Quadrant II – Transcript and Related Materials

Programme: Bachelor of Science

Subject: Chemistry

Paper Code: CHC 109

Paper Title: Inorganic Chemistry

Unit: Spectra and Magnetic Properties

Module Name: Applications: Ligand field strength, Colour of complexes, Cis – Trans isomerism, Geometry of complexes

Module No: 23

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Notes ------------------

Introduction:

The important applications of interpretation of electronic spectra are as follows:

1)Determination of Ligand field strength

2)Explanation for colour of complexes

3)Distinguish cis and trans isomers of the complex

4)Determination of the geometry of complexes

Ligand field strength

Crystal field splitting depends upon the nature of ligands which are attached to the metal ion in the complex.

Ligands which cause only a small degree of splitting of the 'd' orbitals are termed weak ligands. Ligands which cause a large degree of splitting of the 'd' orbitals are termed strong ligands

The electronic spectra of a series of complexes of the same metal ion with different ligands are examined. It is seen that the position of the absorption band and hence the value of Δ varies with the nature of ligands which are attached to it.

• **Complex**	**$\Delta_{\circ}$ (Kj mol^{-1})**
$[Cr(H_2O)_6]^{+3}$	**213**
$[Cr(NH_3)_6]^{+3}$	**259**
$[Cr(CN)_6]^{-3}$	**314**

The common ligands are arranged in ascending order of their splitting power.

The order remains practically constant for different metals and this order is known as Fajan –Tschida spectrochemical series.The arrangement of the ligands in respect of their field strengths is as follows:

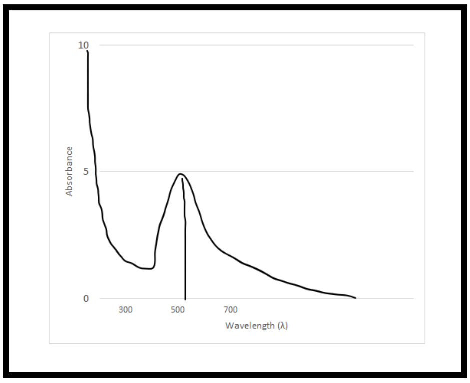
$I^- < Br^- < S^{-2} < Cl^- < NO_3^- < F^- < OH^- <$ oxalate $< H_2O <$ EDTA $< NH_3 <$ en $<$ dipyridine $< CN^- < CO$

Colour of complexes

Electronic spectra also gives explanation for colour of complexes.

Example : $[Ti(H_2O)_6]^{+3}$ ion

The aqueous solution of Ti^{+3} ion is violet. This is because the aqueous solution of titanium (III) contains $[Ti(H_2O)_6]^{+3}$ ion.The absorption spectrum of $[Ti(H_2O)_6]^{+3}$ (see figure) shows that the observed colour arises because of absorption of green portion of incident white light.



Absorption spectrum of $[Ti(H_2O)_6]^{+3}$

This can be explained by the fact that absorption of light of wavelength 500nm causes the promotion of single 'd' electron from lower t_2g to higher eg orbital.

Tetrahedral complexes (of the same ion) can be distinguished from octahedral complexes due to their more intense colour as compared to octahedral complexes.

Example: $[CoCl_4]^{-2}$ is blue while $[Co(H_2O)_6]^{+2}$ is light pink.

This variation can be explained on the basis of selection rules.

Tetrahedral complexes have no centre of symmetry and therefore Laporte selection rule does not apply but it applies to octahedral symmetry.Also, light pink colour of $[Mn (H_2O)_6]^{+2}$ is on basis of spin selection rule

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Cis and trans isomerism

Electronic spectra is used to distinguish cis and trans isomers of the complex

The spectrum of cis and trans isomers of $[Co(en)_2F_2]NO_3$ is shown in figure

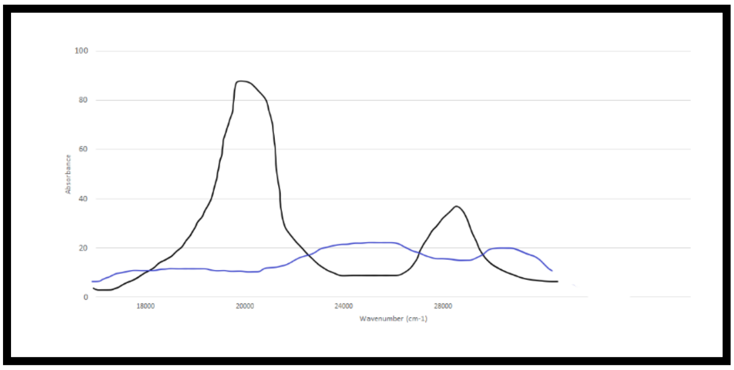
Cis isomer is violet and trans isomer is green .This colour difference can be explained by interpreting the spectrum.

Cis isomer has no centre of symmetry but trans has.Hence absorption band of cis isomer is more intense than that of trans.

The first band of the complex has two maxima in the trans isomer but one in the cis.This is due to to the fact that axial substituents split the octahedral levels of the complex twice in the trans as compared to the cis orientation.

In general ,trans isomer which is centrosymmetric gives less intense bands compared to cis isomer.

Electronic spectrum of cis and trans $[Co(en)_2F_2]NO_3$



Geometry of complexes

The position,intensity and number of bands in the electronic spectra can be used to determine information regarding geometry of complexes.

Tetrahedral complexes do not have centre of symmetry and hence Laporte restriction is not applicable. So, more intense bands are expected from tetrahedral than octahedral complexes of the same metal ion.Also the splitting of 'd' orbitals in tetrahedral field is smaller than in octahedral field.

Hence electronic transition in tetrahedral complexes will involve lower energy transition,sometimes even in infrared region

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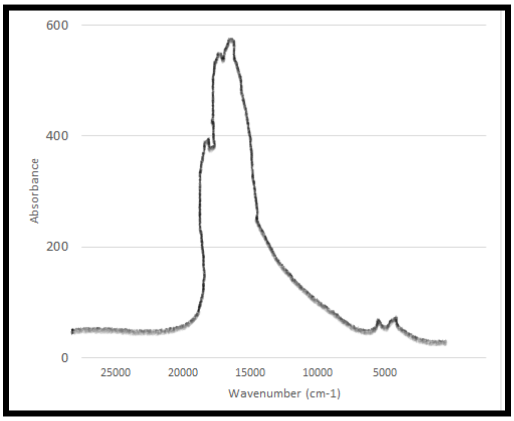
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25000
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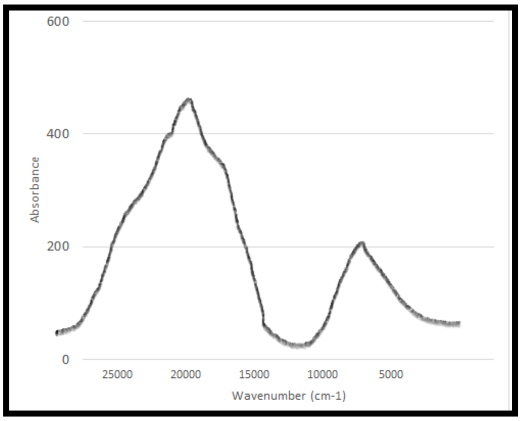
Wavenumber (cm-1)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