Quadrant I – Notes

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Selection Rules for Electronic Transitions in complexes

Transition metal complexes show variety of colours based on transitions taking place. The electronic transitions in complexes are governed by two sets of rules.

- Spin selection rule
- The Laporte orbital rule

Spin selection rule

Transitions in which there is change in the number of unpaired electrons in going from a lower to a higher energy state are referred as spin or multiplicity forbidden.

This means that transitions to only those excited state are to be considered which have the same spin multiplicity as the ground state.

$\Delta s = 0$ Spin allowed transitions

$\Delta s \neq 0$ Spin forbidden transitions

The Laporte orbital rule:

The transitions which involve a change in the subsidiary quantum number ie $\Delta l = \pm 1$ are Laporte allowed transitions.

The transitions which do not involve a change in the subsidiary quantum number ie. $\Delta l = 0$ are called Laporte forbidden transitions.

This rule suggests that transition metal complexes should not give d-d transitions and show colour.

Although transition take place with the help of slight relaxation in Laporte rule.

The intensity of such transitions is very weak.

Eg. $[Co(NH_3)_5Cl]$

This has irregular octahedral structure and do not possess a centre of symmetry. d –d transitions with varying amounts of p –character take place giving colour to the compound.

i) If the structure is slightly distorted, the centre of symmetry is destroyed and then mixing of d and p –orbital of the metal ion occurs. In such cases, the transitions are no more d-d transitions.

$[MnCl_4]^{2-}$ and $[MnBr_4]^{2-}$ are tetrahedral complexes which do not possess a centre of symmetry. Hence intense transitions are observed that results in deep colouration.

Mixing of d and p orbitals does not occur in case of perfectly octahedral complexes like $[Co(NH_3)_6]^{3+}$ and complex appear light coloured.

ii) A complex with perfect octahedral structure also exhibits absorption spectrum because the bonds in transition metal complexes are not rigid but undergo vibrations that temporarily change the centre of symmetry. The vibrations continue and the molecule possess distorted octahedral symmetry so that mixing of d and p orbital occur and therefore low intensity is observed.

These transitions are called vibronically allowed transitions and the effect is vibronic coupling.

In $[Mn(H_2O)_6$ complex, all transitions are spin multiplicity forbidden and Laporte forbidden but the complex ion is pale pink in colour. This is explained by vibronic coupling with very low intensity transitions.

Laporte allowed transitions are very intense while Laporte forbidden transitions are of weak intensity.