

❖ Charge Transfer Spectra

A charge transfer band may be defined as the peak arising from the transition in which an electron is transferred from one atom or group in the molecule to another one.

In other words, the transition occurs between molecular orbitals that are essentially centered on different atoms or groups. These transitions are neither Laporte nor spin-forbidden in nature; and therefore, show very intense absorption. Charge transfer transitions are primarily classified in four types as:

➤ Ligand to Metal Charge Transfer

The ligand to metal charge transfer (LMCT) in metal complexes arises when the electrons are transferred from a molecular orbital with a ligand-like character to those with metal-like character. This type of transfer is predominant if the following conditions are fulfilled:

- i) The ligands should have lone pair of electrons with relatively high-energy such as O^{2-} , Cl^- , Br^- , S^{2-} or Se.
- ii) The metal should be in a high oxidation state and must have low-lying empty orbitals.

These conditions imply that the acceptor level is available and low in energy. Moreover, the charge transfer transitions for octahedral and tetrahedral complexes are different; therefore, these two types of ligand to metal charge transfer are quite important and must be discussed in detail.

1. LMCT in octahedral complexes: Before we discuss the ligand to metal charge transfer in octahedral complexes, the molecular orbital diagram for σ and π -bonding in ML_6 geometry should be recalled. The electrons can be excited, not only from the t_{2g}^* to e_g^* but also from the bonding molecular orbitals of σ and π nature that are predominantly associated with the ligands. The latter two types of excitation modes result in

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the charge transfer spectra, labeled as the ligand to metal charge transfer. This type of transition results in a formal reduction of the metal.

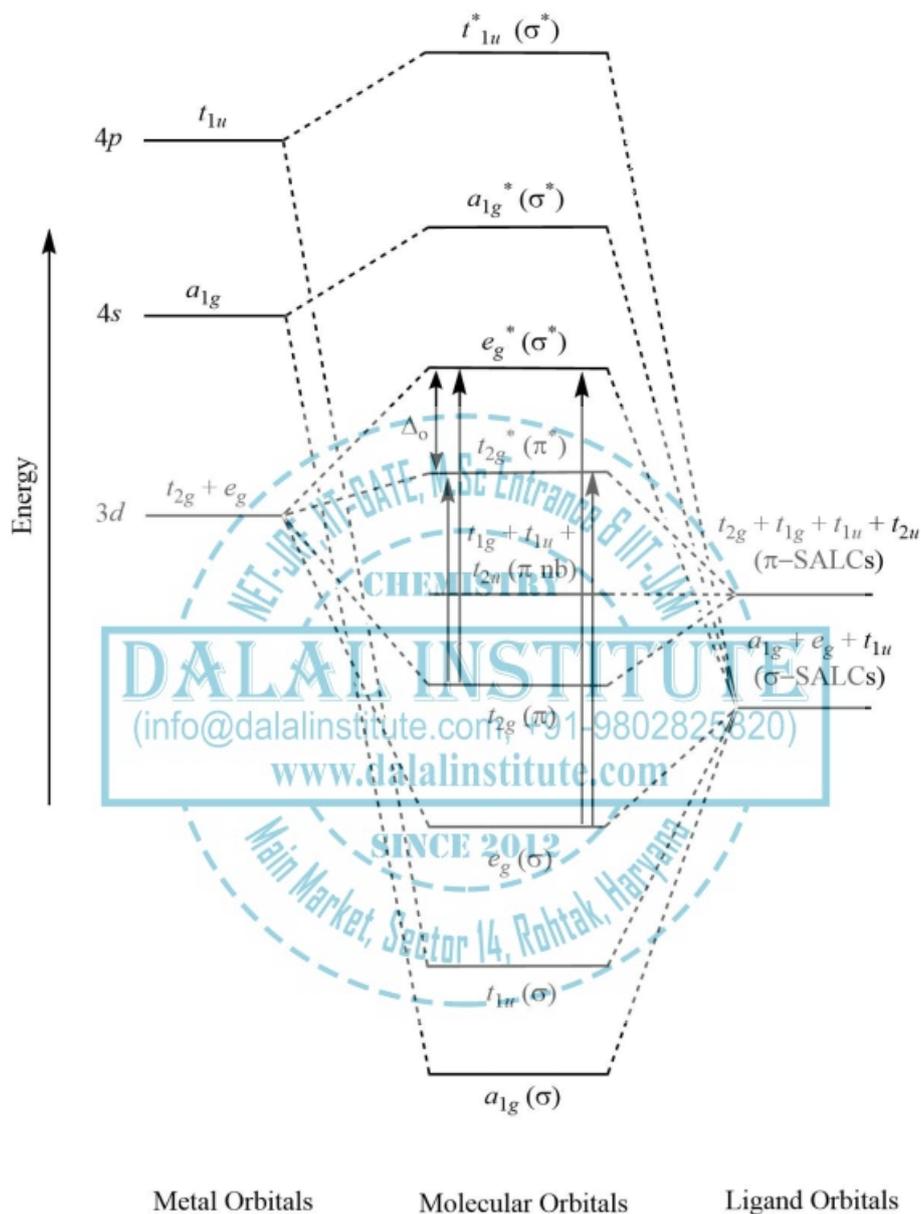


Figure 71. Ligand to metal charge transfer in octahedral (ML_6) complexes.

Consider a d^6 octahedral complex, such as $[Co(NH_3)_5(X)]^{2+}$ ($X = F^-$, Cl^- , Br^- or I^-), whose t_{2g}^* levels are filled. As a consequence, an intense absorption band in $[Co(NH_3)_5F]^{2+}$ is observed above 40000 cm^{-1} ; and that is corresponding to a transition from ligand σ -bonding molecular orbital to the empty e_g^* molecular orbital. However, in $[Co(NH_3)_5Cl]^{2+}$ this intense band with two components is observed above 30000 cm^{-1} .

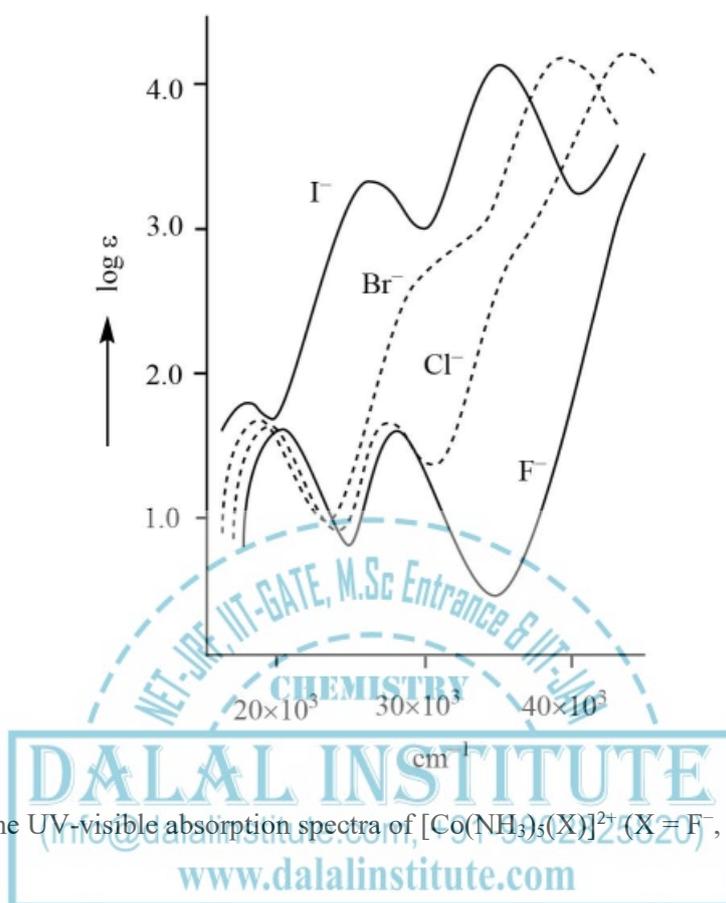


Figure 72. The UV-visible absorption spectra of $[\text{Co}(\text{NH}_3)_5(\text{X})]^{2+}$ ($\text{X} = \text{F}^-$, Cl^- , Br^- or I^-).

The charge-transfer bands appear at lower energy for $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$ and at still lower energy for $[\text{Co}(\text{NH}_3)_5\text{I}]^{2+}$, overlapping with ligand-field bands and masking their higher energy peaks. It must be noted that the ligand-field peaks shift slightly according to the increasing strength of the crystal field of X, but the charge-transfer bands show very large shifts. The shifts in the energies of the LMCT transitions in $[\text{Co}(\text{NH}_3)_5(\text{X})]^{2+}$ correspond to the changes in ease of removal of the electron (oxidation) from X^- . Though the transition corresponds to the transfer of an electron from X^- to Co^{3+} ; and therefore, no net oxidation-reduction occurs because of the very short lifetime of the excited state. Nonetheless, this process, provide a mechanism for photochemical decomposition that occurs for many complexes stored in strong light. A similar pattern has been observed in the case of $[\text{Cr}(\text{NH}_3)_5(\text{X})]^{2+}$ ($\text{X} = \text{F}^-$, Cl^- , Br^- or I^-).

2. LMCT in tetrahedral complexes: Before we discuss the ligand to metal charge transfer in tetrahedral complexes, the molecular orbital diagram for σ and π -bonding in ML_4 geometry should be recalled. The electrons can be excited, not only from the e^* to t_2^* , but also from the π -bonding molecular orbitals of t_2 -symmetry and nonbonding π -SALCs of t_1 -symmetry; both of which are predominantly associated with the ligands. The latter two types of excitation modes result in the charge transfer spectra, labeled as the ligand to metal charge transfer. This type of transition results in a formal reduction of the metal.

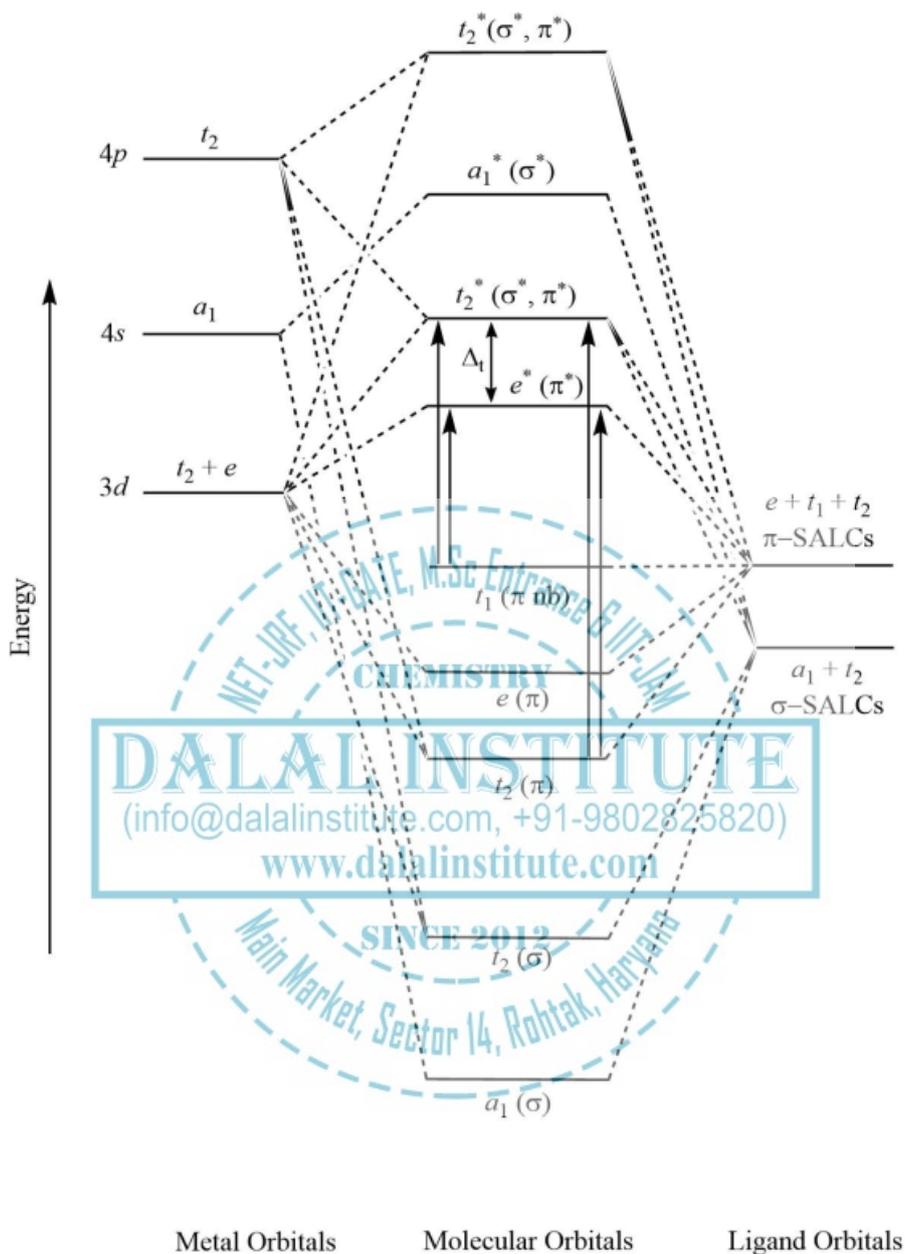


Figure 73. Ligand to metal charge transfer in tetrahedral (ML_4) complexes.

Consider a d^0 tetrahedral complex, such as MnO_4^- , whose e^* and t_2^* levels are totally empty. As a consequence, very intense absorption spectra in permanganate is obtained and all of the four ligand-to-metal-charge-transfer (LMCT) transitions are observed. However, it must be noted that three out of four peaks happen to arise in the ultra-violet region and only $t_1 \rightarrow e^*$ transition belongs to the visible range. Moreover, this particular transition is also responsible for the deep purple color of permanganate ion.

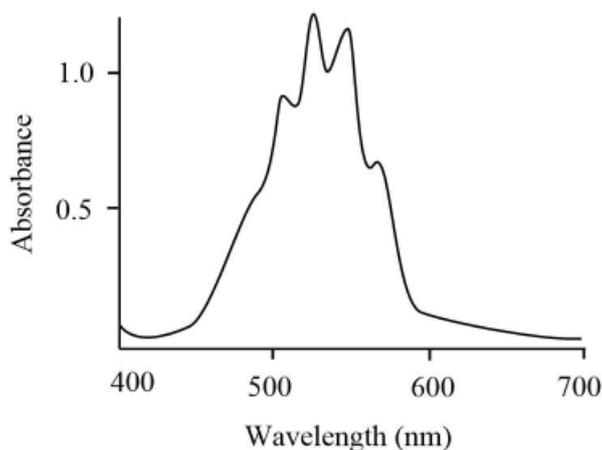


Figure 74. The UV-visible absorption spectra of MnO_4^- .

The complete profile of absorption spectra of MnO_4^- ion is given below as:

Table 15. The type of transition and their wavenumbers of the absorption peaks for MnO_4^- .

Transition type	Wavenumber (cm^{-1})
$L(t_1) \rightarrow M(e^*)$	17700
$L(t_1) \rightarrow M(t_2^*)$	29500
$L(t_2) \rightarrow M(e^*)$	30300
$L(t_2) \rightarrow M(t_2^*)$	44400

A similar pattern has been observed in the case of CrO_4^{2-} . The energies of transitions correlate with the order of the electrochemical series. Lower energy absorption is expected for the metal ions which are reduced more easily. The abovementioned trend is in accordance to the transfer of electrons from the ligand to the metal, and hence resulting in a reduction of the metal center by the ligand attached.

Oxidation state	Complexes			
+7	MnO_4^-	TcO_4^-	ReO_4^-	↓ Blue shift
+6	CrO_4^{2-}	MoO_4^{2-}	WO_4^{2-}	
+5	VO_4^{3-}	NbO_4^{3-}	TaO_4^{3-}	
→ LMCT shows blue shift				

➤ **Metal to Ligand Charge Transfer**

The metal to ligand charge transfer (MLCT) in metal complexes arises when the electrons are transferred from a molecular orbital with a metal-like character to those with a ligand-like character. This type of transfer is predominant if the following conditions are fulfilled:

- The ligands should have high-energy empty π^* orbitals such as CO , CN^- , SCN^- or NO .
- The metal should be in a low oxidation state and must have high-lying filled orbitals.

These conditions imply that the empty π^* orbitals on the ligands become the acceptor orbitals on the absorption of light. The available acceptor level is relatively high in energy. However, before we discuss the ligand to metal charge transfer in transition metal complexes, the molecular orbital diagram for σ and π -bonding in ML_6 geometry should be recalled.

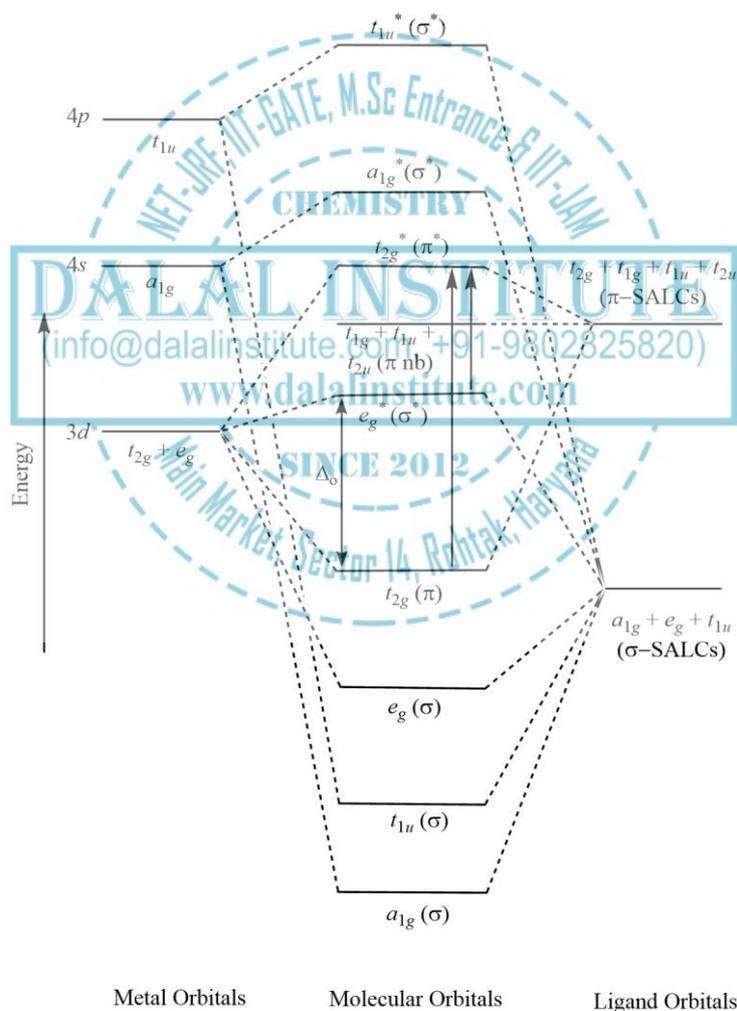


Figure 75. Metal to ligand charge transfer in octahedral (ML_6) complexes.

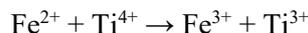
The electrons can be excited, not only from the t_{2g} to e_g^* , but also from the bonding molecular orbitals of π and antibonding molecular orbitals of σ nature (predominantly associated with the ligands) to antibonding π^* . The latter two types of excitation modes result in the charge transfer spectra, labeled as the metal to ligand charge transfer. This type of transition results in formal reduction of the metal. The common type of ligands taking part in MLCT include 2,2'-bipyridine (bipy), 1,10-phenanthroline (phen), CO, CN^- and SCN^- . Examples of these complexes include: Tris(2,2'-bipyridyl) ruthenium(II), $\text{W}(\text{CO})_4(\text{phen})$, $\text{K}_4[\text{Fe}(\text{CN})_6]$, $\text{K}_3[\text{Fe}(\text{CN})_6]$, $[\text{Fe}(\text{phen})_3]^{3+}$, $[\text{Fe}(\text{acac})_3]$ and $\text{Fe}(\text{CO})_3(\text{bipy})$.

An orange-colored complex of bivalent ruthenium, $[\text{Ru}(\text{bpy})_3]^{2+}$, is being analyzed because the excited electronic state that results from this charge transfer has an average life-time around microseconds and the complex can act as an adaptable photochemical reagent. The photo-reactivity of these complexes arises from the nature of the reduced ligand and oxidized metal center. Now although the states of MLCT complexes such as $[\text{Ru}(\text{bipy})_3]^{2+}$ and $\text{Re}(\text{bipy})(\text{CO})_3\text{Cl}$ were intrinsically not that much reactive, there are many MLCT complexes which are characterized by reactive MLCT states. Vogler and Kunkely proposed that a MLCT complex can be considered as an isomer of the ground state, that possesses a reduced ligand and oxidized metal. Hence, many reactions like electrophilic attack, oxidative addition at the metal ion due to the reduced ligand, the radical reactions on the reduced ligand, or the outer-sphere charge-transfer reactions can be attributed to states arising from metal-to-ligand-charge-transfer transitions. The reactivity of MLCT states usually depends on the oxidation of the metal center. The succeeding processes include exciplex formation, cleavage of metal-metal bonds, associative ligand substitution.

➤ **Metal to Metal Charge Transfer**

The metal to metal or inter-valence charge transfer may simply be defined as the excitation and subsequent transfer of an electron from a low oxidation state cation to a neighboring cation of a higher oxidation state.

The transfer is usually excited by a certain visible portion of the light of and produces a characteristic color. The electron then drops back down, giving off the extra energy as a small amount of heat. An example is corundum with the coupled substitution. The simplified chemical equation representing various oxidation states can be given as:



This reaction absorbs red photons and gives sapphire its characteristic blue color. In hematite, the process absorbs all visible photons. Materials that exhibit this property retain their dark color regardless of how finely they are ground. Materials exhibiting metal to metal charge transfer (MMCT) are also conductors. MMCT generally shows a strong sloping spectral signature in the range 500-1000 nm. Edge-shared octahedral geometries generally exhibit MMCT in the range 700-800 nm, while face-shared octahedral complexes exhibit it in the range of 800-900 nm. In order for metal-to-metal-charge-transfer (MMCT) to occur, orbital must overlap so electrons can flight back and forth. Examples of the systems displaying metal to metal charge transfer are:

Table 16. The type of transition and their wavenumbers of the absorption peaks for MnO_4^- .

System	Absorption maxima (nm)
$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ (edge-shared)	700-800
$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$ (face-shared)	800-900
$\text{Ti}^{3+} \rightarrow \text{Ti}^{4+}$	600-800
$\text{Mn}^{2+} + \text{Ti}^{4+} \rightarrow \text{Mn}^{3+} + \text{Ti}^{3+}$	380-450

The most popular example of inter-valence charge transfer is “Prussian blue”. This compound has the formula $\text{KFe}[\text{Fe}(\text{CN})_6]$ and shows a very intense blue color owing to the transfer of an electron from Fe^{2+} to Fe^{3+} . In the crystal structure of Prussian blue, the Fe^{2+} ions are bonded with N atom while the Fe^{3+} ions are bonded with C atom of octahedrally surrounding of CN^- ligands. Therefore, the charge transfer takes place through the cyanide bridge.

➤ **Ligand to Ligand Charge Transfer**

The ligand to ligand or inter-ligand charge transfer may be defined as the excitation and subsequent transfer of an electron from a one ligand orbitals to a neighboring ligand orbital.

The ligand to ligand charge transfer (LLCT) or inter-ligand charge transfer transitions are quite uncommon and rarely observed. In comparison to the enormous literature on metal-to-ligand and ligand-to-metal charge transfer, very little has been published on LLCT. In most of the cases, LLCT peaks are difficult to detect in UV-visible absorption spectra; which can be attributed to the fact that these peaks may be obscured or hidden under absorption bands of different origins, or they may occur at a position very distinct from those ordinarily analyzed. The LLCT bands are of low intensity due to the poor overlap between the participating orbitals. Molecular orbitals with dominant ligand characters may have some amount of metal character also, and a transition that is labelled as ligand to ligand may in fact also involve the metal to some point. However, if the LLCT is pure, it would have transition energy that does not change considerably when the metal is changed. A more specific form of $\text{L}_{\text{red}}-\text{M}-\text{L}_{\text{ox}}$ complexes is mixed-valence compounds (ligand-based), which possesses the same ligand in two different redox states. In this case, the interaction between ligands may yield a partial or complete electron delocalization between the oxidized and reduced form of the ligands. Therefore, the LLCT loses its charge-transfer character because now it is occurring between delocalized orbitals.

One of the recent examples of metal complexes involving ligand to ligand charge transfer is (CuTpAsPh_3) . The emission and UV-visible absorption spectra of (CuTpAsPh_3) , contain low-energy bands (with a band maximum at $16\,500\text{ cm}^{-1}$ in emission and a weak shoulder at about $25\,000\text{ cm}^{-1}$ in absorption) that are not present in the corresponding spectra of the phosphine or amine complexes. The peaks are assigned to the ligand to ligand charge transfer (LLCT) may have some contribution from the metal.

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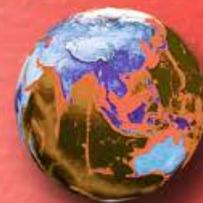
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Volume I

MANDEEP DALAL



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