

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

Unit-1 Electronic Spectra of Transition metal Complexes

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→ Spectrochemical Series

Complex ions or compounds having the same central metal atom/ion and geometry but having ligands of different crystal field splitting strengths show that the position of absorption peaks/values of crystal field stabilization energy (Δ) change with the magnitude of crystal field splitting power of the ligands. The ligands (e.g. CN^-) having splitting power, i.e., stronger ligands to split the d-orbitals of the central metal atom/ion have higher of Δ (CFSE) while, ligands (e.g. I^-) having lower splitting power, i.e., weaker ligands have lower value of Δ .

The ligands can be arranged in a series on the basis of their increasing splitting power, i.e., Δ values, called spectrochemical series. Thus, "the arrangement of ligands in order of their increasing CFSE (Δ) values is called spectrochemical series".

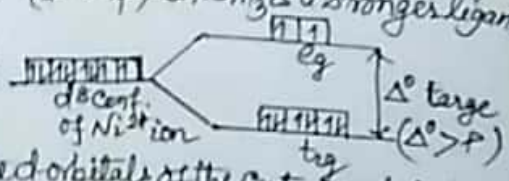
The series is given below: $\text{I}^- < \text{Br}^- < \text{NO}_3^- < \text{Cl}^- < \text{SCN}^- < \text{F}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{ethan gly} < \text{py} < \text{NH}_3 < \text{en} < \text{H}(\text{lig}) < \text{bpy} \sim \text{Ophen} < \text{NO}_2^- < \text{CN}^- < \text{CO}$.

The order of field strength of the ligands is independent of the nature of metal ion and the geometry of the complex. For example,

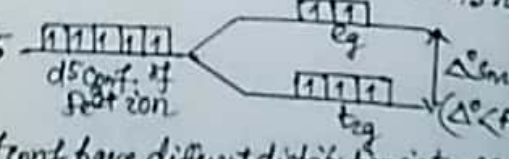
Octahedral complexes:	$[\text{NiBr}_6]^{4-}$	$[\text{NiCl}_6]^{4-}$	$[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$	$[\text{Ni}(\text{NH}_3)_6]^{2+}$	$[\text{Ni}(\text{en})_3]^{2+}$
Δ value (in cm^{-1})	7000	4200	8500	10800	14500
Ligand field strength	: $\text{Br}^- < \text{Cl}^- < \text{H}_2\text{O} < \text{NH}_3 < \text{en}$ (Strength of ligands increases)				

→ Applications: This series is applied in the following.

1. To decide distribution of d^x electrons in t_{2g} & e_g orbitals in the complex: Ligands situated RHS of the series, i.e. stronger ligands (e.g. NH_3 , en , NO_2^- , CN^-) split the d-orbitals of the central metal atom/ion have higher CFSE (Δ) values. The energy difference between t_{2g} & e_g orbitals is relatively high or large and hence distribution of d^x electrons in t_{2g} & e_g orbitals does not take place in accordance with Hund's rule. For example, $[\text{Ni}(\text{NH}_3)_6]^{2+}$ has Ni^{2+} (d^8 conf.) ion. NH_3 is a stronger ligand, so Δ value is large and hence distribution of d^8 electrons in t_{2g} & e_g orbitals does not take place in accordance with Hund's rule, i.e., electronic conf. is $t_{2g}^6 e_g^2$.



On the other hand, weaker ligands (e.g. F^- , H_2O) split the d-orbitals of the central metal atom/ion have lower Δ values, i.e., energy difference between t_{2g} & e_g orbitals is relatively small and hence distribution of d^x electrons in t_{2g} & e_g orbitals take place in accordance with Hund's rule. For example $[\text{FeF}_6]^{3-}$ has Fe^{3+} (d^5 conf.) ion. F^- is a weaker ligand, so Δ value is small and hence distribution of d^5 electrons in t_{2g} & e_g orbitals take place in accordance with Hund's rule, i.e., electronic conf. is $t_{2g}^3 e_g^2$. It is noted d^4 & d^9 confs. have different distribution in t_{2g} & e_g .

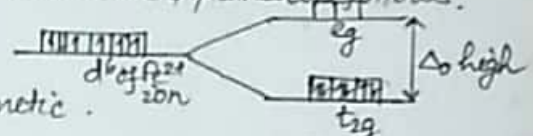


2. To decide high spin & low spin complexes: Ligand on RHS of the series are stronger (higher Δ values), so d^x electrons distribution/ele. conf. does not follow Hund's rule. Hence, the complexes are

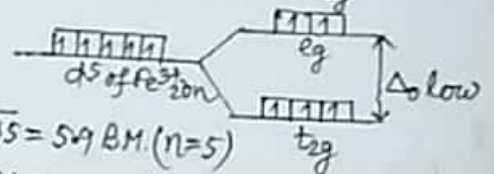
low spin or spin paired (less number of unpaired electrons). On the other hands, complexes with weaker ligands (LHS of the series) have low Δ^0 values. So distribution of d^x electrons follows Hund's rule. Hence, the complexes are high spin or spin free (more unpaired electrons). In above examples, $[\text{Ni}(\text{NH}_3)_6]^{2+}$ is low spin complex ion while $[\text{FeF}_6]^{3-}$ is high spin complex ion.

3. To decide magnetic properties of complexes: Magnetic properties of the complexes are mainly paramagnetism and diamagnetism. Paramagnetism arises due to presence of one or more unpaired electron in the complexes. It is expressed in term of magnetic moment (μ_s). $\mu_s = \sqrt{n(n+2)} \text{ BM}$ (where n = number of unpaired electrons). Diamagnetic substances have only paired electrons, i.e; $n=0$ ($\mu_s=0$). Complexes with stronger ligands (i.e; high Δ values) are diamagnetic or low paramagnetic (μ_s value). On the other hand, complexes with weaker ligands (i.e; low Δ values) are paramagnetic. For example, $[\text{Fe}(\text{CN})_6]^{4-}$ is diamagnetic while $[\text{FeF}_6]^{3-}$ is paramagnetic. This can be explained as follows:

(i) $[\text{Fe}(\text{CN})_6]^{4-}$ has Fe^{2+} ion (d^6 conf. $t_{2g}^6 e_g^0$) and stronger ligand CN^- . Since all the electrons are paired in t_{2g} orbitals, so it is diamagnetic.



(ii) $[\text{FeF}_6]^{3-}$ has Fe^{3+} ion (d^5 conf. $t_{2g}^3 e_g^2$) and weaker ligand F^- . Here five unpaired electrons (two in e_g & three in t_{2g} orbitals) present in Fe^{3+} or $[\text{FeF}_6]^{3-}$ ion, so it is paramagnetic. $\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.9 \text{ BM}$ ($n=5$)

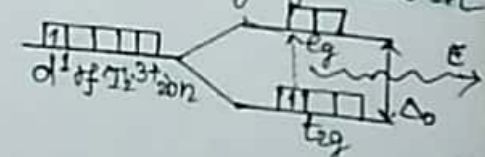


4. To explain colour of the complexes: The absorption of light by coloured complexes takes place in the visible region (4000-7000 Å). The absorbed visible radiation excites electron from the lower energy t_{2g} orbitals to higher energy e_g orbitals in octahedral complexes. Colour (λ_{trans}) of the complex depends upon Δ_0 value (i.e; crystal field splitting power of ligand). Hence, for colour of complex, $\lambda_{\text{trans}} (\text{Colour}) \propto \Delta_0 (\text{in cm}^{-1})$

The excitation energies for the complexes: $[\text{Co}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Co}(\text{NH}_3)_6]^{3+}$ and $[\text{Co}(\text{CN})_6]^{3-}$ follows the order: $[\text{Co}(\text{H}_2\text{O})_6]^{3+} < [\text{Co}(\text{NH}_3)_6]^{3+} < [\text{Co}(\text{CN})_6]^{3-}$; the CFSE (Δ_0) of the ligands (H_2O , NH_3 & CN^-) is in the order: $\text{H}_2\text{O} < \text{NH}_3 < \text{CN}^-$.

Consider a case of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ complex ion, in which Ti^{3+} ion has only one electron in 3d ($t_{2g}^1 e_g^0$) orbitals. Its spectrum shows a single absorption peak at about 5000 Å which corresponds to an energy of about 240 kJ mol^{-1} . $[E = h\nu = hc/\lambda = (6.02 \times 10^{23}) \times (6.62 \times 10^{-34}) \times (3 \times 10^8) / (5000 \times 10^{-10})] = 239.1 \text{ kJ mol}^{-1}$

Energy (E) is greater than Δ_0 value and is sufficient to excite the electron from t_{2g} to e_g orbital. In this case, green and yellow portions of the light are absorbed and the solution of the complex acquires purple colour which is a complementary colour of the radiation absorbed.



Assignments for students:

- Write the distribution of electrons in t_{2g} & e_g for following ions in octahedral complexes: & magnetic property
 - d^4 (strong field)
 - d^6 (weak field)
 - d^7 (strong field)
- Explain: $[\text{CoF}_6]^{3-}$ is paramagnetic but $[\text{Co}(\text{NH}_3)_6]^{3+}$ is diamagnetic
- Explain: $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ is blue coloured.