CHAPTER-7

CHARGE TRANSFER SPECTRA

Charge Transfer Spectra

An electronic transition between orbitals that are centred on different atoms is called charge transfer transition and absorption band is usually very strong. These transitions involve electron transfer from one part of a complex to another. More specifically, an electron moves from an orbital that is mainly ligand in charcter to one that is mainly metal in character (ligand-to-metal charger transfer, LMCT) or vice versa (metal-to-ligand charger transfer, MLCT). Unlike *d-d* transitions, those involving charge transfer are fully allowed and hence give rise to much more intense absorptions. When these absorptions fall within the visible region, they often produce rich colors. In these electronic transitions, the electronic transitions are laporte and spin allowed, i.e., $\Delta l = \pm 1$ and $\Delta S = 0$

A charge transfer transition may be regarded as an internal redox process.

Types of Charge Transfer Spectra

(1) Ligand to Metal Charge Transfer (LMCT)
(2) Metal to Ligand Charge Transfer (MLCT)
(3) Intermetal Charge Transfer or Metal to Metal Charge Transfer
(4) Interligand Charge Transfer

(1) Ligand to Metal Charge Transfer (LMCT)

If the migration of electron is from ligand to the metal, then the cahrge transer is called ligand to metal charge transfer (LMCT). To make the electron transfer from ligand to metal more favorable, we require a metal with a relatively high ionization energy so that it would have empty orbitals at fairly low energies. The metals would be transition or posttransitions metals, or metals of main group with low ionisation energy, especially in higher oxidation states. An ideal ligand would be a nonmetal with a relatively low electron affinity, which would mean that it would have filled orbitals of fairly high energy and would be readily oxidizable. Chalcogenides or heavier halides or oxygen sulphur would be examples of good choices. The net result of such a metal-ligand combination would be that the orbitals involved in an LMCT process would be close enough in energy that the transition could be induced by a photon in the visible or near-ultrviolet region.

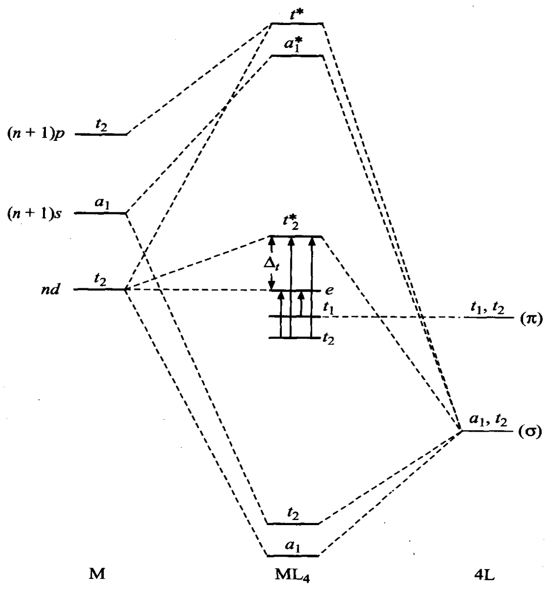


Figure (1)

The permanganate ion, MnO_4^-, Manganese is in a formal oxidation state of + 7 and combined with four oxide ions. The molecular orbital diagram for tetrahedral complexes in figure (1) allows us to identify possible LMCT transitions. In any tetrahedral complex, the four lowest energy σ-bonding orbitals will be filled and will be primarily ligand in character. Next there are two sets of σ-nonbonding MO's, one ligand-centered and one metal-centered. The permanganate, these orbitals would correspond to filled oxygen π_p orbitals and empty manganese 3*d* orbitals, respectively. All of the higher energy antibonding molecular orbitals would be unoccupied for a manganese (VII) complex. Hence there are four possible ligand-to-metal transitions:

$$L(t_1) \longrightarrow M(e)$$

$$L(t_1) \longrightarrow M(t_2^*)$$

$$L(t_2) \longrightarrow M(e)$$

$$L(t_2) \longrightarrow M(t_2^*)$$

For MnO_4^- all four of these transitions have been observed: 17,700 cm^{-1} ($t_1 \rightarrow e$); 29500 cm^{-1} $(t_1 \rightarrow t_2^*)$; 30,300 cm^{-1} $(t_2 \rightarrow e)$; and 44,400 cm^{-1} $(t_2 \rightarrow t_2^*)$. Only the absorption at 17,700 cm^{-1} falls within the visible range (14,000 – 28,000 cm^{-1}), and it is responsible for the familiar deep purple colour of MnO_4^-.

In a similar way, the charge transfer spectrum of organge CrO_4^{2-} ion can be analyzed, the LMCT process being facilitated by the high oxidation state of chromium (VI). Many iodide salts also are colored becaused of charge transfer transitions of this type. Examples are HgI_2 (red), BiI_3 (orange-red) and PbI_2 (yellow). The metal ions in these substances certainly are not outstanding oxidizing agents, but the transitions occur because the iodide ion is easily oxidized. (e.g. FeI3, $[CO(H_2O)_6]^{3+}$, $Pb_3(SbO_4)_2$, $[IrBr_6]^{2-}$ & $[RuCl_6]^{2-}$.

Pigments in which colour is produced by LMCT are given below :

Pigment	Primary orbitals involved
Cadmium yellow (CdS)	Ligand $\pi_p \longrightarrow$ metal 5*s*
Vermilion (HgS)	Ligand $\pi_p \longrightarrow$ metal 6*s*
Naples yellow [$Pb_3(SbO_4)_2$]	Ligand $\pi_p \longrightarrow$ metal 5*s* or 5*p*
Massicot (PbO)	Ligand $\pi_p \longrightarrow$ metal 6*s*
Chrome yellow ($PbCrO_4$)	Ligand $\pi_p \longrightarrow$ metal 3*d*
Red and yellow ochres (iron oxides)	Ligand $\pi_p \longrightarrow$ metal 3*d*

If the energy difference between the lowest unoccupied molecular orbital (LUMO) centered on the metal ion and the highest occupied molecular orbital (HOMO) centered on the ligand is very small (less than 10,000 cm^{-1}), total electron transfer between the two many occur. This will be the case if the metal ion is a sufficiently good oxidizing agent and the ligand a good enough reducing agent to cause a spontaneous redox process. The result is breakdown of the complex. Examples of complexes in which this occurs are $[Co(H_2O)_6]^{3+}$ and FeI_3: Water is oxidized by Co^{3+} and the iodide ion is oxidized by Fe^{3+}.

Figure (2) shows the visible and UV spectrum of the less symmetric complex $[CrCl(NH_3)_5]^{2+}$. From this spectrum we can recognize the two ligand-field, *d-d*, bands in the visible region. The replacement of one NH_3 ligand by a weaker field Cl^- ligand moves the lowest energy *d-d* bands to lower energy than those of $[Cr(NH_3)_6]^{3+}$. Also, a shoulder appears on the high-energy side of one of the *d-d* bands as a result of the reduction in symmetry from O_h to C_{4v}. Another new feature in the spectrum is the strong absorption maximum in the ultraviolet, near 42,000 cm^{-1}. This band is at lower energy than the corresponding band in the spectrum of $[Cr(NH_3)_6]^{3+}$ and has been assigned as an LMCT transition from the Cl^- ligand to the metal. The LMCT character of similar bands in $[CoX(NH_3)_6]^{2+}$ is confirmed by the decrease in wavenumber in steps of about 8000 cm^{-1} as X is varied from Cl to Br to I. In this LMCT transition a lone-pair electron of the halide ligand is promoted into a predominantly metal orbital.

Charge-transfer transitions are identified by their high intensity and the sensitivity of their energies to solven polarity.

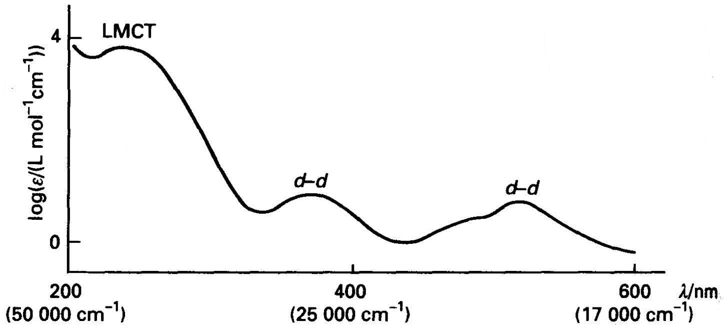


Figure (2)

CT transitions are generally intense compared with ligand-field transitions. Charge-transfer bands in the visible region of the spectrum (and hence contributing to the intense colors of complexes) may occur if the ligands have lone pairs of relatively high energy (as in sulfur and selenium) or if the metal has low-lying empty orbitals. The color of the artists pigment ‘cadmimum yellow’, CdS, for instance, is due to the transition Cd^{2+} (5*s*) ← S^{2-} (π). Similarly, HgS is red as result of the transition Hg^{2+} (6*s*) ← S^{2-} (π) and ochers are iron oxides that are colored red and yellow by the transition Fe (3*d*) ← O^{2-} (π).

The tetraoxoanions of metals with high oxidation numbers (such as MnO_4^-) provide what are probably the most familiar examples of LMCT bands. In them, an 0 lone-pair electron is promoted into a low-lying empty *e* metal orbital. High metal oxidation states correspond to a low *d*-orbital population (many are d^0), so the acceptor level is available and low in energy. The trend in LMCT energies is:

Oxidation Number	
+ 7	$MnO_4^- < TcO_4^- < ReO_4^-$
+ 6	$CrO_4^{2-} < MoO_4^{2-} < WO_4^{2-}$
+ 5	$VO_4^{3-} < NbO_4^{3-} < TaO_4^{3-}$

The energies of the transitions correlate with the order of the electrochemical series, with the lowest energy transitions taking place to the most easily reduced metal ions. This correlation is consistent with the transition being the transfer of an electron from the ligands to the metal, corresponding, in effect, to the reduction of the metal ion by the ligands.

Polymeric and monomeric oxoanions follows the same trends, with the oxidation number of the metal the determining factor.

The variation in the position of LMCT bands can be expressed in terms of the optical electronegativities of the metal, χ_{metal} and the ligands, χ_{ligand}. The wavenumber of the transition is then writeen as the difference between the two electronegativities:

$$\tilde{\nu} = |\chi_{\text{ligand}} - \chi_{\text{metal}}|\tilde{\nu}_o$$

Optical electronegativities have values comparable to pauling electronegativities if we take the constant $\tilde{\nu}_0$ to be 3.0 × 10^4 cm^{-1}. If the LMCT transition terminates in an e_g orbital, Δ_0 must be added to the energy predicted by this equation. Electron pairing energies must also be taken into account if the transition results in the population of an orbital that already contains an electron. The values for metals are different in complexes of different symmetry, and the ligand values are different if the transition originates from a π orbital rather than a σ orbital.

Ligand-to-metal transitions are observed when the metal is in a high oxidation state and ligands contain lone-pair electrons, the variation in the position of LMCT bonds can be parametrized in terms of optical electronegativities.

The spectra of $RuCl_6^{2-}$ and $IrBr_6^{2-}$ (d^4 and d^5 complexes, respectively) show two sets of bands that have been assigned to transitions from the weakly bonding π orbitals on the ligands to the antibonding t_{2g}^{*} and e_{g}^{*} orbitals of the metal atom. In $IrBr_6^{2-}$ (a d^6 complex), the t_{2g}^{*} orbitals are filled, and only the transition to the e_{g}^{*} orbitals can be observed.

In the halogenopentaammine complexes of the type $[Co(NH_3)_5X]^{2+}$, strong charge-transfer bands are observed in the ultraviolet region. These bands appear at progressively lower frequencies on going from the chloro to the bromo to the iodo complex, as one might expect from the trend in reduction potentials for these halogens. Indeed, in $[Co(NH_3)_5I]^{2+}$, the charge-transfer bands largely obscure the weaker *d*-*d* transitions.

(2) Metal to Ligand Charge Transfer (MLCT)

If the migration of electron is from metal to ligand, then charge transfer is called metal to ligand charge transfer (MLCT). Charge transfer processes in the opposite direction, from metal to ligand, are favored in complexes that have occupied metal-centered orbitals and vacant low lying ligand-centered orbitals. Prime examples are complexes in which the ligands have empty π antibonding orbitals. Ligands falling into this category include CN^-, SCN^- carbon monoxide, pyridine, bipyridine, pyrazine, *o*-phenanthroline, dithiolene ($S_2C_2R_2$), dithiocarbamate (S_2CNR_2) shows possible MLCT transitions for an octahedral complex in which both the t_{2g} and e_g orbitals are occupied.

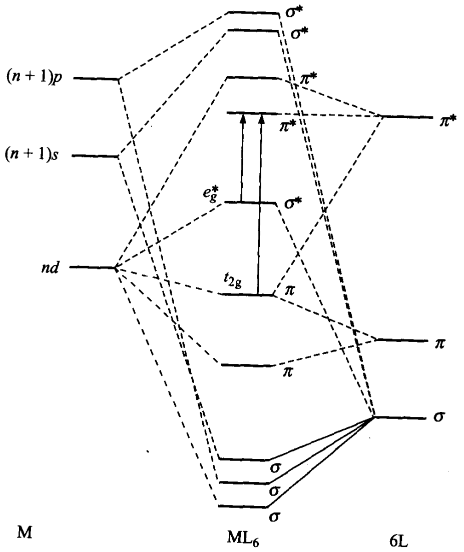


Figure (3)

An example of an MLCT transition is the one responsible for the red color of tris(bipyridyl)iron(II), the complex used for the colorimetric analysis of Fe(II). In this case, an electron makes a transition for a *d* orbital of the central metal into a π^* orbital of the ligand.

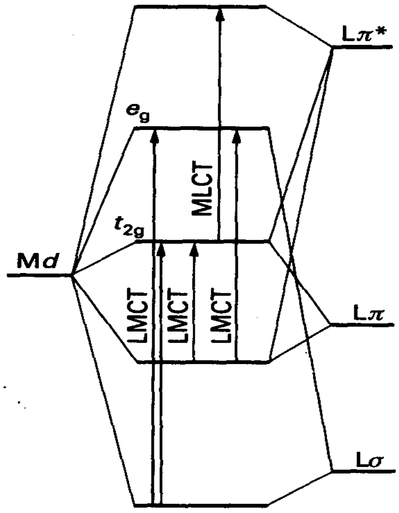
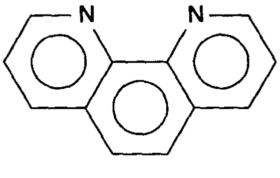


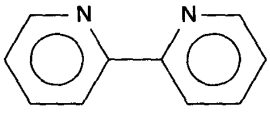
Figure (4)

Diamines, which have two N donor atoms: two important examples are 2, 2'-bipyridine and 1, 10-phenanthroline. Complexes of diimines with strong MLCT bands include tris(diimine) species such as tris (2, 2'bipyridyl)ruthenium(II), which is orange on account of its MLCT band. A diimine ligand may also be easily substituted into a complex with other ligands that favor a low oxidation state. Two examples are [W(CO)$_4$(phen)] and [Fe(CO)$_3$(bipy)]. However, the occurrence of MLCT transitions is by no means limited to diimine ligands. Another important ligand type that shows typical MLCT transitions is dithiolene, $S_2C_2R_2$. Resonance Raman spectroscopy is a powerful technique for the study of MLCT transitions, particularly of diimine complexes.

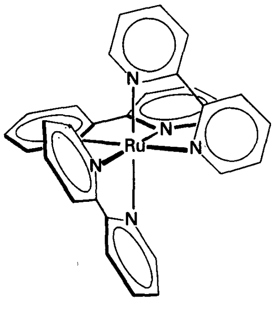
Charge transfer transitions from metal to ligand are most commonly observed in complexes with ligands that have low lying π* orbitals specially aromatic ligands.



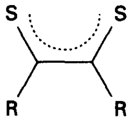
5 1,10–Phenthroline (phen)



4 2,2′–Bipyridine (bipy)

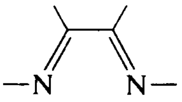


6 [Ru(bipy)$_3$]$^{2+}$



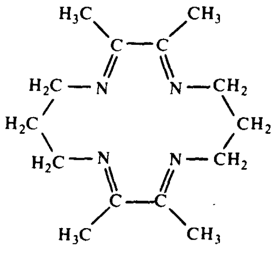
7 Dithiolene

The visible absorption spectra of iron(II) complexes with ligands containing the α-diimine unit



have intense charge-transfer bands associated with the transfer of charge from metal t_{2g} orbitals to the antibonding orbitals of the α-diimine group. In the case of the 1, 10-phenanthroline complex $\mathrm{Fe(phen)_3^{2+}}$, the transition occurs at 19,600 $\mathrm{cm^{-1}}$. A series of 6-coordinate iron(II) complexes containing the tetraimine macro-cyclic ligand (TIM) shown below, have been prepared with various monodentate liands occupying the two axial sites. The band maxima of these complexes, corresponding to metal-to-TIM charge transfer, are given below. It can be seen that the transition energy is a function of the π-acceptor ability of the axial ligands. As the π-acceptor ability increases, the energy of the d_{xz} and d_{yz} orbitals decreases relative to that of the π (TIM) orbital, causing the $t_{2g} \to \pi$ (TIM) charge-transfer band to move to higher energies.

Complex	**Band maximum $\mathrm{cm^{-1}}$**
$\mathrm{Fe(TIM)CH_3CN(CO)^{2+}}$	23,200
$\mathrm{Fe(TIM)(P(OEt)_3)_2^{2+}}$	19,500
$\mathrm{Fe(TIM)(CH_3CN)_2^{2+}}$	18,200
$\mathrm{Fe(TIM)(imidazole)_2^{2+}}$	15,200
$\mathrm{Fe(TIM)(NH_3)_2^{2+}}$	14,300



TIM

Spectra of Compounds with Metal-Metal Bonds or (Intervalence transitions)

Compounds which contain metal-metal bonds are intensely colored. For example $\mathrm{Mn_2(CO)_{10}}$ is bright yellow, $\mathrm{Re_2Cl_8^{2-}}$ is deep blue, $\mathrm{Co_2(CO)_8}$ is purple-black, $\mathrm{Mo_2Cl_8^{4-}}$ is cherry red, and $\mathrm{Fe_2(CO)_9}$ is gold; the observed transitions for these compounds are of the types $\sigma \to \sigma^*$, $\pi \to \pi^*$ and $\delta \to \delta^*$ and are fully allowed. In the case of $\mathrm{Mn_2(CO)_{10}}$, the $\sigma \to \sigma^*$ band peaks at 29,400 $\mathrm{cm^{-1}}$. One expects that this excitation should be accompanied by weakening or dissociation of the Mn-Mn bond. Indeed, ultraviolet irradiation of $\mathrm{Mn_2(CO)_{10}}$ in carbon tetrachloride solution leads to the intermediate formation of $\mathrm{Mn(CO)_5}$ radicals, which abstract chlorine atoms from the solvent to form the chlorine-substituted mononuclear complex:

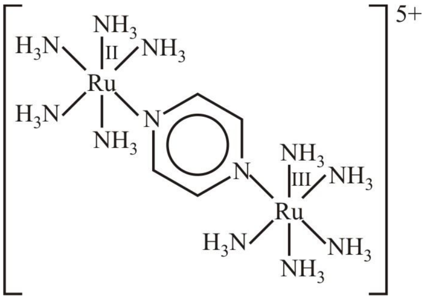
$$\mathrm{Mn_2(CO)_{10}} \xrightarrow[\mathrm{CCl_4}]{h\nu} \mathrm{2Mn(CO)_5Cl}$$

Photochemical cleavage of metal-metal bonds is fairly common in metal cluster compounds. However, it appears that excitation to the relatively weakly antibonding π* and δ* states is ineffective for such cleavage.

(3) Intermetal Charge Transfer

Potassium ferrocyanide is used to test for iron in solution. $\mathrm{Fe^{2+}}$ ions give a white precipitate of $\mathrm{K_2Fe^{II}[Fe^{II}(CN)_6]}$, but $\mathrm{Fe^{3+}}$ ions give deep blue $\mathrm{KFe^{III}[Fe^{II}(CN)_6]}$ known as Prussian blue. A deep blue colour is also produced by $\mathrm{Fe^{2+}}$ with $\mathrm{K_3[Fe^{III}(CN)_6]}$, and this is known as Turnbull's blue $\mathrm{KFe^{II}[Fe^{III}(CN)_6]}$. Both have been used as pigments in ink and paint. Recent X-ray work, infrared and Mossbauer spectroscopy have shown that Turnbull's blue is identical to Prussian blue. The intense colour arises from electron transfer between Fe(+II) and Fe(+III).

Another example is Creutz-Taube ion. $[(NH_3)_5Ru - Pyz - Ru(NH_3)_5]^{5+}$ where p_{yz} is bridging pyrazine ligand. In this complex e– transfer occurs from Ru(II) to Ru(III) through p_{yz}.



Red Lead (Pb_3O_4) contain Pb (II) and Pb (IV). Due to electron transfer from Pb (II) to Pb (IV) it gives intense red colour.

(4) Interligand Charge Transfer

The ligand itself may have a chromophore and still another type of absorption band, an intraligand band, may be observed. These bands may sometimes be identified by comparing the spectra of complexes with the spectra of free ligands. However, coordination of ligand to a metal may significantly alter the energies of the ligands orbitals, and such comparisons may be difficult, especially if charge-transfer bands overlap the intraligand bands. Also, it should be noted that not all ligands exist in the free state; some ligands owe their existence to the ability of metal atoms to stabilize molecules that are otherwise highly unstable.

Some Other Examples of Charge Transfer Spectra

1. In the (+1) state of Cu most of the simple compounds and complexes are diamagnetic and colourless because the ions have a d^{10} configuration. There are a few coloured compounds. For example, Cu_2O is yellow or red, Cu_2CO_3 is yellow and CuI is brown. In these cases the colour arises from charge transfer bands and not from *d-d* spectra.

2. There are several blue proteins which contain Cu. They act as electron transfer agents by means of a Cu^{2+}/Cu^{+} couple. Their colour is much more intense than would be expected for *d-d* spectra. The colour is thought to be caused by charge transfer between Cu and S. Examples include plastocyanin and azurin. Plastocyanin occurs in the chloroplasts of green plants.

3. Zn, Cd and Hg have a d^{10} electronic configuration and so cannot produce *d-d* spectra. Thus many of their compounds are white. However, some compounds of Hg (+II) and a smaller number of Cd (+II) are highly coloured due to charge transfer from the ligands to the metal.

4. HgI_2 exists in red and yellow forms. The colour is due to charge transfer.

5. The orange colour of SnI_4 is caused by the absorption of blue light, the reflected light thus containing a higher proportion of red and orange. The energy absorbed in this way caused the transfer of an electron from I to Sn. (This corresponds to the temporary reduction of Sn(IV) to Sn(III). Since transferring an electron to another atom is transferring a charge, such spectra are called charge transfer spectra. This occurs in SnI_4 and GeI_4 because the atoms have similar energy levels. This would be expected because they are close in the periodic table, and have similar sizes. Charge transfer spectra do not occur with the other halides.

6. Almost all manganese compounds are coloured. Mn^{2+} is pale pink, and MnO_2 is black, both becauseof ***d-d*** transitions. The (+ VII) oxidation state has a d^0 configuration and would be expected to be colourless. Whilst perrhenates ReO_4^- containing Re (+VII) are colourless, permanganates MnO_4^- containing Mn (+VII) are intensely coloured. The purple-black colour arises from charge transfer spectra.

7. The permanganate MnO_4^- ion has an intense purple colour. Mn (+VII) has a d^0 configuration, so the colour arises from charge transfer and not from ***d-d*** spectra.

8. $KMnO_4$ is a very dark purple-black solid. The MnO_4^- ion is deep purple coloured due to charge transfer spectra. In contrast solutions of TeO_4^- and ReO_4^- are colourless, as the charge transfer band occurs at higher energy in the UV region. However solutions of $HReO_4$ become yellow-green when they are concentrated, and $HTcO_4$ has been isolated a red solid. These colours arise because the tetrahedral ReO_4^- ion becomes less symmetrical when undissociated HO—ReO_3 is formed.

9. $Cr_2O_7^{2-}$ is an orange solid, CrO_4^{2-} is yellow solid, CrO_3 is a bright orange solid. The colour arises from charge transfer (not ***d-d*** spectra as Cr (+VI) has a d^0 configuration.

10. V_2O_5 is orange or red coloured due to charge transfer.