CHAPTER V

TETRAD EFFECT IN THE BINARY AND MIXED LIGAND COMPLEXES
1. Tetrad Effect in Lanthanides

Some properties of Ln(III) cations do not vary smoothly over the Ln(III) series. The variation profiles usually show a discontinuity at Gd(III) (4f$^7$ configuration or half-filled 4f shell); minor discontinuities may be observed at Nd(III) - Pm(III) (4f$^3$ - 4f$^4$ configuration or one-fourth filled 4f shell) and at Ho(III) - Er(III) (4f$^{10}$ - 4f$^{11}$ configuration or three-fourth filled 4f shell) also. These discontinuities divide the entire Ln(III) series into four segments or 'tetrads' f$^0$-f$^3$, f$^4$-f$^7$, f$^7$-f$^{10}$ and f$^{11}$-f$^{14}$. This tetradic phenomenon has, therefore, been called 'tetrad effect' or 'double double effect'. Earlier the term 'Gd-break' was used to designate the discontinuity at Gd(III).

The presence of tetrad effect has been shown in separation coefficients, free energy changes of binary complex formation and extraction, enthalpies and entropies of extraction, free energy of crystallization and hydration of Ln(III) ions, unit cell volumes of Ln(III) compounds, IR stretching frequencies, deprotonation constants of Ln(III) complexes, Racah parameters of Ln(III) ions, ionization potentials, energy of the f$^n$-f$^{n-1}$d transitions and the (II-III) and (III-IV) redox potentials of lanthanides.

The presence of tetrad effect may be detected by (i) property versus 4f$^n$ plots, (ii) straight line approximation method, (iii) differential plot method and (iv) inclined
systematics. The simple property versus \(4f^n\) plots may not be able to exhibit the break due to tetrad effect, especially the two minor ones at \(4f^3-4f^4\) and \(4f^{10}-4f^{11}\) stages. The straight line approximation method is a good statistical tool for locating the presence of tetrad effect. The method is based on the fact that deviations in property are observed due to tetrad effect as compared to linearly interpolated values due to Ln(III) contraction alone. The deviations \(\Delta\) are given by

\[
\Delta = P_{\text{exptl}} - P_{\text{int}} \quad \text{(1)}
\]

where, \(P_{\text{exptl}}\) and \(P_{\text{int}}\) refer to the experimental and interpolated values of the property in the four tetrads, \(f^0-f^3\) (tetrad I), \(f^6-f^7\) (tetrad II), \(f^7-f^{10}\) (tetrad III) and \(f^{11}-f^{14}\) (tetrad IV). In the Ln(III) series the configurations \(f^3, f^4, f^7\) and \(f^{10}, f^{11}\) are more stable and hence deviations are frequently observed at other configurations. Thus \(\Delta\) is expected to be a negative quantity (\(\Delta < 0\)) for the configurations \(f^1, f^2, f^5, f^6, f^8, f^9, f^{12}\) and \(f^{13}\); positive values of \(\Delta\) (\(\Delta > 0\)) are expected for the \(f^3, f^4, f^7, f^{10}\) and \(f^{11}\) configurations.

In the differential plot method the values of \(\Delta P/\Delta r\) (where \(\Delta P = \text{difference between the values of experimental property}\ P\ \text{of two successive Ln(III) ions and } \Delta r = \text{corresponding difference in the ionic radii})\) are plotted against \(r + \frac{1}{2}\Delta r\) or \(4f^n\) to obtain the so-called 'differential plot'. In this plot well-marked depressions are obtained at one-fourth and three-fourth filled shell besides at half-filled shell in the presence of tetrad effect.

The so-called inclined -W hypothesis (or inclined -W systematics) aims at correlating Ln(III) properties with their total
orbital angular momentum values. The quantum number L is itself a non-linear periodic function of $4^N$. Since L-correlation with a property, which gradually increases (or decreases) across the Ln(III) series, yields a plot which looks like an inclined $-W$, the correlation is termed inclined $-W$ systematics.

Some attempts have been made to theorise the occurrence of tetrad effect. These include the correlation of Gd-break with change in coordination number of Ln(III) cations$^{24,25}$ dependence of Gd-break on the change in hydration number of Ln(III) cations$^{26-28}$ and changes in inter-electronic repulsions$^{29,30}$. The inadequacies of these explanations have been pointed out by Siekierski$^{6,9,11,31}$, Dzurinskii$^{32}$, Spitsyn$^{33}$ and Poluektov$^{34}$. There is a difference of opinion between Jorgensen$^{29}$ and Yatsimirskii$^{35}$ about the possibility of ligand field splitting contributing to the tetrad effect. It has been suggested$^{32}$ that L-S coupling may also be responsible for the occurrence of this phenomenon. Hydration appears to be involved in some way$^{36}$.

A microperiodicity has been detected$^{37}$ recently for the mixed ligand lanthanide complexes with $\beta$-diketones and EDTA expressed as linear dependence of stability constants on the orbital quantum number L for each tetrad. Oulum et al.$^{38}$ have used literature data to evaluate changes in stability constants of Ln(III) ion complexes with six different aromatic sulphonated ligands by means of inclined $-W$ theory of Sinha, double double theory of Siekierski and tetrad effect theory of Peppard. In yet another study$^{39}$ plots of stability constants of Ln(III) complexes vs atomic number have been examined and the Gd-break occurring in these plots has been attributed to spin-orbit interactions.
2. Tetrad Effect in the Solution Stabilities of Binary and Ternary Complexes

In chapter IV of the thesis while discussing the trends in formation constants it has been mentioned that the observed log\(K_{ML}^M\) and log\(K_{MAL}^A\) values in all the binary and ternary systems lie in the order La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Eu(III) > Gd(III) < Tb(III) < Dy(III) indicating the presence of tetrad effect in the solution stabilities. The problem is analysed in greater depth in this chapter. Each series is considered separately for this purpose.

(A) Ternary Systems with Catechol, 4-Methylcatechol and Pyrogallol

The variation profiles of the formation constants of binary ML and ternary MAL complexes with cat, m-cat and pyr for all the three binary systems and three representative ternary systems across the Ln(III) series are shown in figure 5.1. These log\(K\) vs \(4f^n\) plots exhibit a clear dip at Gd(III) but no depressions are observed for the \(f^3-f^4\) stage. (It has not been possible to scan the other end of the Ln(III) series due to nonavailability of the higher lanthanides). The plots, however, clearly indicate the presence of tetrad effect in the solution stabilities of the complexes.

A different approach may be followed for studying the tetradic phenomenon. Plots of log\(K_{ML}^M\) or log\(K_{MAL}^A\) vs standard entropy \(S_0^M\) of the Ln(III) cations are reproduced in figure 5.2. These plots serve a dual purpose. They indicate the presence of tetrad effect at Gd(III) where a sharp discontinuity is observed. An almost linear variation with standard entropy in two segments may
FIG. 5.1 : Variation in formation constants with the no. of 4f electrons ($4f^n$) of Ln(III) ions.
(A) Binary [Ln(III).L] systems
(B) Representative ternary [Ln(III).A.L] systems
FIG. 5.2: Variation in formation constants with the standard entropy, \( S^\circ_M \) (cal deg\(^{-1}\) mole\(^{-1}\)) of Ln(III) ions.

(A) Binary [Ln(III).L] systems

(B) Representative [Ln(III).A.L] systems
FIG. 5.3 : Variation in $\Delta (\Delta G_{\text{exptl}} - \Delta G_{\text{int}})$ values with the no. of 4f electrons (4f$^n$) for different segments (straight line approximation method)
FIG. 5.4: Variation in $\Delta \log K/\Delta r$ with the no. of 4f electrons ($4f^x$) of Ln(III) ions (Differential plot method).
FIG. 5.5 : Variation in formation constants with the total orbital angular momentum, $L$ of Ln(III) ions (Inclined -W plots)
be regarded as an evidence of predominant entropy stabilization of these complexes.

The presence of tetradeffect has been detected by using the straight line approximation method also. The values of the deviation $\Delta$ as given by equation (1) above have been calculated for all the $4f^n$ configurations. The $\Delta$ vs $4f^n$ plots for the segments $f^0-f^3$, $f^4-f^7$, $f^2-f^5$ and $f^6-f^8$ are shown in figure 5.3. The results are quite satisfactory; solid lines indicating agreement and broken lines disagreement with the expected direction of deviation. In general, negative values of $\Delta$ have been obtained for the configurations $f^1$, $f^2$ and $f^5$, $f^6$ and positive values for $f^3$, $f^4$ and $f^7$ configurations confirming the presence of tetradeffect at the $f^3-f^4$ stage also besides prominently at the $f^7$ stage.

The differential plots have been reproduced for the binary as well as ternary complexes of the first series in figure 5.4. In all these plots deep minima are observed at half-filled shell stage, i.e. at Gd(III) ($f^7$) but more significantly well-marked minima are seen at the one-fourth filled shell stage ($f^3-f^4$) also.

Application of inclined-W systematics has been made for studying the $\Lambda$-correlation with the formation constants of binary and ternary complexes. Variation in total orbital angular momentum quantum number $\Lambda$ along with the number of $4f$-electrons of Ln(III) ions is tabulated below.
\[
\begin{array}{cccccccc}
\text{Ln(III)} & \text{La}^{3+} & \text{Ce}^{3+} & \text{Pr}^{3+} & \text{Nd}^{3+} & (\text{Pm}^{3+}) & \text{Sm}^{3+} & \text{Eu}^{3+} \\
4f^n & 0 & 1 & 2 & 3 & 4 & 5 & 6 \\
\text{L (value)} & 0 & 3 & 5 & 6 & 6 & 5 & 3 \\
\text{L (symbol)} & S & F & H & I & I & H & F \\
\end{array}
\]

\[
\begin{array}{cccccccccccc}
\text{Ln(III)} & \text{Gd}^{3+} & \text{Tb}^{3+} & \text{Dy}^{3+} & \text{Ho}^{3+} & \text{Er}^{3+} & \text{Tm}^{3+} & \text{Yb}^{3+} & \text{Lu}^{3+} \\
4f^n & 7 & 8 & 9 & 10 & 11 & 12 & 13 & 14 \\
\text{L (value)} & 0 & 3 & 5 & 6 & 6 & 5 & 3 & 0 \\
\text{L (symbol)} & S & F & H & I & I & H & F & S \\
\end{array}
\]

The periodic nature of L quantum number is evident. The values of L for a given 4f\(^n\) configuration for the Ln(III) series may be calculated using the expressions:

\[
L = \frac{1}{2} [ n \left( \frac{N}{2} - n \right) ] \ldots \quad \ldots(2)
\]

for the values of n lying in the range 0 < n < N/2 and

\[
L = \frac{1}{2} [ (n - N/2) (N - n) ] \ldots \quad \ldots(3)
\]

for the values of n lying in the range (N/2 + 1) < n < N, where N = 14 for the Ln(III) series.

A plot between number of 4f-electrons (4f\(^n\)) of the Ln(III) ions and their L values is of inclined-W (\(\equiv\)) type (plot not shown).

It appears, therefore, that properties which gradually increase or decrease with 4f\(^n\) should give the so-called inclined-W plots. In the present case, such plots between log\(_M\) or log\(_{MAL}\) and L quantum number are shown in figure 5.5. The fourth segment in these plots has been indicated tentatively by a broken line because there are no experimental points on this segment. Although these L correlation
plots are inclined-W type, they are devoid of symmetry and linearity within segments. The second segment \((r^4-r^7)\) appears to be more curved with a hump at Eu(III). It has been claimed by Sinha\(^{20,23,41}\) that the W-plots are symmetrical and possess linearity within the segments. A hump at Eu(III) may be due to a partial reduction of Eu(III) \((4f^5)\) to Eu(II) \((4f^7)\) in the ligated systems.

The characteristics of these plots is that the three vertices of inclined-W coincide with the configurations \(f^3-r^4\), \(r^7\) and \(f^{10}-r^{11}\), where the tetrad effect occurs. The \(\log K_{\text{MAL}}^{\text{MA}}\) values (or any other property in which tetrad effect is present) seem to vary smoothly for the terms S \((L = 0)\) and I \((L = 6)\), but discontinuity occurs corresponding to the terms F \((L = 3)\) and H \((L = 5)\). The even values of terms are associated with relatively stable Ln(III) configurations and odd values with the configurations where deviations occur easily\(^{42}\).

The problem of linearity of the segments has been examined by evaluating the values of correlation coefficients \((r)\) for various segments of inclined-W plots. These values are recorded in table 5.1. The values of \(r\) for segments I and III show good linearity on statistical basis. It is only in segment II where the values of \(r\) are much less than unity indicating significant departure from linearity.

(B) Ternary Systems with Resorcinol, Orcinol and Phloroglucinol

The \(\log K_{\text{ML}}^M\) and \(\log K_{\text{MAL}}^{\text{MA}}\) values with res, orc and phl have been found to increase in the order La(III) < Ce(III) < Pr(III) < Nd(III) < Sm(III) < Eu(III) > Gd(III) < Tb(III) < Dy(III).
Table 5.1: Inclined-W systematics - calculated values of correlation coefficients (r) for various segments of Ln(III) series.

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<td>[Ln(III).HEDTA. m-cat]</td>
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<td>[Ln(III).CDTA. pyr]</td>
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<td>II. Sm$^{3+}$- Gd$^{3+}$(f$^4$- f$^7$)...</td>
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<td>III. Gd$^{3+}$- Ho$^{3+}$(f$^7$- f$^{10}$)...</td>
<td>0.9922</td>
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FIG. 5.6 : Variation in formation constants with the no. of 4f electrons ($4f^n$) of Ln(III) ions.

(A) Binary [Ln(III).L] systems
(B) Representative ternary [Ln(III).A.L] systems
FIG. 5.7: Variation in formation constants with the standard entropy, $S^0_M$ (cal deg$^{-1}$mole$^{-1}$) of Ln(III) ions.

(A) Binary [Ln(III).L] systems

(B) Representative [Ln(III).A.L] systems
FIG. 5.8: Variation in $\Delta (\Delta G_{\text{exptl}} - \Delta G_{\text{int}})$ values with the no. of 4f electrons ($4f^n$) for different segments (straight line approximation method)
FIG. 5.9: Variation in $\Delta \log K/\Delta r$ with the no. of 4f electrons ($4f^n$) of Ln(III) ions (Differential plot method).
FIG. 5.10: Variation in formation constants with the total orbital angular momentum, $L$ of Ln(III) ions (Inclined -W plots)
A decrease in stability at Gd(III) is a manifestation of tetrad effect. The variation profiles may be seen in the logK vs $4f^n$ plots reproduced in figure 5.6. These plots contain a well-marked dip at Gd(III) i.e. $4f^7$ configuration, but no break is visible at $4f^3-4f^4$ stage.

The plots of logK vs standard entropies $S^0_M$ of Ln(III) cations are shown in figure 5.7. These plots are linear in two segments. The break corresponds to the presence of tetrad effect at Gd(III) and the linearity of plots indicates entropy stabilization of the complexes.

The presence of tetrad effect may be demonstrated by applying the straight line approximation method also. The deviations $\Delta (= \Delta G_{\text{exptl}} - \Delta G_{\text{int}})$ have been worked out for all configurations and its calculated values have been plotted against $4f^n$ for the segments $f^0-f^3$, $f^4-f^7$, $f^2-f^5$ and $f^6-f^8$. Negative values of $\Delta$ for the configurations $f^1$, $f^2$, $f^5$, $f^6$ and positive values at $f^3$, $f^4$ and $f^7$ indicate the presence of tetrad effect. Figure 5.8 containing $\Delta$ vs $4f^n$ plots shows a fairly satisfactory agreement with the expected trend.

Differential plots are reproduced in figure 5.9. These plots clearly show depressions at the end of the first tetrad i.e. $f^3-f^4$ stage also, besides deep minima at the end of the second tetrad. This method establishes the presence of tetrad effect not only at the half-filled shell stage but also at the quarter-filled shell stage in the present case.

The L-correlation plots between the formation constants
and the total orbital angular momentum L are reproduced in figure 5.10 for the three binary and representative ternary systems. The inclined-W plots so obtained are again devoid of symmetry. There appears to be a significant departure from linearity within the segments, especially in second segment. The values of correlation coefficient 'r' have been presented in table 5.2. This statistical approach shows a good linearity for the first and third segments only. The curvature in second segment associated with a hump at Eu(III) may be due to a partial reduction of Eu(III) into Eu(II).

(C) Ternary Systems with $\alpha$-, $\beta$- and $\gamma$-Resorcylic Acids

The variation profiles of $\log K_{ML}^M$ and $\log K_{MAL}^{MA}$ with $4f^n$ for the ternary systems containing $\alpha$-, $\beta$- or $\gamma$- resorcylic acid are shown in figure 5.11. In these plots also only the dip at Gd(III) is clearly visible.

The formation constant vs standard entropy plots (figure 5.12) are as usual two segmented linear plots with a break at Gd(III) due to tetrad effect. Linear variation in $\log K$ with the standard entropies leads to the conclusion that the complexes are predominantly entropy stabilized.

The deviations between the experimental and the interpolated values of the free energy changes of complex formation when plotted against $4f^n$ for various segments ($f^0$-$f^3$, $f^4$-$f^7$, $f^2$-$f^5$ and $f^6$-$f^8$) yield the plots reproduced in figure 5.13. The $\Delta$ values are negative or positive as expected from the straight line approximation method. The presence of tetrad effect at the $f^3$-$f^4$ stage is also indicated although there are some disagreements with the method.
Table 5.2: Inclined-W systematics - calculated values of correlation coefficients (r) for various segments of Ln(III) series.

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FIG. 5.11: Variation in formation constants with the no. of 4f electrons ($4f^n$) of Ln(III) ions.

(A) Binary [Ln(III).L] systems
(B) Representative ternary [Ln(III).A.L] systems
FIG. 5.12: Variation in formation constants with the standard entropy, $S_M^o$ (cal deg$^{-1}$ mole$^{-1}$) of Ln(III) ions.

(A) Binary [Ln(III).L] systems

(B) Representative [Ln(III).A.L] systems
FIG. 5.13: Variation in $\Delta (\Delta G_{\text{exptl}} - \Delta G_{\text{int}})$ values with the no. of 4f electrons ($4f^n$) for different segments.

(straight line approximation method)
FIG. 5.14: Variation in $\Delta \log K/\Delta r$ with the no. of 4f electrons ($4f^n$) of Ln(III) ions (Differential plot method).
FIG. 5.15: Variation in formation constants with the total orbital angular momentum, L of Ln(III) ions (Inclined -W plots)
Table 5.3: Inclined-W systematics - calculated values of correlation coefficients (r) for various segments of Ln(III) series.

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<tr>
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<td>III. Gd³⁺ - Ho³⁺(f⁷ - f¹⁰) ...</td>
<td>0.9802</td>
<td></td>
<td>III. Gd³⁺ - Ho³⁺(f⁷ - f¹⁰) ...</td>
<td>0.9972</td>
</tr>
<tr>
<td>[Ln(III).γ-res]</td>
<td>I. La³⁺ - Nd³⁺(f⁰ - f³) ...</td>
<td>0.9403</td>
<td>[Ln(III).NTA. γ-res]</td>
<td>I. La³⁺ - Nd³⁺(f⁰ - f³) ...</td>
<td>0.9105</td>
</tr>
<tr>
<td></td>
<td>II. Sm³⁺ - Gd³⁺(f⁴ - f⁷) ...</td>
<td>0.3533</td>
<td></td>
<td>II. Sm³⁺ - Gd³⁺(f⁴ - f⁷) ...</td>
<td>0.1742</td>
</tr>
<tr>
<td></td>
<td>III. Gd³⁺ - Ho³⁺(f⁷ - f¹⁰) ...</td>
<td>0.9818</td>
<td></td>
<td>III. Gd³⁺ - Ho³⁺(f⁷ - f¹⁰) ...</td>
<td>0.9991</td>
</tr>
</tbody>
</table>
FIG. 5.16 : Variation in formation constants with the no. of 4f electrons (4f^n) of Ln(III) ions.

(A) Binary [Ln(III).L] systems
(B) Representative ternary [Ln(III).A.L] systems
FIG. 5.17: Variation in formation constants with the standard entropy, $S_M^0$ (cal deg$^{-1}$ mole$^{-1}$) of Ln(III) ions.

(A) Binary [Ln(III).L] systems

(B) Representative ternary [Ln(III).A.L] systems
FIG. 5.18 : Variation in $\Delta (\Delta G_{\text{exptl}} - \Delta G_{\text{int}})$ values with the no. of 4f electrons ($4f^n$) for different segments (straight line approximation method)
FIG. 5.19: Variation in $\Delta \log K/\Delta r$ with the no. of 4f electrons ($4f^n$) of Ln(III) ions (Differential plot method).
FIG. 5.20: Variation in formation constants with the total orbital angular momentum, L of Ln(III) ions (Inclined W plots)
stage also besides a clear indication at the $f^7$ stage.

The differential plots reproduced in figure 5.19 more clearly indicate the occurrence of tetrad effect in the solution stabilities with well-marked minima at the $f^3$-$f^4$ stage besides deep minima at the $f^7$ stage in each case.

The inclined-W plots for the binary and representative ternary systems of the series are shown in figure 5.20. The plots are devoid of symmetry. The linear nature of the segments may be seen from the values of correlation coefficient recorded in table 5.4. Once again statistical evidence supports linearity of segments I and II only.

It may be concluded on the basis of above treatment of the formation constant data that the solution stabilities of the binary as well as mixed ligand complexes are influenced by the presence of tetrad effect. The differential plot method appears to be more powerful than the statistical straight line approximation method.

The inclined-W plots in practically all the cases lack symmetry. The second segment ($f^4$-$f^7$) of these plots has always been found to be sufficiently curved, with correlation coefficient values lying much away from unity. The originator of the inclined-W hypothesis, Sinha$^{20,23,41}$ is of the opinion that the inclined-W plots should be symmetrical and linear within the segments. Sinha has actually used the L-linearization scheme of inclined-W plots for calculating and predicting ionization potentials$^{43}$ and other properties$^{41}$ of Ln(III) cations.

Fidelis$^{44}$, Siekierski$^{31}$ and Dzhurinskii$^{32,45}$ are of the
Table 5.4: Inclined-W systematics - calculated values of correlation coefficients (r) for various segments of Ln(III) series.

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ln(III).ARS]</td>
<td>I. La(^{3+}) - Nd(^{3+})(f(^0) - f(^3))...</td>
<td>0.9912</td>
<td>[Ln(III).DTPA. ARS]</td>
<td>I. La(^{3+}) - Nd(^{3+})(f(^0) - f(^3))...</td>
<td>0.9312</td>
</tr>
<tr>
<td></td>
<td>II. Sm(^{3+}) - Gd(^{3+})(f(^4) - f(^7))...</td>
<td>0.3496</td>
<td></td>
<td>II. Sm(^{3+}) - Gd(^{3+})(f(^4) - f(^7))...</td>
<td>0.4213</td>
</tr>
<tr>
<td></td>
<td>III. Gd(^{3+}) - Ho(^{3+})(f(^7) - f(^10))...</td>
<td>0.9998</td>
<td></td>
<td>III. Gd(^{3+}) - Ho(^{3+})(f(^7) - f(^10))...</td>
<td>0.9888</td>
</tr>
<tr>
<td>[Ln(III).IMDA]</td>
<td>I. La(^{3+}) - Nd(^{3+})(f(^0) - f(^3))...</td>
<td>0.9372</td>
<td>[Ln(III).EDTA. IMDA]</td>
<td>I. La(^{3+}) - Nd(^{3+})(f(^0) - f(^3))...</td>
<td>0.9507</td>
</tr>
<tr>
<td></td>
<td>II. Sm(^{3+}) - Gd(^{3+})(f(^4) - f(^7))...</td>
<td>0.5353</td>
<td></td>
<td>II. Sm(^{3+}) - Gd(^{3+})(f(^4) - f(^7))...</td>
<td>0.4932</td>
</tr>
<tr>
<td></td>
<td>III. Gd(^{3+}) - Ho(^{3+})(f(^7) - f(^10))...</td>
<td>0.9772</td>
<td></td>
<td>III. Gd(^{3+}) - Ho(^{3+})(f(^7) - f(^10))...</td>
<td>0.9997</td>
</tr>
<tr>
<td>[Ln(III).ATP]</td>
<td>I. La(^{3+}) - Nd(^{3+})(f(^0) - f(^3))...</td>
<td>0.9001</td>
<td>[Ln(III).NTA. ATP]</td>
<td>I. La(^{3+}) - Nd(^{3+})(f(^0) - f(^3))...</td>
<td>0.9646</td>
</tr>
<tr>
<td></td>
<td>II. Sm(^{3+}) - Gd(^{3+})(f(^4) - f(^7))...</td>
<td>0.5349</td>
<td></td>
<td>II. Sm(^{3+}) - Gd(^{3+})(f(^4) - f(^7))...</td>
<td>0.5961</td>
</tr>
<tr>
<td></td>
<td>III. Gd(^{3+}) - Ho(^{3+})(f(^7) - f(^10))...</td>
<td>0.9990</td>
<td></td>
<td>III. Gd(^{3+}) - Ho(^{3+})(f(^7) - f(^10))...</td>
<td>0.9945</td>
</tr>
</tbody>
</table>
opinion that the inclined-W plots are accidental and the total
dependence of property showing tetrad effect on the L-quantum
number is questionable.\footnote{36}

The choice of L-quantum number for correlating the
Ln(III) properties may be justified\footnote{20,43} because the ground state
configurations of Ln(III) ions are without exception $4f^n$ and their
L-values are intrinsic non-linear (periodic) property for the series.
The ground states are more than 98% pure L=5 states. The ground
states of wave function of Ln(III) ions are only nominally perturbed
on complexation due to little or perhaps no involvement of $4f$-orbitals
in M-L bonding.\footnote{43}

(3) \textbf{Mechanistic Aspects of Tetrad Effect}

The first attempt made for explaining the occurrence of
Gd-break (before the advent of tetrad effect) sought to correlate its
existence with a decrease in coordination number of Ln(III) ions at
Gd(III)\footnote{24,25}. The Ln(III) complexes were believed to be isostructu-
ral on either side of the $4f^7$ stage. The possibility of change in
coordination number in the Ln(III) series was, however, soon
discarded on the basis of X-ray crystallographic data\footnote{46} on their
solid EDTA chelates, acid dissociation constants related to studies on
Ln(III).EDTA complexes\footnote{47}, and also as a result of study of molecular
models\footnote{48}.

Three independent groups of workers, viz. Staveley and
co-workers\footnote{26}, Choppin and co-workers\footnote{27}, and Grenthe\footnote{28} suggested
that Gd-break is a consequence of change in hydration number
(H.N.) of Ln(III) ions on going from 'Ce subgroup' to 'Y subgroup'.
Retaining the essential ideas of the "iceberg" model of the hydration sphere by Frank and Evans, Spedding and Atkinson proposed two different hydration sphere structures for the 'lighter' and the 'heavier' lanthanides.

Jorgensen has proposed an inter-electronic repulsion theory in terms of which tetrad effect is present in a property of Ln(III) ions due to changes in nephelauxetic ratio. The ground state of 4f^n configuration of Ln(III) is stabilized by an amount \( H_{st} \) given by the expression

\[
H_{st} = K_1 E^1 + K_3 E^3 \quad ... \tag{4}
\]

where

\[
K_1 = \text{coefficient of } E^1 = 18/13.5 (S - \frac{1}{2}),
S = \text{spin quantum number of Ln(III) ions}
K_3 = \text{coefficient of } E^3 = L/180 [L(222 - 48L) - 234]
\]

The terms \( E^1 \) and \( E^3 \) stand for Racah parameters. In the above expression the term \( K_1 E^1 \) is related to the 'spin part' of stabilization energy \( H_{st} \) and the term \( K_3 E^3 \) to the 'radial part'. Jorgensen has defined a quantity 'spin pairing energy' \( D \), which is given by

\[
D = 9/8 E^1 \quad ... \tag{5}
\]

Jorgensen has studied the effect of change in \( D \) and \( E^3 \). In a separate investigation Nugent has studied the variations in the spin and orbital parts, i.e. in \( K_1 E^1 \) and \( K_3 E^3 \) over the Ln(III) series. It has been shown that the discontinuity at \( f^7 \) configuration occurs due to changes in \( K_1 E^1 \) and that at the \( f^3 - f^4 \) & \( f^{10} - f^{11} \) stages due to changes in \( K_3 E^3 \).
In a recent study Sickierski\textsuperscript{14} has shown that tetrad effect is present separately in the Racah parameters as well as in the coefficients of Racah parameters of the Ln(III) cations. This is a significant observation because the coefficients (\(k\)'s) are related to the 'angular part' of 4f\(^n\) wave functions and the Racah parameters (\(E^k\)'s) to the 'radial part'. Tetrad effect may, therefore, be regarded as an intrinsic property of the 4f orbitals. When a change in chemical environment occurs, \(K_1E^1\) and \(K_3E^3\) alter causing a change in the nephelauxetic ratio.

Dzhurinskii\textsuperscript{32} is of the opinion that the theories of Nugent\textsuperscript{30} and Jorgensen\textsuperscript{29} are inadequate; even the latter which is more detailed does not take into account the L-S coupling. He has suggested that the ligand field effect, as pointed out by Yatsimirskii\textsuperscript{35}, may also be significant, but Jorgensen\textsuperscript{29} refutes this possibility.

R.J.P. Williams\textsuperscript{36} has emphasised the involvement of hydration in some way in the occurrence of tetrad effect in the properties of Ln(III) ions in solution. It appears that a comprehensive and universally acceptable explanation of the occurrence of tetradic phenomenon has yet to come.

As explained above the discontinuities at the \(f^7\) and \(f^3-f^4\) & \(f^{10}-f^{11}\) stages occur due to changes in two different quantities, the spin part (\(K_1E^1\)) and the orbital part (\(K_3E^3\)) of the ground state stabilization energy of Ln(III) ions. The changes in \(K_1E^1\) appear to be larger and those in \(K_3E^3\) much smaller. The property vs \(4f^n\) plots, therefore, usually fail in displaying breaks at the \(4f^3-4f^4\) and \(4f^{10}-4f^{11}\) stages. The linear deviations worked out in straight line
approximation method also at times, prove to be insufficient in revealing these small discontinuities. In the differential plot method the small changes when expressed as their derivatives get magnified and hence this method appears to be more powerful in locating the presence of tetrad effect even when it is weak, particularly at the $f^3-f^4$ and $f^{10}-f^{11}$ stages.

In order to examine the influence of hydration on the occurrence of tetrad effect hydration numbers of Ln(III) cations have been calculated by using a recently published method assuming that there are three concentric zones of hydration around each Ln(III) ion$^{49,52}$. The calculated values of hydration numbers are presented in table 5.5.

The hydration numbers of Ln(III) ions are much larger as compared to other metal ions because in their case (Ln(III)) three hydration zones are involved. The total hydration number varies from about 21.91 to 24.22 across the series. Plots of $\log K_{MA}^M$ vs H.N. for all the ternary complexes with catechol and also for the representative ternary complexes with other secondary ligands studied in present work are reproduced in figure 5.21 (A) and (B), respectively. Prominent discontinuities at $f^4$ and $f^7$ stages are seen in these plots. These discontinuities show the influence of hydration on the formation constant values in leading to irregularities at the said configurations.

In figure 5.22(A) plots between $\log K_{MA}^M$ and standard entropies ($S^o_M$) of lanthanides are drawn to show smooth variations in $\log K_{MA}^M$ with $S^o_M$ values indicating that the Ln(III) complexes are basically entropy stabilized. The values of $\log K_{MA}^M$ used for drawing
Table 5.5: Hydration numbers (H.N.) of Ln(III) ions.

<table>
<thead>
<tr>
<th>Hydration number</th>
<th>La$^{3+}$</th>
<th>Ce$^{3+}$</th>
<th>Pr$^{3+}$</th>
<th>Nd$^{3+}$</th>
<th>(Pm$^{3+}$)</th>
<th>Sm$^{3+}$</th>
<th>Eu$^{3+}$</th>
<th>Gd$^{3+}$</th>
<th>Tb$^{3+}$</th>
<th>Dy$^{3+}$</th>
<th>Ho$^{3+}$</th>
<th>Er$^{3+}$</th>
<th>Tm$^{3+}$</th>
<th>Yb$^{3+}$</th>
<th>Lu$^{3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H.N. 1</td>
<td>2.87</td>
<td>2.88</td>
<td>2.88</td>
<td>2.89</td>
<td>2.89</td>
<td>2.89</td>
<td>2.90</td>
<td>2.91</td>
<td>2.92</td>
<td>2.92</td>
<td>2.92</td>
<td>2.92</td>
<td>2.94</td>
<td>2.94</td>
<td></td>
</tr>
<tr>
<td>H.N. (total)</td>
<td>21.91</td>
<td>22.24</td>
<td>22.42</td>
<td>22.51</td>
<td>22.60</td>
<td>22.69</td>
<td>22.88</td>
<td>23.08</td>
<td>23.29</td>
<td>23.51</td>
<td>23.62</td>
<td>23.62</td>
<td>24.11</td>
<td>24.22</td>
<td></td>
</tr>
</tbody>
</table>

Note: The total H.N. values have been used for studying correlations with Ln(III) properties.
FIG. 5.21: Variation profiles of formation constants, \(\log K_{\text{MAL}}^{\text{MA}}\) (exptl values) vs hydration number (H.N.) of Ln(III) ions across the Ln(III) series.

[A] [Ln(III).A.cat] systems, (B) [Ln(III).A.L] representative systems-
A: [Ln(III).NTA.res], B: [Ln(III).HEDTA.B-res], C: [Ln(III).CDTA.ARS],
D: [Ln(III).EDTA.IMDA], E: [Ln(III).DTPA.pyr].
these plots have been taken from literature (Appendix-III). Plots between $\log K^M_{MA}$ and hydration number of lanthanides are shown in figure 5.22(B). The breaks at $f^4$ and $f^{10}$ stages are clearly seen in these plots. It may be concluded, therefore, that the H.N. values at these stages contribute to discontinuities in the variation profiles of Ln(III) properties in solution, for example, the formation constants. The trends in changes in H.N. also appear to add to the magnitude of tetrad effect (in solution) at the three stages dividing the Ln(III) series into four tetrads.
FIG. 5.22: Variation profiles of formation constants, $\log K_{MA}^{M}$ (literature values) vs [A] standard entropy, $S_{M}^{0}$ (cal deg$^{-1}$mole$^{-1}$), and (B) hydration number, H.N. (total) of the Ln(III) ions across the Ln(III) series.
References


