

M.Sc. Semester II, Paper: CC-06 (Inorganic Chemistry)

Unit-1 Electronic spectra of transition metal complexes

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The colours of complex compounds are closely related to the magnitude of the spacing between energy levels. Since this spacing between energy levels depends on a number of factors viz. geometry of the complex, nature of ligands, oxidation state of the central metal atom/ion etc. Hence, electronic spectra of complexes can provide valuable information related to bonding and structure of complexes. The number of absorption peaks expected for a given complex can be known by the accurate energy level diagram for a complex and knowing the selection rules governing electronic transitions.

To explain the electronic spectra of complexes generally three types of energy level diagrams are used:

1. Orgel diagram
2. Tanabe-Sugano diagram
3. Correlation diagram.

→ Orgel diagram

Orgel diagram was given by Leslie Orgel. Orgel diagram is a correlation diagram which shows the relative energies of electronic terms in transition metal complexes. It is the simplest among the three diagrams used to explain electronic transitions. It provides a convenient means of ^{predicting} the number of spin allowed absorption bands to expect in a visible spectrum for a complex. It is much simpler because excited state of different multiplicities to that of ground states are excluded and only weak field cases are included. The d^n & d^{10-n} have the same set of Russell-Saunders's terms which are called hole equivalents of one another.

Tetrahedral crystal field splitting is the inverse of the octahedral crystal field. Hence, the Orgel diagram for tetrahedral field are obtained by inverting the splitting pattern of a particular Russell-Saunders's terms of a given d^n ion in octahedral field. Hole formalism indicates an equivalence of d^n electronic configuration with d^{10-n} (p-orbital) configuration.

$$d^n(\text{Oct}) \text{ diagram} = \text{Inverse of } d^{10-n}(\text{Oct}) \text{ diagram}$$

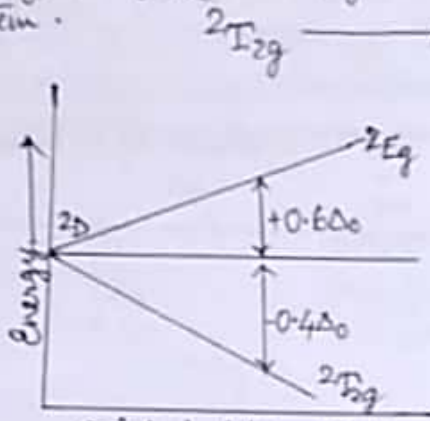
So, $d^2(\text{Oct})$ diagram = inverse of $d^8(\text{Oct})$ diagram = $d^8(\text{tet})$ = $d^2(\text{Oct})$ = inverse of $d^7(\text{Oct})$ = inverse of $d^3(\text{Oct})$ = $d^7(\text{tet})$.

Terms with identical symmetry will mix, with the extent of mixing being inversely proportional to the energy difference between them. The energies of two states deviate from the values would have been in the absence of mixing. The upper level is raised in energy while the lower level falls. For tetrahedral complexes in the absence of mixing the two T_2 terms gradually approach each other as Δ_t increases which is just opposite to that of octahedral complexes. As a result, the extent of mixing is greater for tetrahedral complexes.

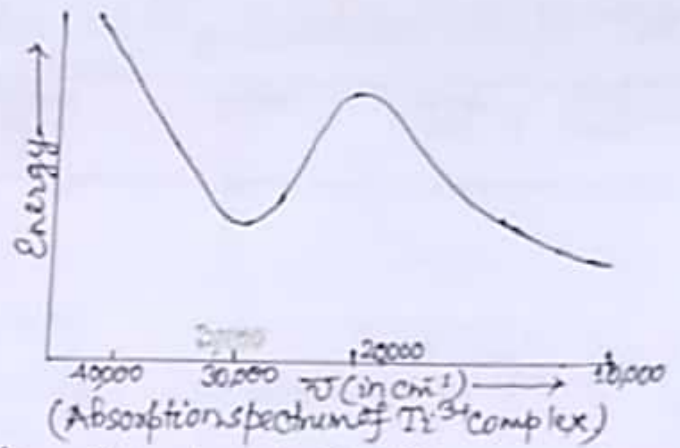
* Discussion of spectra of Octahedral Complexes: (i) d^1 system or Ti^{3+} salt - The spectroscopic ground state term of Ti^{3+} ion (d^1 system) is 2D which splits into T_{2g} & E_g . Two arrangements of electron (t_{2g}^1) & (e_g^0) are possible, the corresponding crystal field terms being-

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${}^2T_{2g}$ & 2E_g . The T_{2g} state lies $0.4\Delta_0$ below and the E_g state $0.6\Delta_0$ above, the values of the energies of the five d-orbitals in a spherical field. The value of Δ_0 corresponds to the promotion of an electron from a t_{2g} orbital to an e_g orbital. In d^1 system, the ground state $(t_{2g})^3(e_g)^0$ is triply degenerate, it can be $(d_{xy})(d_{yz})(d_{xz})(e_g)^0$; $(d_{yz})(d_{xz})(d_{xy})(e_g)^0$ or $(d_{xy})(d_{yz})(d_{xz})(e_g)^0$ and the excited state $(t_{2g})^2(e_g)^1$ is doubly degenerate, it can be $(t_{2g})^0(d_{xy})^2(d_{z^2})^0$ or $(t_{2g})^0(d_{xy})^0(d_{z^2})^2$. A single electronic band is expected for d^1 system.



Octahedral ligand field
(Orgel diagram of d^1 system/ Ti^{3+} ion)

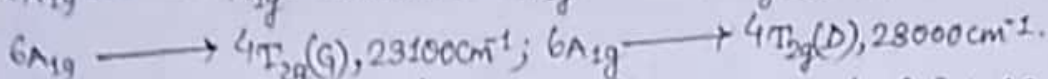
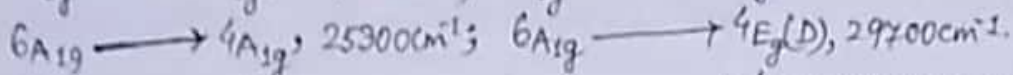
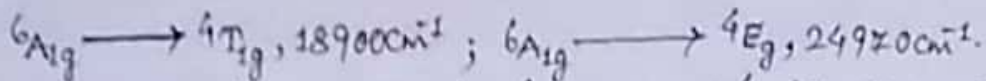


Magnitude of Δ_0 depends on the nature of ligands and affects the energy of transition, and hence λ_{max} . As Δ_0 increases, the energy for the transition ($T_{2g} \rightarrow E_g$) in absorption and ($E_g \rightarrow T_{2g}$) in emission increases. Thus, the peak occurs at 13000 cm^{-1} in $[TiCl_6]^{3-}$, 18900 cm^{-1} in $[TiF_6]^{3-}$, 20300 cm^{-1} in $[Ti(H_2O)_6]^{3+}$ and 22300 cm^{-1} in $[Ti(CN)_6]^{3+}$. The amount of splitting caused by various ligands is related to their position in the spectrochemical series. $[Ti(H_2O)_6]^{3+}$ gives solutions of purple colour which is complementary colour of green as the energy 57 kcal/mole (20300 cm^{-1}) is equal to the energy difference (Δ_0) between t_{2g} & e_g levels.

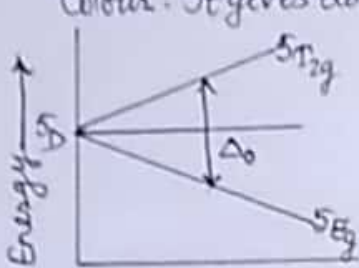
(ii) d^5 system/ Mn^{2+} complexes: In high spin octahedral complexes formed with weak ligands, e.g. $[MnF_6]^{4-}$ five unpaired electrons are present with parallel spins. Any electronic transition within the d level will need a reversal of spins and hence is spin forbidden transitions, therefore absorption bands will be extremely weak. This accounts for the pale pink colour of $Mn(II)$ salts. The ground state term of d^5 system is 6S .

In Orgel diagram, only the quartet terms 4G , 4F , 4D & 4P are included, because transitions to the other states are doubly spin forbidden. The ground state 6S is not split and transforms into the ${}^6A_{1g}$ state which are also horizontal lines on the diagram. So their energies are independent of the crystal field strength. $10Dq$ varies about a mean value. Hence, the absorption bands are broad. The degree of the broadening of the peaks is related to the slope of the lines on the Orgel diagram. Since the slope of the ground state term, ${}^6A_{1g}$ is zero and the slopes of the ${}^4E_g(G)$, ${}^4A_{1g}$, ${}^4E_g(D)$ and ${}^4A_{2g}(F)$ terms are also zero, transitions from the ground state to these four states should give rise to sharp peaks. The bands are assigned as follows:

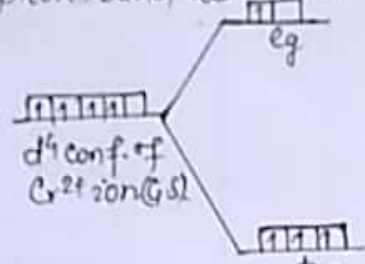
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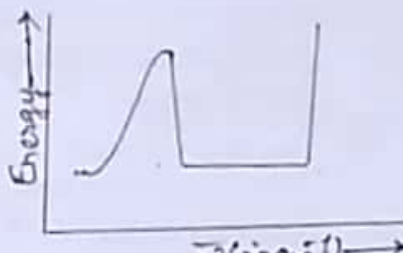
(D) d^1 system (High spin): d^1 system or Cr^{2+} ion in octahedral field (high spin) may be considered as having one hole in the upper e_g level. The spectrum of d^1 system e.g. $[\text{CrCl}_6]^{4-}$ shows the expected single absorption band with a maximum at $10,200\text{cm}^{-1}$ with no apparent splitting. It also give one absorption band in the electronic spectrum, corresponding to transition: $5E_g \rightarrow 5T_{2g}$. Its solution is of light blue colour. It gives absorption band at $\sim 15000\text{cm}^{-1}$.



Energy level splitting of d^1 system



In octahedral ligand field (Strong).

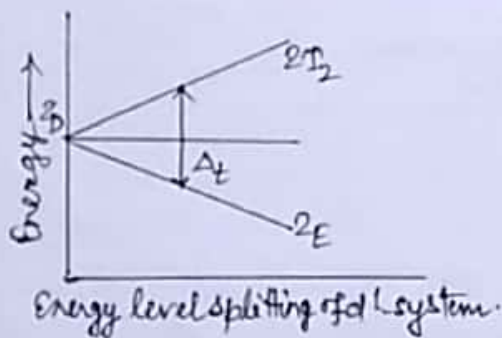


(Absorption spectrum of d^1 system)

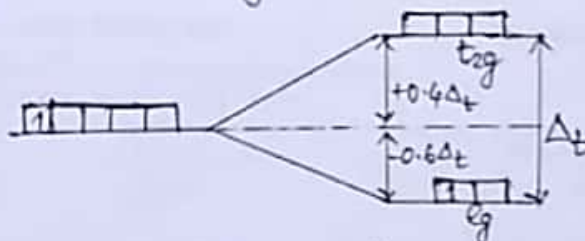
Spectra of Tetrahedral Complexes: Tetrahedral complexes show intense bands due to d-d mixing. The tetrahedral complexes have no centre of symmetry hence d-d transitions are Laporte's allowed transition and a change in the dipole moment will take place in d-d transitions. The order of splitting in tetrahedral complexes are opposite to that of octahedral complexes but the splitting pattern of the orbitals is same as in octahedral field.

(i) d^1 system: In d^1 system, the ground state is $2D$ splits up into $2T_2$ & $2E$ states.

The ground state configuration is shown as $e_g^1 t_{2g}^0$ and the two electronic arrangements can be given to the ground state $(d_{x^2-y^2})^1 d_{z^2}^0 t_{2g}^0$ and $(d_{x^2-y^2})^0 d_{z^2}^1 t_{2g}^0$ and the ground state is $2E$. The configuration of excited state $e_g^0 d_{xy}^1 d_{yz}^1 d_{zx}^1$, $e_g^0 d_{xy}^1 d_{yz}^0 d_{zx}^1$ and $e_g^0 d_{xy}^0 d_{yz}^1 d_{zx}^1$, and the excited state is T_2 state. The electronic transition can be expressed as $2E \rightarrow 2T_2$ corresponding to Δ_t .



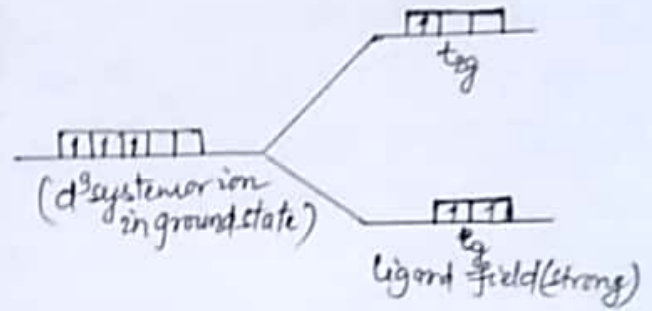
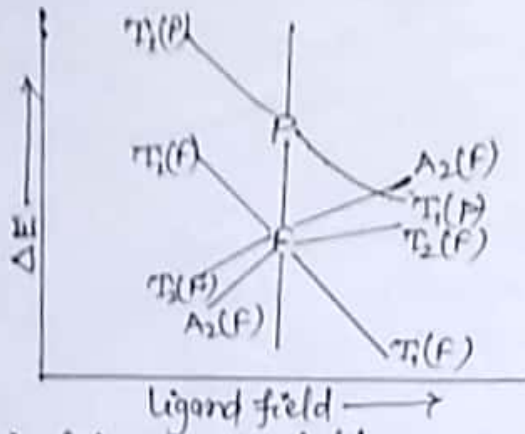
Energy level splitting of d^1 system.



(Tetrahedral ligand field)

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(i) d^3 system: In d^3 system, the ground state is 4F and another state of same multiplicity is 4P . The ground state configuration is $e_g^2 t_{2g}^1$. Three electronic arrangements can be given as $e_g^2 d_{xy}^1 d_{xz}^0 d_{yz}^0$, $e_g^2 d_{xy}^0 d_{yz}^1 d_{xz}^0$ and $e_g^2 d_{xy}^0 d_{yz}^0 d_{xz}^1$ which correspond to ${}^4T_1(F)$. Three transitions are possible in d^3 system are:



Limitations of Orgel diagram:

Orgel diagram is useful for interpreting electronic spectra, but they suffer from the following limitations:

1. They treat only high spin (weak ligand field) cases.
2. They are useful for spin allowed transitions when the number of observed peaks is greater than or equal to the number of empirical parameters. It is possible to add low spin states to an Orgel diagram.