

## 8.5.3: Charge-Transfer Spectra

### Charge Transfer Transitions

$\text{Zn}^{2+}$		$d^{10}$ ion	white
$[\text{Cu}(\text{MeCN})_4]^+$	Cu(I)	$d^{10}$ ion	colourless
$[\text{Cu}(\text{phen})_2]^+$	Cu(I)	$d^{10}$ ion	dark orange
$\text{TiF}_4$		$d^0$ ion	white
$\text{TiCl}_4$		$d^0$ ion	white
$\text{TiBr}_4$		$d^0$ ion	orange
$\text{TiI}_4$		$d^0$ ion	dark brown
$[\text{MnO}_4]^-$	Mn(VII)	$d^0$ ion	extremely purple
$[\text{Cr}_2\text{O}_7]^-$	Cr(VI)	$d^0$ ion	bright orange

Figure 8.5.3.1: Some examples of complexes with  $d^0$  and  $d^{10}$  electron configurations, and their colors. Attribution: E.R. Schofield.

We are still not done with our electronic spectra. Thus far, we have only considered transitions of d-electrons between d-orbitals, and their terms. These are called d-d transitions. However, there are also so-called charge transfer transitions possible, which are not d-d transitions. We can easily see that there must be transitions other than d-d transitions when we look at the colors of  $d^{10}$  and  $d^0$  ions. For those, there are no d-d transitions possible. Therefore, they all should be colorless. However, that is not always true. Some of these ions are indeed colorless, but some are not (Figure 8.5.3.2). For example,  $\text{Zn}^{2+}$ , a  $d^{10}$  ion, is colorless in complexes, but not Cu(I), which is also  $d^{10}$ . While tetrakis(acetonitrile)copper(+) is colorless, bis(phenanthrene) copper(+) is dark orange.  $d^0$  ions have similar properties: While  $\text{TiF}_4$  and  $\text{TiCl}_4$  are colorless,  $\text{TiBr}_4$  is orange, and  $\text{TiI}_4$  is brown. Some  $d^0$  species are even extremely colorful, for example, permanganate with  $\text{Mn}^{7+}$ , which is extremely purple, and dichromate with Cr(VI), which is bright orange.

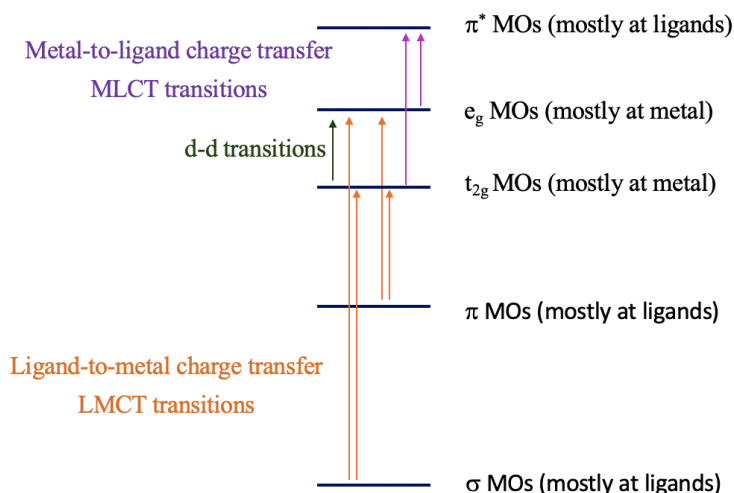


Figure 8.5.3.2: Charge-transfer transitions. Attribution: E.R. Schofield.



The explanation for these phenomena is charge-transfer transitions (8.5.3.2). There are two types of charge-transfer transitions: ligand-to-metal (LMCT) and metal-to-ligand (MLCT) charge transfer transitions. For the ligand-to-metal transitions, electrons from bonding  $\sigma$  and  $\pi$ -orbitals get excited into metal d-orbitals in the ligand field, for example the  $t_{2g}$  and the  $e_g$  orbitals in an octahedral complex. If the energy difference between the  $\sigma/\pi$ -orbitals and the d-orbitals is small enough, then this electron transition is associated with the absorption of visible light. The transition is called a ligand-to-metal transition because the ligand  $\sigma/\pi$ -orbitals are mostly located at the ligands, while the metal-d-orbitals in a ligand field are mostly located at the metal. Vice versa, the metal-to-ligand transition involves the transition of an electron from metal d-orbitals in a ligand field to ligand  $\pi^*$ -orbitals. This

essentially moves electron density from the metal to the ligand, hence the name ligand-to-metal-charge transfer transition. If the energy-difference between the ligand  $\pi^*$  and the metal orbitals is small enough, then the absorption occurs in the visible range. Charge-transfer transitions are usually both spin- and Laporte allowed; hence, if they occur, the color is often very intense. How can we distinguish between d-d and charge transfer transitions? Charge transfer transitions often change in energy as the solvent polarity is varied (solvatochromic), as there is a change in polarity of the complex associated with the charge transfer transition. This can be used to distinguish between d-d transitions and charge-transfer bands.

## LMCT Transitions

Can we predict when the energy windows between the bonding molecular orbitals and the metal d-orbitals are small enough for LMCT transitions in the visible to take place? Generally, it would be desirable if the energy of the metal orbitals were as low as possible and the energy of the bonding ligand orbitals were as high as possible. The energy of metal d-orbitals decreases with increasing positive charge at the metal because the effective nuclear charge on the metal increases. This means that very high metal oxidation states favor LMCT transitions. The d-orbitals should have few or no electrons, so that electrons can be promoted into the orbitals, and orbital energy decreases because electron-electron repulsion is minimized. Examples are Mn(VII), Cr(VI), and Ti(IV). The energy of MOs from bonding ligand orbitals increases when the ligand orbitals have high energy; this is typically the case for  $\pi$ -donor ligands with a negative charge (Fig. 8.2.21).

Ligand properties	Metal ion properties
Ligand MOs: high energy	Valence orbitals: low energy
$\pi$ -donor electrons	high positive charge
Negatively charged ligands	Few or no d electrons
$O^{2-}$ , $Cl^-$ , $Br^-$ , $I^-$	Eg. Mn(VII), Cr(VI), Ti(IV)

8.5.3.1: The properties of the metal ions and ligands suitable for LMCT transitions.  $MnO_4^-$  is deep purple due to LMCT transitions (Attribution: Benjah-bmm27 / Public domain <https://commons.wikimedia.org/wiki/File:Permanganate-sample.jpg>) and (Attribution: Pradana Aumars / CC0 <https://commons.wikimedia.org/wiki/File:Entrations.jpg>), respectively.

Examples of ligands are oxo- and halo ligands. This explains, for example, the LMCT transitions in permanganate. The Mn is in the very high oxidation state +7, and the ligands are oxo-ligands, which are  $\pi$ -donors with a 2- negative charge. The transitions are both Laporte and spin-allowed, leading to a very high intensity of light absorption, and thus color (Fig. 8.2.21).

## MLCT Transitions

What are favorable metal ion and ligand properties for a metal-to-ligand transition, then? In this case we would like to keep the energy of the metal orbitals as high as possible so that the energy difference between a metal d-orbital and a  $\pi^*$ -orbital is minimized. This is accomplished when the positive charge at the metal ion is small, and there are many d-electrons that can repel each other, thereby increasing orbital energies, for example Cu(I), Fig. 8.2.22.

#### Metal ion properties

low metal ion charge

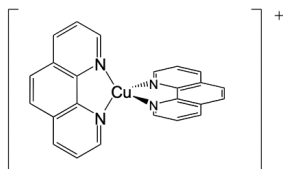
many electrons

Cu(I),  $d^{10}$  ion

#### Ligand properties

$\pi$ -acceptor ligand with low-lying  $\pi^*$  orbitals

1,10-phenanthroline,  $CN^-$ , CO,  $SCN^-$



$[Cu(phen)_2]^+$ , dark orange

#### 8.5.3.3: bis(phenanthroline) copper(+). Attribution: E.R. Schofield.

The ligand should be a  $\pi$ -acceptor with low-lying  $\pi^*$ -orbitals - for example, phenanthroline,  $CN^-$ ,  $SCN^-$ , and CO. The bis(phenanthroline) copper(+) ion, for instance, is dark orange and has an MLCT absorption band at 458 nm. This MLCT transfer is both spin and Laporte-allowed.

It should be mentioned that some complexes allow for both metal-to-ligand and ligand-to-metal transitions. For example, in the  $Cr(CO)_6$  complex, the  $\sigma$ -orbitals are high enough and the  $\pi^*$ -orbitals are low enough in energy to allow for light absorption in the visible range. Finally, intraligand bands are also possible when the ligand is a chromophore.

Dr. Kai Landskron ([Lehigh University](#)). If you like this textbook, please consider to make a donation to support the author's research at Lehigh University: [Click Here to Donate](#).

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- [8.2: Term splitting in ligand fields, selection rules, Tanabe-Sugano diagrams. Metal to ligand, and ligand to metal transitions](#) by Kai Landskron is licensed CC BY 4.0.