

## Periodicity in the properties of lanthanoids: Review of theory, systematics and the role of nephelauxetic effects

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### Abstract

Developments in the phenomenon of tetrad or double-double effect in periodicity in the properties of lanthanoids (Lns) and its recent quantum chemical explanation have been reviewed. A five-parameter semi-empirical equation based on interelectronic repulsion Racah parameters has also been used and discussed to calculate the 'extrastabilization' ( $\partial E_M$ ) at specific  $f^q$  configurations and the 'nephelauxetic ratio' ( $\partial E^3/\partial E^1$ ) for Lns in different ligand environments. The possibility of dependence of  $\partial E_M$  on ligand basicity has been examined with prospects of developing a nephelauxetic series for Lns. The nomadic behaviour of Y(III) with respect to Ln(III)s has also been discussed.

**Keywords:** Lanthanoids, f-block, periodicity, systematics, extrastabilization, nephelauxetic ratio.

### 1. Introduction

The lanthanoids (Lns) (Ce-Lu; atomic number,  $Z = 57-71$ ) are unique among the elements, except for the closely similar actinoids, resembling each other so markedly, both in elemental and in compound states, that changes across the series are more in degree than in kind. The electronic configuration<sup>1,2</sup> of a neutral Ln atom amounts to a [Xe] core with subshells  $(n-1)d$ , partly filled  $(n-2)f$  and  $ns$ , where  $n = 6$ . The configuration, however, varies for the entire series with beginner, middle and end members having different configurations with regard to the occupancy of the  $d$  shell than the rest of the series, viz.,  $(n-1)d^1ns^2$  for La,  $(n-1)d^1(n-2)f^qns^2$ , where  $q = 1, 7, 14$  for Ce, Gd and Lu, respectively, and  $(n-2)f^qns^2$ , where  $q = 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13$  for Pr, Nd, Pm, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, respectively. The  $4f$  orbitals are initially well outside the [Xe] core and are unoccupied. However, the development of a deep potential energy well near the nucleus draws the  $f$  orbitals into the atoms, thus permitting their occupancy and hence the existence of a series of 14 Ln elements. La(III) with unoccupied  $f$  orbitals is also included in the series, making the total number 15.

These 15 elements, though kept in one group in the periodic classification, exhibit an interesting periodicity within the series itself in their physicochemical properties. This periodicity has a significant role in determining the general characteristics of these metals, their ions, their bonding patterns, biological significance, extraction behaviour and

technology, but has so far been unable to acquire significant place in texts of chemistry. The present article is an effort to compile at one place the growth and development of the subject, its significance, theoretical considerations and a note on the future areas.

## 2. Systematics: Historical developments and theoretical considerations

Historically, the first systematization of the lanthanoids (rare earths) was done in 1895 by Rotger<sup>4</sup>, who classified the elements into one group showing their very similar nature. Klemm<sup>4</sup> put forward the diad grouping, while Noddak<sup>4</sup> proposed the triad classification in Lns. The earliest tetradic classification of Lns was made by Enders<sup>4</sup> in 1932. An interesting grouping and pairing of these metals was also evident from their separation process<sup>5</sup> during their discoveries.

Preobrazenskii<sup>6</sup> published valuable information on the separation factors of the Ln(III) ions in solution. Dzhurinskii<sup>6</sup> observed that the separation factor  $\beta$  defined as the ratio of extraction coefficients of two neighbouring ions,  $D_{z+1}/D_z$ , is equal to the ratio of the stability constants ( $K$ ) of their complexes,  $K_{z+1}/K_z$ , and demonstrated the occurrence of a break close to Gd(III) on the variation profiles of  $\beta$  vs  $Z$ . Bandurkin<sup>6</sup>, from an examination of a large number of compounds, showed that the composition and/or structure most frequently change in the region of Nd-Sm, Gd or Dy-Ho. It was suggested that the middle of the Ce and Y subgroups would appear unique for other properties of Ln elements or their ions.

After the discovery of the so-called 'Gd break'<sup>7,8</sup>, immense interest has been shown in this field. The first definition of the phenomenon of periodicity in the properties of Lns was given by Peppard and co-workers<sup>9</sup>, who introduced the term 'tetrad effect'. They defined it as: "In systems involving 15 Ln(III) elements, the points on a plot of the logarithm of a suitable numerical measure of a given property of these elements vs  $Z$  may be grouped through the use of a smooth curve without inflexion, into four tetrads, with the Gd point being common to the second and third tetrads and the extended smooth curves intersections, additionally in the 60-61 and 67-68  $Z$  regions".

Fidelis<sup>10,11</sup> in 1970 put forward an explanation that 'regularities lie in the internal features of the free  $f$  electron ions and not in their immediate environment, although the immediate environment may influence the magnitude of the effect'. On the basis of this, a new term was introduced (based on the sequence of ground terms—explanation given later in the text) called the 'double-double effect' (D-D effect), which reflects the symmetrical character of the alternation of the terms  $S$  and  $L$  and the properties relative to the  $S$  term of Gd. Simultaneously, Siekierski<sup>12</sup> proposed a statistical approach to demonstrate the discontinuities occurring as a result of the D-D effect, pointing out that there are only a few ligands for which regularities are observed throughout the Ln series, and there are many ligands for which these regularities are observed only for a part of the series. The average values of the functions used for the study were, e.g., average values of free-energy changes on complexation, or average values of specific cell volumes of the unit cell. The presentation is significant when the graphs are plotted using the differences between the experimental and the interpolated values of the properties.

Sinha<sup>13</sup> on a close perusal of the tetrad plots expressed doubts about the tetrad classification on the basis that 'the theory is not refined enough to define the function  $f(Z)$ , the property used for correlation'. Sinha suggested the existence of a microsymmetry within the series. To search for a more suitable property for correlation, unlike  $Z$ , which would be an intrinsic parameter differentiating between the elements and their ions and also permitting a simple relationship between the property under study and the parameter, Sinha realized that the total orbital angular momentum quantum number ( $L_{Ln}$ ) of the free trivalent Lns not only shows periodicity but also generates rythemics, *i.e.*, properties arranged and occurring in an orderly manner showing periodicity. The classification of trivalent Lns on the basis of their  $L$  values not only confirms the diad division of Kiern<sup>4</sup> and the generally accepted Gd break<sup>7,8</sup>, but also presents the microsymmetry within the series.

Recently, a differential plot method<sup>14,15</sup> has been proposed from our laboratory to locate the discontinuities occurring as a result of the tetrad effect. It indicates a variation in the ratio of the rate of change of the property under study to that of the change in the ionic radius of the Ln cation as a function of  $4f^q$ . These plots demonstrate better the occurrence of discontinuities at half-filled (Gd), 1/4 filled (Pr-Nd) and 3/4th filled (Ho-Er) stages of the  $4f$  shell.

The theoretical consideration of the above-mentioned approaches, Gd break, corresponds to a greater stabilization of the half-filled  $4f$  shell as a result of the reduced interelectronic repulsion parameter. Initially, Nyholm<sup>16</sup> preferred calling it as 'f effect'. It was also assumed that the change in coordination number<sup>17, 18</sup> on going from lighter Lns to the heavier ones, as a result of Ln contraction, may probably be a cause of Gd break. The Ln coordination number (CN) is often taken as being synonymous with the hydration number, *i.e.*, water molecules<sup>19</sup> in the first coordination shell of the metal ion in dilute solutions devoid of the coordinating ligands other than water. Although this problem is still open for new ideas, it has been tentatively established<sup>20</sup> by X-ray analysis of Ln(III) aqua complexes in solid state that the CN for La-Nd is preferably 9 and that for Tb-Lu is preferably 8, whereas the central elements Sm-Dy show transitional coordination numbers from 9 to 8. There is, however, no confirmatory approach but for the neutron scattering studies<sup>21</sup>, which enabled to find out the exact CN in aqueous solutions<sup>22,23</sup>. Recent X-ray studies on Ln(III)-EDTA<sup>24</sup> and Ln(III)-ethylsulphate<sup>25</sup> complexes have revealed a constant CN for Ln(III) ions in these complexes throughout the series.

The change in the hydration numbers of Ln(III) ions was also proposed to be the cause of Gd break. A statistical mechanical model based on the bulk properties of water was proposed by Williams<sup>26</sup>. It may, however, be stated that a significant compensational effect<sup>27</sup> in the thermodynamic properties of Ln(III) complexes may minimize the effect of changes in hydration sphere on the final  $\Delta G$  values. A possible contribution from crystal field stabilization energy (c.f.s.e.) towards the projection of Gd break can be ruled out in view of the strong shielding of the  $4f$  orbitals by the outer-lying orbitals<sup>5</sup>. In the light of these observations, it may be stated that a probable cause of the said discontinuities may be on account of the ground term values and their variation across the series.

The D-D effect is based on the explanation<sup>11</sup> that 'there is a definite correlation between the regularities and the sequence of the ground term. The terms *S* and *I* correspond to a smooth change in the experimental quantity with a change in *Z* values and the terms *F* and *H* to a change which is not smooth' (see Table I).

Hence, it is obvious that the D-D or tetrad effect consists of singularities<sup>28</sup> in specific  $f^q$  configurations at the stages  $q = 3, 4; 7, 10, 11$ . Preference for the term D-D effect

Table I

Variations in *S* and *L* quantum numbers and term values for Ln(III)s

1st half								
<i>Ln</i>	<i>La</i>	<i>Ce</i>	<i>Pr</i>	<i>Nd</i>	<i>Pm</i>	<i>Sm</i>	<i>Eu</i>	<i>Gd</i>
$f^q$	0	1	2	3	4	5	6	7
Term	S	F	H	I	I	H	F	S
<i>S</i>	0	1/2	1	3/2	2	5/2	3	7/2
<i>L</i>	0	3	5	6	6	5	3	0
2nd half								
<i>Ln</i>	<i>Gd</i>	<i>Tb</i>	<i>Dy</i>	<i>Ho</i>	<i>Er</i>	<i>Tm</i>	<i>Yb</i>	<i>Lu</i>
$f^q$	7	8	9	10	11	12	13	14
Term	S	F	H	I	I	H	F	S
<i>S</i>	0	3	5	6	6	5	3	0
<i>L</i>	7/2	3	5/2	2	3/2	1	1/2	0

Note: *L* = 0, 6 (S, I) corresponds to smooth change and 3, 5 (F, H) to deviation.

rather than for the tetrad effect was shown by Siekierski *et al*<sup>11,12</sup> in view of the nature of regularities and singularities of certain configurations exhibited by the Ln(III)s. Limaye and Saxena<sup>29</sup> have studied a large number of fundamental properties of Ln(III) elements and their compounds and the properties of Ln(III) ions and have developed an opinion that the properties as a whole exhibit two types of periodicities. Some properties exhibit a preference for one of the two regularities, but no generalized rule seems to be followed. The final effect in both the cases is no different.

The linear interpolation method of Siekierski<sup>30</sup> takes cognizance of the fact that in Ln(III) ions the  $4f^q$  configurations for  $q = 1, 2; 5, 6; 8, 9; 12, 13$  are relatively extrastabilized. The Ln series is divided into four segments (or tetrads)  $q = 0-3; 4-7; 7-10; 11-14$ . The difference  $\Delta$  (where  $\Delta = P_{\text{expt}} - P_{\text{inter}}$ ) in the experimental ( $P_{\text{expt}}$ ) value of the property ( $P$ ) under study and its interpolated ( $P_{\text{inter}}$ ) value at each  $4f^q$  configuration (for  $q = 1, 2; 5, 6; 8, 9; 12, 13$ ) has been worked out. The value of  $\Delta$  for these configurations is expected to be negative ( $\Delta < 0$ ) in the presence of tetrad effect. Similarly,  $\Delta$  may be calculated for the set of  $4f$  configurations with  $q = 3, 4; 7, 10, 11$  using the segments  $q = 2-5, 6-8; 9-12$ . The value of  $\Delta$  for these configurations is expected to be positive ( $\Delta > 0$ ) in the presence of the tetrad effect.

Guillaumont and Hubert<sup>31</sup> have, however, suggested such linear correlations, considering the 'extrastabilization' of specific electronic configurations due to the 'nephelauxetic effect' (explained later in the text) vs the number of  $f^q$ -electrons with that of the hypothetical case where the effect is zero. Spitsyn<sup>32</sup> pointed out a large approximation in the linear interpolation technique. Limaye and Saxena<sup>29,33</sup> have applied the linear interpolation technique for detecting the presence of tetrad effect in a large number of properties of Ln elements, Ln(III) ions and their solid complexes, as well as the solution stabilities of binary and ternary complexes and their thermodynamic parameters. They are of the opinion that besides a few cases of disagreement, the method is effective in detecting minor discontinuities at 1/4th filled and 3/4th filled stages also. The observed disagreements may be on account of the experimental error in the property under study or the environmental effect as a whole on the specific configuration. The parameter  $\Delta$ , however, has a significant use in determining the magnitude<sup>34</sup> of the tetrad effect.

The 'inclined-W' hypothesis of Sinha is based on the realization that the total orbital angular momentum ( $L$ ) values of the trivalent Lns (at a fixed oxidation state) show periodicity and generate rythemics. Selection of ground state configurations and their respective  $L$  state is suggested to be appropriate. As for the trivalent Lns, the ground states are over ~98% pure LS state. The spin-orbit coupling being negligible as compared to the electrostatic interaction, the  $L$  character of the ground state is preserved. The variation in the  $L$  values with  $f^q$  can be expressed as in the form of equation<sup>35</sup>:

$$L = -0.5q(q - 7) \quad \text{for } 0 < q < 7, \quad (1)$$

$$L = -0.5q(q - 7)(q - 14) \quad \text{for } 8 < q < 14. \quad (2)$$

This correlation of property vs  $L$  led to inclined  $W(\Sigma)$  type of plots where the three vertices of inclined  $W$  correspond to the  $f^q$  configurations for  $q = 3, 4, 7, 10, 11$ . Discontinuities due to tetrad effect occur at these configurations only. Sinha expected these plots to be symmetrical with linearity within the segments. Limaye and Saxena<sup>36</sup> have examined the inclined  $W$  plots for a number of systems and observed the hypothesis to be markedly effective in expressing the occurrence of the tetrad effect. However, the symmetrical nature of the plots and linearity within the segments are not always found. Sinha<sup>37</sup> has argued that 'the lines within a given tetrad must be least-square lines and should not join the originating and the terminating Ln members in a tetrad like a cord in the bow'. A probable partial reduction of  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  (giving rise to a stable  $4f^7$  configuration) in the presence of organic ligands was also suggested to be a cause for the deviations from linearity in the second segment (Pm(III)-Gd(III)). The correlation is useful in determining<sup>20</sup> the missing intermediate values of the property for the metal ions in the series. It also confirms the position of Gd(III) in the second or third segment on the basis of values (for Gd(III)) obtained from least squares. Sinha also suggested to correlate the slope values obtained for different segments for a set of ligands having similar coordination

<sup>35</sup>The values of ionic radii have been revised and reported by Shannon *et al.* [Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, R. D. Shannon, *Acta Crystallographica*, 1976, **32**, 751]. These values of ionic radii (CN = 9) also yield similar differential plots; however, Goldschmidt's values were taken for reference in the preliminary studies.

tendencies. A detailed analysis of the slope values obtained for a set of ligands and their related parameters is presently being carried out by the authors. Fidelis<sup>38</sup> and Dzhurinskii<sup>39</sup> are, however, critical of the hypothesis for the reason that the correlations obtained from the properties of Ln(III) metal and ion with the  $L$  values are only accidental.

An attempt to demonstrate the regularities within the Ln(III) series with the help of the differential plot method has been made successfully for a number of cases<sup>40</sup>. A plot of  $\delta P/\delta r$  vs  $4f^q$  (where  $P$  is the property under study and  $r$  is the ionic radius<sup>4</sup> (Goldschmidt's values of ionic radii for Ln(III) ions) and  $\delta P$  and  $\delta r = P_{z+1} - P_z$  and  $r_{z+1} - r_z$ , respectively) shows a deep minimum at the half-filled shell stage with significant minima at 1/4th filled and 3/4th filled stages also. The plots are helpful in locating the discontinuities occurring due to the tetrad effect and also in studying the symmetrical pattern of the variation along the two halves in the Ln series. The basis of differential plots is the assumption that since the tetrad effect is an intrinsic feature of  $f$  electrons (which remain shielded from the ligand field), the changes in the properties of Ln elements and their compounds throughout the series are, in fact, the reflections of subsequent roles of  $f$  orbitals at each  $f^q$  configuration as may be observed in Ln contraction, added with the environmental effects on specific  $f^q$  configurations. The cumulative effect of this is termed as the tetrad effect.

### 3. Theory of tetrad effect

The studies reported earlier indicate the efforts made to demonstrate the occurrence of the tetrad effect with possible theoretical consideration. Jorgensen<sup>41</sup> and Nugent<sup>42</sup> simultaneously proposed the theoretical cause for this phenomenon. Jorgensen suggested the occurrence to be on account of 'nephelauxetic effect'. However, Nugent extended an explanation based on the variation in the spin and orbital part of the stabilization energy of the ground term of Lns with  $4f^q$ .

An effective shielding of  $4f$  orbitals by the outer orbitals leads to a very small crystal field splitting in Ln(III) complexes. Under these conditions the ground term values and their variation become dominant giving rise to observed microsymmetries or singularities in specific  $f^q$  configurations.

Jorgensen suggested that the ground state of the  $4f^q$  configuration is stabilized by a certain amount which varies with the number of  $f^q$  electrons. The energy below the baricentre for maximum  $S$  can be written as a definite multiple of the interelectronic repulsion parameters expressed by Racah (IERP-Racah)<sup>43</sup>. The change in the nephelauxetic effect (*i.e.*, a decrease in the phenomenological parameters of interelectronic repulsion) causes the occurrence of the tetrad effect:

$$E = \sum_{n=3}^{n=0} K_n E^k, \quad (3)$$

where  $E^k$  is the Racah parameter<sup>b</sup> and  $K_n$  are the quantum-number-dependent coefficients expressed as

$$K_0 = [q(q-1)]/2, \quad (4a)$$

$$K_2 = 0, \quad (4b)$$

$$K_1 \text{ and } K_3 = S\text{-related and } L\text{-related coefficients, respectively,} \quad (4c)$$

where  $S$  being the spin quantum number and  $L$  the total orbital angular momentum quantum number.

In the context of eqn (3), Racah proposed an expression

$$K_1 = 9(q-v)/2 + (v(v+2)/4) - S(S+1) \quad (4d)$$

involving 'seniority number'  $v$ , where  $v = q$  for most terms below 7 ( $q < 7$ ), but some terms have  $v$  decreased to a non-negative value, viz., 2, 4 or 6 units lower. The ground terms have always  $v = q$  for  $q > 8$ , so that the first of the three contributions to  $K_1$  vanishes, and the sum of the last two is also zero. Later, Racah transcribed it to an energy relative to the energy of all the states,

$$K_1^* = (9/8) [3q(14-q)52 - S(S+1)], \quad (4e)$$

of the  $f^q$  configuration. The factor reminds one of the spin-pairing energy parameter  $D = 9E^1/8$ . The value of  $K^*$  is  $-90/13$  for ground term  ${}^6\text{H}$  of  $f^5$ ,  $-135/13$  for  ${}^7\text{F}$  of  $f^6$ , and  $-189/13$  for  ${}^8\text{S}$  of  $f^7$ . The use of eqns (3) and (4a-c) may have some limitations: (i) comparison of the variation along  $q$  and  $q+1$  is approximate, and (ii) the correction term<sup>c</sup> introduced by Racah<sup>43</sup> for  $q = 8-12$  has not been considered.

Thus, the energy of stabilization by the decreased interelectronic repulsion relative to the baricentre of the whole  $f^q$  configuration is given by

$$E_{st} = E_B + K_1(S)E^1 + K_3(L)E^3, \quad (5)$$

where variation of  $K_1$  and  $K_3$  with  $f^q$  is shown in Table II.

The term  $E_B$  in eqn (5) is given by

$$E_B = [q(q-1)/2]E^0 + qV + C. \quad (6)$$

From the variation in the values of  $K_1$  and  $K_3$ , it is evident that  $K_1$  or  $K_3 < 0$  and  $E^1$  and  $E^3 > 0$ ;  $E_{st}$  will have a negative value, indicating a stabilization of the ground term relative to the baricentre when  $K_1$  and  $K_3$  (or one of them) is not zero. Thus, it can be stated that a greater negative value of  $K_1$  and  $K_3$  will lead to a greater stabilization of the ground terms than the relative negative or positive values.

<sup>c</sup>There are two significant features of the Racah parameter that make it more suitable to use: (i) the dependence of the ground term on  $S$  and  $L$  is separated into different coefficients of  $K_s$ , and (ii)  $K_2 = 0$  according to the values of  $s$ ,  $q/2$  or  $14-q/2$ <sup>43</sup>.

**Table II**  
Variation of  $K_1$  and  $K_3$  with  $f^q$

$q$	0, 14	1, 13	2, 12	3, 11	4, 10	5, 9	6, 8	7
Ln	La, Lu	Ce, Yb	Pr, Tm	Nd, Er	Pm, Ho	Sm, Dy	Eu, Tb	Gd
$K_1$	0	0	-9/13	-27/13	-54/13	-90/13	-135/13	-189/13
$K_3$	0	0	-9	-21	-21	-9	0	0

Using the values of  $E^1$  and  $E^3$  for the trivalent Ln (or actinoid) aqua ions, the energy of the ground terms  $E_{st}$  can be calculated<sup>d</sup> using eqn (5). It may be emphasized that regularities in  $E_{st}$  values are generated by the variation in  $K_1$  and  $K_3$  values, which, in turn, are affected by the variation in the  $S$  and  $L$  values.

The generation of the tetradic phenomenon and its relationship with the nephelauxetic effect of Jorgensen<sup>41</sup> ('nephelauxetic effect' means 'cloud expansion', a term suggested by Prof. K. Barr) suggests that when Ln(III) ion is attached to a ligand (or even water/H<sub>2</sub>O molecule in aqua complexes), the  $f$  electrons get spread under the ligand field depending upon the strength of the field and the deformability of these  $f$  orbitals under the changed environment or external field. The difference in the relative stabilization of the ground terms, however, generates an irregular pattern showing the tetradic pattern of variation. This deformation in  $f$  orbitals causes a change in the interelectronic repulsion values of the  $f$  electrons, consequently changing the IERP-Racah ( $\partial E^i$ ) parameters. The stabilization energy as a result of complexation attains the form

$$E_{st} = K_1 \partial E^1 + K_3 \partial E^3, \quad (7)$$

where  $\partial E^1$  and  $\partial E^3$  are the changes in the corresponding Racah parameters as a result of the change in the immediate environment of  $f^q$  electrons. Since  $\partial E^1$  and  $\partial E^3$  are negative,  $\partial E_{st}$  becomes negative, representing destabilization. Usually, a decrease of -1% in  $E^1$  and  $E^3$  is reported<sup>41,42</sup> to have expressed the appearance of tetradic variation. The variation in these quantities is very small, yet one expects<sup>c</sup> a correlation between the variation of these parameters and the ligand characteristics, viz., basic strength, polarizing power, type of donor atom, nature of ligand, effective charge on the donor atom, softness values, etc.

#### 4. Magnitude of tetrad effect

It is evident from eqn (7) that the parameters  $\partial E^1$  and  $\partial E^3$  contribute to the magnitude of  $E_{st}$  (tetrad effect). This has been expressed as 'extrastabilization' of certain  $f$  configurations under the ligand field.

On account of the variation in  $\partial E_{st}$ , an approximate range  $R$  of the tetrad effect can be estimated rearranging eqn (7) as

$$E_{st} = [K_1 + K_3(q)R] \partial E^3, \quad (8a)$$

where  $R = \partial E^3 / \partial E^1$  is called the range of tetrad effect. Assuming  $\partial E^1$  as constant and

<sup>d</sup>For  $q = 8-12$  necessitates the use of a correction parameter,  $A^* = E + (9E^1/13)$  with coefficient  $K_0 = q^2q - 1/2$ .



taking into account the conservation of difference of sign between the adjacent values of  $\partial E_{st}(q)$  within each half of the  $f$  shell, the range of tetrad effect is found to be

$$-0.134 < R < 0.234. \quad (8b)$$

It is observed<sup>46</sup> that the factor  $K_1 \partial E^1$  ( $\partial E^3$  is very small and negligible) plays a dominant role in regulating the magnitude of the tetrad effect.<sup>f</sup>

A study of complexation equilibria in the light of the above observations where an aqua molecule from aqua complex is replaced by the ligand causing a change in the environment of Ln(III) ion (from aqua complex to the ligand's donor atoms), the probable role of ligand in the magnitude of tetrad effect or 'extrastabilization'  $\partial E_{st}$  may be expected in two ways<sup>47</sup>:

(i) by causing a change in  $\partial E^3/\partial E^1$  (within the limits expressed by eqn (8b)), i.e., in the 'nephelauxetic ratio', and

(ii) by involving the metal ion in a (partial) probable covalent bonding.

Taking into consideration the above observation, an approximate correlation may be expected between the magnitude of tetrad effect and the nature of ligand or donor group/atoms. The magnitude of tetrad effect (calculated using eqn (5)) for specific  $f^q$  configurations with  $q = 3, 10; 4, 11$  and  $7$ , for some Ln(III) carboxylic aminopolycarboxylic acid complexes has been calculated (Table III).

The values of  $\partial E_{st}$  observed for the present series of ligands with respect to  $f^q$  configuration follow the sequence,  $f^7 \gg f^3 - f^4 \approx f^{10} - f^{11}$ , which is in agreement with the interelectronic repulsion theory<sup>42</sup>, whereas the values of  $\partial E^4$  ( $\partial E^3$  and  $\partial E^1$  values are not reported) are also in good agreement with the stated range<sup>42</sup> of  $\partial E^1$  or  $\partial E^3$ , i.e.,  $\sim 1\%$  of  $E^1$  and  $E^3$ . The ratio  $\partial E^3/\partial E^1$  is also found to lie in the stated range<sup>46,47</sup> of

$$-0.134 < \partial E^3/\partial E^1 < 0.234.$$

The plots of  $\partial E_{st}$  vs  $4f^q$  exhibit a conventional 'inverted organ pipe' ( $\wedge$ ) for  $K_1 \partial K^1$  and 'inverted tulip' type ( $\cup$ ) for  $K_3 \partial E^3$ . The agreement with the calculated and the observed values shows the validity of the present approach.

The observed sequence in the extrastabilization values,  $\partial E_{st}$  with respect to the ligands may be expressed as follows, which is an approximate order of their basic strengths:

1. FOR  $\gg$  ACE  $\approx$  HS - GLY  $\ll$  GLYCL < GLYCN
2. LACT < MAL < GLY < SAL

<sup>f</sup>Use of correction terms as expressed in eqns (4d) and (4e) has no significant effect on the output; therefore, the calculated values reported in Table III are without correction terms. The details of the correction terms are, however, discussed elsewhere<sup>44</sup>.

<sup>g</sup>A quantitative explanation for the nephelauxetic effect is yet to be found. One cannot correlate crystal field parameters and the 'nephelauxetic ratio', whereas the spectrochemical series, following the order of ligands, also does not seem to correlate with 'nephelauxetic series' and thus it is felt necessary to undertake a theoretical effort<sup>45</sup> to solve this problem similar to that for crystal field theory.

3. Di-PICOL < PICOL < GLYCN < IMDA  
 4. NTA < EDDA < HEDTA < IMDA  
 5. EEDTA < NTA < PDTA < CDTA < EDTA  $\approx$  OXAL > TTHA  
 6.  $\text{Cl}^- < \text{PO}_4^{3-} < \text{OH}^-$ .

Table III

Extrastabilization values ( $\partial E_{st}$ ) calculated using eqns (5) and (6) for specific  $f^q$  configurations ( $q = 3, 10, 4, 11; 7$ ) and  $\partial E^7/\partial E^1$  for various ligand environments

Ligand	$\partial E_{st}$	$\partial E^7/\partial E^1$			
		q=3, 10	4, 11	7	
Formic acid	(FOR)	7	24	217	-0.119
Acetic acid	(ACE)	9	9	25	0.116
Glycolic acid	(GLY)	171	246	527	0.125
Thio-glycolic acid	(HS-GLY)	21	21	56	0.181
Lactic acid	(LAC)	118	169	356	0.125
Malic acid	(MAL)	45	160	380	-0.092
Salicylic acid	(SAL)	376	475	692	0.277
I-acetic acid	(I-ACE)	140	178	250	0.275
Mandelic acid	(MANDL)	40	147	338	-0.101
Tartaric acid	(TAR)	46	79	231	0.039
Oxydiacetic acid	(OXI-ACE)	118	136	246	0.232
Acetylacetone	(ACAC)	26	162	363	0.035
Oxalic acid	(OXAL)	51	214	1139	-0.067
Glycine	(GLYCN)	388	502	799	0.236
Picolinic acid	(PIC)	57	134	375	0.246
Di-picolinic acid	(DI-PIC)	6	40	231	0.081
Iminodiacetic acid	(IMDA)	150	378	840	0.195
Ethylenediaminediacetic acid	(EDDA)	215	313	687	0.117
Hydroxyethyl-ethylene diamine triacetic acid	(HEDTA)	148	369	755	0.239
Nitrilotriacetic acid	(NTA)	61	160	561	0.098
Oxibis(ethylenenitrilo) tetra acetic acid	(EEDTA)	105	231	489	0.228
Cyclohexylenediamine tetra acetic acid	(CDTA)	135	343	868	0.174
Propylenediamine tetra acetic acid	(PDTA)	83	218	781	0.094
Ethylenediamine tetra acetic acid	(EDTA)	169	430	1169	0.155
Diethylenetriamine penta acetic acid	(DTPA)	58	152	525	0.101
Triethylene triamine hexa acetic acid	(TTHA)	38	123	591	-0.054
Hydroxyl	(OH)	128	204	534	0.067
Chloride	(Cl)	122	137	103	0.072
Phosphate	(PO <sub>4</sub> )	47	93	328	-0.005

Note: (1)  $\partial E_{st}$  values reported in calories.

(2) Parameter  $\partial E^7/\partial E^1$  corresponds to 'nephelauxetic effect'.

A novel approach has been attempted for determining the dependence of extrastabilization on the Ln(III) metal ion environment or ligand donor atom characteristics. The values of extrastabilization (for  $f^7$  configuration) have been correlated with total partial charge<sup>48</sup> on the ligand donor atoms (Table IV).

<sup>48</sup>The role of spin-orbit coupling<sup>46</sup>, however, has a considerable contribution towards the free energy of complexation, but does not contribute to the tetradic feature of  $f$  electrons.

A gradual increase in the values of extrastabilization (cf. Table IV) (at  $4f^7$  configuration) with total partial charge on the ligand is indicative of a direct dependence of extrastabilization on the metal ion environment *vis-à-vis* the ligand's donor atom characteristics. The magnitude of extrastabilization  $\partial E_{st}$  which constitutes  $\partial E^k$  parameters ( $\partial E_{st} = K_1 \partial E^1 + K_2 \partial E^3$ ) gets directly affected by the total partial charge on the ligand donor atoms brought into the vicinity of metal ions as a result of complexation. There are, however, deviations (Table IV, values marked with †); yet the dependence of extrastabilization on total partial charge gives a new direction to the studies<sup>44</sup>. A finer analysis of the

Table IV

Variation in the extrastabilization  $\partial E_{st}$  (for  $f^7$  configuration) with total partial charge on the ligand donor atoms

Ligand	Total partial charge*	$\partial E_{st}$
<i>O = O donors</i>		
Formic acid	0.214	.217
Tartaric acid	0.219	231
Oxy-diacetic acid	0.232	246
Iodo-acetic acid	0.252	250
Mandelic acid	0.280	338
Acetylacetone	0.293	363
Oxalic acid	0.352	1139
<i>O = N donors</i>		
Glycine	0.259	799†
Di-picolinic acid	0.248	231
Picolinic acid	0.273	374
MDA	0.600	424
EEDTA	0.766	489
EDDA	0.798	687
NTA	0.819	561†
HEDTA	1.111	755
EDTA	1.252	1169
PDTA	1.302	781†
TTHA	1.312	591
CDTA	1.453	868†
DTPA	1.675	525

\*Values, supplied by Prof. P. P. Singh, Bareilly College, are in esu.

†Values showing deviations.

hypothesis using the difference between the polarizing power of  $H_2O$  and the ligand or the difference between the softness values of water and ligand is under study.

The authors feel it appropriate to discuss here about the itinerant (nomadic) behaviour of Y(III) with respect to Ln(III) series. On account of ionic radius, Y(III) acquires a position ~Ho-Er in Ln(III) series, and Y may retain its position for all physicochemical properties, including the formation constants. It resembles Ln(III) in forming a predominantly ionic bond. The deviation in the position of Y(III) from the encompassing Ln(III)s may

indicate a greater stabilization of Ln(III)-L system as compared to Y(III)-L, partly due to deviation in the bonding pattern in Ln(III)-L from the electrostatic model to a partial covalent type due to a probable partial involvement of the f-orbital in bonding<sup>44-47</sup>. The parameter  $\partial E^3/\partial E^1$ , as studied by the authors, is expected to be helpful in this regard. Similarly, a comparison of Cm(III) ([Xe] 5f<sup>7</sup>) (suggested by Gschneider<sup>49</sup>), In(III) ([Kr] 4d<sup>10</sup>5s<sup>2</sup>5p<sup>1</sup>) (suggested by Jorgensen<sup>49</sup>) and Sc(III) ([Ar] 3d<sup>1</sup>4s<sup>2</sup>), Th(IV) ([Rn]6d<sup>1</sup>7s<sup>2</sup>) with the corresponding Ln(III) or An(III) series can also be made to draw information about the bonding patterns and other similarities. The non-availability of comparable data and the difference in their fundamental characteristics are, however, barriers to be overcome to seek a relevant correlation. Yet a detailed study of the hypothesis is under investigation.

## 5. Conclusions

It may be concluded that periodicity in the properties of Lns (or actinoids), which originates on account of variation in *S* and *L* quantum numbers or the coefficients of interelectronic repulsion parameters, is an intrinsic feature of f electrons. A negligible c.f.s.e. due to strong shielding of f orbitals (4f > 5f) and low spin-orbit coupling project the role of ground term values in explaining the presence of periodicity. The relativistic<sup>50</sup> and inter-configurational mixing effects, though substantial, have negligible effect on the phenomenon of periodicity. Spitsyn<sup>51</sup> has observed the effect of relativistic factors on variation in  $\partial E^3/\partial E^1$ , which is found to be significant but does not appear to influence the tetradic feature.

As regards the determination of  $\partial E^k$  values using the formation constants and the free-energy changes, it may be stated that any free-energy contribution of the type  $-2.303RT \log_{10} K$  might remain detectable and significant in the background of the enormous effect of Racah parameters and in particular spin-pairing energy. It may be stated that the observed free-energy change is, in fact, the total result of the minor insignificant and the major significant factors involved in the transition of a cation from one environment to another. The use of the given five-parameter expression can, however, be made<sup>51</sup> to back-calculate the distribution of energy factors involved in complexation with an approximate magnitude of variation in the  $\partial E^k$  and nephelauxetic ratio  $\partial E^3/\partial E^1$ . The validity of the equation has been verified<sup>52</sup> with the experimental (spectroscopic) and calculated (semiempirical values). Though the magnitudes differ, the sequence of their variation for a set of ligands is found to be the same.

In the light of the nephelauxetic phenomenon, the periodicity expressed as extrastabilization ( $\partial E_{st}$ ) of specific f<sup>*q*</sup> configurations is due to changes in interelectronic repulsion (Racah) parameters ( $\partial E^k$ ). As a result of the change in the metal ion environment, the ratio  $\partial E^3/\partial E^1$  gives the susceptibility of the metal ion orbitals to different environments. As regards the formation constants, it may be stated that besides various ligand- and metal-ion-dependent factors, the dependence of  $\partial E_{st}$  on ligand donor groups/atoms, or the ligand characteristics as a whole, supports the aforesaid hypothesis. The extent of covalency and the quantitative role of f orbitals in Ln(III) complexes is, however, uncertain, but the evaluated parameter  $\partial E^3/\partial E^1$  studied in the present case may be able to throw light on the

$\text{Ln(III)-L}$  bonding pattern. The nephelauxetic effect, which is an environment-dependent phenomenon, is directly or indirectly linked to chemical bonding at least in the framework of LCAO theory and valence shell nature of the orbitals. Thus, the solution of the problem of periodicity in the f shell property lies in the study of the effect of the nature of metal ion environment, its electrical properties, dielectric conditions, coordination polyhedra, the ligand/crystal geometries and ion site of interaction on the  $4f^q$  configuration and their excited states. The parameters associated with these operators may have minor individual effect on the phenomenon, but their total effect seems to be important. Framing of a consolidated explanation using these operative factors, combined according to their weightage, may lead to a quantitative explanation to the nephelauxetic effect and the tetrad effect. A further extensive analysis of the phenomenon is felt necessary.

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