Learning outcomes

After studying this module, you shall be able to

- Know what are charge transfer transitions
- Learn about the origin of charge transfer transitions
- Identify the difference between LMCT and MLCT transitions
- Analyze the complexes that show charge transfer spectrum

What are charge transfer bands?

In case of transition metal complexes with octahedral geometry the most important type of electronic transition taking place is the d-dtransition where **transition of an electron takes place** from the lowert_{2g} level is the upper e_g level. Mostly it is this transition which imparts the color to the complex since it occurs in the visible or ultraviolet part of the spectrum. But the value of molar extinction coefficient, ε for these transitions, the value of molar extinction coefficient, ε for d-d transitions, the value of molar extinction coefficient, ε ranges from 0.5 to 20 Lmol - 1 cm - 1. But there are cases where the absorption bands in the visible or ultraviolet regions ranges between molar extinction coefficient (ε) value of 1000 to 55,000 Lmol - 1 cm - 1. For these cases such high value of absorption have been suggested due to charge transfer bands which are so much intense since they are allowed transitions that impart exceptionally deep colors to the respective transition metal complex. Charge transfer transitions but they impart color if the transitions fall in the visible region of the spectrum.

Examples include KMnO₄, K_2CrO_4 , [Fe(bipy)₃]2+, $Cr(CO)_6$, [Ir(Br)₆]2-, [Ni(CI)₄]2-, etc. In charge transfer transition either electrons are donated from the low-lying orbitals of the ligand to the metal or from orbitals of the metal to the ligand. Both of these transitions are feasible and in some of the complexes both can co-exist.

Charge transfer Spectrum

What is Charge Transfer?

The color of complexes can be explained on the basis of the concept of d-d transition or on the basis of concept of charge transfer. Here, we shall discuss charge transfer concept only.

There are many complexes in which either the metal ion is highly oxidizing & the ligand is highly reducing or the metal ion is highly reducing & the ligand is highly oxidizing. In such complexes there occurs transfer of charge(electron) from the

reducing partner to the oxidizing partner, i.e.; the transfer of electron may occur either from the metal ion to the ligand or from the ligand to the metal ion.

Thus, charge transfer involves redox process. High intensity bands with $E_{max} > 10^4$ & occurring in the near UV region are charge transfer bands. These bands are Laporte allowed. If $E_{max} = 10^4$, this bands are also spin allowed.

Charge transfer bands may be observed in the visible region, if the metal is easily oxidizable and the ligand is readily reduceable. Complexes showing charge transfer appear colored to our eyes only when the charge transfer transitions of complexes occur in the visible region.

Charge transfer transitions may appear in metal complexes having metal with d0, incomplete d – orbitals and d10 configuration. For example, $VO_2^{+i-pale \, yellow[V^{+5}=3d^0],i}$ $CrO_4^{2-i-yellow[Cr^{+6}=3d^0],i}$ $MnO_4^{-i[i \, solution]-intense \, purple[Mn^{+7}=3d^0]i}, MnO_4^{-i[i \, solid]-almost \, black[Mn^{+7}=3d^0],i}$ [Fe(dipy)₃]²⁺ - dark red (Fe⁺² = 3d⁶), $HgI^{2-i-brickred\,ii}$

Greater is the oxidizing power of the metal ion and reducing power of the ligand, lower is the energy and hence the frequency at which the charge transfer bands appear.

Origin of the spectrum

These types of transitions are very intense in nature as compared to the other transitions such as d- d transitions. The reason for **their intensity is the fact that they are fully allowed transitions** which have very high value of molar extinction coefficient (ε). The following table shows the difference in the value of ε for the various transitions possible. From the table it can be seen that charge transfer bands are quite profound as compared to d-d transitions with large ε values.

Types of transition	Typical ε_{max} $(dm^3 mol^{-1} cm^{-1})$	Example
Spin forbidden 'd – d'	<1	[Mn(H₂O)₅]²⁺ (high spin d⁵)
Laporte – forbidden, spin allowed 'd – d'	1 – 100 1 – 1000	Centrosymmetric complexes, e. g. [Ti(OH₂)₅]³+ (d¹) Non – Centrosymmetric complexes, e. g. [NiCl₄]²-
Charge transfer (fully allowed)	1000 – 50000	[MnO₄] [.]

Types of charge transfer spectra

The charge transfer transitions can be of two types namely ligand to metal charge transfer (LMCT) and metal i ligand charge transfer (MLCT). In the case of *LMCT transitions*, their origin lies in the transfer of the electrons from the low-lying molecular orbital that are principally ligand in disposition to the orbitals that are chiefly metal in nature. Other way round in case of *MLCT transitions* the transfer of electrons occurs from the molecular orbitals that are mainly on the metal to the empty π^{i} orbitals of the ligand which are comparatively higher in energy as compared to the metal orbitals. The comparative relationship between the two has been shown in the figure below (figure 2)

Figure 2: Origin of charge transfer bands



MLCT = Transfer of electrons from the $e_g \wedge t_{2g}$ ligand set to low – lying π^i orbitals on the ligands.

LMCT = Transfer of electrons from filled ligand-based orbitals to the $e_g \wedge t_{2g}$ Sets.

There are chiefly three types of charge transfer spectrum

- a) Ligand to metal chare transfer spectrum (LMCT)
- b) Metal to ligand charge transfer spectrum (MLCT)
- c) Metal to metal charge transfer spectrum (MMCT)

Ligand to metal charge transfer spectrum (LMCT)

In these types of transitions, the transfer of electron occurs from the orbitals that are ligand based to the orbitals that are metal based. An example of these type of complexes include [Cr(NH3)6]3+, [Cr(CI)(NH3)5]2+. The LMCT charge transfer spectrum has been shown in figure 3.



Figure 3. Example of coordination complex showing LMCT charge transfer bands

Mostly in these cases the ligands are $good \sigma \lor \pi donors$. Generally, the transitions lead to metal reduction takes place. Thus, metal which is easily reduced combines

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with the ligand that is easily oxidized giving rise to a transition low in energy. Therefore, anions that are easily oxidized like I^{-ii} often form complexes where charge transfer absorption in the visible region is guite appreciable. The examples include TiI_4 which is bright violet, HgI_2 red and AgI that is vivid yellow in color. The trend in frequency of absorption of a series of similar complexes can be explained in terms of the ease of oxidation of the ligand. For example, $TiCl_6^{2-ii}$ has a higher absorption frequency in comparison to $TiBr_6^{2-ii}$ because Br^{-ii} ligand is readily oxidized as compared to Cl^{-ii} . Similar trends are observed when the metal cation is strongly oxidizing, where the frequency of absorption follows the oxidizing strength of the metal ion. This has been shown in the following figure 4, which shows that 3dmetal ions are comparatively more readily reduced as compared to their respective analogous 4d and 5d metal ions. Because of this the charge transfer bands of 3dmetal ions will be of larger intensity as compared to that of 4d and 5d metal ions present in the series. Also, more is the oxidation state of the metal ion, more is the tendency of the metal ion to get reduced and hence large is the intensity of absorption of the respective charge transfer band.

Comparison of $3d$, metal ions shows the comparatively easy	4 <i>d</i> and5 <i>d</i> pat 3 ga re to be reduce	ed	4d		5d	Ţ
as compared to 4 d	^5MnO₄⁻	<	TcO₄ ⁻	<	ReO₄⁻	• M ⁷⁺
	٨		٨		٨	
	CrO ₄ ²⁻	<	MoO 4 ²⁻	<	WO 4 ²⁻	M ⁶⁺
	۸		٨		۸	
	VO 4 ³⁻	<	NbO ₄ ³⁻	<	TaO₄³-	M ⁵⁺

Figure 4. Sequence of metal ions showing ease of reduction

Consider a complex with π donor ligands. The origin of the LMCT transitions is shown in the figure 5 drawn below. In this case the prospect of excitement of the electrons from the low lying π orbitals of the ligands to the t2g or eg orbitals of the metal takes place giving rise to the charge transfer bands.



Figure 5. Origin of LMCT charge transfer bands

Metal to Ligand Charge Transfer spectrum (MLCT)

In these types of transitions basically the metal orbitals are involved that can easily supply their electrons present in the low-lying molecular orbital to the empty π^* orbitals of the ligand. Example of complexes showing these type of transitions are [Fe(CO)₃(bipy)], [Ru(bipy)₃]2+, [W(CO)₄(phen)] etc. in all these cases the π^* empty orbital present on the ligand becomes the receptor of electrons with the introduction of light and the absorption process. The absorption spectrum of the [Ru(bipy)₃]2+ complex possessing the MLCT transitions is shown in the figure 6.



Figure 6. Example of [Ru(bipy)₃]2+ complex showing MLCT charge transfer bands

In the process of charge relocation the metal is oxidized and the ligand is reduced, therefore for this type of charge transfer phenomenon, it is important that the metal oxidation as well as ligand reduction is quite feasible. Easily reducible ligands are those which have a low lying, vacant π^* orbital, such as pyridine, which then forms sturdy colored complexes with the metal ions that are easily oxidized such as Fe²⁺ and Cu⁺. Depending on the number of electrons in the d orbital of the metal ion, two different transitions are possible; the t2g to π^* and eg to π^* which both may be observed depending on the conditions. An illustration of the phenomenon is given below (figure 7) which shows the transfer of electrons from the molecular orbital primarily present on metal to the unoccupied π^* orbital of the ligand.



Origin of MLCT charge transfer bands

Figure 7. Origin of MLCT charge transfer bands

3.1.1 Metal to metal charge transfer spectrum (MMCT)

Metal to Ligand Charge Transfer spectrum (MLCT)

Some compounds possess metal ions in two different oxidation states. In these compounds, a charge transfer transition may occur when the electron moves from one metal ion to the other, with one metal ion acting as the reducing agent and the other acting as the oxidizing agent. Compounds of this nature are generally very intensely coloured, such as Prussian Blue, KFeIII[FeII(CN)6].

Effect of solvent on charge transfer spectrum

A charge transfer band depicts the transition energy of the transition occurring and depends on the solvating capability of the solvent. In a solvent with high polarity, the shift in the wavelength occurs to the lower value or higher frequency. Polar solvent molecules align their dipole moments maximally or perpendicularly with the ground state or excited state dipoles. If the ground state or excited state is polar an interaction will occur that will lower the energy of the ground state or excited state

by solvation but if the ground state and the excited state are neutral a shift in wavelength is not observed since now polar solvent won't be able to align its dipole with a neutral ground and excited state. Three cases arise when either ground state or excited state or both are polar (figure 8).

- a) If the excited state is polar, but the ground state is neutral the solvent will only interact with the excited state. This allows alignment of the dipole with the excited state and thus decrease in the energy by solvation will occur. This will shift the wavelength to higher energy and lower frequency.
- b) If the ground state is polar but excited state is neutral, the polar solvent will align its dipole moment with the ground state. Highest interaction will take place and hence energy of the ground state will be reduced. If the excited state is neutral no change in energy will occur. Since like dissolves like the polar solvent won't be able to align its dipole with a neutral excited state. Overall increase in energy will take place, because the ground state is lower in energy.
- c) If the ground state as well as excited state both are polar, the polar solvent will align its dipole moment with the ground state. Maximum interaction will occur and the energy of the ground state will be lowered. The dipole moment of the excited state would be perpendicular to the dipole moment of the ground state, since the polar solvent dipole moment is aligned with the ground state. This interaction will raise the energy of the polar excited state.





Figure 8. Effect of solvent polarity on charge transfer bands

Summary

- i. d-d transitions impart the color to the complex since it occurs in the visible or ultraviolet part of the spectrum. But the value of molar extinction coefficient, ϵ for these transitions is quite low since, these are Laporte forbidden transitions.
- ii. There are cases where the absorption bands in the visible or ultraviolet regions ranges between ε value of 1000 to 55,000 Lmol⁻¹cm⁻¹. For these cases such high value of absorption have been suggested due to charge transfer bands which are so much intense since they are allowed transitions that impart exceptionally deep colors to the respective transition metal complex.
- iii. Charge transfer transitions are generally much higher in energy as compared to the normal crystal field transitions but they impart color

if the transitions fall in the visible region of the spectrum (figure 1) Examples include $KMnO_4$, K_2CrO_4 , $[Fe(bipy)_3]2+$, $Cr(CO)_6$, $[Ir(Br)_6]2-$, $[Ni(Cl)_4]2-$, etc.

- iv. The charge transfer transitions can be of two types namely ligand to metal charge transfer (LMCT) and metal to ligand charge transfer (MLCT).
- v. In case of LMCT transitions, their origin lies in the transfer of the electrons from the low lying molecular orbital that are principally ligand in disposition to the orbitals that are chiefly metal in nature.
- vi. Other way round in case of MLCT transitions the transfer of electrons occur from the molecular orbitals that are mainly on the metal to the empty π^* orbitals of the ligand which are comparatively higher in energy as compared to the metal orbitals.
- vii. A charge transfer band depicts the transition energy of the transition occurring and depends on the solvating capability of the solvent.
- viii. In a solvent with high polarity, the shift in the wavelength occurs to the lower value or higher frequency. Polar solvent molecules align their dipole moments maximally or perpendicularly with the ground state or excited state dipoles.
- ix. If the ground state or excited state is polar an interaction will occur that will lower the energy of the ground state or excited state by solvation but if the ground state and the excited state are neutral a shift in wavelength is not observed since now polar solvent won't be able to align its dipole with a neutral ground and excited state.