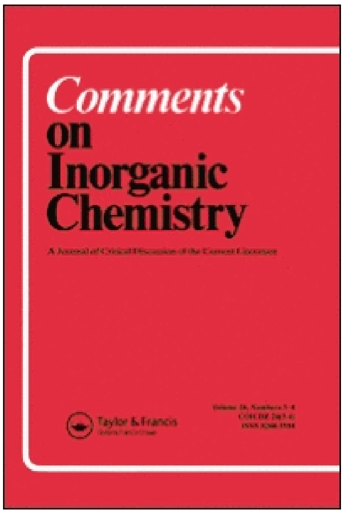

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The “Regular” and “Inverse” Tetrad Effect

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The "Regular" and "Inverse" Tetrad Effect

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A correlation between the direction of the tetrad (double-double) effect in the lanthanide and actinide series and coordination number (CN) is discussed on experimental and theoretical grounds. Some examples of determining the CN values of the f-block elements in solution complexes using the tetrad effect are reviewed. Except for the CN implication, the tetrad effect of the inner transition elements is presented in terms of effective crystal radius, covalent shortening, nephelauxetic and ligand field effects, spin-orbit coupling, hydration, etc.

Key Words: *tetrad effect, coordination number, lanthanides, actinides(III)*

Background information on the subtle effect discovered in this laboratory, called, at first, regularities in stability constants[1] and then the tetrad or double-double effect, is supplied by some previous review articles.[1-3] The effect has been demonstrated for Gibbs energies of complex formation, extraction and ion exchange, enthalpies and entropies of extraction, unit cell volumes of lanthanide and actinide compounds, Gibbs energies of solubility and co-crystallization, Gibbs energy of hydration of the Ln(III) ions, band intensities of IR spectra, protonation constants of lanthanide(III) chelates, etc.[1] Although the tetrad effect, as related to the number of f-electrons (q), concerns all oxidation states of the f-block ele-

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ments, it is usually discussed for the Ln(III) and An(III) series. To give a simple definition of the effect, it suffices now to assume that the lanthanide(III) and actinide(III) contraction vs. q follow a faint two-humped downward curve with the f^7 configuration (Gd^{3+} and Cm^{3+}) as the central point with the two additional minor dips, in the same direction as for the half-filled f-shell, at the ions with the f-shell filled in 1/4 and 3/4. Obviously, the effect should occur for all ionic radius dependent properties of the inner transition elements.

The effect originates mainly from the interelectronic repulsion energy of the f^q electrons. It can be described in terms of the Racah parameters E^1 and E^3 and the dependence of the coefficients of these parameters, $k_1(q)$ and $k_3(q)$, on the quantum numbers L and S. The resulting stabilization energy, E_{st}, of the ground terms in the Russell–Saunders basis for the S-L coupling mode, with regard to the weighted average expectation value (i.e., barricenter) for each f^q configuration,[1–3]

$$E_{st} = k_1(S)E^1 + k_3(L)E^3, \tag{1}$$

displays the same symmetry as the tetrad effect.

For chemical equilibria in solutions involving changes in ligand surroundings of the f-block central ions, it is the difference in stabilization energies, ΔE_{st}, between reaction products and left-hand-side complexes (reaction substrates) which accounts for the tetrad effect:[1–3]

$$\Delta E_{st} = E_{st}^{prod} - E_{st}^{subs} = k_1(q)\Delta E^1 + k_3(q)\Delta E^3 \tag{2}$$

and[2]

$$\Delta E_{st} = (18/13)S(1/2 - S)\Delta E^1 + (L/180)[L(222 - 48L) - 234]\Delta E^3. \tag{3}$$

The tetrad effects reported[1] are differential in nature, viz. they correspond to Eq. (2). The nephelauxetic ratio always decreases for a gaseous f-block ion transferred to a crystal lattice, resulting in negative ΔE^1 and ΔE^3 values, and a destabilization of compounds of the f-block elements for which the f-shell is filled in 0/4, 1/4, 2/4, 3/4 and 4/4. Such a tetrad effect, with downward curves, observed, e.g., for the lanthanide(III) and actinide(III) contraction, is called, by the present author, the "regular" tetrad effect. Usually, e.g., for the Gibbs energy of extraction or complex formation vs. q, where a central ion environment is changed from this in the ionic aquo ion to a somewhat less hard one in the complex formed, the ΔE^1 and ΔE^3 values are negative and the "regular" tetrad effect is recorded. It is characterized, *inter alia*, by a less stable complex of Gd(III) than that resulting from a linear interpolation between stability constants of the respective Eu(III) and Tb(III) complexes. In some cases, for ligand substitution reactions and resulting bidifferential, in fact, tetrad effects (viz. contrary to monodifferential effects, which are always "regular" as, e.g., for the unit cell volumes[1]), the reaction products are more ionic than the reaction substrate complexes. This means that the nephelauxetic effect is less pronounced for the products, and the respective ΔE^1 and ΔE^3 values are positive. It results in the "inverse" tetrad effect, viz. upward tetrad bends, and extra-stabilization of, e.g., Ho(III)($4f^{10}$) and Er(III)($4f^{11}$) complexes (i.e., the 3/4-filled shell effect) with regard to the stabilities corresponding to a linear interpolation for the neighboring ions. (For a more illustrative definition of the "regular" and "inverse" resultant tetrad effect than that based upon the sign of the ΔE_{st} value in Eqs. (2) and (3), see Fig. 1.)

Sawada *et al.*[4] have reported, with no figure given, the tetrad effect within all four tetrads for the logarithmic first protonation constants of 1:1 lanthanide(III) complexes of nitrilotris(methylenephosphonic acid) ($\mathrm{Ln(ntmp)}^{3-}_{aq}$). In this connection a question arises: What indication, concerning the protonated and unprotonated complexes, results from the tetrad effect observed by the Miyamoto group?[4] Another question is: What is the reason for abnormal behavior of Sc(III) reported[4] which gives more or less the same $\log K_{\mathrm{MH(ntmp)}^{2-}}$ value as that for protonation of the Y(III) and Ho(III) nitrilotris(methylenephosphonates)?

The protonation equilibria under discussion, where M stands for all rare earths (La to Lu, Sc and Y) can be given as follows:

$$(\mathrm{H_2O})_x\mathrm{M(ntmp)}^{3-}_{aq} + [(\mathrm{H_3O})(\mathrm{H_2O})_n]^{+}_{aq} \Leftrightarrow (\mathrm{H_2O})_y\mathrm{MH(ntmp)}^{2-}_{aq} + (x - y + n + 1)\mathrm{H_2O}. \quad (4)$$

The $-RT\,\Delta \ln K$ vs. q variations for Eq. (4) display the "regular" tetrad effect within all four tetrads as presented in Fig. 1.

The consistent mode of writing the reaction equations, e.g., according to the convention used by Martell and Smith[5] followed by the present author, viz. placing the H^+_{aq} ion and, generally, the simpler species on the left hand side of the equilibrium equation, is essential for a correct interpretation of the direction of the tetrad effect.

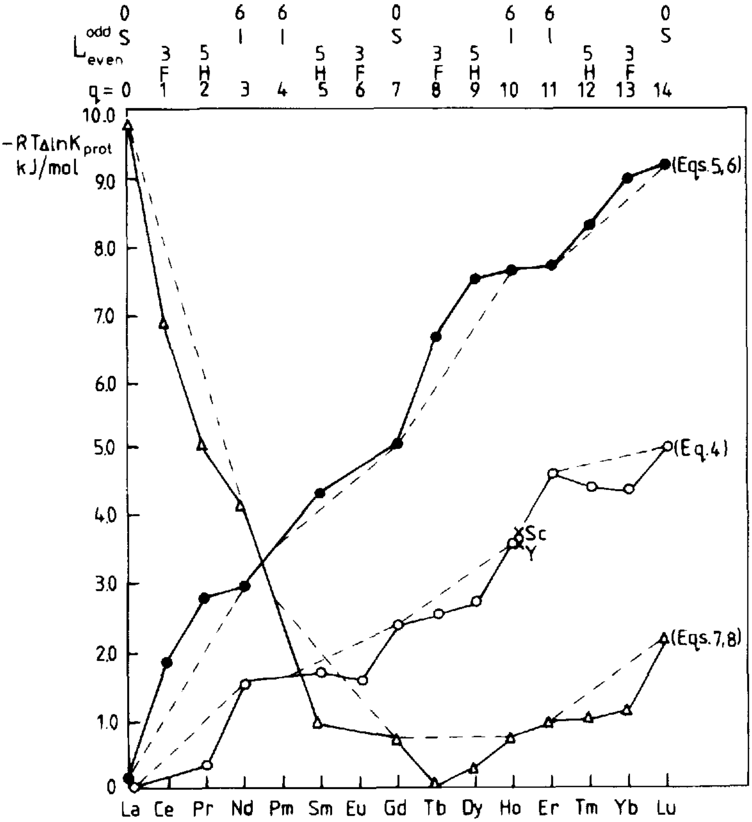

FIGURE 1 $-RT\,\Delta \ln K$ variations vs. number of f-electrons q, total orbital quantum number L and ground terms of lanthanides(III), at imprecision of about ±0.17 kJ/mol. ○—For Eq. (4), i.e., for protonation constants of the Ln(ntmp)^{3-} complexes with × indicating the position of Sc and Y. The "regular" tetrad effect with the downward arcs, unusual for $\Delta(\Delta G)$ increasing with q. The direction of the effect indicates extra-destabilization of the complexes of the Ln(III) ions with the f-shell filled in 0/4, 2/4, 3/4 and 4/4. ●—For Eqs. (5) and (6), i.e., for protonation constants of the Ln(dcta)^{-} complexes. The "inverse" tetrad effect with the upward curves, indicating extra-stabilization of the chelates of the Ln(III) ions with $q = 3, 4, 10$ and 11 in addition to those with $q = 0, 7$ and 14. Δ—For Eqs. (7) and (8), i.e., for the relative Gibbs energy of formation of the $\text{(HO)Ln(dcta)}^{2-}_{aq}$ mixed complexes. The "regular" tetrad effect, with the downward curves, out of the ordinary direction at the third and fourth tetrad where $\Delta(\Delta G)$ increases with q.

On the right hand side of the equilibrium (4), water is specified just to lay emphasis on the entropic gain impelling the protonation. This increase in the reaction entropy, as the protonation (4) proceeds, is caused by dehydration of the H^+_{aq} clusters: $[(H_3O)(H_2O)_n]^+_{aq}$ of the *n* number equal probably to 3 with the doubly hydrated hydroxonium ion at ambient temperature:[6] $[(H_3O)(H_2O)_3]H_2O^+$.

The main objective of this paper is to elucidate how to interpret location and direction of the tetrad effect to determine coordination number (CN) of the f-block elements, which is of importance especially for complexes in dilute solutions. The detailed discussion is exemplified for the "regular" and "inverse" tetrad effect in variations of the first protonation constants of the lanthanide(III) nitrilotris(methylenephosphonates) and diaminocyclohexanetetraacetates. Some other cases of applying the correlation between the tetrad effect and CN are briefly reviewed, and some supporting literature evidence based on routine methods is cited.

RESULTS AND DISCUSSION

The protonation constants for the equilibria (4) have been determined potentiometrically by Sawada *et al.*,[4] using a glass electrode at 298.15 K and at an ionic strength of 0.1 mol*dm^{-3} KNO_3. The data[4] are presented in Table I and plotted in Fig. 1, as confronted with the present author's data,[7,8] measured potentiometrically at 298.15 K and at an ionic strength of 1 mol*dm^{-3} KCl, using the H^+/H_2 on Pt/Pt black indicator electrode for protonation and hydroxo-complexation of the $Ln(dcta)^-_{aq}$ chelates, where dcta denotes trans-1,2-diaminocyclohexanetetraacetic acid.

Lanthanide(III) Diaminocyclohexanetetraacetates

The equilibria dealing with the $Ln(dcta)^-_{aq}$ chelates in 0.01M solutions (Table I, Fig. 1), where the coordination number (CN) of Ln(III) and the inner sphere hydration numbers for the reactants along the lanthanide(III) series were deduced within the specified ranges of the series by the present author by interpreting the direction of the tetrad effect,[7,8] are given below:

$$\text{La–Sm:}\quad (H_2O)_3Ln(dcta)^-_{aq} + H(OH_2)^+_n \Leftrightarrow (H_2O)_4HLn(dcta)_{aq} + (n-1)H_2O,$$

$$CN = 9 \qquad\qquad CN = 10 \qquad (5)$$

TABLE I

Variations of the $-RT\,\Delta\ln K^{*}$ values for equilibria (4)–(8)

	Eq. (4)		Eqs. (5, 6)		Eqs. (7, 8)	
M(III)	$lgK_{\mathrm{MH(ntmp)}^{2}}$	$\Delta(\Delta G)$	$lgK_{\mathrm{LnH(dcta)}}$	$\Delta(\Delta G)$	$lgK_{\mathrm{Ln(OH)(dcta)}^{2-}}$	$\Delta(\Delta G)$
	kJ/mol		kJ/mol		kJ/mol	
La	7.82	0	2.82 ± 0.02	0	1.73 ± 0.01	10.0
Ce	–	–	2.57 ± 0.02	1.7	2.26 ± 0.01	7.0
Pr	7.74	0.4	2.40 ± 0.02	2.7	2.58 ± 0.01	5.2
Nd	7.52	1.7	2.37 ± 0.02	2.9	2.74 ± 0.01	4.5
Sm	7.49	1.8	2.13 ± 0.01	4.2	3.31 ± 0.01	1.0
Eu	7.51	1.7	–	–	–	–
Gd	7.37	2.5	2.00 ± 0.01	5.0	3.36 ± 0.01	0.7
Tb	7.34	2.7	1.72 ± 0.01	6.6	3.49 ± 0.02	0
Dy	7.31	2.9	1.56 ± 0.01	7.5	3.44 ± 0.01	0.3
Ho	7.16	3.7	1.53 ± 0.01	7.7	3.35 ± 0.01	0.8
Er	6.98	4.8	1.52 ± 0.01	7.7	3.31 ± 0.01	1.0
Tm	7.01	4.6	1.42 ± 0.01	8.3	3.30 ± 0.01	1.1
Yb	7.02	4.5	1.29 ± 0.01	9.0	3.27 ± 0.01	1.2
Lu	6.90	5.2	1.25 ± 0.01	9.3	3.09 ± 0.01	2.3
Y	7.15	3.8	–	–	–	–
Sc	7.12	4.0	–	–	–	–

*K is the stoichiometric stability constant.

$$\text{Dy–Lu:}\quad (H_2O)_2Ln(dcta)^-_{aq} + H(OH_2)^+_n \Leftrightarrow (H_2O)_3HLn(dcta)_{aq} + (n-1)H_2O.$$
$$\text{CN} = 8 \qquad\qquad \text{CN} = 9 \qquad (6)$$

The "inverse" tetrad effect was observed in the $-RT\,\Delta \ln K$ vs. q variations in the whole series both for (5) and (6) equilibria.

$$\text{La–Sm:}\quad (H_2O)_3Ln(dcta)^-_{aq} + (OH)(OH_2)^-_n \Leftrightarrow H_2O\,(HO)Ln(dcta)^{2-}_{aq} + (n+2)H_2O.$$
$$\text{CN} = 9 \qquad\qquad \text{CN} = 8 \qquad (7)$$

The "regular" tetrad effect was recorded for Eq. (7) in the first tetrad.

$$\text{Dy –Lu:}\quad (H_2O)_2Ln(dcta)^-_{aq} + (OH)(OH_2)^-_n \Leftrightarrow (HO)\,Ln(dcta)^{2-}_{aq} + (n+2)H_2O.$$
$$\text{CN} = 8 \qquad\qquad \text{CN} = 7 \qquad (8)$$

The "regular" tetrad effect in the third and fourth tetrads for increasing $\Delta(\Delta G)$ values vs. q was a major indication for deducing the CN values in Eq. (8).

In the intermediary range of Eu–Tb, around the middle of the series, the following equilibria exist which result from the change in the inner sphere hydration number of the Ln(III) ions:

$$\text{Eu–Tb:}\quad [(H_2O)_2Ln(dcta)]^-_{aq} + H_2O \Leftrightarrow [(H_2O)_3Ln(dcta)]^-_{aq}.$$
$$\text{CN} = 8 \qquad\qquad \text{CN} = 9 \qquad (9)$$

This change in CN from 9 to 8 in the Eu–Tb range has been established[7] using auxiliary ligands of glycine (gl^-) and iminodiacetic acid (ida^{2-}), and resolving that $dcta^{4-}$ and ida^{2-} are hexa-[9] and tridentate, respectively, from La to Lu. The equilibrium (9) is shifted entirely into the $[(H_2O)_3\,Ln(dcta)]^-_{aq}$ species in the La–Sm range, and into the left hand side chelates of CN = 8, and of the inner sphere hydration number 2, in the Dy–Lu range. The equilibria for the mixed complex formation are as follows:[8]

$$\text{La–Sm:}\quad (H_2O)_3Ln(dcta)^-_{aq} + gl^- \Leftrightarrow (H_2O)\,(gl)Ln(dcta)^{2-}_{aq} + 2H_2O.$$
$$\text{CN} = 9 \qquad\qquad \text{CN} = 9 \qquad (10)$$

The "regular" tetrad effect in the first tetrad was reported[7,8] for Eq. (10).

$$\text{Dy–Lu:}\quad (H_2O)_2Ln(dcta)^-_{aq} + gl^- \Leftrightarrow (H_2O)\,(gl)Ln(dcta)^{2-}_{aq} + H_2O$$
$$CN = 8 \qquad\qquad CN = 8 \qquad (11)$$

The "regular" tetrad effect in the fourth tetrad was shown[7,8] for Eq. (11).

$$\text{La–Sm:}\quad (H_2O)_3Ln(dcta)^-_{aq} + ida^{2-} \Leftrightarrow (ida)\,Ln(dcta)^{3-}_{aq} + 3H_2O.$$
$$CN = 9 \qquad\qquad CN = 9 \qquad (12)$$

The "regular" tetrad effect in the first tetrad was a decisive indication for the CN determination for Eq. (12).

$$\text{Dy–Lu:}\quad (H_2O)_2Ln(dcta)^-_{aq} + ida^{2-} \Leftrightarrow (ida)\,Ln(dcta)^{3-}_{aq} + 2H_2O$$
$$CN = 8 \qquad\qquad CN = 9 \qquad (13)$$

The "inverse" tetrad effect in the third and fourth tetrads was reported[7] for Eq. (13).

The CN = 9 of Eu in the $[(ida)Eu(dcta)]^{3-}_{aq}$ species,[7] and the presence of the two Eu(III) complexes of CN = 8 and CN = 9, according to the equilibrium

$$[(H_2O)_2Eu(dcta)]^-_{aq} + H_2O \Leftrightarrow [(H_2O)_3Eu(dcta)]^-_{aq} \qquad (14)$$

was confirmed later on by Horrocks *et al.*[10] (The double peak in their Fig. 4 of the selective laser excitation spectra of the $^7F_0 \Rightarrow {}^5D_0$ electronic transition of the $Eu(dcta)^-_{aq}$ chelates.)

The present author's[7] data for the $[(gl)Ln(dcta)]^{2-}_{aq}$ complexes (Eqs. (10) and (11)) have been confirmed by Dash *et al.*[11] Instead of glycine, they used norleucine, i.e., butylglycine. Dash *et al.*[11] also observed the tetrad effect of the "regular" direction in the first and fourth tetrads but, as all other authors, they did not make use of this information for discussion of CN in their ternary complexes in dilute solutions. The indication concerning the chelate stoichiometry, arising from the recorded tetrad effect, was neglected by Limaye *et al.*[12] as well.

For the analogous $Ln(edta)^-_{aq}$ chelates, Bukietyńska and Mondry[13] confirmed a difference in the structure between the light (Nd) and heavy

(Ho,Er) lanthanide(III) species on the basis of supersensitive transitions. Of the same opinion on these chelates are Kiraly and Brücher.[14]

Although in the solid phase the $[(H_2O)_nLn(dcta)]^-_s$ chelates have not been studied yet by X-ray diffraction, since they form glassy precipitates, the analogous $[(H_2O)_nLn(edta)]^-_s$ crystals display a change in n from 3 in the La–Dy range to 2 in the Ho–Lu range.[15,16] This supports the present author's conclusion[7] (Eq. (9)) on the $[(H_2O)_nLn(dcta)]^-_{aq}$ chelates.

Thus, the early conclusions concerning CN of the Ln(III) ions, based on the direction of the tetrad effect,[7] have been supported by routine methods[10–16] at other laboratories.

It appears, however, that contrary to the Hoard *et al.*[9] suggestion on similar edta chelates of La(III) in the solid phase, in the protonated chelates, the $(H_2O)_{3-4}$ $HLn(dcta)_{aq}$ (Eqs. (5) and (6)), proton preferably does not coordinate next to the unbonding oxygen atom of the carboxylic group but on the opposite "hemisphere" of the Ln(III) ions free of dcta.[8] On this hemisphere the proton probably migrates by the relay (i.e., tunnel) mechanism between oxygen atoms of the *aqua* molecules, stabilizing the chelates and, in particular, the hydration hemisphere of the central Ln(III) ions. This hydration hemisphere is supposed to contain energetically privileged species of $H_9O_4^+$ (La–Sm) and $H_7O_3^+$ (Dy–Lu) analogous to those postulated for the free H^+_{aq} ion.[6–8]

Similar equilibria to those given by Eqs. (5)–(13) seem to be valid for the respective $Ln(edta)^-_{aq}$ complexes[7–9] at room temperature.

As in the case of the H^+_{aq} ion, and for the same reasons, the anomalous behavior of the OH^-_{aq} ion, and the high entropic stability[7,8] of the hydroxo-complexes (Eqs. (7) and (8)) can be explained in terms of the proton transfer reaction: $HO^- + H{-}O{-}H \Leftrightarrow H{-}O{-}H + OH^-$. ($n$ is probably 3 in Eqs. (7) and (8), i.e., the $[(OH)(OH_2)_3]^-_{aq}$ ion is formed.)

Lanthanide(III) Nitrilotris(methylenephosphonates) and Comparison of Both Protonation Variations

In Fig. 1, the comparison of the relative $-2.303\ RT\Delta\ \lg K$ values vs. q plots for protonation of the nitrilotris(methylenephosphonate) complexes, $Ln(ntmp)^{3-}_{aq}$ (Eq. (4)), with those for the $Ln(dcta)^-_{aq}$ chelates (Eqs. (5) and (6)) is given. It shows that in both cases the "stoichiometric" relative Gibbs energy of the first protonation increases from La to Lu. It means that the stability of protonation of the Ln(III) complexes decreases with lanthanide contraction, viz. with the decreasing basicity of the Ln(III) ions along the series. In both cases, as the lanthanide series is traversed, the $-RT\Delta \ln K$ variations display the tetrad grouping which amounts to 0.4–0.7 kJ/mol, i.e., well above the imprecision limit reaching ±0.02 log K that corresponds to 0.17 kJ/mol. However, a more interesting feature is the opposite direction of the tetrad effects in the protonation cases discussed (Eq. (4)) vs. Eqs. (5) and (6)) as revealed in Fig. 1. It can be seen that in the protonated complexes for which the $4f^q$-shell of the Ln(III) ions is occupied in 0/4 (f^0; La), 1/4 ($f^{3,4}$; Nd, Pm), 2/4 (f^7; Gd), 3/4 ($f^{10,11}$; Ho, Er) and 4/4 (f^{14}; Lu), the protonation is destabilized for the respective $\text{LnH(ntmp)}^{2-}_{\text{aq}}$ complexes (the "regular" tetrad effect, i.e., downward bends), while it is stabilized in case of the $\text{LnH(dcta)}_{\text{aq}}$ series (the "inverse" tetrad effect, i.e., four upward curves).

Most often, the resultant stability of lanthanide(III) complexes increases with q and with increasing ionic potential of the central ion as in case of the hydroxo-complexation for lighter lanthanides (Fig. 1, Eq. (7)). In such a case the complexes of the Ln(III) ions with extra-stabilized $4f^q$ configurations (i.e., f^0, f^3, f^4, f^7, f^{10}, f^{11} and f^{14}) of higher symmetry and of lower repulsion energy than for linearly interpolated neighboring ions, are destabilized. It is so, since the "extra-shrinkage" of these configurations is accompanied by a decrease in the effective nuclear charge and an "extra-expansion" of the outer shells and of the whole Ln(III) ion.[8,17] In other words, a smaller radius of the 4f-shell means better screening of the 5s and 5p orbitals from the positively charged core, and this better, screening corresponds to a larger ionic radius. Thus, the "extra-compression" of the stabilized 4f orbitals, viz. of $\langle r_{4f}\rangle$, is accompanied by a mirror "extra-extension" of the outer 5p orbitals, viz. of $\langle r_{5p}\rangle$ and of $r_{\text{Ln(III)}}$[8,17] of the tetrad pattern. For the product stability increasing with q, CN usually decreases and, in consequence, the nephelauxetic tetrads are more pronounced for the reaction products than for the left-hand-side complexes. Hence, the resultant tetrad effect is manifested by a destabilization of complexes of the Gd(III) ion and of the other Ln(III) ions of extra-stabilized f-configurations.

Such a "regular" double-double effect is also exhibited as the simplest (i.e., mono-differential) effect, with respect to the gaseous ions, in the crystallographic ionic radii and crystal lattice parameter variations with q revealed by Siekierski[18] (a minute effect at the 1/4 and 3/4 points) and illustratively plotted by David[19] both for the Ln(III) and An(III) series. In the crystal lattice the magnitude of the effect increases as the nephelauxetic effect and the average radius of the partly filled shell increase, i.e., with decreasing parameters of interelectronic repulsion E^1 and E^3. It means that the nephelauxetic/tetrad effect increases with increasing "softness" of coordinating ligands in the crystal lattice which is correlated with the CN dependent internuclear distances. The decreasing CN produces a decrease in central ion—donor atom distances R, and consequently in crystal cationic r_M and, to a lesser extent, anionic radii r_A.[20] This decrease in the R value is accompanied by an increase in an overlap integral between the buried 4f-shell with a small average radius r_{4f} and the ligand orbitals, viz. Ψ_{4f} and Ψ_{lig}. In consequence, an increase in the r_{4f} value (i.e., cloud expansion) and a decrease in the $r_{Ln(III)}$ value[8,17] occur. This small additional decrease in the effective ionic radius for a given CN is designated as the nephelauxetic effect[21] or, more generally, "the covalent shortening".[20] It is of importance whether the position of a ligand in the nephelauxetic series, and electronegativity of its donor atoms, is of smaller or larger consequence than CN variations for the f-block elements as far as the effect of covalency on shortening of the M–X bonds is concerned.

The OH^- ion, as slightly more ionic, i.e., harder, precedes water in the nephelauxetic series of ligands for the same CN. In spite of this, it results, from Fig. 1, that the monohydroxy complexes display a "regular" tetrad effect, i.e., they are more covalent than the left-hand-side 1:1 complexes (Eqs. (7) and (8)). It is so because the OH^- ion replaces two molecules of water in the left-hand-side complexes of $Ln(dcta)^-_{aq}$[7]. Consequently, in the $(HO)Ln(dcta)^{2-}_{aq}$ complexes, CN is decreased by 1, and in spite of the presence of the OH^- ion, which is harder than water, the average distance of Ln-donor atoms becomes shorter with respect to that for the $Ln(dcta)^-_{aq}$ complexes. On the other hand, for the ions of heavy Ln(III), the iminodiacetate ions (ida^{2-}),[7,8] distincly preceded by hard *aqua* in the nephelauxetic series, produce the harder mixed complexes $(ida)Ln(dcta)^{3-}_{aq}$ (CN = 9, Eqs. (12) and (13)) with regard to the substrate complexes, $(H_2O)_2Ln(dcta)^-_{aq}$ of CN = 8. In the latter case two water molecules result in a more covalent action than a tridentate ida anion. This is proved by the "inverse" tetrad effect[7,8] for heavy lanthanides(III). So, it is once more the CN change which is the decisive factor for the differential nephelauxetic effect and the direction of the resultant tetrad effect. For the f-block trivalent ions with well-shielded f-orbitals, neither the charge of the complex nor electronegativity of the donor atom and the position of a ligand in the nephelauxetic series can prevail over the influence of the CN change.

Therefore, hard oxygen in the soft crystal lattice of cubic C-type Ln_2O_3 (CN = 6) generates the nephelauxetic effect even slightly more distinct than soft iodine in LnI_3 (CN = 8). This results implicitly from the nephelauxetic series of ligands of increasing covalency with respect to the Pr(III) ion reported by Jørgensen[21]: Pr^{3+}_{gas}(0; 1.0) < (La, Pr)F_3(9; 0.970) < $[Pr(OH_2)_9](C_2H_5SO_4)_3$(9; 0.962) < (La, Pr)$Cl_3$(9; 0.958) < (Gd, Pr)$Cl_3$ (9; 0.955) < (La, Pr)Br_3(9; 0.954) < PrI_3(8; 0.944) < C–Pr_2O_3(6; 0.943) < $BaPr_2S_4$(6; 0.928). (In parentheses the CN values and decreasing β nephelauxetic ratios, specified by the present author, are given.)

Implications of the "Inverse" Tetrad Effect in the Ethylsulfate System

Besides the $(ida)Ln(dcta)^{3-}_{aq}$ complexes[7,8] in the Dy–Lu range (Eq. (13)), the resultant stability of lanthanide(III) and actinide(III) compounds decreases with q,[22,23] and the "inverse" tetrad effect has been observed also for the relative Gibbs energy of co-crystallization and crystallization of ethylsulfates of heavy lanthanides, viz. in the third and fourth tetrads. This has also been attributed[22,23] to an increase in CN from 8 for the left-hand-side aquo-ions of the D_{4d} symmetry point group: $[Ln(OH_2)_8]^{3+}_{aq}$ (Ln = Tb–Lu) and $[An(OH_2)_8]^{3+}$ (An = Fm–Lr) to CN = 9 in the solid (s) phase lattice of the products being crystalline salts and pure aquo-complexes, i.e., $[(Ln,M)(OH_2)_9](C_2H_5SO_4)_3$ (C_{3v}). For the ethylsulfate co-crystallization (Eq. (15)) and crystallization (Eq. (16)), the following equilibria are valid:[22,23]

$$M^{3+}_{aq} + [Ln(H_2O)_9](C_2H_5SO_4)_{3,s} \Leftrightarrow Ln^{3+}_{aq} + [M(H_2O)_9](C_2H_5SO_4)_{3,s}, \quad (15)$$

$$Ln^{3+}_{aq} + 3C_2H_5SO^-_{4,aq} + 9H_2O \Leftrightarrow [Ln(H_2O)_9](C_2H_5SO_4)_{3,s} \quad (16)$$

The "reverse" tetrad effect in the third and fourth tetrads was recorded for the both equilibria (15) and (16).

Taking into consideration the behavior in the special ethylsulfate system with water as the only inner sphere ligand in both phases, the slightly higher symmetry of D_{3h} in the flexible nonaaqua-ions (as compared with that distorted of C_{3v}/C_{3c} in the hydrogen bonding bound crystal lattice of the nonahydrates) is probably held in the $[M(OH_2)_9]^{3+}_{aq}$ aquo-ions. M concerns Ln and An ions from the La–Pm and U–Cm ranges. The aquo-ions of CN = 8 are more covalent, i.e., they display a larger nephelauxetic effect than those of CN = 9, resulting in the "inverse" tetrad effect in the Gd–Lu range[22,23] for the relative Gibbs energy vs. q variations for Eqs. (15) and (16). So, for comprehension:

$$\text{Ln} = \text{Sm, Eu, Gd} \quad [\text{Ln(OH}_2)_8]^{3+}_{\text{aq}} + \text{H}_2\text{O} \Leftrightarrow [\text{Ln(OH}_2)_9]^{3+}_{\text{aq}}, \quad \text{CN} = 8\,(D_{4d}) \quad \text{CN} = 9\,(D_{3h} \text{ rather than } C_{3v} \text{ or } C_{3h}) \tag{17}$$

$$\text{An} = \text{Bk, Cf, Es} \quad [\text{An(OH}_2)_8]^{3+}_{\text{aq}} + \text{H}_2\text{O} \Leftrightarrow [\text{An(OH}_2)_9]^{3+}_{\text{aq}}. \quad \text{CN} = 8\,(D_{4d}) \quad \text{CN} = 9\,(D_{3h} \text{ rather than } C_{3v} \text{ or } C_{3h}) \tag{18}$$

The equilibria (17) and (18) concern ambient temperature, and with increasing temperature the transition zones of Sm–Gd and Bk–Es tend to broaden.

It has been concluded (Eqs. (17) and (18)) that for M standing for Sm, Eu, Gd, Bk, Cf and Es, CN in the aquo-ions is between 8 and 9,[8,22,23] while for the largest trivalent cation of the Periodic Table, i.e., Ac(III), which is about 9% larger than La(III),[20] CN = 10 is suggested by the present author.[8] The exceptional CN for $[\text{Ac(OH}_2)_{10}]^{3+}_{\text{aq}}$ is probably responsible for the anomalous behavior of the Ac(III) ion in some systems.[24]

The increase of the relative Gibbs energy with q for protonation of the $\text{Ln(dcta)}^-_{\text{aq}}$ chelates (Table I, Fig. 1, Eqs. (5) and (6)), accompanied by the "inverse" resultant tetrad effect, has been also (viz. as in Eqs. (15) and (16) for heavy Ln) interpreted in terms of the CN increased by one for the reaction products due to linking the oxonium H_3O^+ ion for the 1:1 lanthanide(III) chelates of dcta from La to Lu[7,8] in the result of protonation.

To the best of the author's knowledge, the slightly decreasing resultant stability of the lanthanide(III) complexes with q, accompanied by the "regular" tetrad effect, has been observed rather exceptionally only for hydroxo-complexation of the $\text{Ln(dcta)}^-_{\text{aq}}$ chelates of heavy lanthanides[7] (Table I, Fig. 1., Eq. (8)) and for protonation of the $\text{Ln(ntmp)}^{3-}_{\text{aq}}$ complexes in the entire lanthanide(III) series (Table I, Fig. 1, Eq. (4)).

What Results from the "Regular" Tetrad Effect in the Protonation Constants of the $\text{Ln(ntmp)}^{3-}_{\text{aq}}$ Species?

What results from the "regular" tetrad effect and what is its physical meaning in the case of protonation of the $\text{Ln(ntmp)}^{3-}_{\text{aq}}$ complexes reported by the Miyamoto group?[4] The discussion must be analogous to that given[7,22,23] for the equilibria (5)–(8), (10)–(13) and (15) and (16). The direction and magnitude of the resultant tetrad effect depends upon a difference in the overlap integrals of 4f-electrons with ligand orbitals between the reaction products and left-hand-side complexes, i.e., between the $(H_2O)_yMH(ntmp)^{2-}_{aq}$ and $(H_2O)_xM(ntmp)^{3-}_{aq}$ respective species (Eq. (4)). Hence, the present "regular" tetrad effect for the $-RT\ \Delta \ln K_{prot}$ vs. q variation (Eq. (4), Fig. 1) gives evidence that, contrary to the $Ln(dcta)^{-}_{aq}$ vs. $HLn(dcta)_{aq}$ chelates, the protonated Ln(III) complexes of ntmp are more covalent with regard to the unprotonated ones in the entire lanthanide series. In other words, the nephelauxetic effect is more distinct and the nephelauxetic ratio is smaller for the protonated complexes ($E^1_{prod}/E^1_{subst} < 1$ and $E^3_{prod}/E^3_{subst} < 1$). The coordinating group of ligands $(H_2O)_yH(ntmp)^{5-}_{aq}$ is a softer Pearson's base (more reducing, more polarized, more enhancing slightly covalent bonding) with respect to the Ln(III) ions, and this group must be located behind the left-hand-side group of $(OH_2)_x(ntmp)^{6-}_{aq}$ (Eq. (4)) in the nephelauxetic series of ligands.

It results from the above discussion that the observed direction of the tetrad effect can be explained by a shorter distance between the central Ln(III) ion and the donor atoms of ntmp in the protonated complexes, which could be caused by a decrease in CN for the protonated complexes (Eq. (4)).

According to Shannon,[20] an increase in CN for the Ln(III) ions from 8 to 9 is accompanied by an increase in the effective ionic radius by about 5%. It means that this increase is about twice as large as predicted by Pauling.[25] In case of the Ln(III) ions for a change in CN from 6 to 8, a radius multiplier of 1.16 must be used, and for an increase from the standard CN = 6 to CN = 12, this multiplier even amounts to 1.33.[20]

The donor atom–central ion distances R and, in consequence, the ionic radii $r_{Ln(III)}$ must be smaller for the protonated complexes, thereby allowing a greater orbital overlap of the *eigenfunctions* of Ψ_{4f} and Ψ_{lig}. It gives a more distinct covalent shortening, viz. an additional decrease of the effective ionic radius, associated with the "regular" tetrad effect which is displayed by the relative Gibbs energy vs. q variations for equilibria given by Eq. (4) and illustrated in Fig. 1.

Contrary to the protonation of the $Ln(dcta)^{-}_{aq}$ chelates, which, as endothermic,[7,8] is destabilized by the enthalpy of protonation, protonation of the $Ln(ntmp)^{3-}_{aq}$ species must be slightly exothermic. In addition to the obvious entropic contribution, it should also be stabilized enthalpically due to the postulated lower CN and shorter distances, Ln(III)–donor atoms, for the reaction products across the lanthanide series (Eq. (4)).

Thus, the "regular" direction of the tetrad effect for the logarithmic first protonation constants of the $Ln(ntmp)_{aq}^{3-}$ complexes (four downward curves vs. q in Fig. 1) indicates the decrease in CN for all the protonated chelates from La to Lu. It has been clearly demonstrated by Sawada *et al.*[4] by routine methods that this decrease in CN could be attributed only to the rupture of the weak Ln–N bond, by the betaine type proton (as for Mg(II), Ca(II), Sr(II) and Ba(II), but contrary to the softer d-block M(II) ions). This proton starts the protonation with attack for the highly basic nitrilo nitrogen of ntmp. It could be expected that the Ln–N bond is weaker than the Ln–O bonds (N is less electronegative and softer than O) since for the hard Ln(III) cations the "hard-hard" interactions are energetically privileged. In consequence of the CN decrease by 1, all the Ln–O bonds become shorter by about 5%,[20] and consequently more covalent, resulting in the "regular" tetrad effect. In other words, it results from the direction of the tetrad effect that the increase in covalency, additive in nature, produced by shortening of all the Ln–O bonds due to the decreased CN, prevails over the decrease in covalency due to the absence of the softer Ln–N bond. A small covalent contribution into the ionic bond is exhibited even by the Ln(III) and An(III) aquo ions.[8,22,23] Thus, again the CN factor predominates over the position of a ligand in the nephelauxetic series when the direction of the resultant tetrad effect is concerned. Probably for the $Ln(dcta)_{aq}^{-}$ and $Ln(edta)_{aq}^{-}$ complexes, the initial increase of CN by 1 due to protonation, and the H_3O^+ ion bonded (Eqs. (5) and (6)) at very low pH, is also followed by the decrease in CN and in dentacy of $dcta^{4-}$ and $edta^{4-}$, the decrease of which is caused by the two weakest Ln–N bonds ruptured.

In conclusion, the evidence given by Sawada *et al.*[4] on the Ln–N bonding ruptured by protonation in the $Ln(ntmp)_{aq}^{3-}$ series must be completed by the CN decrease by 1 in the whole series, indicated by the direction of the tetrad effect.

Going from the aminopolycarboxylic ligands to their aminopolyphosphonic analogues, e.g., from nitrilotris(acetic acid), nta, to nitrilotris (methylenephosphonic acid), ntmp, a higher stability of the 1:1 Cu(II) and Zn(II) complexes of ntmp by 5 and 6 orders of magnitude, respectively, has been observed.[26] It must be mainly due to a twice higher charge of the phosphonic groups ($ntmp^{6-}$ vs. nta^{3-}). Most likely, the Y(III) ion in the crystal lattice of insoluble and triply protonated $YH_3(ntmp)$ $*3H_2O$[27] displays CN = 9 with 6 oxygen atoms of the "short bite" bidentate phosphonic groups of ntmp and 3 oxygen atoms of H_2O as donors. In aqueous solution, deprotonation of $YH_3\ (ntmp)_{aq}$ is probably accompanied by a general shrinkage of the coordination sphere of the Y(III) ion,[9] followed by a compelled monodentacy of all three phosphonic groups of $ntmp^{6-}$, and finally by the N–Y bonding after deprotonation of the third proton. If analogy with the respective basic complexes of $(HO)Ln(dcta)^{2-}_{aq}$ (Eq. (8)) is held, then Y in the $Y(ntmp)^{3-}_{aq}$ complex should probably be of CN = 7, i.e., with three water molecules coordinated in the first coordination sphere. Therefore, Eq. (4), at least for Y(III) and heavy lanthanides of the yttrium group, may be given in the following hypothetical form:

$$\begin{aligned}&(H_2O)_3Ln\{N[CH_2P(O)_2(O)]_3\}^{3-}_{aq} + [(H_3O)(H_2O)_3]^{+}\\&\qquad\Leftrightarrow (H_2O)_3Ln\{{}_3[(O)(O)_2PCH_2N]H\}^{2-}_{aq} + 4H_2O.\\&\quad CN = 7 \qquad\qquad\qquad\qquad\qquad\qquad CN = 6\end{aligned} \tag{19}$$

For the light (i.e., larger) Ln(III) ions, CN probably decreases from 8 to 7 with the constant inner sphere hydration number of 4, resulting in the tetrad effect of the "regular" direction.[28,30]

It has been suggested that three PO_3^{2-} groups of $ntmp^{6-}$ are monodentate with regard to the alkaline earth[26] and rare earth(III)[4] cations. Since the second protonation constants change very little with $r_{Ln(III)}$ (log K for $LnH_2(ntmp)^{-}$ = 5.7–5.4),[4] the second proton probably stays at the unbonding oxygen atom of the phosphonic group: $O = P\ (O)^{2-}$. In the second coordination sphere of the Ln(III) ions, at a distance of about 6.5 Å, it is "insensitive" to the lanthanide contraction which from La to Lu reaches 0.18 Å for CN = 8.[20]

Quasi-Lanthanide Behavior of Sc(III)

In order to explain a quasi-heavy-lanthanide behavior of Sc(III) in the system under consideration (Table I; Fig. 1), an increase in CN of Sc(III) must be assumed for the protonated complexes.[31,32] Such an increase is possible, provided the small Sc(III) ion is bound in the $Sc(ntmp)^{3-}_{aq}$ complex only by the oxygen atoms of the monodentate phosphonic groups as for Be(II).[26] In such a case the mechanism of protonation of the $\mathrm{Sc(ntmp)}_{\mathrm{aq}}^{3-}$ species would be analogous to that given by Eqs. (5) and (6), viz. with the oxonium water, H_3O^+, joined. It is difficult to say whether in this case, from a statistical point of view, a proton preferably stays next to the nitrogen atom or on the opposite "hemisphere" of the Sc(III) ion as the stabilized $H_7O_3^+$ species, e.g.,

$$\begin{aligned}
&(\mathrm{H_2O})_2\mathrm{Sc}\{{}_3[(\mathrm{O})(\mathrm{O})_2\mathrm{PCH_2}]\mathrm{N}\}_{\mathrm{aq}}^{3-} + \mathrm{H_9O_4^+}\\
&\qquad\qquad \Leftrightarrow \mathrm{H}(\mathrm{H_2O})_3\mathrm{Sc}\{{}_3[(\mathrm{O})(\mathrm{O})_2\mathrm{PCH_2}]\mathrm{N}\}_{\mathrm{aq}}^{2-} + 3\mathrm{H_2O}.\\
&\qquad \mathrm{CN} = 5 \qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathrm{CN} = 6
\end{aligned} \tag{20}$$

If the proven decrease in CN by one, due to rupturing of the M–N bond in the lanthanide(III) series and Y(III), is accompanied by the postulated increase in CN by 1 for Sc(III) by bonding the H_3O^+ ion (as for protonation of $\mathrm{Ln(dcta)}_{\mathrm{aq}}^{-}$ given by Eqs. (5) and (6)), the Sc(III) behavior must be similar to that reported by Sawada *et al.*[4] It results from the Shannon's[20] values of the effective crystal radii that the Sc(III) radius for CN = 6 is 0.745 Å while for CN = 8 it amounts to 0.870 Å, exceeding that of Yb(III) for CN = 6. The decrease in CN by 1 for the Ln(III) and Y(III) ions and the increase in CN by 1 for Sc(III), in result of protonation, as given by Eqs. (19) and (20), yields two CN units of difference. This has as a consequence a quasi-holmium behavior of scandium, i.e., the log $K_{\mathrm{MH(ntmp)}^{2-}}$ value for Sc(III) close to that for the first protonation of nitrilotris(methylenephosphonato) complexes of Y(III) and Ho(III) (Table I, Fig. 1).

Hence, the position of Sc(III) with respect to the Ln(III) and An(III) series is a purely thermodynamic, and independent of the tetrad effect, indicator of CN of Y(III), Sc(III) and of the f-block elements in solution complexes[31,32] even at low concentrations, e.g., of 0.01M.

SOME GENERAL REMARKS

Recapitulating, the direction of the resultant tetrad effect, corresponding to chemical equilibria in solutions, e.g., for log K, ΔG, ΔH, ΔS and plots of other ionic radius (r) dependent quantities, results from the course of the lanthanide (and actinide) contraction within two series of the Ln(III) (and An) complexes: reaction products and left-hand-side reactants (see, e.g., Eqs. (4)–(8), (10)–(13), (15) and (16)). It implies that this course, referred to the gaseous/free cations, and its slope are very sensitive to the CN changes in the complexes involved. The covalent shortening of the tetrad pattern is correlated mainly with the CN for the reaction products vs. left-hand-side complexes and, to a lesser degree, with a nephelauxetic position of ligands in both series of complexes in question. As discussed above, the CN factor contravenes the position of a ligand in the nephelauxetic series, and it is the CN influence which always prevails as in the case of the $HLn(ntmp)^{2-}_{aq}$, $(HO)Ln(DCTA)^{2-}_{aq}$ and $(IDA)Ln(DCTA)^{3-}_{aq}$ series.

Tetrad Effect and Ligand Field

The tetrad effect certainly bears close resemblance to the ligand field effect for the d-block elements. Both effects show, e.g., destabilization of compounds of the ions with the half-filled f- or d-shell. It is produced by an extension of the ions with the half-filled shell, e.g., of Gd(III)($4f^7$), Cm(III)($5f^7$), and Fe(III)($3d^5$) or Mn(II)($3d^5$). It can be seen for r vs. q variation[19] or, e.g., for the respective enthalpy of hydration or crystal lattice energy plots. However, these destabilizations are of quite different origin. For the d-block elements, the ligand field effect is usually discussed in terms of stabilization of configurations other than d^5 by splitting d orbitals into the t_{2g} and e_g levels in the octahedral crystal field. This produces two-humped curves (downward with increasing q) for high spin complexes with unchanged, i.e., relatively destabilized, Fe(III) (or Mn(II)) compounds in the middle of the plot. For the f-block elements, the destabilization of, e.g., Gd(III) ($4f^7$) complexes, due to the tetrad effect results from the stabilization and "extra-compression" of the f^7 orbitals by the spin pairing energy which, as the E^1 dependent contribution to the stabilization energy (Eqs. (1)–(3)), explains the half-filled shell effect. This "extra-compression" of the $4f^7$ orbitals, produced by the smaller interelectronic repulsion, is accompanied by the mirror "extra-expansion" of the outer orbitals of the $5s^25p^6$ octet, of the $5d^0$ orbital, viz. of the whole Gd(III) ion. Therefore, although the two-humped ligand field effect in r vs. q variations has the same direction as the respective four-curve tetrad effect, these effects counteract, e.g., for the Gd(III) (or Fe(III)) ion. The direction of the ligand field stabilization, and that of the tetrad effect, would be the same, e.g., for the crystal lattice parameters, only if the ligand field effect would not concern the shielded 4f-shell but an outer 5d-shell, but this is not the case. Therefore, the ligand field effect, the absolute magnitude of which for the f-block elements is over 20 times smaller than the f-electronic repulsion energy of the tetrad pattern, must relatively diminish the half-filled shell effect. Since the ligand field stabilizes all the configurations, except for f^0, f^7 and f^{14}, it augments by a "mirror image" all the Ln(III) ions except for La(III), Gd(III) and Lu(III). The ligand field reaches the maximum stabilization energy and destabilization of complexes of the respective ions for the f^3, f^4, f^{10}, f^{11} configurations (e.g., for crystals of the symmetry point groups: D_{3h}, C_{3h}, D_{6h}, O_h). Hence, contrary to some estimates,[2,29] the ligand field effect enhances, to some extent, the essence of the tetrad effect, viz. the effect of the f-shell filled in 1/4 and 3/4. Consequently, it relatively reduces the effect of the f-shell filled in 0/4, 2/4 and 4/4. These are the changes in the Racah parameters ΔE^3 in the reaction products with regard to the left-hand-side complexes (Eq. (3)) which explain[28,29] the effect of the f-shell filled in 1/4 and 3/4. Small contributions from the ligand field and quite minute ones from the spin-orbit (SO) coupling are very likely, especially for the An(III) ions where these contributions are about twice as large as those for the Ln(III) ions. The An(III) ions have the radial extent of 5f orbitals larger by about 60% than for the better shielded 4f orbitals of the Ln(III) ions of similar size. It must be emphasized that the crucial role for the tetrad effect is played by the E^3 parameter, in spite of the $E^1/E^3 \cong 10$ ratio.[21,28]

It is difficult to explain unequivalent nephelauxetic changes in the E^3 value with respect to the E^1 variation. According to Jørgensen,[28] when passing from the Ln(III) aquo-ions into the respective Ln(III) extraction complexes in the organic phase, the E^3 parameters decrease to a 4–5 times greater extent than the E^1 parameters, resulting in a $\Delta E^3/\Delta E^1$ ratio of about 0.4–0.5. However, some theoretical estimates[29] have proved that the $\Delta E^3/\Delta E^1$ ratio has its strict physical limitations, and it can change but from -0.136 to 0.214. The negative value of -0.136 implies a possible occurrence of an alternating tetrad effect that has never been observed. For such an effect the E^1 dependent spin pairing energy, and the half-filled shell bend, would show the opposite direction with regard to the two minor dips for the f-shell filled in 1/4 and 3/4, originating in the E^3 variations for an eventual ligand.

In the great majority of extraction systems[29] (e.g., Ln(III)-TBP-HNO_3; Ln(III)-HDEHP-HNO_3; Ln(III)-HEHØP-HNO_3, etc.[1]) a decrease in the E^1 parameter for a more covalent organic phase environment (viz.

mostly due to a decreased CN in the organic phase complexes) by about 0.5% is accompanied by a decrease in the more sensitive E^3 parameter by about 1%, with an $\Delta E^3/\Delta E^1$ value of 0.18–0.19, i.e., close to the upper physical limit. In practice, however, $0.058 < \Delta E^3/\Delta E^1 < 0.231$.[29] In the present author's opinion, the higher values of the experimentally observed limits for the tetrad effect presumably result not only from the discussed contribution from the ligand field stabilization but also from the SO coupling share.

Tetrad Effect and Spin-Orbit Coupling

The spin-orbit coupling coefficient, $k_\xi(q)$, displays a similar symmetry with respect to the f-shell filled in 1/4 and 3/4 as the coefficient $k_3(q)$ from Eq. (2). Consequently, a stabilization energy of the ground states for the Ln(III) aquo-ions, derived from the $k_\xi(q)\xi$ term, amounts to about 50% of that originating in the $k_3(q)E^3$ term[33] in Eq. (2).

Thus, due to the SO coupling stabilization, the primary effect (Eq. (1)) of the 4f-shell filled in 1/4 and[34] 3/4 is increased by about 50%. For the An(III) ions in crystal matrices, this relativistic effect is about twice as large, since the number of protons is higher by 32, as that of the respective Ln(III) ions. Consequently, for the An(III) ions the value of $k_\xi(q)\xi$ is more or less the same as the $k_3(q)E^3$ value from Eq. (2), although it is still about 6 times smaller than the $k_1(q)E^1$ term responsible for the half-filled shell effect. On the other hand, for the An(III) ions the quantum mechanical interelectronic repulsion energy of the q electrons in each $5f^q$ configuration amounts to 2/3 of the respective energy for the Ln(III) ions,[29] while ξ_{5f} parameter, as determined spectroscopically, is 2–2.5 times larger than the respective ξ_{4f} value. However, analysis of the ξ_{4f} value[35] has shown that this SO parameter is virtually constant for different Ln(III) compounds, Ln^{3+}_{aq} aquo-ions, and Ln^{3+} admixtures at various crystals included. In addition, the $k_\xi(q)$ value is insensitive to q changes. When going from Pr^{3+} ($4f^2$) to Nd^{3+}($4f^3$), $k_\xi(q)$ changes by 0.5 while $k_3(q)$ changes by 12.[29] As a result, the SO coupling is virtually negligible as far as the resultant tetrad effect is concerned. An enhancement of the relativistic SO coupling occurs for the wave function in the direct vicinity of the nucleus, and this part of the wave function gives the main contribution to the ξ value, while ligands influence an outer, i.e., "tail", density of the relativistic electrons. Consequently, the integral for the ξ value contains the r^{-3} factor whereas that for the Racah parameters E^1

and E^3 that of r^{-1}. Therefore, the Racah or related Slater integrals are very sensitive to changes in coordination number (CN) of complexes of the f-block elements. For ligand substitution and protonation equilibria, resulting in the differential tetrad effect (Eq. (3)), it is not the absolute energy values (Eq. (1)) which count but their differences for varying ligand environment, and CN in particular, between reaction products and left-hand-side reagents.

The simplified theoretical approach to the tetrad effect, summarized in Eq. (3), is based on the possibility of separating the spin from the orbital contribution into the wave function, according to the Russell–Saunders classification, and resulting $^{2S+1}L_J$ terms. In spite of a substantial shift from the $\mathbf{S} + \mathbf{L} = \mathbf{J}$ to $\mathbf{s} + \mathbf{l} = \mathbf{j}$ and $\mathbf{J} = \Sigma\mathbf{j}$ coupling, S and L are sufficiently "good" quantum numbers for low energy levels of both Ln(III) and An(III) ions. The ground multiplet, e.g., of $Pr^{3+}(4f^2)$, consists in 99% from levels originating in the splitted ground term of ^3H.[35] For $U^{3+}(5f^3)$ ca. 70% concerns the ground term of ^4I, and for $Cm^{3+}(5f^7)$ still ca. 60% is of the ^8S term.[36] Except for the stabilization energy, caused by repulsion between q electrons (viz. resulting in the ^{2S+1}L terms given in Fig. 1), SO coupling ($^{2S+1}L_J$), ligand field (which splits the J levels depending on the M_J value up to about 100 cm^{-1} (Ce, Sm, Tb, Yb), 250 cm^{-1} (Nd) and 400 cm^{-1} (Eu, Tm)[37]), and o-o, s-o and s-s interactions (i.e., the orbital-orbital, spin-other orbital and spin-spin interactions which as quite negligible quantities are not discussed here), the term for the remaining energy is simply a quadratic monotonically increasing function of q and cannot account for the tetrad effect.

As mentioned above, the half-filled shell effect is attributable mainly to the spin pairing, $k_1(S)E^1$, stabilization (Eqs. (1)–(3)) due to spin coupling of the f electrons in the total spin momentum: $\mathbf{S} = \Sigma\, \mathbf{s}_i$ and $\mathbf{S} = \hbar\ [(S(S+1)]^{1/2}$, where S is the total electron angular momentum quantum number in the Russell–Saunders basis for the f^q configuration.

The discontinuities at the 1/4 and 3/4 filled f-shell are attributable mainly to the $k_3(L)E^3$ stabilization (Eqs. (1)–(3)) which is due to the summation of the orbital momenta of f-electrons in the total orbital momentum: $\mathbf{L} = \Sigma\, \mathbf{l}_i$, quantified with the L quantum number, i.e., $\mathbf{L} = \hbar[(L(L+1)]^{1/2}$.

To be quite explicit about the matter, the Russell–Saunders coupling into the total momentum, $\mathbf{S} + \mathbf{L} = \mathbf{J}$, where $\mathbf{J} = \hbar[(J(J+1)]^{1/2}$, gives rise to the spin-orbit (SO) stabilization, $k_\xi(q)\xi$, of the analogous symmetry to that of the $k_3(q)E^3$ variations. Although for An(III), $\xi \cong E^3$, for a change in the stabilization energy of transfer of an An(III) ion from a left-hand-side complex (usually an aquo-ion) into a reaction product, the following relations are roughly held: $\Delta E^1 \cong 10\Delta\xi$, $\Delta E^3 \cong 20\Delta\xi$ and $\Delta E_\xi = k_\xi\ (S,\ L,\ J)\ \Delta\xi \ll \Delta E_{st}$, where $\Delta E_{st} = \Delta E^1_{st} + \Delta E^3_{st}$ is defined by Eq. (3). By analogy, in such a qualitative approach for the ligand field contribution, extremely sensitive to changes in CN, although $E^1 \cong 10E^3 \cong 20V_{lig}$, the respective differential quantities for the total tetrad stabilization energy could often be of the order $\Delta E^1_{st} \cong 3\Delta E^3_{st} \cong 6\Delta V_{lig} \cong 15\Delta E_\xi$.

Some Other Examples of Covalency of the f-Block Elements

Except for the tetrad effect, a subtle covalent contribution into bonding of the f-block elements, and a correlation between this contribution and coordination number (CN), is manifested, e.g., in the solubility/reactivity in acids of the Ln and Th hydroxides and oxides, obtained as a mixture from bastnaesites.[8,38] Here, the leaching of the f-block cations using nitric acid decreases with temperature and drying time[38] of the Ln bastnaesite concentrate in consequence of increasing "softness" of the crystal lattices. This Pearson's softness is directly correlated with CN, covalent shortening, valency state and 4f- or 5f-shell involved, and increases with the "inertness" of bastnaesite concentrate components as follows: $Ln(OH)_3$ < A-Ln_2O_3 < C-Ln_2O_3 < CeO_2 < ThO_2. As expected, in the crystal lattices of the above series, the covalent shortening for the Ln(III) ions increases as CN decreases from 9 to 6 (indicated below by the Roman numerals) in the respective crystal units of decreasing ability to be leached off from the roasten bastnaesite concentrate with nitric acid: $Ln(OH)_3^{IX} > Ln_2O_3^{VII}$ (A-type) $> Ln_2\ O_3^{VI}$(cubic C-type). This effect can even be applied in the rare earth technology.[8,38] Due to a higher oxidation state, the regular molecular orbital formed, and a smaller size,[20] Ce(IV) in calcined CeO_2, in spite of CN = 8, is less soluble/reactive in acids than the lanthanide sesquioxides of the C-type of CN = 6. In spite of smaller size, the Ce(IV) as CeO_2, is still more soluble in acids and less covalent, viz. "harder", than completely unreactive Th(IV) of CN = 8 in insoluble calcined ThO_2.[38]

In general, the covalency of the f-block elements in their compounds decreases in the tetrad pattern as f-electron localization becomes stronger, i.e., with atomic number. Being more pronounced for actinides than for lanthanides, it decreases with increasing CN, and it increases with increasing oxidation state. Therefore, the expected nephelauxetic series of increasing covalency for the inner-transition ions in their complexes for the same CN is expected to be as follows: Er(II) < Eu(II) < Pr(II) < Ce(II) < Fm(II) < Cf(II) < Am(II) < Tm(III) < Er(III) < Ho(III) < Sm(III) < Nd(III) < Pr(III) < Cm(III) < Am(III) < Pu(III) < Tb(IV) < Bk(IV) < Pu(IV) < Am(VI) < Pu(VI) < Am(VII). This series, where the ions contain at least two f-electrons for interelectronic (i.e., nephelauxetic) repulsion, correlates closely with the exceptionally distinct tetrad effect in the crystal lattice parameters of AnF_4,[1] the well-known covalency of UF_6 and demi-covalency of UF_4. Assuming one C_5H_5 or C_8H_8 aromatic ring as a CN unit in f-metalorganic compounds is not quite exact. The well-known ionic character, viz. a covalency of about 5%, as for the respective chlorides, of, e.g., $Ln(C_5H_5)_3$, $An(C_5H_5)_3$, $Ln(C_8H_8)_2^-$, $An(C_8H_8)_2^-$, $An(C_8H_8)_2$, etc., can be explained by a very high CN of 15 and 16 involved (and not CN = 3 or 2 as is formally assumed). This high CN results in rather long M–C distances, making virtually negligible the orbital overlaps (in spite of their additivity) of the Π electrons of the rings with the deeply buried f orbitals of the central ions.

The respective nephelauxetic series of increasing covalency for the ligands with the oxygen donor atoms, coordinating the Ln(III) ions, would be as follows (CN given by the Roman numerals, and in parentheses some examples are specified): $^{XII}O^{2-}$ (double nitrates) < $^{IX}OH^-$ ($Ln(OH)_3$) < $^{IX}OD_2$ < $^{IX}OH_2$ < $^{VIII}OD_2$ < $^{VIII}OH_2$ (aquo-ions of La–Pm (IX) and Tb–Lu (VIII), hydrates of, e.g., Ln(III) chlorides, nitrates and sulphates) < $^{VII}O^{2-}$(A-Ln_2O_3) < $^{VI}O^{2-}$(C-Ln_2O_3, organic phase complexes of Ln(III) with TBP, HDEHP, HEHΦP,[1] etc., responsible for high separation factors and for the distinct tetrad effect in the thermodynamic parameter variations for the liquid-liquid extraction).

The discovery of the double-double effect in this laboratory, confirmed by Peppard *et al.*, in the separation factor α vs. q variations for liquid-liquid extraction of the Ln(III) ions with TBP, HDEHP and HEHΦP,[1] was possible since the difference in lanthanide CN between the aquo-ions and the respective organic phase complexes was substantial. Presumably, this difference was 3 in the La–Pm range and 2 in the Gd–Lu range of the series. Therefore, it appears that a further increase in the α values for Ln(III) and An(III) separations, and for the chemical isotope effect as well, e.g., for the U^{3+}/U^{4+}, Ce^{3+}/Ce^{4+}, Eu^{2+}/Eu^{3+} systems,[39] can be achieved, provided CN of the f-block elements is increased in the aquo-ions from 8–9 to, e.g., 12. On the other hand, it appears that CN in the respective organic phase complexes can be decreased to 4 or even 3 for some bulky monodentate ligands with flexible dents and accessible donor atoms, e.g., similar to those well-known of $\mathrm{Nd[OC(^tBu)_3]_3}$ and $\mathrm{Nd[N(SiMe_3)_2]_3}$ but still stable in some liquid extraction or ion-exchange systems.

Other evidence for slightly covalent character of the bonding (virtually with no directional bonds and variable CN of 3, 4, 6, 7, 8, 9, 10, 11, 12) displayed by the f-block elements is the "nomadic" behavior of Y(III) (and to a lesser degree that of Sc(III)[31,32]) in numerous Ln(III) and An(III) systems, studied exhaustively by Siekierski *et al.*[40,41] However, the position of yttrium within or out of the Ln(III) series may be, in some cases, a somewhat misleading indicator of covalency. This position depends not only on the participation of the f-electrons in bonding, resulting in shifts of the Ln(III) and, to a greater extent, An(III) series with respect to "purely ionic" Y(III) for a series of compounds. Such a shift depends mostly on CN and electronegativity of donor atoms. For ligand substitution reactions, the shift of Y(III) within the f-block series also depends on the slope of, e.g., $\Delta(\Delta G)$ vs. q plot. For an extreme case, provided the $\Delta(\Delta G)$ vs. q value is nearly constant, it is difficult to say whether Y falls out of La or out of Lu in such a plot, and the experimental precision is essential.

It results from the present discussion that the direction of the tetrad effect and its presence (or absence as, e.g., in the first tetrad of the ethylsulfate system,[22,23] where CN and the ligand surrounding is nearly the same in both phases) in a given tetrad, and some related covalency effects, e.g., the Y(III) shifts, as well as the position of Sc(III) in the respective plots,[31,32] can be used as purely thermodynamic indicators of CN in the complexes involved.[8] It is of importance especially for complexes of the f-block elements in dilute solutions (e.g., 0.01M[7]) where even X-rays of synchrotron radiation (e.g., the EXAFS method) are useless.

The conclusions of the author,[7] based on the direct correlation between direction of the tetrad effect and CN, given in Eqs. (4)–(13), were confirmed later on by other methods.[10–16] The same situation took place with the author's early conclusion[22,23] on the controversial Ln(III) and An(III) aquo-ions, summarized in Eqs. (15)–(18), which was afterwards supported by X-ray and neutron diffraction data, and other routine methods, for the $\mathrm{[An(H_2O)_x]^{3+}_{aq}}$ [43,44] and $\mathrm{[Ln(H_2O)_x]^{3+}_{aq}}$ [45–57] species.

SUMMARY

The opposite directions of the tetrad (double-double) effect in variations of the logarithmic first protonation constants for 1:1 lanthanide(III) nitrilotris(methylenephosphonates) (ntmp) and diaminocyclohexanetetraacetates (dcta) along the Ln series have been elucidated. While the "inverse" tetrad effect (upward bends) for protonation of the $\mathrm{Ln(dcta)^{-}_{aq}}$ species indicates an increase in coordination number (CN) for the protonated chelates, the "regular" effect (downward curves) for protonation in the $\mathrm{Ln(ntmp)^{3-}_{aq}}$ series must be interpreted in terms of the decreased CN. The protonation constant for $\mathrm{Sc(ntmp)^{3-}_{aq}}$, close to the respective value for the Y(III) and Ho(III) complexes, is due to the opposite change in CN for Sc(III) with regard to Ln(III) and Y(III) in result of protonation. In this instance the original method of interpretation has been presented, making it possible to use location and direction of the tetrad effect for determination of CN in complexes of the f-block elements even in dilute solutions. Except for $\mathrm{M(ntmp)^{3-}_{aq}}$ and $\mathrm{MH(ntmp)^{2-}_{aq}}$, the method is also exemplified by finding CN and the primary hydration number of the protonated and unprotonated lanthanide (III) 1:1 chelates of dcta, mixed lanthanide(III) complexes of dcta with iminodiacetate ($\mathrm{ida^{2-}}$), glycine ($\mathrm{gl^{-}}$) and hydroxide ions, and for the Ln(III) and An(III) aquo-ions. In an up-to-date look at the tetrad effect, correlations between tetrad effect, CN, effective crystal radii, covalent shortenings for the f-block elements, nephelauxetic effect, ligand field effect, spin-orbit coupling, hydration and reactivity are discussed, and the crucial role of the CN changes in reaction products vs. left-hand-side reactants for ligand substitution equilibria is emphasized. It is indicated that the SO coupling stabilization energy, although of similar absolute value to the interelectronic repulsion stabilization energy for the 5f-subshell filled in 1/4 and 3/4, is negligible for the resultant tetrad effect. On the other hand, the minute ligand field stabilization energy, as very sensitive to the CN changes, slightly increases the tetrad effect for the f-subshell filled in 1/4 and 3/4.

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