

❖ Spectrochemical and Nephelauxetic Series

➤ The Spectrochemical Series

The spectrochemical series is a list of ligands arranged on basis of ligand strength and a list of metal ions based on oxidation number, group and its identity.

In crystal field theory, ligands change the difference in energy between the d -orbitals (Δ) called the ligand-field splitting parameter or crystal-field splitting parameter for ligands, which is primarily reflected in differences in color of similar metal-ligand complexes. However, there are many ligands which do not form complexes with a particular metal ion and the vice-versa is also true. It clearly means that the value of crystal field splitting energy for these complexes cannot be calculated experimentally. Therefore, an empirical method must be used to find out their Δ values. In this method, two empirical parameters have been suggested for different metal ions and ligands.

Table 12. Values of parameters g and f for different metal centers and ligands.

Metal ion	g	Ligands	f
Co^{2+}	9.3	3acac	1.21
Co^{3+}	19.0	$6\text{H}_2\text{O}$	1.00
Cr^{3+}	17.0	$6\text{CH}_3\text{COO}^-$	0.96
Cu^{2+}	12.0	3en	1.28
Fe^{2+}	10.0	6OH^-	1.70
Mn^{2+}	8.5	6Cl^-	0.80
Ni^{2+}	8.9	6F^-	0.90

Now, on the basis of experimental and empirical results, not only the metal ions but also the ligands can be arranged in the increasing or decreasing order of Δ -values. The empirical formula to calculate the magnitude of crystal field splitting energy is given below.

$$\Delta_o = f \times g \times 10^3 \text{ cm}^{-1}$$

i) For $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$

$$\Delta_o = 8.9 \times 1.00 \times 10^3 \text{ cm}^{-1}$$

$$\Delta_o = 8900 \text{ cm}^{-1}$$

This value is pretty close to what has been observed experimentally (8700 cm^{-1}).

ii) For $[\text{Co}(\text{en})_3]^{3+}$

$$\Delta_o = 19 \times 1.28 \times 10^3 \text{ cm}^{-1}$$

$$\Delta_o = 24320 \text{ cm}^{-1}$$

This experimental value of Δ for $[\text{Co}(\text{en})_3]^{3+}$ is 23000 cm^{-1} which is pretty much comparable.

1. Spectrochemical series of ligands: The proposal of the spectrochemical series was first given in the year of 1938 by analyzing the results of UV-visible absorption spectra of cobalt complexes. A simple spectrochemical series ordering of ligands from small Δ to large Δ is given below.

$\text{O}_2^{2-} < \text{I}^- < \text{Br}^- < \text{S}^{2-} < \text{SCN}^-$ (S-bonded) $< \text{Cl}^- < \text{N}^{3-} < \text{F}^- < \text{NCO}^- < \text{OH}^- < \text{C}_2\text{O}_4^{2-} \approx \text{H}_2\text{O} < \text{NCS}^-$ (N-bonded) $< \text{CH}_3\text{CN} < \text{py}$ (pyridine) $< \text{NH}_3 < \text{en}$ (ethylenediamine) $< \text{bipy}$ (2,2'-bipyridine) $< \text{phen}$ (1,10-phenanthroline) $< \text{NO}^{2-} < \text{PPh}_3 < \text{CN}^- < \text{CO}$

Ligands placed on the left side of this spectrochemical series are usually considered as weak-field ligands and cannot cause the electron-pairing within $3d$ shell and thus form spin-free octahedral complexes. On the other hand, ligands lying at the right end are stronger ligands and form spin-paired octahedral complexes due to forcible pairing of electrons within $3d$ level and therefore are called low spin ligands. However, it should also be noted that the spectrochemical series is definitely backward from what it should be for a reasonable prediction based on the assumptions of crystal field theory. This deviation from crystal field theory highlights the reliability of the main assumption crystal field theory's that purely ionic bonds exist between metal and ligand. The order of the spectrochemical series can be obtained from the understanding that ligands are frequently classified by their donor or acceptor abilities.

Some, like NH_3 , are σ -bond donors only, with no orbitals of appropriate symmetry for π -bonding interactions. Bonding by these ligands to metals is relatively simple, using only the σ -bonds to create relatively weak interactions. Another example of a σ -bonding ligand would be ethylenediamine, however, ethylenediamine has a stronger effect than ammonia, generating a larger crystal field split, Δ . Ligands that have filled p -orbitals are potentially π -donors. These types of ligands tend to donate these electrons to the metal along with the σ bonding electrons, exhibiting stronger metal-ligand interactions and an effective decrease of Δ . Most halide ligands, as well as OH^- and H_2O , are primary examples of π -donor ligands. When ligands have vacant π^* and d orbitals of suitable energy, there is the possibility of π -backbonding, and the ligands may be π -acceptors. This addition to the bonding scheme increases Δ . Ligands that do this very effectively include CN^- , CO and many others.

2. Spectrochemical series of metals: Like the ligands, different metal ions can also be ordered in increasing Δ , and this order is independent of the identity of the ligand to a large extent.

$\text{Mn}^{2+} < \text{Ni}^{2+} < \text{Co}^{2+} < \text{Fe}^{2+} < \text{V}^{2+} < \text{Cu}^{2+} < \text{Fe}^{3+} < \text{Cr}^{3+} < \text{V}^{3+} < \text{Co}^{3+}$

In general, it is almost impossible to claim whether a given ligand will exert a strong or a weak field on a given metal ion. Nevertheless, if we consider the metal ion, it has been observed that the magnitude of ligand field splitting energy increases with increasing oxidation number, and also as we move down the group.

➤ **The Nephelauxetic Series**

The nephelauxetic series is a list of ligands or metal ions ordered on the basis of the strength of their nephelauxetic effect.

In the inorganic studies, the term “nephelauxetic effect” is very frequently used for transition metal complexes. This refers to a decreasing Racah parameter (B), a measure of inter-electronic repulsion, that occurs when a free transition-metal ion forms a complex with different types of ligands. The label "nephelauxetic" is for cloud-expanding in the Greek language. The presence of the nephelauxetic effect brings out the drawbacks of crystal field theory, as this suggests a somewhat covalent character in the metal-ligand bonding.

The declining value of the Racah parameter hints that in a metal complex, there is less repulsion between the two electrons in a given doubly occupied metal d -orbital than what is in the free ion counterpart, M^{n+} ; which consecutively implies that the orbital size is larger after complexation. Two reasons for electron-cloud-expansion effect may be given; one is that the effective positive charge on the metal is reduced by any negative charge on the ligands, the d -orbitals can expand a slight manner; the second is the considers the overlapping with ligand orbitals and creation of covalent bonds increases the size of the orbital.

The reduction of B from its free ion value is normally reported in terms of the nephelauxetic parameter, β , as:

$$\beta = \frac{B'(\text{Complex})}{B(\text{Free ion})}$$

Moreover, it is also observed experimentally that the magnitude of the nephelauxetic parameter always follows a certain order with respect to the nature of the ligands attached. However, there are many ligands which do not form complexes with a particular metal ion and the vice-versa is also true. It clearly means that the value of the Racah parameter for these complexes cannot be calculated experimentally. Therefore, an empirical method must be used to find out their B values. In this method, two empirical parameters have been suggested for metal ions and ligands.

Table 13. Values of parameters k and h for different metal centers and ligands.

Metal ion	k	Ligands	h
Co^{2+}	0.24	6CN^-	2.0
Co^{3+}	0.35	3en	1.5
Cr^{3+}	0.21	$6\text{H}_2\text{O}$	1.0
Mn^{2+}	0.07	6NH_3	1.4
Ni^{2+}	0.12	6F^-	0.8

The empirical formula to calculate the magnitude of the Racah parameter for any metal ion in complexation is given below.

$$B' = B(1 - kh) \text{ cm}^{-1}$$

Where, B and B' are the Racah parameters for free ion and metal center in complexation, respectively.

i) For $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$

$$B' = 1080(1 - 0.12 \times 1.0) \text{ cm}^{-1}$$

$$B' = 950 \text{ cm}^{-1}$$

This value is pretty close to what has been observed experimentally (905 cm^{-1}).

ii) For $[\text{Co}(\text{en})_3]^{3+}$

$$B' = 1400(1 - 0.35 \times 1.5) \text{ cm}^{-1}$$

$$B' = 665 \text{ cm}^{-1}$$

This experimental value of B for $[\text{Co}(\text{en})_3]^{3+}$ is 568 cm^{-1} .

The values of Racah parameter (B) for transition metal ion in the gaseous state can be noted from the table given below.

Table 14. Racah parameters for different free transition metal atoms or ions.

Metal	M^0	M^{1+}	M^{2+}	M^{3+}	M^{4+}
Ti	560	681	719	-	-
V	579	660	765	860	-
Cr	790	710	830	1030	1040
Mn	720	872	960	1140	-
Co	789	879	1117	-	-
Ni	1025	1038	1080	-	-
Cu	-	1218	1239	-	-
Fe	805	870	1059	-	1144

Now, on the basis of experimental and empirical results, not only the metal ions but also the ligands can be arranged in the increasing or decreasing order of β -values.

1. Nephelauxetic series of ligands: The list is shown below list commons ligands (with increasing nephelauxetic effect):



Although parts of this series may seem quite similar to the spectrochemical series of ligands, that is not true. for instance; the fluoride, ethylenediamine and cyanide seem to occupy almost similar positions; Some other ligands such as chloride, iodide and bromide, are arranged very differently. Roughly, we can say that the ordering reflects the capability of the ligands to form better covalent bonds with metals; means ligands at the end of the series i.e. with large nephelauxetic effect have better tendency to form covalent bond than the ligands present at the start of the series.

2. Nephelauxetic series of metal ions: The nephelauxetic effect does not only depend upon the ligand type but also upon the central metal ion. These too can be arranged in order of increasing nephelauxetic effect as follows:



It is obvious that as the oxidation number for the metal ion increases, the nephelauxetic effect also increases.

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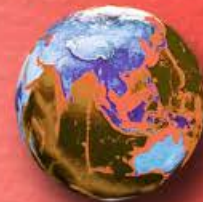
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