# 210. An Answer to the Article 'On the Misleading Interpretation of the Properties of the f-Electron Elements'[1][2]

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*Summary*

The position of the 'Inclined W theory', *i.e.*, the linear correlation of the properties ($P_i$) of the lanthanide and the actinide ions with their ground state total orbital angular quantum numbers (L), $P_i = w_i L + k_i$, where $w_i$ and $k_i$ are the slopes and intercepts of the least squares lines, is made clear. The position of gadolinium is ambivalent, and it can be a common point for the symmetric 'Inclined W plots' or it may either belong to the second or the third tetrad depending on the system investigated. The propionate and the isobutyrate systems are used to elucidate the 'Inclined W concept'. The 'Inclined W parameters' for the solvent extraction of the lanthanides with PMBP ligand have been calculated.

In an article in this journal, *Fidelis* [1] questions the 'Inclined W theory' proposed by me in 1975 [2] and subsequently developed and used to interpret a great variety of experimental data on the lanthanides and the actinides [3]. This article [1] essentially summarizes the arguments developed in a previous paper by her [4][3]). *Fidelis* seems to ignore the linear L-correlation presented [3] for many available experimental data on the lanthanides:

(i) Cocrystallization of ethylsulfate hydrates; (ii) Extraction constants for TBP, HEHØP, HIB, HIMBUT, MIBK; (iii) Formation constants for acetate, propionate, isobutyrate, HIB, lactate, diglycolate, HIMBUT, phthalate, HIMDA, IMDA, NTA, HEDTA, EDTA, DPA, EEDTA, EDDA, EGTA, DTPA, DCTA, En; (iv) Oxidation and ionization potentials; (v) Racah, spin-orbit coupling parameters, $\langle r^{-3} \rangle$, $\langle r^n \rangle$, $|A_n^m \langle r^n \rangle|$, $f^n \rightarrow f^{n-1}d$ transitions, photoelectron spectra; (vi) M-N stretching frequencies, lattice parameters, *etc.*

and on the actinides:

(i) Hydration enthalpies, entropies of $M^{3+}$ and $M^{4+}$ ions; (ii) Crystal lattice parameters of $MF_3$ and $MF_4$; (iii) Separation factors for lactate, HEHØP, HDEHP, HIB; (iv) Formation constants for chloride, acetate, thiocyanate; (v) Spectroscopic parameters $F_2$, $\zeta_{5f}$; (vi) Oxidation potentials.

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[1]) See [1].

[2]) The editor declares that this communication terminates the controversy between Ms. *Irena Fidelis* and Mr. *Shyama P. Sinha.*

[3]) Wrong data were used in this paper [4] to criticize the 'Inclined W theory' *(cf. Fig. 4).*

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In [1], the 'Inclined W theory' is again misinterpreted. According to this theory, we neither draw chords joining the two extreme elements within a tetrad, nor plot the difference of the properties of the adjacent elements ($P_{Z+1}-P_Z$), but *always* draw the least squares lines taking into account all experimental points [3] [5] [6].

The *Figure* for the lanthanide propionate system [7] illustrates that the schematic pattern presented in [1] is *not* always a true representative of the lanthanide systems and that the so called gadolinium break is not concentrated at or around Gd only. The formation constants, $\log K_1$, are plotted: (a) against the atomic numbers, Z, as in the tetrad plot; (b) as ($P_{Z+1}-P_Z$) *vs.* Z, where $P_Z=\log K_1$; (c) as $\log K_1$ *vs.* L according to the 'Inclined W theory'. To demonstrate that the latter fits well, the differences between the experimental and the calculated $\log K_1$ values are plotted in *Figure, d.* These are very small indeed. The following least squares lines satisfy the experimental data [7] for the propionate system: La-Nd tetrad: $\log K_1=0.062L+1.51$; Pm-Gd tetrad: $\log K_1=0.037L+1.85$; Gd-Ho tetrad: $\log K_1=-0.039L+1.84$; Er-Lu tetrad: $\log K_1=-0.01L+1.66$. Predicted value for Pm: $\log K_1=2.07$; Standard deviation for the whole series is 0.02. Here, the gadolinium break occurs as early as in Sm, and the downward trend continues until about Er *(Fig., a).* Such

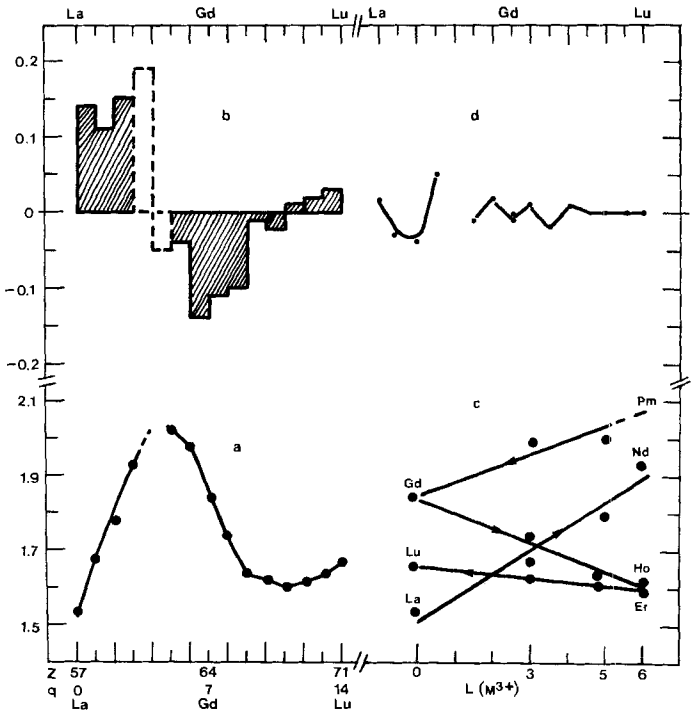


Figure. *Formation constants* ($\log K_1$) *of the lanthanide-propionates.*
(a) Normal tetrad plot of $\log K_1$ *vs* Z. (b) Histogram showing ($P_{Z+1}-P_Z$) *vs.* Z, where $P=\log K_1$. The unshaded area under the broken lines is calculated from the $\log K_1$ value of Pm as obtained from an 'Inclined W plot' (see c). (c) 'Inclined W plot' of $\log K_1$ *vs.* $L(M^{3+})$. (d) The difference between the experimental $\log K_1$ and that calculated by using the 'Inclined W theory'.

trends are common for simple ligands like acetate and isobutyrate [3]. The isobutyrate system [8] is represented as: La-Nd tetrad: $\log K_1 = 0.057L + 1.63$; Pm-Gd tetrad: $\log K_1 = 0.036L + 1.87$; Gd-Ho tetrad: $\log K_1 = -0.028L + 1.88$; Er-Lu tetrad: $\log K_1 = -0.022L + 1.82$. Predicted value for Pm: $\log K_1 = 2.09$; standard deviation for the whole series is 0.013. It should be noted here that for the propionate and the isobutyrate systems Gd serves as a common point for both second and the third tetrads.

Once and for all, I would like to make clear the position of the 'Inclined W theory':

(1) 'Inclined W systematics' present the correlation of the experimental data with the ground state L values of the corresponding lanthanide and the actinide ions in different states of oxidation [2–6] [9];

(2) Usually, a linear correlation of the properties ($P_i$) with the ground state L values is obtained within the four tetrads (i = 1–4)

$$P_i = w_i L + k_i \tag{1}$$

$w_i$ and $k_i$ are called the 'Inclined W parameters';

(3) The position of Gd (Z = 64) is *ambivalent.* Depending on the system, the Gd point may fall on the second (Pm-Gd) or on the third (Gd-Ho) tetrad. Hence, the Gd point *cannot always* serve as the common point between the second and the third tetrad [2] [3] [9], except in the case of a *symmetric* [2] 'Inclined W plot';

Stating certain things which are *not* claimed by me [2] [3], *Fidelis* [1] puts a *wrong* concept in my theory;

(4) 'Inclined W concept' can be reasonably extended to the d-transition series making this concept a more general one [10].

Readers must be aware of the fact that *Fidelis* or *Siekierski* make use of the *differentials* of the properties ($P_{Z+1} - P_Z$), to emphasize the curvature in their plots. Often double differentials are used [11] [12], and as correctly pointed out by *Wallace* [13] if applied in general, the procedure would lead to the sought for regularities where none exist, and would not tell much about the chemistry of the lanthanides.

As shown here and elsewhere [5] [6] [9] [10] there is *no* arbitrary nature of the straight lines drawn for the tetrads within the framework of my theory (eq. 1). On examining the statistical approach in the case of the double double procedure one is confronted with disastrous statistics. As tabulated by *Siekierski* [14], the probability of an individual element following the double double pattern could be as low as 28%!

| | | |
|---|---|---|
| (a) | $M + X \rightleftarrows MX$: | Tb 57%, Dy 43%, Tm 57%, Yb 64% |
| (b) | $MX + X \rightleftarrows MX_2$: | Tb 72%, Dy 67%, Tm 28%, Yb 41% |
| (c) | $MX_2 + X \rightleftarrows MX_3$: | Ce 71%, Eu 67%, Tb 63%, Dy 67% |

*Fidelis* refers to a recent paper by *Roy & Nag* [15] where the authors have pointed out the relevance of the 'Inclined W plots' in connection with the solvent extraction behaviour of the lanthanides with 4-benzoyl-3-methyl-1-phenyl-5-pyrazolone (HPMBP). They quite correctly state that the 'correlation proposed by *Sinha,* which

is based on experimental data of different workers and is also supported by the present study is a justified one'. I have analyzed their $\log K^{*}_{3,0}$ data and the calculated 'Inclined W parameters' are the following. La-Nd tetrad: $w_1 = 0.203$, $k_1 = -7.28$; Pm-Gd tetrad: $w_2 = -0.072$, $k_2 = -5.20$, calculated value for Pm: 5.64; Gd-Ho tetrad: $w_3 = 0.084$, $k_3 = -5.20$; Er-Lu tetrad: $w_4 = -0.051$, $k_4 = -4.25$. The standard deviation for the whole series is 0.075, showing the internal consistency of the experiment [15]. It is gratifying to note that the ligand PMBP follow the 'Inclined W theory' like other extraction systems, *e.g.*, TBP, HEHØP, HIB, TTA [2] [3] [9].

## REFERENCES

[1] *I. Fidelis,* Helv. *62,* 2046 (1979).
[2] *S. P. Sinha,* Helv. *58,* 1978 (1975).
[3] *S. P. Sinha,* Struct. Bonding *30,* 1 (1976).
[4] *I. Fidelis,* Inorg. nucl. Chemistry Letters *12,* 475 (1976).
[5] *S. P. Sinha,* Inorg. chim. Acta *22,* L5 (1977).
[6] *S. P. Sinha,* Inorg. chim. Acta *27,* 253 (1978).
[7] *G. R. Choppin & A. J. Graffeo,* Inorg. Chemistry *4,* 1254 (1965).
[8] *W. R. Stagg & J. E. Powell,* Inorg. Chemistry *3,* 242 (1964).
[9] *S. P. Sinha,* Invited Plenary Lecture, EUCHEM Conference on the Chemistry of the Rare Earths, May 29, 1978, Helsinki. See also Kemia-Kemi (Helsinki) *5,* 238 (1978).
[10] *S. P. Sinha & A. Bartecki,* Inorg. chim. Acta *33,* 77 (1978).
[11] *I. Fidelis & S. Siekierski,* J. inorg. nucl. Chemistry *29,* 2629 (1967).
[12] *S. Siekierski & I. Fidelis,* J. inorg. nucl. Chemistry *34,* 2225 (1972).
[13] *R. M. Wallace,* Inorg. nucl. Chemistry Letters *7,* 305 (1971).
[14] *S. Siekierski,* J. inorg. nucl. Chemistry *32,* 519 (1970). Actually, in several cases the numbers of ligands that show exactly the opposite effect are twice as large as expected for the double double plots.
[15] *A. Roy & K. Nag,* J. inorg. nucl. Chemistry *40,* 331 (1978). The straight line drawn by these authors for the fourth tetrad is too steep, and one should use the $w_4$ and $k_4$ values in the text to draw the least squares line.