Electronic Spectra of Coordination Compounds

***Selection rules :* Transitions of electrons to be allowed should be occurred from**

**singlet to singlet, or triplet to triplet states and so on, but a change in spin**

**multiplicity is forbidden. Laporte selection rule: There must be a change in parity:**

**allowed transitions: g $ u forbidden transitions: g $g, u$ u, and, thus, allowed**

**transitions are *s p, p d* and *d***

***f;* forbidden transitions are *s s, p***

***d***

***d, f***

***f , s***

***d, p***

***f …etc.* Since these selection rules must be strictly**

**obeyed, why do many d-block metal complexes exhibit ‘d–d’ bands in their**

**electronic spectra? A spin-forbidden transition becomes ‘allowed’ if, for example,**

**a singlet state mixes to some extent with a triplet state. This is possible by spin–**

**orbit coupling but for first row metals, the degree of mixing is small and so**

**bands associated with ‘spin-forbidden’ transitions are very weak . Spin-allowed**

**‘d–d’ transitions remain Laporte-forbidden and their observation is explained by**

**a mechanism called ‘vibronic *coupling’.***

**تكون الأنتقالات الألكترونية مسموحة عندما يحصل الأنتقال بين مستويات الكترونية لها نفس تعددية البرم مثلا من الأحادية الى الأحادية او من الثلاثية الى الثلاثية وتكون مسموحة برميا مثل الطيف الألكتروني لمعقدات العناصر الأنتقالية في المنطقة المرئية وتتميز بأن لها شدة واطئة وذات معامل أمتصاص مولاري قليل.**

**أما القاعدة الأخرى لقواعد الأختيار (لابورت) تنص أن الأنتقال الألكتروي يكون مسموحا بين المستويات المتماثلة ومحظورة أوربتاليا عندما يكون نقل الألكترون بين نفس النوع من الأوربتالات فمثلا أنتقالات**

**d-d.f-f و p-p تكون محظورة**

**An octahedral complex possesses a centre of symmetry, but molecular**

**vibrations result in its temporary loss. At an instant when the molecule does not**

**possess a centre of symmetry, mixing of *d* and *p* orbitals can occur. Since the**

**lifetime of the vibration (10\_13 s) is longer than that of an electronic transition**

**(10\_18 s), a ‘d–d’ transition involving an orbital of mixed pd character can occur**

**although the absorption is still relatively weak . In a molecule which is noncentro**

**symmetric (e.g. tetrahedral), *p–d* mixing can occur to a greater extent and so the**

**probability of ‘d–d’ transitions is greater than in a centro symmetric complex.**

**This leads to tetrahedral complexes being more intensely colored than octahedral**

**complexes.**



***p,***

**Absorption bands in electronic spectra are usually broad; the absorption of a**

**photon of light occurs in 10\_18 s whereas molecular vibrations and rotations**

**occur more slowly. Therefore, an electronic transition is a ‘snapshot’ of a**

**molecule in a particular vibrational and rotational state, and it follows that the**

**electronic spectrum will record a range of energies corresponding to different**

**vibrational and rotational states.**

**Absorption bands are described in terms of *λmax* corresponding to the**

**absorption maximum *Amax*; the wavelength, *Amax* , is usually given in *nm,* but the**

**position of the absorption may also be described in terms of wave numbers,**

**(cm*\_1*). The molar extinction coefficient (or molar absorptivity) "*εmax* of an**

**absorption must also be quoted; " *εmax* indicates how intense an absorption is**

**and is related to Amax by equation below where *c* is the concentration of the**

**solution and ‘ℓ is the path length (in cm) of the spectrometer cell ( Fig. 1 ). Values**

**of "*εmax* range from close to zero (a very weak absorption) to >10 000 *dm\_3 mol\_1***

***cm\_1* (an intense absorption). Table – 1**

***εmax* = *Amax***

**cx *ℓ***

**Some important points shall be considered are that the electronic spectra of:**

**1- *d 1, d 4 , d 6*, and *d 9* complexes consist of one absorption;**

**2- *d 2*, *d 3, d 7* and *d 8* complexes consist of three absorptions;**

**3- *d 5* complexes consist of a series of very weak, relatively sharp absorptions.**

***Fig. 1 Absorption in the electronic spectrum of a***

***molecule or molecular ion***



***Table – 1 Some examples of electronic transitions with their values of εmax***



***Charge Transfer Transitions:* There is another important class of transition in**

**which the electron moves from a molecular orbital centered mainly on the ligand**

**to one centered mainly atom , or *vice versa .* In these the charge distribution is**

**considerably different in ground and excited states, and so they are called *Charge***

***Transfer Transitions.***

**هناك نوع اخر ومهم للانتقالات الالكترونية يدعم التداخل بين الفلز واالليكند من خلال ظهور امتصاصات عالية الشدة في بداية المنطقة المرئية ونهاية الاشعة فوق البنفسجية وهي ثلاث انواع.**

**The metal on charge transfer (CT) gives rise to intense absorptions, whereas**

**‘d–d’ bands are much weaker. In some spectra, CT absorptions mask bands due**

**to ‘d–d’ transitions, although CT absorptions (as well as ligand-centred *n – π\****

**and *π – π\** bands) often occur at higher energies than ‘d–d’ absorptions.**

**There are two classes of these bands ; ligand to metal ( L**

**M ) and metal**

**to ligand ( M**

**L ). In general , most of CT are of the first class. Charge transfer**

**transitions usually lie at the extreme blue end of the visible spectrum, or in the**

**ultraviolet region. Also, nearly all observed CT transitions are fully allowed,**

**hence the CT bands are strong, and the extinction coefficient are typically 103 to**

**104 , or more . There are of course many forbidden CT transition that give rise to**

**weak bands; these are seldom observed because they are covered up by the**

**strong CT bands, which lie between 400nm corresponds to 25 000 cm\_1; 200nm**

**corresponds to 50 000 cm\_1**



***Ligand to metal ( L***

***M ):* Most of metal complexes had this type of transition**

**which can be expected to be divided to four types of transitions in octahedral**

**configuration. Fig. 2, shows a partial MO diagram for such complexes, and each of**

**transitions shown is a group of transitions, since the excited orbital configuration**

**gives rise to several different of similar but not identical energies.**

**Transition of the *ν1* type will obviously be of lowest energy. Second since the**

***π* and *π\** orbitals involved are both approximately non bonding , they will not vary**

**steeply with M – L distance as the ligand vibrate. The bands for these transitions**

**should be relatively narrow. A third factor that should assist in identifying the *ν1 .***

**Set of bands is that they will be missing whenever the *π\*(t2g* ) orbitals are filled (d *6***

**complexes). The energies for *ν1* will be decrease in the sequence *MCl6, MBr6* and**

***MI6* which is the order of decreasing the ionization potentials( easier oxidizability )**

**of the halogen atoms. As the oxidation state of the metal increase ( easier**

**oxidizability ) like RuCl6-3, RuCl6-2 ,its orbitals should be deeper , thus the transition**

**should go to lower energy.**

**Transition of the *ν2* type should give the lowest energy CT bands in *t2g6***

**complexes like those for PtX6-2 complexes. Since the transition is from a mainly the**

**nonbonding level to a distinctly antibonding one, the bands should be fairly broad.**

**The transition assigned to the *ν2* sets all have half – widths of 2000 cm\_1 to 4000**

**cm\_1. The shift of energy in these bands with change of halogen and change of**

**metal oxidation state are again as expected for L**

**M transitions.**

**Transition of the *ν3* set are all expected to be broad and weak and are not**

**observed. The *ν4* transitions have been observed in a few cases, but in many cases**

**they must lie beyond the range of observation.**



***Fig. 2 Partial MO diagram for octahedral complex***



**In tetrahedral complexes like NiX4-2, CoX4-2 and MnX4-2 a strong L M**

**spectra can be observed and assigned in much the same way as for octahedral**

**complexes. For *d 8* complexes like HgCl 4-2, HgBr4-2 and HgI4-2 a strong CT for L**

**M transition and showed bands at 43,700 , 40,000 and 31,000 cm\_1**

**In the previous lecture Fig. 2 showed the spectrum of [Cr(NH3)6]+3 ,when**

**one NH3 ligand replaced by one weaker ligand (Cl - ) moves the lower energy**

**band to lower energy than that for [CrCl(NH3)5]+2 . That arises because the Cl-**

**ligands have *π* lone pair electrons that are not directly involved in bonding. The**

**band is an example of an LMCT transition in which a lone pair electron of Cl- is**

**promoted into a predominantly metal orbital. The LMCT character of similar**

**bands in is [CrX(NH3)5]+2 confirmed by the decrease in energy in steps equivalent**

**to about 8000 cm\_1 as X is varied from Cl to Br to I .**

***Metal to Ligand( M L ):* A transfer of charge of electrons from metal to ligands**

**is most commonly observed in complexes with ligands that have low lying *π\****

**orbitals, especially carbonyl ( CO ) , cyanide ( CN ) and aromatic ligands ( diimine,,**

**phenanthroline and dithiolene) Fig. 3. If the metal ion have a low oxidation**

**number, in which case the d orbitals will be relatively high in energy, the**

**transition will occur at low energy. A diimine ligand may also be easily**

**substituted into a complex with other ligands that favor a low oxidation state.**

**Two example are , [ W(CO)4(phen)] and [ Fe(CO)3(bipy )] .**

**In the case of octahedral metal carbonyl such as Cr(CO) *6* and Mo(CO)*6* pair**

**of intense bands at 35,800 and 44,500cm\_1 for the former and 35,000 and 43,000**

**cm\_1 for the later which can be assigned to transition from bonding (mainly**

**metals) to the antibonding( mainly ligands)components of the metal ligands *π***

**bonding interactions.**

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***Fig. 3***

