# 216. Gadolinium Break, Tetrad and Double-double Effects were here, What next?

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*Summary.* It has been found that the properties of the lanthanide and actinide ions and their complexes vary linearly with the L-values (the total angular momentum). Usually plots resembling a four segmented «inclined W» are obtained for the whole series, where the data are available. Although some deviation from a symmetrically «inclined W» plot occured in a few cases, the linearity is maintained within the four segments. It is suggested that in future, for correlating the properties of the lanthanide and actinide series, the L-values rather than the atomic number (Z) or number of the f-electrons, should be used.

It is a known fact, that the plots of the stability constants for the lanthanides show discontinuity around the middle of the series. This discontinuity is known to the chemists as the gadolinium break. Much has been written on this topic but no unique explanation for its occurance has as yet been found [1]. Examination of the thermodynamic quantities ($\Delta H_1^0$, $\Delta S_1^0$) for EDTA and related ligands failed to throw any light on this problem. The $\Delta H_1$ values [1] for the heavier lanthanides are smaller than those for the lighter members. If the stabilization of the half-filled 4f shell in Gd(III) is the dominating factor, then one would expect a lower $\Delta H_1$ value for Gd(III) complex with respect to the heavier members of the series. However, this is ***not*** the case and the crystal field stabilization due to the half-filled shell cannot possibly be the main factor causing this break. In fact the gadolinium break is not limited to the stability constant plots, but virtually any property of the series shows such break and this has been demonstrated by the author [1] in plots for oxidation potential ($E^0$), $F_2$, $\zeta_{4f}$ and others for the lanthanide series.

Recent interest in this topic stems from a series of papers by *Siekierski et* al. [2-6] and *Peppard et* al. [7] [8]. Both groups succeeded in showing that certain regularities exist when diverse properties like unit cell volumes, separation factors, stability constants, $\Delta G^0$ of the complex formation are plotted against the atomic numbers (Z). These curves show two branches more or less symmetrically spaced around gadolinium. Each branch, in turn, consists of two segments joined by the pairs Nd–Pm in the first half and Ho–Er in the second half of the series. *Fidelis & Siekierski* [3] [5] coined the name double-double effect for this regularity, while *Peppard et al.* [7] [8] preferred to call this effect as the tetrad effect. The generic form of these plots consists of four convex curves, although the nature of these convex forms varies from one plot to another.

In examining these plots, it became obvious that the four convex curves resulted due to plotting of nonlinear functions against a linear function *e.g.* the atomic numbers (Z). In our search for an intrinsic nonlinear property for the series we found that the total angular momentum (L) is a function, varying nonlinearly within the series and dividing the series in four segments:

| Ground term | S | F | H | I |
|---|---|---|---|---|
| L | 0 | 3 | 5 | 6 |
| $\Delta$L | 3 | 2 | 1 | |
| $f^n$ | La | Ce | Pr | Nd |
| $f^{7-n}$ | Gd | Eu | Sm | Pm |
| $f^{7+n}$ | Gd | Tb | Dy | Ho |
| $f^{14-n}$ | Lu | Yb | Tm | Er |
| Difference in f-electrons | 7 | 5 | 3 | 1 |

Attempts were then made to correlate the observed properties of the lanthanide series with the L-values. Striking linear correlation has been found for most plots. We shall discuss only a few cases here. A plot of the *Zachariasen's* [9] ionic radii (i.r.) and the effective ionic radii (e.i.r.) (CN = 6,8) [10] [11] for the M(III) ions is made in Fig. 1. The linear correlation within each of the four segments are more than gratifying. The generic form of "*inclined W*" is preserved for plots of such diverse properties as oxidation potential ($E^0$), spectroscopic parameters ($E^3$, $\zeta_{4f}$), stability constants (log $K$), extraction constant ($K_{ex}$), molecular volume (V/Z), lattice parameters ($a$, $c$), M–N stretching frequencies *etc.* (Fig. 2–5). Some deviations from a symmetrically "*inclined W*" plot have, however, been observed (Fig. 2d, 3c, 4c, 4d) but we want to emphasize that the linearity within each of the four segments is still preserved.

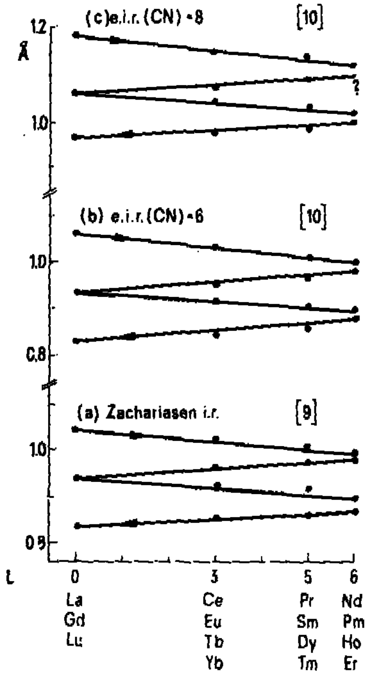

Fig. 1. *A plot of the ionic radii for the tripositive lanthanides* vs. *the value of the total angular quantum numbers* (L) *showing linear relationship*

Extension of this concept of plotting the observable properties against the L-values has been made to the actinide series. It is highly gratifying to see that the generic form of the *"inclined W"* is also present for the trivalent actinides (Fig. 6) when hydration enthalpies ($\Delta H_h$) and the entropies ($\Delta S_h$) for the whole series [12] are plotted against the L-values. Other available data for part of the actinide series (M(III) and M(IV)) also confirm the linear relationship existing within each of the

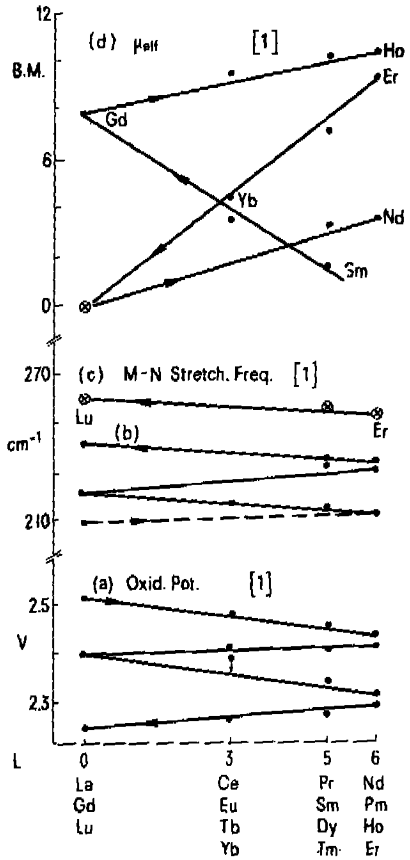

Fig. 2. *Graph showing the variation of* (a) *oxidation potential,* (b) *M–N stretching frequencies for the 2,2'-dipyridyl complexes* (c) *the same as* (b), *but the positions of the second peak for Er, Tm and Lu ions are plotted* (d) *the effective magnetic moments for the ethylsulfate (or cyclopentadienyl) complexes of the lanthanides with the L-values*

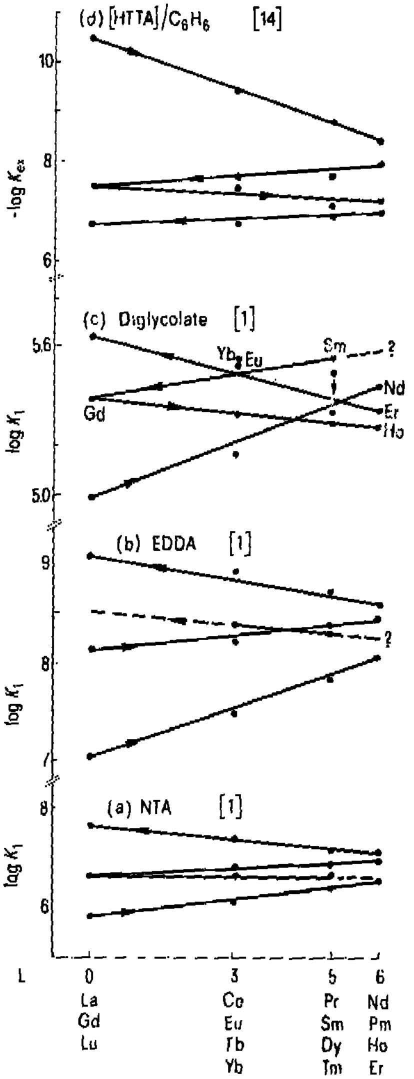

Fig. 3. *Variation of the stability constants* (*log* K$_1$) *for* (a) *NTA* (b) *EDDA* (c) *diglycolate complexes and* (d) *the extraction constants* (– *log* K$_{ex}$) *for the thenoyltrifluoroacetonate complex* (*in* $C_6H_6$) *of the lanthanides with the L-values*

four segments and this has been illustrated in Fig. 7 using the crystal parameters (*a*, *c*) and molecular volume (V/Z) for $MF_3$ and $MF_4$ complexes of the actinides [13].

To summarize, it has been shown that:

(i) Linear correlation exists between the measurable properties for the lanthanide and the actinide ions and the L-values;

(ii) Most plots for the whole series consist of four linear segments connected in a way to resemble an *"inclined W"*;

(iii) In certain cases deviation from a symmetrically *"inclined W"* plot has been observed, but linearity within each segment is usually preserved. This property is very useful in predicting the missing value for a member of the series,
and it is suggested that:

(i) In future use should be made of the L-values in correlating the properties of the lanthanide series, and eventually those of the actinides as well, rather than the conventional parameters, the atomic numbers (Z) and the number of the f-electrons ($f^n$), used at present;

(ii) For symmetrically *"inclined W"* plots arrows should be used to indicate the direction of change of the property with respect to the L-values;

(iii) For others, at least the terminal members be indicated on the plots, as has been done for some of the present cases, to avoid ambiguity.

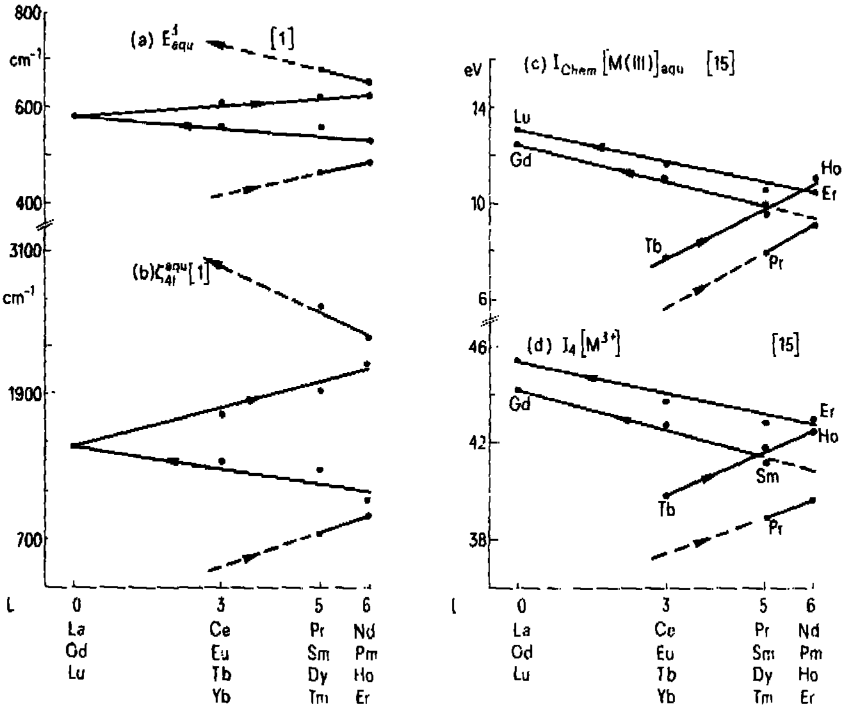

Fig. 4. *Variation of the spectroscopic parameters* (a) *Racah* $E^3$ (b) *spin-orbit coupling parameter* ($\zeta_{4f}$) (c) $I_{chem}$ *of the M(III) aquoion and* (d) *fourth ionization potential* ($I_4$) *of the* $M^{3+}$ *ions*

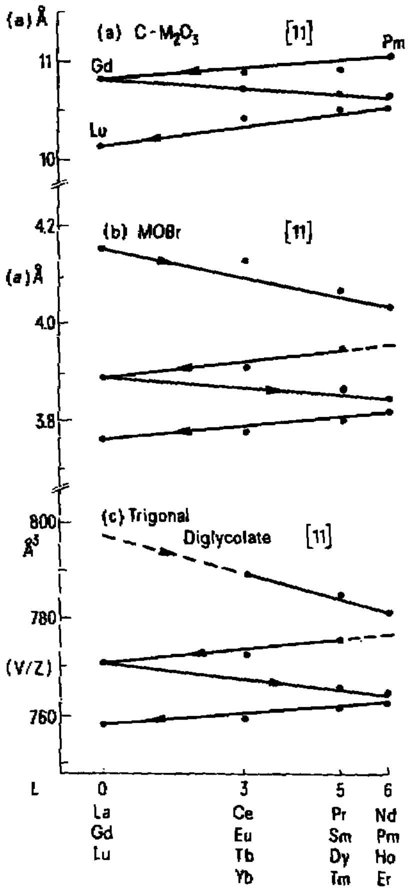

Fig. 5. *Lattice parameter* (a) *for C—$M_2O_3$ and MOBr and molecular volume* (*V/Z*) *for trigonal* (*R32*) *diglycolate complexes as a function of the L-values of the Lanthanides*

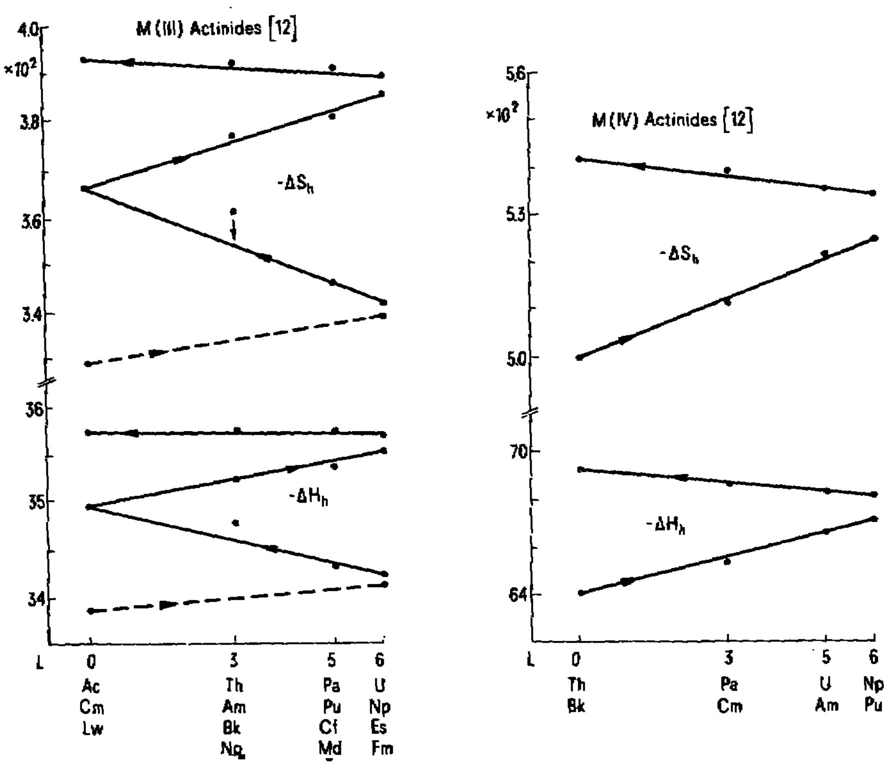

Fig. 6. *Variation of the hydration enthalpies* (kJ/mol) *and the entropies* (J/K/mol) *for the trivalent and quadrivalent actinides with their L-values*

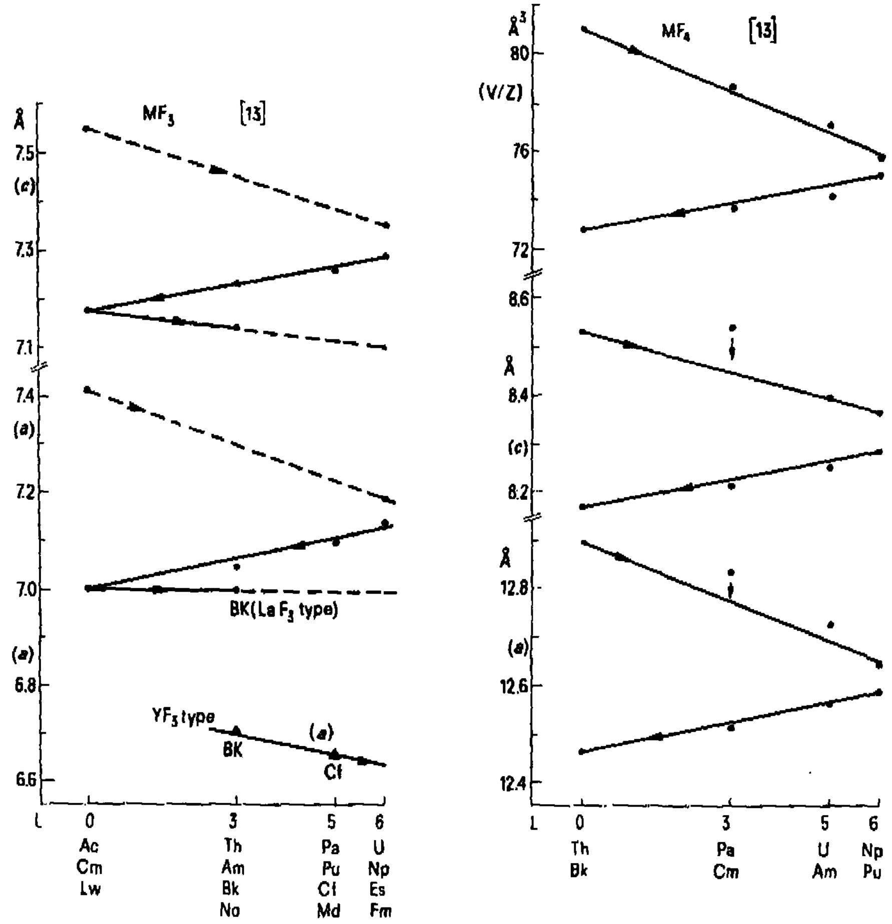

Fig. 7. *Crystallographic parameters for the trifluorides and tetrafluorides of the actinides as a function of the L-values*

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