be checked against the solid-state spectral profile to be sure that no structural alteration has been taken place. These alterations could result in ligand displacement by solvent, ligand rearrangement, or an increase in the coordination number due to solvation. Very reliable information about the ligand environment in transition metal complexes can be found from their electronic spectrum. Some of the main sources of structural information from the UV-visible spectrum of transition metal complexes are given below.

➢ *Molar Absorptivity of assigned Bands*

The intensities of electronic transitions depend upon the wavefunctions of the ground and excited states; and provide important information about the electronic structure. Ligand field transitions that are forbidden in octahedral complexes may partly be allowed in tetrahedral complexes due to significant *d-p* mixing. The intensity of spin-allowed, as well as spin-forbidden d-d transitions in tetrahedral complexes, is 10-100 times more than in octahedral complexes. However, the values of molar extinction coefficients for *d-d* transitions in tetrahedral complexes are still lower than what we observe for charge transfer bands. This is because of the fact that the intensities in the former largely depend upon the ligand contribution to e and t_2 orbital sets, which is approximately 30% in magnitude. On the other hand, charge transfer transitions occur from an orbital which is largely p to an orbital with large d-character. The values for molar extinction coefficients for different types of transitions are given below.

Table 9. The order of magnitude for the molar extinction coefficient for different types of transitions.

Type	Extinction coefficient
d-d spin forbidden, Laporte forbidden (O_h)	0.1
d-d spin forbidden, Laporte allowed (T_d)	1
d-d spin allowed, Laporte forbidden (O_h)	10
d-d spin allowed, Laporte allowed (T_d)	100
Charge transfer, spin allowed and Laporte allowed	1000

Therefore, as the asymmetry around metal center increases, the intensity of various bands is also enhanced and a superficial shortlisting between tetrahedral and octahedral coordination can be done just on the basis of intensity and number of bands observed. It should also be noted that many complexes that ideally belong to a non-centrosymmetric point group usually have only a small asymmetric contribution to the crystal

field. On the basis of the magnitude of this asymmetric contribution, the intensity lies between that of a truly centrosymmetric and a complex with a highly asymmetric crystal field, such as a square-pyramidal or distorted tetrahedral complex. If geometric distortion is so small that it is in the range of vibrational amplitudes, the intensities of the spectral band would not be much greater than those in typical centrosymmetric compounds. For example, peak intensities in tris-chelate complexes of ethylenediammine are not much more intense than their hexa-ammine counterparts. When asymmetry is the result of a difference in the ligand type on either side of the metal, the deviation depends on how different the ligands actually are. The bands in the spectrum of a complex such as the cis-Co[(NH$_3$)$_4$Cl$_2$]$^+$ ion are two to three times as intense as those in the corresponding trans complex; and Thus, the two isomers can be distinguished on the basis of intensity only. Tetrahedral complexes can easily be distinguished from hexa-coordinated counterparts on the basis of the intensity of the bands. The complex Ni{OP[N(CH$_3$)$_2$]$_3$}$_4$Cl$_2$ could have tetrahedral or distorted octahedral geometries but the similarity of its electronic spectrum to that of [NiCl$_4$]$^{2-}$ implied that this was the first cationic, tetrahedral nickel(II) complex ever synthesized. Further confirmation of the structure comes from the similarity of its x-ray powder diffraction patterns with tetrahedral zinc(II) complexes.

Consistent structural information can be obtained from the electronic spectra of Co(II) complexes. Hexa-coordinated complexes of Co(II) are usually high-spin and the Orgel diagram for d^7-configuration should be used to assign different peaks. The ground state is $^4T_{1g}$ and a considerable magnitude of spin-orbit coupling is expected in $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions. Being a two-electron transition $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, its intensity is pretty low and hardly observed. The electronic spectrum of octahedral [Co(H$_2$O)$_6$]$^{2+}$ and tetrahedral [CoCl$_4$]$^{2-}$ are shown in the following figure.
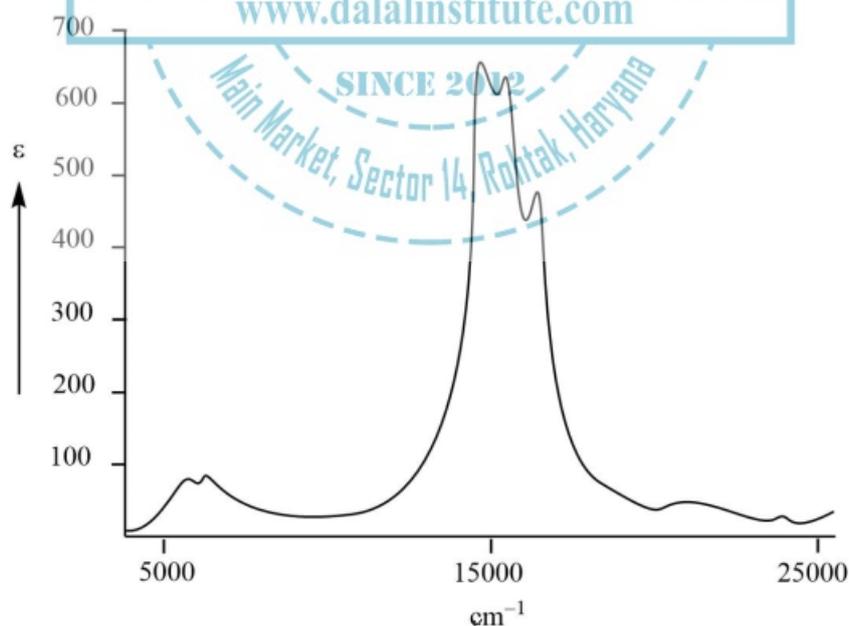
Figure 53. Electronic spectrum of tetrahedral [CoCl$_4$]$^{2-}$.
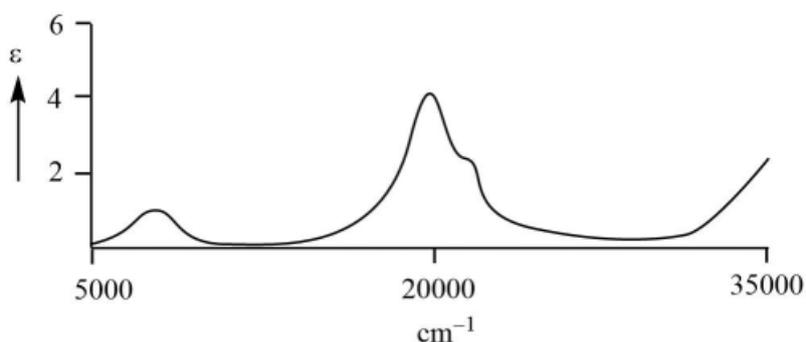
Figure 54. Electronic spectrum of octahedral $[Co(H_2O)_6]^{2+}$.

Tanabe and Sugano diagram for d^7-configuration has to be used to explain the electronic spectrum of tetrahedral complexes of Co(II) which are always high-spin in nature. The absorption at 15000 cm^{-1} may be attributed to $^4A_2(F) \rightarrow {}^4T_1(P)$ and fine structure can be explained in terms of to spin-orbital coupling of the T electronic state. The presence of spin-orbital interaction also permits some quartet → doublet transitions to happen. The other peak shown is assigned to $^4A_2(F) \rightarrow {}^4T_1(F)$ transition while the expected $^4A_2(F) \rightarrow {}^4T_2(F)$ transition is predicted to result in a peak at 3000-4500 cm^{-1}. However, most of the UV-visible spectrophotometers cannot record them as they are out of detectable range and usually overlap with the infrared bands of attached ligands. On the other hand, the main peak in the UV-visible spectrum of $[Co(H_2O)_6]^{2+}$ is at about 20000 cm^{-1} and is allocated to the $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transition. The shoulder owes to the lifting of degeneracy due to spin-orbital coupling in the excited $^4T_{1g}(P)$ state. The second band at 8350 cm^{-1} is ascribed to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ transition.

➤ *Splitting Pattern of Assigned Bands*

The splitting pattern of absorption peaks provides useful information not only on the symmetry but also on the relative σ and π bonding nature of the attached ligands. The effects of decreased ligand-field symmetry in a mixed ligand metal complex can easily be explained by the analysis of UV-visible spectra of the $[Co(en)_3]^{3+}$, cis-$[Co(en)_2F_2]^{1+}$ and trans-$[Co(en)_2F_2]^{1+}$. Although the complex $[Co(en)_3]^{3+}$ belongs to D$_3$ point group symmetry, its ligand field pretty close to O$_h$ symmetry. Therefore, the Tanabe-Sugano diagram for d^6-configuration should be used to interpret the electronic spectrum which is comprised of two symmetric bands due to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively. The spectrum of cis-$[Co(en)_2F_2]^{1+}$ is somewhat similar to what is observed for $[Co(en)_3]^{3+}$; however, both bands are broader and slightly shifted to lower energy value. In case of trans-$[Co(en)_2F_2]^{1+}$, the lower energy band is obviously split into two components; and the peak intensities are slightly lesser than those of cis-$[Co(en)_2F_2]^{1+}$ and $[Co(en)_3]^{3+}$ which obviously comply with the fact that the former complex does possess a center of symmetry so that the electronic transitions are formally Laporte forbidden.
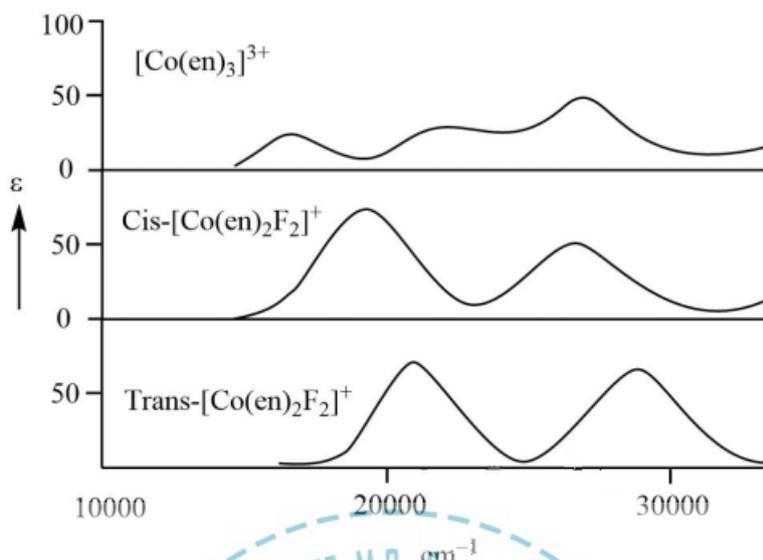
Figure 55. Electronic spectrum of trans-$[Co(en)_2F_2]^{1+}$, cis-$[Co(en)_2F_2]^{1+}$ and $[Co(en)_3]^{3+}$ in aqueous solution.

The main cause of the splitting of bands in trans-$[Co(en)_2F_2]^{1+}$ is the loss of degeneracy of excited states due to the lowering of ligand-field symmetry; which can be explained in terms of the effect of an increasing tetragonal component of the ligand field on the $^1T_{1g}$ and $^1T_{2g}$ states. The whole schematic is shown in the energy level diagram given below. The two lower energy peaks of trans-$[Co(en)_2F_2]^{1+}$ may be ascribed to the $^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1A_{2g}$ transitions, respectively. It is worthy to note that both excited states in the tetragonal field, ^1E_g and $^1A_{2g}$, are the components of $^1T_{1g}$ state of O_h-symmetry. Moreover, as the splitting of $^1T_{2g}$ state is quite insignificant, the two corresponding transitions ($^1A_{1g} \rightarrow {}^1E_g$ and $^1A_{1g} \rightarrow {}^1B_{2g}$) are not resolved even in the trans complex.

Now, the angular overlap method states that it is the "holohedrized" symmetry that governs the energy levels in a complex; or in other words, d-orbital energies depend on the sum of the effects of the ligands along each axis. Therefore, the magnitude of the tetragonal component in the ligand field of the trans-complex is twice that what is active in the cis counterpart. This gives rise to much more overlapping transitions in the spectrum of cis-$[Co(en)_2F_2]^{1+}$ and no clear splitting of the bands can be resolved. Even though it is not evident in the solution spectra, the sign of ligand field splitting in cis-isomer is different than the trans-isomers. The energy level diagram given in this section is actually for the situation in which the in-plane ligand field is stronger than the axial field, just like in the case of trans-$[Co(en)_2F_2]^{1+}$ complex. The degree of the splitting is correlated to the difference in σ and π-bonding ability of the in-plane and axial ligands. Thus, the peak splitting profile for mixed-ligand complexes offers a powerful means of obtaining metal-ligand bonding parameters.
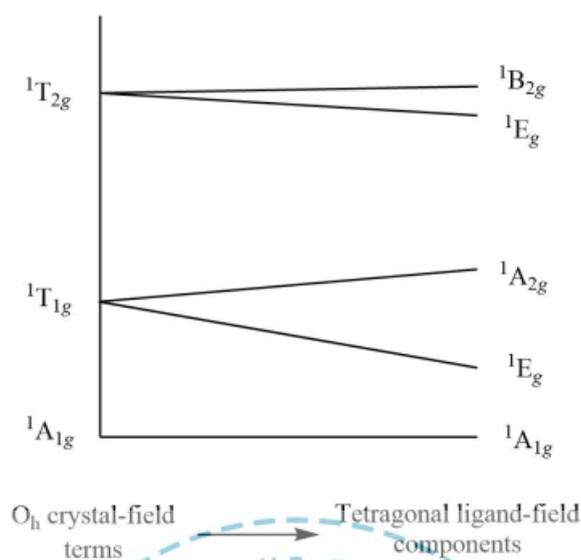
Figure 56. The splitting pattern of $^1T_{1g}$ and $^1T_{2g}$ terms of octahedral Co^{3+} complex in increasing the tetragonal ligand field.

In order to analyze the system in a precise manner, the assignment of different bands must be done properly; and if possible, this is best achieved by recording single-crystal polarized spectra. The average position of the split components of the $^1T_{1g}$ is approximately 18000 cm^{-1} and of $^1T_{2g}$ is 26000 cm^{-1} for trans-$[Co(en)_2F_2]^{1+}$. These values of band positions are rather similar to those of cis-$[Co(en)_2F_2]^{1+}$ and give a ligand field splitting 21000 cm^{-1}.

This result is also supported by "the rule of average environment" which states that the magnitude of ligand field splitting in a mixed-ligand complex is around the weighted average of the octahedral ligand fields associated with a complete set of each ligand. For example, the value of crystal field splitting in MA_nB_{6-n} complex can be given as:

$$\Delta = \frac{[n\Delta(MA_6) + (6-n)\Delta(MB_6)]}{6}$$

Putting the values of crystal field splitting values of $[Co(en)_3]^{3+}$ and $[CoF_6]^{3-}$ in the above equation, we get the expected magnitude of Δ for $[Co(en)_2F_2]^{1+}$.

$$\Delta = \frac{[4(23000) + 2(13000)]}{6} = 19667 \text{ cm}^{-1}$$

Which is pretty close to the experimentally observed value of 21000 cm^{-1} and therefore confirms the practical applications in structure determination.

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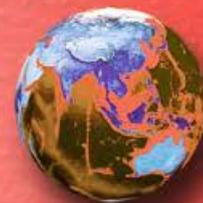
A TEXTBOOK OF INORGANIC CHEMISTRY

Volume I

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