M.Sc. Semester-II, Paper: CC-6 (Inorganic Chemistry)

Unit: 1 Electronic spectra of Transition metal Complexes (Contd.)

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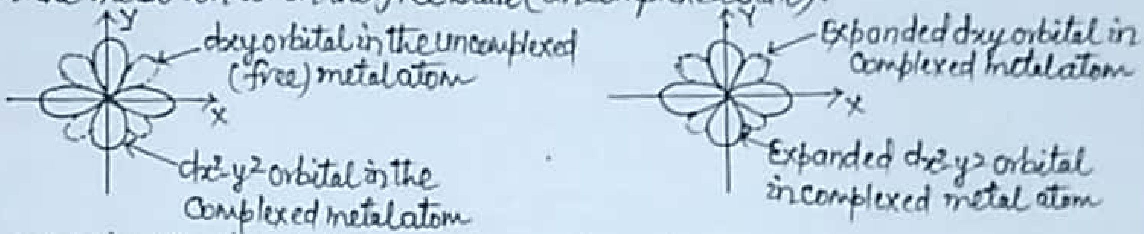
⇒ Nephelauxetic Effect

Nephelauxetic effect is indirect evidence of the existence of covalent bonding character in metal ligand bond in complexes. Electrons present in partially filled d-orbital of a metal ion repel one another. This repulsion is called d-d inter electronic repulsion. It has been found experimentally that when a metal ion gets coordinated with the ligands and forms a complex, the repulsion existing between d-electrons of the complexed metal ion becomes less than when the metal ion is in the free state (uncomplexed state).



Due to the expansion of metal d-orbitals into the region of ligand orbitals, the overlap of metal d-orbitals with ligand orbital takes place and metal-ligand bonds acquire some covalent character in metal-ligand bond.

Thus, complexed metal d-electrons spend sometime on the ligands, i.e., metal d-electrons are partially delocalised into ligand orbitals. This effect of ligands in expanding metal d-electron cloud is known as Nephelauxetic (a Greek word meaning 'cloud expanding') effect. The capability of a ligand to expand metal d-electron cloud differs from one ligand to the other.

⇒ Nephelauxetic ratio (β)

Due to the overlap of metal ion d-orbitals with the ligand orbitals, delocalisation of d-electrons from the metal ion to the ligand occurs. The extent of delocalisation of d-electrons is called Nephelauxetic ratio, and expressed by symbol 'β'. It is the ratio of the inter-electronic repulsion Racah parameter of the complexed metal ion (B′) to that of the free metal ion (B).

$$\text{Thus, Nephelauxetic ratio}(\beta) = \frac{\text{Inter-electronic repulsion Racah parameter of the complexed metal ion}}{\text{Inter-electronic repulsion Racah parameter of the free metal ion}}$$

$$\text{Or, } \beta = \frac{B'}{B} \quad \text{——(1)}$$

When a metal ion gets complexed, the size of d-orbitals of the metal ion increases. Due to this increase in the size of d-orbitals of the metal ion, the inter electronic repulsion amongst d-electrons of the complexed metal ion is decreased. Therefore, the value of B′ is always less than that of B. Consequently, β is always less than 1.

The approximate value of Racah parameter of a metal ion present in a complex ion (i.e., value of B′) is given by $B' = B(1 - h_M k_L) \times 10^3$ ——(2)

(Where B = Racah parameter for the free metal ion, h_M = Arbitrary parameter for the free metal ion, k_L = Arbitrary parameter for the ligands present in the complex ion.)

Empirical values of h_M for different metal ions/cations are given below:

Metal ion	Co^{2+}	Co^{3+}	Cr^{3+}	Fe^{3+}	Mo^{3+}	Ni^{2+}
h_M value	0.23	0.35	0.21	0.24	0.07	0.12

k_L values (empirical) for different ligands are given below:

Ligand	$6CN^-$	$6Br^-$	$6Cl^-$	$6OH^-$	3en	$6H_2O$
k_L value	—	2.3	2.0	2.0	1.5	1.4

→ Nephelauxetic Series

A series of ligands in the decreasing order of β-values/in the increasing order of their ability to expand metal d-electron cloud is called Nephelauxetic (Greek word, meaning cloud expanding) Series. The series is as follows:

$$F^- > H_2O > urea > NH_3 > C_2O_4^{2-} \sim en \sim NCS^- > Cl^- > CN^- > Br^- > I^-$$

The above order is independent of the nature of the metal ion. In this series as we move from left to right (i.e., F^- to I^-), the ability of the ligands to expand metal d-electron cloud in the region of ligand orbitals increases and hence delocalisation of metal d-electrons into ligand orbitals also increases, which increases covalent character of metal-ligand bond in complexes. Thus, covalent character in M-I bond in iodo complex of a given metal (M) is more than that of M-F bond in fluoro complex of the same metal.

This series is valid for most of the metal ions. The decreasing order of β values from left to right in the series indicates that the complexes having low value of β are covalent in nature.

→ Calculation of Δ_o, Dq, Racah parameter (B') & Nephelauxetic ratio (β): Consider $[Ni(H_2O)_6]^{2+}$ complex ion,

Racah parameter of a metal ion in a complex ion $(B') = B(1 - h_M k_L) \times 10^3$

for Ni^{2+}, B = Racah parameter of free Ni^{2+} ion $= 1080\ cm^{-1}$, $h_M = 0.12$, $k_L = 1.4$

$\therefore B' = 1080(1 - 0.12 \times 1.4) \times 10^3 = 1080(1 - 0.168) \times 10^3 = 1080 \times 0.832 \times 10^3 = 898.56 \times 10^3\ cm^{-1}$.

Nephelauxetic ratio $(\beta) = \frac{B'}{B}$ $\quad \therefore \beta = \frac{898.56 \times 10^3}{1080} = 0.832 \times 10^3 = 832.$

* Crystal field stabilization energy for Octahedral Complexes, $(CFSE)_{oct} = \Delta_o = +0.6 n_{eg} - 0.4 n_{t_{2g}}$

(where n_{eg} = number of electrons in eg set, $n_{t_{2g}}$ = number of electrons in t_{2g} set of orbitals)

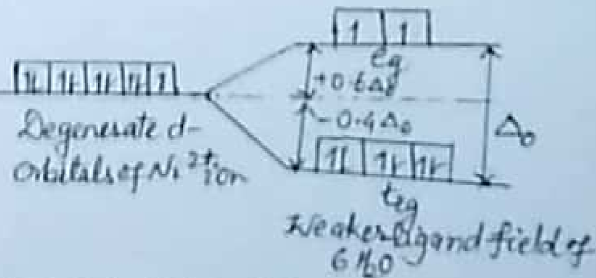
$\Delta_o = 10 D_q$ & $\Delta_t = 4/9 \Delta_o$ or $4.5 D_q$.

$[Ni(H_2O)_6]^{2+}$ has Ni^{2+} ion (d^8 system)

Ele. Conf. of Ni^{2+} in the complex ion: $t_{2g}^6 e_g^2$

Here $n_{t_{2g}} = 6$, $n_{eg} = 2$

$(CFSE)_{oct}, \Delta_o = +0.6 n_{eg} - 0.4 n_{t_{2g}}$



∴ Change of energy in $\Delta_o = +0.6 \times 6 - 0.4 \times 2 = 3.6 - 0.8 = 2.8$. (for $t_{2g}^6 e_g^2$ conf.)

Change of energy in $D_q = 2.8 \times 10 = \underline{28}$.

→ Assignments for Students:—

1. Calculate CFSE in Δ_o & D_q for $[Co(NH_3)_6]^{3+}$ ion.
2. Calculate the value of Racah parameter (B') & Nephelauxetic ratio (β) for $[Fe(en)_3]^{3+}$.

Given: Racah parameter of the free Fe^{3+} ion = cm^{-1}, $h_M = 0.24$, $k_L = 1.5$.