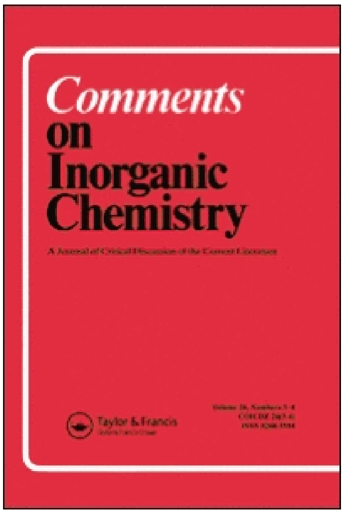

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Quasilanthanide(III) Behavior of Scandium(III) and Coordination Number

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Quasilanthanide(III) Behavior of Scandium(III) and Coordination Number

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The variable position of scandium(III) with regard to the lanthanides(III) on plots of thermodynamic parameters of complex formation and solubility vs. atomic number of Ln has been explained in terms of coordination number (CN) and effective ionic radii ($r_{M(III)}$) variations. The emphasis is given to the quasi-heavy-lanthanide behavior of Sc(III) as far as the enthalpies of solution of anhydrous rare earth halides MX_3 in water are concerned. It is indicated that this peculiar behavior is due to the constant CN = 6 of Sc(III) in the aqueous phase and in the solid phase of anhydrous ScX_3, whereas the CN of heavy lanthanides(III) decreases from 8 in the aquoions to 6 in the crystal lattice of anhydrous LnX_3. It appears that in the series of increasing softness, Sc(III) occupies the place between Y(III) and Ln(III): Y(III) < Sc(III) < Ln(III) < An(III). Covalent shortening has a small influence on the "nomadic" behavior of Sc(III). The relative decrease of CN of Ln(III) by 2 with regard to Sc(III), connected with the corresponding decrease of the effective ionic radii of the Ln(III) ions, must also be assumed to explain the quasi-heavy-lanthanide(III) behavior of Sc(III) for the first protonation constant of 1:1 lanthanide(III) nitrilotris(methylenephosphonates). Such a relative decrease of CN of the Ln(III) ions with regard to Sc(III) can even reach 5 and, in consequence, their effective ionic radii can be relatively decreased by about 30%. This would explain the Sc(III) behavior as an ion quasi "lighter"/larger than La(III). In such cases tetrahedral coordination is suggested for the Sc(III) species in some nonaqueous solutions: Sc_2Cl_6 (in 2-butylamine and diethylamine), $(CH_3OH)ScI_3$, $[(CH_3)_2SO]ScCl_3$.

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Key Words: *scandium(III), yttrium(III), lanthanides(III) displacements, coordination number, effective ionic radii, scandium(III) as a quasilanthanide(III), rare earth trihalides, solution enthalpies, solubilities*

1. OPENING REMARKS

Chemical interactions of the lanthanide(III) ions (Ln(III): $4f^q5s^25p^65d^0$) are electrostatic in nature and all are very similar. *Differentia specifica* of these ions consists in a gradual increase of ionic potential and decreasing basicity from La(III) ($[Xe]4f^0$) to Lu(III) ($[Xe]4f^{14}$) due to the lanthanide contraction. Therefore, the long and stable Ln(III) series offers unique possibilities for studying parameters which theory correlates with ionic radii as those for thermodynamics of hydration, complex formation, liquid–liquid extraction, ion-exchange, solubility, cocrystallization, etc., connected on the molecular level with changes in coordination number (CN), hydration number, hydrate number and generally with the structure of the Ln(III) species.[1] Of special interest are deviations from the purely ionic model, appearing in the double–double(tetrad) effect,[2] and some minor variations of the effective ionic radii of Ln(III), An(III) and Y(III) ions in environments of varying Pearson's hardness. Internuclear distances R, known precisely for solid phases and concentrated solutions from X-ray and neutron diffraction data, are shared more or less arbitrarily between a central ion $r_{M(III)}$ and donor atoms r_A. It is well-known that in the "softer" crystal lattice of, e.g., anhydrous lanthanide(III) chlorides,[3] the Y(III) ion is slightly larger than the Dy(III) ion, whereas in the "harder" oxychloride and oxide lattices its dimension is between that for Dy and Ho, and in the least covalent fluoride it is between Ho and Er. This variation in effective radii amounts to only about 0.03 Å, and the location of Y(III) within the Ln(III) (and An(III)) series can serve as a sensitive measure of the f-electron effect on bonding.[4] This f-electron effect is designated generally as covalent shortening[5] or more specifically as the nephelauxetic effect.[6] The origin of the tetrad effect and of the "nomadic" behavior of Y(III) amongst Ln(III), and to a greater extent along a somewhat more covalent An(III) series,[7] is the same. It is mainly f-electronic repulsion energy variation for compounds of the f-block elements. The interelectronic repulsion energy decreases with the increasing "softness" of the donor atoms, i.e., mostly with decreasing CN and, to a lesser degree, with increasing electronegativity of donor atoms.[1] Since both cation and anion radii decrease substantially with CN for trivial reasons, for lower CN the overlap integral, ψ_f and ψ_{lig}, becomes more pronounced. It results in an increase of the f-shell, $\langle r_f \rangle$ (the nephelauxetic effect), and in a minor additional decrease of the central ion, $\langle r_{M(III)} \rangle$ (the covalent shortening), the core of which becomes less effectively shielded[8] by the augmented f-orbitals. It appears that highly electronegative oxygen in the cubic C-type Pr_2O_3 (CN = 6) generates the nephelauxetic effect even slightly greater than the iodine in anhydrous PrI_3 (CN = 8).[6] Interactions within aquoions of originally less covalent heavy lanthanides(III) are more covalent due to CN = 8 than those for the La–Pm range where CN = 9 has been established, and analogous behavior is also expected for the An(III) aquoions.[9,10]

In the nephelauxetic series of cations of increasing "softness": Y(III)[Kr] < Ln(III)[Xe]$4f^q$ < An(III)[Rn]$5f^q$, demonstrated on the basis of migration of the Ln(III) and An(III) series with regard to Y(III),[7] the position of Sc(III)[Ar], the least (and, unfortunately, the least studied) of rare earths(III) is unknown.

The major objective of this paper is to explain why in some peculiar systems Sc(III) displays a quasilanthanide(III) behavior.

2. ENTHALPIES OF SOLUTION OF SCANDIUM, YTTRIUM AND LANTHANIDE TRIHALIDES

According to the most reliable data of Shannon,[5] for CN = 6 the effective ionic radius of Sc(III) is 0.745 Å, viz. it amounts to 86.5% of the respective radius of the Lu(III) ion (0.861 Å).

In general, the Sc(III) complexes are more stable than Ln(III) complexes.[11] This means that the Gibbs energy of complex formation from gaseous components becomes more exothermic with $1/r_{M(III)}$ faster/steeper than the respective Gibbs energy of hydration of the $M(III)_{gas}$ ions does. The latter, in turn, similarly as the Gibbs energy for solvents other than water, $\Delta G_{solvation}$, becomes more negative with $1/r_{M(III)}$ faster than the Gibbs energy of crystal lattice of equilibrium solid phases for heavier/smaller Ln(III) ions and Sc(III). This is why the solubility of scandium nitrate,[12] sulfate, fluoride, chloride, bromide and iodide in water,[13] and in nonaqueous solvents[14] is higher than the solubility of the respective Ln(III) salts.

Burgess and Kijowski[15] have reported very precise calorimetric enthalpies of solution of anhydrous trihalides of Ln, Y and Sc in water and in some nonaqueous solvents at 298.2 K for final concentrations of 1.0 to 3.5 × 10^{-3} mol dm^{-3}. Their solution enthalpies, the trends of which vs. q (or atomic number) of Ln(III) are supported by some early data,[16] are presented in Fig. 1. It can be seen in Fig. 1 that the enthalpies of solution of anhydrous $LnCl_3$, $LnBr_3$ and LnI_3 are negative and that the exothermic effect increases from chlorides to iodides, and it smoothly increases for all three halide series from La to Lu.

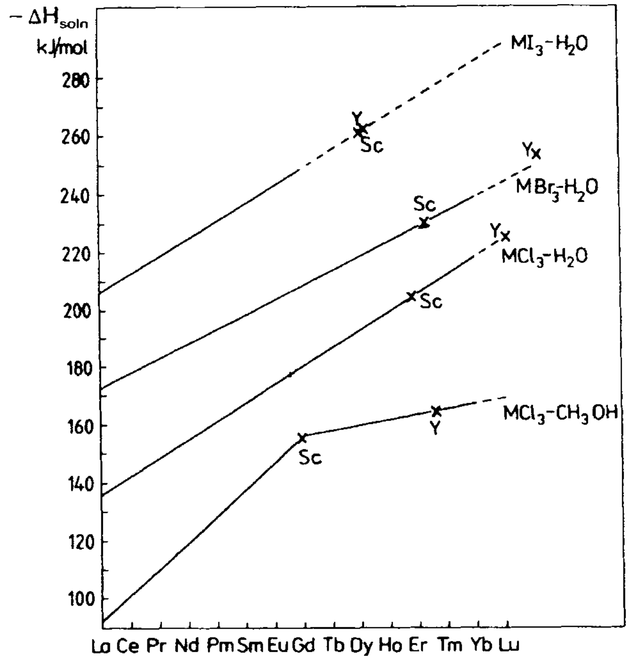

FIGURE 1 Enthalpies of solution of scandium, yttrium and lanthanide trihalides, according to Burgess and Kijowski (Ref. 15).

For consistency, according to the common convention for complexes,[11] the reaction equation (1) is given not for dissolution but for crystallization of the virtually anhydrous solid halides:

$$M^{3+}_{aq} + 3X^{-}_{aq} = MX_{3,s} \tag{1}$$

where M stands for Ln, Y and Sc, X for Cl, Br and I, and subscripts aq and s denote aqueous and solid phase.

Unexpectedly, but positively, in all three halide systems Sc(III) behaves like a heavy lanthanide(III) (Fig. 1). The enthalpies of solution of scandium halides correspond to the values interpolated, respectively, for $ErCl_3$, $ErBr_3$ and DyI_3, while those for yttrium halides to $LuCl_3$ and DyI_3. For the MBr_3–H_2O system the enthalpy value for YBr_3 slightly falls behind with the enthalpy of solution of anhydrous $LuBr_3$ in Fig. 1. This irregularity is probably due to an experimental error, e.g., the presence of small amounts of an interfering hydrate of YBr_3. The interpolated position of the solution enthalpy for YBr_3 is around the respective $TmBr_3$ value.

The shift of the enthalpy of solution of the yttrium halides from Lu in the MCl_3–H_2O system to Dy in the MI_3–H_2O system can be explained in terms of "softer" (more covalent, more nephelauxetic, more polarized/polarizing, more reducing the central ion charge +3, of larger covalent shortening) interactions in the crystal lattice of the iodides in comparison with the respective interactions of the chloride ions. A displacement of Y(III) in the same direction by at least two q (or atomic number) units also results from the early, and less precise, data of Bommer and Hohmann for MCl_3 and MI_3.[16]

The effects of the halide ions in the crystal lattices of MX_3 are fully comparable in the present case since in all the discussed heavy lanthanide(III) and yttrium(III) halides, the Ln(III) and Y(III) ions display CN = 6. The anydrous triiodides for M = Sm to Lu and Sc crystallize in the hexagonal (rhombohedral) BiI_3 structure with the space group $R\bar{3}$-C^2_{3i}.[17] The same structure of $FeCl_3$ has been reported for the tribromides for M = Tb to Lu, Y and Sc, and for $ScCl_3$ as well. The trichlorides for M = Dy to Lu and Y crystallize in the monoclinic octahedral $AlCl_3$ structure, space group C^2_{3h}-C2/m (a distorted NaCl structure in which two-thirds of the metal atoms are absent). It follows from the foregoing that in the "softer" crystal lattice of LnI_3 the effective ionic radius of Y(III), referred to in the substrate (Eq. (1)) aquoions $[M(OH_2)_8]^{3+}_{aq}$,[9,10] is about the radius value for Dy(III), while in the crystal lattice of $LnCl_3$, the apparent dimension of the Y(III) ion is close to that of Lu(III). This migration of the Ln(III) radii with regard to the Y(III) position, the extension of which but not the general trend[15,16] can be placed in question, due to experimental precision limitations (YBr_3?), is produced by a greater covalent shortening of the Ln–I bonds than the Ln–Cl bonds in comparison with the respective negligible covalent shortenings for the Y(III) ion which does not dispose 4f-orbitals. In other words, the ionic radii of the Ln(III) ions increase to a greater degree when passing in the crystal lattice of LnX_3 (CN = 6) from X = I to X = Cl than the ionic radius of Y(III) does. As expected, the iodine atoms of lower electronegativity generate the more pronounced 4f-"cloud-expansion" than the chlorides do for the same CN = 6 in the crystal lattices of anhydrous heavy lanthanide(III) halides. The lattice parameters a_0 and c_0 and, in consequence, bond lengths directly connected with the enthalpy values, cause YBr_3 to be situated at the $HoBr_3$, and YI_3 between TbI_3 and DyI_3.[17] (For YCl_3 of different structure than the isostructural YBr_3 and YI_3, the parameters of elemental cells were reported to be at the $DyCl_3$ level.) The nephelauxetic effect, greater for the iodides than for other halides at CN = 6, is accompanied by a less effective shielding of the nucleus protons (or the Ln(III) cores) by 4f-electrons,[8] and consequently by a slightly greater decrease of the whole Ln(III) ion in the iodide environment of CN = 6. However, it should be noted that the most covalent of the halides, the iodides LnI_3, are the least stable enthalpicly, resulting in the most exothermic enthalpies of solution in water (Fig. 1). Although the effective ionic radii of Ln(III) for CN = 6 are smallest for the iodides, and in spite of the largest covalent shortenings for both the Ln(III) and I^- ions, the Ln–X distances *R* remain the largest for the iodides and this factor prevails. Therefore, for the "hard" rare earth (III) ions, the "hard–hard" interactions are energetically privileged which is not the case for ions of the Ag(I) type (the molar volume of AgF is 120% of the molar volume of NaF, whereas the volume of Ag_2Se is 72% of that for Na_2Se[5]).

The shift of the Sc(III) position within lanthanides(III) in function of the X^- ion cannot be neglected (Fig. 1), since it amounts two q (or atomic number) units, i.e., from about Er for the chlorides to Dy for the iodides. If this shift is statistically meaningful, and out of the error limits, it would indicate that Sc(III) is slightly more covalent than Y(III) but a little less covalent than the Ln(III) ions. So, the covalency for the same CN and the same ligand would increase as follows: Y(III) < Sc(III) < Ln(III) < An(III), viz. with Sc of highest electronegativity of rare earths situated between Y and Ln. (Within the Ln(III) and An(III) series the nephelauxetic effect decreases with q, and it increases with the oxidation state.)

The major question of this paper is left, i.e., how to explain the exceptional quasilanthanide(III) behavior of Sc(III) in the systems under discussion. Burgess and Kijowski,[18] who considered the enthalpies of solution of ScX_3 [16] insufficiently exothermic, initially suggested[18] the possibility of experimental errors, e.g., hydrolysis of Sc^{3+}_{aq} or the presence of small amounts of lower halides, hydrates or oxochlorides. But on the basis of their verifying re-study,[15] the present author believes that the enthalpic data are very precise and correct except perhaps for too exothermic enthalpy a solution of anhydrous YBr_3 (possibly the solute was a little humid).

The answer is involved in CN variations for the reaction equation (1) and accompanying effective radii changes in the Ln(III) series with regard to Sc(III). It is the Dy–Lu range of the Ln(III) series which is under discussion due to the Sc and Y "nomadic" behavior. As mentioned above, in this range the solid phase (right-hand side of Eq. (1)) is MX_3 with M of CN = 6 for M = Sc, Y and Dy–Lu, and X = Cl, Br, I. Fortunately, the CN of the rare earth substrate aquoions are also known and equal 8 for heavy Ln(III) and Y(III), $[Ln(OH_2)_8]^{3+}_{aq}$ (D_{4d}) [9,10,19] and 6 for $[Sc(OH_2)_6]^{3+}_{aq}$.[20,21] Therefore, as reaction (1) proceeds, the CN of heavy Ln(III) and Y(III) central ions decreases from 8 to 6, while for Sc(III) the CN remains unchanged and equals 6. According to the most reliable data of Shannon,[5] the ionic radius of Lu(III) for CN = 8 is 0.977 Å, and it decreases to 0.861 Å for CN = 6, i.e., by 13.5%. An analogous decrease has been reported for other Ln(III) ions.[5] Thus, the unchanged CN of Sc(III) for the reaction equation (1), and the decrease of CN by two for the Ln(III) and Y(III) ions, correspond to a relative increase of the Sc(III) ion in some percentage in the teens. In addition this rise is enlarged by the respective increase of the anionic radii which also, but to a lesser extent,[5] become larger with CN. It is of interest that the effective ionic radius of Sc(III) for CN = 8 amounts to 0.870 Å,[5] so it is larger than the effective ionic radius of Yb(III) for CN = 6 (0.868 Å). In other words, although both for the enthalpies of hydration and for the crystal lattice enthalpies: $M^{3+}_g \Rightarrow M^{3+}_{aq}$; $M^{3+}_g + 3X^-_g \Rightarrow MX_{3,s}$ (the term for $3X^-_g \Rightarrow 3X^-_{aq}$ is in common) the respective enthalpic values for Sc(III) fall out of the Ln(III) series, the sensitive differential effect given by the reaction equations (2) and (3) results in a quasi-heavy-lanthanide(III) behavior of scandium(III):

$$\underset{CN\,=\,8}{[Ln(OH_2)_8]^{3+}_{aq}} + 3X^-_{aq} = \underset{CN\,=\,6}{LnX_{3,s}} \tag{2}$$

$$\underset{CN\,=\,6}{[Sc(OH_2)_6]^{3+}_{aq}} + 3X^-_{aq} = \underset{CN\,=\,6}{ScX_{3,s}} \tag{3}$$

Therefore, any suggestion[22] of possible CN = 7 for Sc^{3+}_{aq} must be rejected as in contradiction with the present discussion which indicates a substantial difference in CN variations between the Sc(III) and Ln(III) central ions as depicted by the reaction equations (2) and (3).

Usually Sc(III) falls out of Lu(III) for thermodynamic effects of chemical reactions since both CN of heavy Ln(III) remains constant (frequently equal to 8 or 9) and CN of Sc(III) stays unchanged (frequently equal to 6) or CN is changing simultaneously. Even if the CN changes are not quite parallel the relative difference does not exceed 1, and Sc(III) still remains slightly "heavier"/smaller than Lu(III).

The solubility of scandium halides in water, connected with the Gibbs energy of solution, is higher than for the LnX_3 halides.[13] That this must be so follows from the presupposed constancy of CN. Both in the aquoions of heavy lanthanides(III), $[Ln(OH_2)_8]^{3+}_{aq}$ (D_{4d})[9,10,19] and in the equilibrium solid phases of heavy lanthanide(III) halides[13]: $[(H_2O)_6LnCl_2]Cl$, $[(H_2O)_6LnBr_2]Br$, $[Ln(OH_2)_8]I_3$, CN = 8 is preserved, similarly as CN = 6 for Sc, e.g., in $[Sc(OH_2)_6]I_3$ (the final solid phases are specified for ambient temperature, and at a temperature around 273 K, hydrates of higher hydrate numbers but of presumably unchanged CN crystallize[13]). An analogous explanation of the solubility trends with Sc falling behind with Lu is also valid for the fluorides and rare earth(III) salts other than halides, e.g., for the nitrates[12] and sulfates.[13]

Going from water to nonaqueous solvent,[14] one deals with unknown species in solutions, and poorly specified and unstable adducts of unknown structure and of controversial stoichiometries of equilibrium (final) solid phases.

It results from Fig. 1 that the enthalpy of solution of $ScCl_3$ in anhydrous methanol falls in the middle of the Ln series where the hexagonal $LnCl_3$ chlorides of the UCl_3 structure (CN = 9) pass into monoclinic $LnCl_3$ chlorides of the $AlCl_3$ for type (CN = 6). This structural rearrangement is reflected by an inflection point at Gd which is absent for all the aqueous systems illustrated in Fig. 1. This is because of compensation which presumably occurs only in the aqueous systems. The changes in the structures of anhydrous LnX_3 around the middle of the series are accompanied by a more or less parallel change in the structure of the aquoions, Ln^{3+}_{aq}, from $[Ln(OH_2)_9]^{3+}_{aq}(D_{3h})$ for lighter lanthanides to $[Ln(OH_2)_8](D_{4d})$ in the Tb–Lu range of the series.[1,9,10,19,23] Therefore, it may be concluded with moderate confidence that in solvated $LnCl_3$ species in methanol, lanthanides(III) do not change their CN of 9[23] which is higher by 3 than for the respective Sc(III) species, as the whole Ln(III) series is traversed:

$$(CH_4O)_6(Ln,Y)Cl_{3,\text{methanol}} \text{ vs. } (CH_4O)_3ScCl_{3,\text{methanol}}$$

Ultrasonic measurements of 0.2 M solutions of $ScCl_3$, YCl_3 and $LaCl_3$ in aqueous methanol[21] also indicated different behavior of $ScCl_3$.

The solubility of lanthanide trichlorides in methanol[14] increases from 2.44 mol kg^{-1} for $LaCl_3$ to 4.90 mol kg^{-1} for $YbCl_3$ (4.38 mol kg^{-1} for YCl_3 and 5.52 mol kg^{-1} for $ScCl_3$). These solubility values indicate that in the saturated methanolic solution there are about six molecules of methanol per 1 mol of $LuCl_3$. (The limiting solubility for the methanol solvation number 6 is 5.20 mol kg^{-1}, and this value is exceeded for $ScCl_3$. This indicates that $ScCl_3$ must be solvated by less than 6 molecules of methanol.) The equilibrium adducts are reported to be of stoichiometry: $LnCl_3 \cdot 4CH_3OH$,

$YCl_3 \cdot 4CH_3OH$, $ScCl_3 \cdot (2-3)CH_3OH$[14] (the solvate numbers n are controversial). This results from the above considerations and high solubility of $ScCl_3 \cdot (2-3)CH_3OH$ that in these solvates the exceptionally low CN = 6 of $LnCl_3$ ($AlCl_3$ structure) is no longer preserved for heavy Ln(III) and Y(III) adducts. In the equilibrium solid phases of the methanolic solvates the central ions presumably display CN = 9, i.e., the same as in methanolic solution. (The relative variation of CN of Sc with regard to Ln by 1 still situates Sc(III) slightly out of Lu(III).)

The solubility of $ScCl_3$ adducts higher than that of $LnCl_3$ adducts in the case of ethanol, 1-propanol, 2-ethoxyethanol, 1,2-diethoxyethane[14] can be explained *per analogiam*, i.e., the CN and effective radii of the Ln(III) ions both in solution and in the respective $LnCl_3 \cdot nS$ solvates are large (CN = 8 or 9) and basically stay unchanged, similar to CN = 6 of Sc(III) both in $ScCl_3 \cdot nS$ and in $ScCl_{3,\mathrm{solvent}}$ species.

There are, however, some indications[14] that for low solubilities in some solvents of weak, non-specific interactions, the solubility of $ScCl_3$ falls amongst the solubilities of heavy lanthanide(III) halides. This particular case takes place in the MCl_3–diisobutylamine system where the solubility value for $ScCl_3$ is close to that for $TbCl_3$, and in the system of MBr_3–1,4-dioxane (electric dipole moment $\mu = 0$) where the solubility of $ScBr_3$ is situated between the solubility values for $TmBr_3$ and $YbBr_3$. For these solvents radical structural rearrangements of the initial solid phase upon recrystallization probably do not occur, viz. the dissolution is reversible and the original solutes are recovered with heavy Ln(III) ions surrounded in the final solid phase by six chlorine or iodine atoms in the crystal lattice. Hence, the reason for Sc(III) falling among heavy Ln(III) on the Gibbs energy of solution plots vs. q would be the same as that discussed in detail for the enthalpies of solution given in Fig. 1.

It should be noted that the solubility of $ScCl_3 \cdot 3S$ in 2-butanamine and diethylamine has been reported to be lower than for all $LnCl_3$.[14] Similarly, the enthalpies of solution of ScI_3 in methanol and $ScCl_3$ in dimethyl sulfoxide have been reliably reported to be less exothermic[15] than the respective enthalpies for lanthanide(III) halides. Since for these systems the thermodynamic functions become more exothermic with $1/r_{M(III)}$, one can say that Sc(III) behaves as if it was relatively/effectively larger than the La(III) ion. Because a decrease in CN for the Ln(III) ions for the process

$$MX_{3,\text{solvent}} \Rightarrow MX_{3,\text{solid}} \tag{4}$$

by more than three CN units is rather unlikely, a dramatic increase of CN of Sc(III) by changing the tetrahedral into octahedral coordination must be assumed for these cases to keep the hypothesis working. This would raise the total relative CN change for Sc(III) with regard to the Ln(III) ions to 3 + 2 = 5. So, to justify far displacements of the thermodynamic function values for Sc(III) towards the left-hand side of the Ln series, out of La(III), sufficc it to suppose that, as in the case of the isostructural $FeCl_3$ crystals, in nonaqueous polar solvent solutions the tetrahedral $(H_4CO)ScI_3$ and $[(CH_3)_2SO]ScCl_3$ species are present, whereas for the amine solvents dimeric tetrahedral Sc_2Cl_6 species with the chloride bridge occur in solution. Such tetrahedral $ScX_{3,\text{solvent}}$ species would be extremely weakly solvated and hardly soluble, as is the case.

3. LOGARITHMIC FIRST PROTONATION CONSTANTS OF 1:1 Sc(III), Y(III) AND Ln(III) COMPLEXES OF NITRILOTRIS(METHYLENEPHOSPHONIC ACID)

Another well-demonstrated case of a quasi-lanthanide(III) behavior of Sc(III) is that reported recently by Sawada, Kuribayashi and Miyamoto.[24] They determined very accurately, using a potentiometric method and a glass electrode, thc protonation constants for Sc(III), Y(III) and all Ln(III) (but Ce(III)) nitrilotris(methylenephosphonates), $Ln(ntmp)^{3-}_{aq}$, at 298.2 K, and at an ionic strength of 0.1 mol dm^{-3} KNO_3. Except for the enigmatic behavior of Sc(III), which in this system gives a log $K_{MH(ntmp)^{2-}}$ value similar to that for the protonation of the Y(III) and Ho(III) nitrilotris(methylenephosphonates), of special interest is the double–double(tetrad) effect reported by Sawada *et al.*[24] Their reliablc results are illustrated in Fig. 2 as compared with the present author's data measured potentiometrically at 298.2 K, and at an ionic

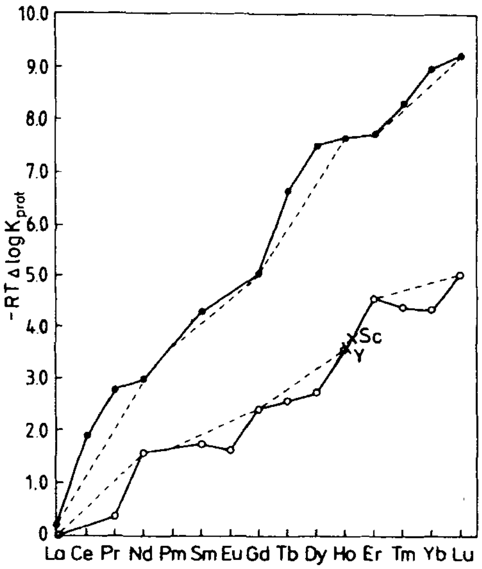

FIGURE 2 – $RT\Delta$ log $K_{\text{protonation}}$ vs. q variations for $\text{Ln(ntmp)}^{3-}_{aq}$ complexes (open circles with × indicating the position of Y and Sc) and for Ln(dcta)^{-}_{aq} complexes (full circles).

strength of 1 mol dm^{-3} KCl, using the H^+/H_2 on Pt/Pt black indicator electrode for protonation of the Ln(dcta)^{-}_{aq} chelates (dcta denotes trans-1,2-diaminocyclohexanetetraacetic acid).

The $-RT\Delta$ log K_{prot} is the "stoichiometric" relative Gibbs energy of protonation (i.e., neglecting variations of activity coefficients along the Ln(III) series at a constant ionic strength).

The direction of the double–double(tetrad) effect for the logarithmic protonation constants of the Ln(dcta)^{-}_{aq} chelates vs. q indicates[25] that in the entire Ln series the CN of Ln(III) increases by 1 due to protonation:

$$(H_2O)_x\text{Ln(dcta)}^-_{aq} + (H_3O)(H_2O)^+_{3,aq}$$

$$= (H_2O)_{x+1}\text{HLn(dcta)} + 3H_2O \quad (5)$$

where x is 3 (CN = 9) in the La–Sm range of the series and 2 (CN = 8) for Dy–Lu.[25] More or less the same mechanism consisting of the addition of the oxonium ion H_3O^+ to the unprotonated chelates (Eq. (5)) appears to be valid also for the analogous $\mathrm{Ln(edta)}^-_{\mathrm{aq}}$ complexes.

It should be noticed that for both the aminopolycarboxylate system of H_4L of dcta[25] and the aminopolyphosphonate system H_6L of ntmp,[24] the tetrad effect amounts to 0.4–0.7 kJ/mol at the imprecision limits reaching ±0.17 kJ/mol. The most important feature, however, is that the tetrad effects presented in Fig. 1 have opposite directions. The protonated complexes for which the $4f^q$-shell 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) are destabilized for the $\mathrm{LnH(ntmp)}^{2-}_{\mathrm{aq}}$ complexes (the "regular" tetrad effect) whereas they are stabilized in the case of the $\mathrm{LnH(dcta)}_{\mathrm{aq}}$ series (the "inverse" tetrad effect).

The "regular" tetrad variation of $-RT\Delta \log K_{\mathrm{protonation}}$ vs. q for the first protonation of the $\mathrm{Ln(ntmp)}^{3-}_{\mathrm{aq}}$ complexes gives evidence that, contrary to the $\mathrm{HLn(dcta)}_{\mathrm{aq}}$ chelates, the protonated complexes $\mathrm{HLn(ntmp)}^{2-}_{\mathrm{aq}}$ are more covalent with regard to the unprotonated ones in the whole Ln(III) series. This means that in the protonated complexes $\mathrm{HLn(ntmp)}^{2-}_{\mathrm{aq}}$ the ligands are "softer" (more reducing the +3 charge of the central ions, e.g., to +2.8, more polarized/polarizing, more enhancing partly covalent bonding and giving more pronounced decreases of the Racah's parameters of f-electronic repulsion energies E^1 and E^3) than for the unprotonated complexes $\mathrm{Ln(ntmp)}^{3-}_{\mathrm{aq}}$ ($E^1_{\mathrm{prot}}/E^1_{\mathrm{unprot}} < 1$, $E^3_{\mathrm{prot}}/E^3_{\mathrm{unprot}} < 1$ and $\Delta E^3 > \Delta E^1$).[1,2] Therefore, it must be assumed that the donor atom–central ion distances R and, in consequence, both the cationic, $r_{\mathrm{Ln(III)}}$ and anionic radii r_A must be smaller for the protonated complexes. This makes the orbital overlap, ψ_{4f} and ψ_{lig}, more effective and the covalent shortening enhanced for the $\mathrm{HLn(ntmp)}^{2-}_{\mathrm{aq}}$ complexes. So, the four downward curves vs. q in Fig. 2, i.e., the "regular" double–double(tetrad) effect, indicate the decrease in the CN of all the Ln(III) ions as a result of protonation of the $\mathrm{Ln(ntmp)}^{3-}_{\mathrm{aq}}$ complexes. It has been clearly shown by the Miyamoto group[24] that this decrease in CN is due to the rupture of the weak Ln–N bond by the betaine type proton. In consequence of the CN decrease by 1, the $r_{\mathrm{Ln(III)}}$ and r_0^{2-} radii decrease and all the Ln–O bonds become shorter by about 5%,[5] only as far as the $r_{\mathrm{Ln(III)}}$ shares are concerned, resulting in the "regular" double-double effect.

The increase of the nephelauxetic effect, additive in nature, produced by shortening of all the Ln–O bonds due to the decreased CN, prevails over the decrease of covalency due to the weak Ln–N bond ("softer" than the Ln–O bond) ruptured:

$$\begin{aligned}
&\mathrm{Ln\{N({}_3[{}_2(O)(O)PCH_2])\}^{3-}_{aq}} + \mathrm{[(H_3O)(H_2O)_3]^{+}_{aq}} \\
&\qquad \mathrm{CN} = \mathrm{X} \\
&\qquad\qquad = \mathrm{Ln\{{}_3[{}_2(O)(O)PCH_2NH]\}^{2-}_{aq}} + 4\mathrm{H_2O} \qquad (6) \\
&\qquad\qquad\qquad \mathrm{CN} = \mathrm{X} - 1
\end{aligned}$$

(X is probably about 8 and may decrease by 1 as the lanthanide contraction proceeds. Dehydration of the hydrated proton, $H_4O_9^+$, emphasizes a substantial increase of entropy for Eq. (6).)

The decrease in CN of the Ln(III) ions by 1 due to protonation (Eq. (6)) is insufficient to explain the exceptional position of Sc(III) amongst lanthanides(III). In order to clear up the quasi-heavy-lanthanide(III) behavior of Sc(III), an increase in CN of Sc(III) must be assumed as a result of protonation. Such an increase is possible, provided the small Sc(III) ion is bound in the $\mathrm{Sc(ntmp)}^{3-}_{aq}$ complex only by the oxygen atoms as for Be(II).[26] In such a case the mechanism of protonation of the $\mathrm{Sc(ntmp)}^{3-}_{aq}$ complex would be analogous to that given by Eq. (5) for protonation of the $\mathrm{Ln(dcta)}^{-}_{aq}$ chelates, i.e., with the oxonium water H_3O^+ added:

$$\begin{aligned}
&\mathrm{Sc\{{}_3[{}_2(O)(O)PCH_2]N\}^{3-}_{aq}} + \mathrm{[(H_3O)(H_2O)_3]^{+}_{aq}} \\
&\qquad \mathrm{CN} = \mathrm{N} \\
&\qquad\qquad = \mathrm{(H_3O)Sc\{{}_3[{}_2(O)(O)PCH_2]N\}^{2-}_{aq}} + 3\mathrm{H_2O} \qquad (7) \\
&\qquad\qquad\qquad \mathrm{CN} = \mathrm{N} + 1
\end{aligned}$$

(N is probably 5, and for the Sc(III) complex the primary hydration number increases by 1 as a result of protonation.)

If the CN of the Ln(III) central ions decreases by 1 (Eq. (6))

and the CN of Sc(III) increases by 1 (Eq. (7)), the relative CN increase for Sc(III) is equal to 2. Thus, the resulting effective radii changes[5] for Sc(III) with regard to the Ln(III) ions cause the protonation constant for Sc(III) to approach the respective constants for the Ho(III) and Y(III) nitrilotris (methylenephosphonates). Hence, the explanation is analogous to that given in detail for the enthalpies of solution of rare earth halides where the structure of both the substrate aquoions and the solid anhydrous halides LnX_3 as the reaction products was well-known.

It should be mentioned that for such a distinct tetrad effect as that observed for protonation of the $Ln(ntmp)_{aq}^{3-}$ complexes (Fig. 2), the protonation constant for the Y(III) complex should be rather closer to that for the Dy(III) or Tb(III) complex than for the Ho(III) complex.

As a result of the foregoing considerations, the data[27] reporting quasilanthanide(III) behavior of Sc(III) in the aqueous isothiocyanate system (i.e., the stability constants of the 1:1 Ln(III) isothiocyanate complexes) must be qualified as doubtful:

$$M_{aq}^{3+} + NCS_{aq}^{-} = M(NCS)_{aq}^{2+} \tag{8}$$

It appears that for Eq. (8) the reaction product complexes keep their CN from the aquoions, viz. probably 6 for Sc(III) and 8 for heavy Ln(III). Even if this CN is decreased for the flexible reaction (8) products, the relative difference in CN variations between the Sc(III) and Ln(III) ions presumably cannot exceed 1. On the same basis, it appears that ethylenebis(oxyethylenenitrilo)-tetraacetic acid, H_4L, egta, $_2(HO_2CCH_2)NCH_2CH_2OCH_2CH_2OCH_2CH_2N(CH_2CO_2H)_2$, analogous to edta (similar stability constants for 1:1 Ln(III) complexes imply it is probably hexadentate) and dcta, cannot reveal a real quasilanthanide(III) behavior of Sc(III).[11,28] Such behavior would be possible if the etheric oxygen atoms of egta were bonding. Only in such a case of the octadentate egta for both Ln(III) and Sc(III) ions, which is improbable, could the relative increase of CN of Sc(III) with regard to Ln(III) be 2, i.e., from 6 for $[Sc(OH_2)_6]_{aq}^{3+}$ to 8 for the 1:1 chelate, and would the reported quasilanthanide(III) behavior of Sc(III) be possible.

4. FINAL REMARKS

To the best of the author's knowledge, this is the first attempt to clearing up the question of the variable position of scandium(III) with regard to lanthanides(III) on plots of thermodynamic parameters of complex formation and solubility vs. Ln atomic number. The theoretical grounds for this qualitative approach (adequate for the experimental precision available) is based upon an early Pauling's equation: $R_{\mathrm{II}}/R_{\mathrm{I}} = \{A_{\mathrm{I}}B_{\mathrm{II}}/A_{\mathrm{II}}B_{\mathrm{I}}\}^{1/n-1}$, as applied to the rare earth(III) complex species, where R or $\langle r_{\mathrm{M(III)}} + r_{\mathrm{A}}\rangle$ denotes the average central atom–donor atom distance, A is the Madelung constant, B is the repulsive coefficient assumed to be proportional to CN (i.e., to the number of contacts between M(III) and donor atoms), n stands for the Born exponent which is connected with repulsive forces of the electron clouds at the closest distance between M(III) and donor ligand atoms. For the present discussion, the differences in Madelung constants for structure I and II can be ignored, since $A_{\mathrm{I}}/A_{\mathrm{II}} \cong 1$. The increase of $r_{\mathrm{M(III)}}$ (and r_{A}, and in particular r_{O}^{2-}) with CN is clearly demonstrated in Shannon's tables of ionic radii[5] based on 1000 experimental interatomic distances. It results from these tables that the value of $r_{\mathrm{La}^{3+}}$ increases with CN from 1.032 Å for CN = 6 to 1.36 Å for CN = 12, i.e., by 32%. (The value of r_{O}^{2-} increases with CN from 1.35 Å for CN = 2 to 1.42 Å for CN = 8, i.e., by 5%.) The enthalpies of solution of rare earth trihalides,[15,16,18] where the structure of both the reaction substrates and products (Eq. (1)) is known, give evidence that Sc(III) becomes a quasi-heavy-lanthanide(III) due to its constant CN = 6 accompanied by a decrease of CN of Ln(III) from 8 to 6. To explain the quasi-heavy-lanthanide behavior of Sc(III) for the first protonation constants of the $\mathrm{M(ntmp)}_{\mathrm{aq}}^{3-}$ complexes, the analogous relative decrease of CN of Ln(III) by 2 and the corresponding effective radii must be assumed. Such a decrease is possible, provided the mechanism of protonation of the $\mathrm{Sc(ntmp)}_{\mathrm{aq}}^{3-}$ complex is different from that of the $\mathrm{Ln(ntmp)}_{\mathrm{aq}}^{3-}$ complexes, and similar to the mechanism studied in detail[1,25] for protonation of the $\mathrm{Ln(dcta)}_{\mathrm{aq}}^{-}$ complexes. Usually the CN changes, if any, are parallel for the Sc(III) and Ln(III) central ions or the relative changes do not exceed 1 CN unit. Therefore, the stability constants and solubility of salts are, as a rule, much higher in the case of Sc(III) than for Lu(III). If the relative decrease of CN of the Ln(III) ions by 1 occurs, Sc(III) is only slightly "heavier"/ smaller than Lu(III) as in the case of the solubility of rare earth nitrates.[12] In the case of the relative decrease of CN of Ln(III) with respect to Sc(III) by 3 or 4, Sc(III) probably behaves as a light lanthanide(III) (the enthalpy of solution in the MCl_3–CH_3OH system[15]). Finally, if Sc(III) falls out of La(III), the relative increase of CN of Sc(III) with regard to Ln(III) by 5 may be presupposed, and the presence of weakly solvated tetrahedral species of ScX_3 in nonaqueous solvents, analogous to those described for isostructural $FeCl_3$ (viz. Fe_2Cl_6 in CS_2 or $(C_2H_5)_2O \Rightarrow FeCl_3^{\cdot}$ in ether) is possible. In other words, the difference between the Gibbs energies of solvation and crystal lattice is more negative (exothermic) for the LaX_3 halides due to extremely weak solvation of the ScX_3 halides in the case of the tetrahedral species: Sc_2Cl_6 (in 2-butylamine and diethylamine[14]), $(CH_3OH)ScI_3$[15] and $[(CH_3)_2SO]ScCl_3$.[15]

Summarizing, one can say that the position of Sc(III) with respect to the Ln(III) series for the thermodynamic function vs. q variations (i.e., a peculiar quasi-heavy-lanthanide behavior, a regular situation corresponding to an ion smaller than Lu(III) or even that quite unexpected of an ion larger than La(III)) can give some valuable information on the CN changes in the systems studied. Such information is supplied also by the presence, magnitude and the direction ("regular" or "inverse" as in Fig. 2) of the tetrad effect, and by yttrium(III) and scandium(III) displacements along the Ln(III) series. The latters should strictly correlate with the magnitude and direction of the differential tetrad effect. This is because both phenomena are strictly connected one with another and with changes in the first coordination sphere of the f-block elements and, consequently, in interelectronic repulsion energies. The double–double effect itself can be considered as minor mutual (or, e.g., with regard to the La(III) ion) displacements of the f-block ions directly dependent upon the environment of these ions, the length of M–L bonds R, CN and electronegativity of donor atoms. All these indications are of special importance for solution species where even X-ray and neutron diffraction data are often deceiving. Therefore, the enthalpies of solution of anhydrous MX_3 (X = Cl, Br, I) in water are worth restudying, at least for the Sc(III), Y(III) and heavy Ln(III) ions, at a maximal experimental precision which is essential for these subtle effects. It seems necessary to confirm that the double–double effect is substantial in this system, and that passing from $[Ln(OH_2)_8]^{3+}_{aq}$ to $LnX_{3,s}$, it increases from X = Cl (CN = 6) throughout X = I (CN = 6). The shift of Y(III) toward light lanthanides for the solution enthalpies, corresponding to the increasing tetrad effect and the most distinct for X = I, is expected to be more pronounced than that for Sc(III). It is of interest whether the shift of Sc(III) is really higher than for Y(III) and slightly lower than for the Ln(III) ions as it results from the present estimate.

Unfortunately, it appears that precise microcalorimetric measurements of the enthalpy of solution of AnX_3 (CN = 6) in water to confirm that the direction of the An(III) displacement on the ΔH_{soln} vs. q plot with regard to the Ln(III) ions is opposite to the respective Y(III) and Sc(III) shifts is impossible.

Some participation of the crystal field effect in the 1/4 and 3/4 filled f-shell effect is possible. The latter, according to common opinion,[29–32] originates in the variations of the Racah parameters, $\Delta E^3 = E^3_{product} - E^3_{substrate}$, in spite of small values of E^3 ($E^1/E^3 \cong 10$). Therefore, the crystal field effect, even if some 20 times lower than the f-electronic repulsion energies in the Racah representation in case of the differential effect, may stabilize $f^{3,4}$ and $f^{10,11}$ configurations and destabilize/increase the corresponding ions due to better shielding of the cores by the stabilized/shrunk configurations.[8] Hence, contrary to some estimates,[29] the differential crystal field effect can relatively decrease to some extent the half-field shell effect.[33] The proper interpretation of the double–double(tetrad) effect is essential for considering the structure of the f-block element complexes.

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