



Review

The size of actinoid(III) ions – structural analysis vs. common misinterpretations



Daniel Lundberg*, Ingmar Persson

Department of Chemistry and Biotechnology, Uppsala BioCenter, Swedish University of Agricultural Sciences, P.O. Box 7015, SE-750 07 Uppsala, Sweden

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ABSTRACT

A fundamental property of ions is their size, a known fact since before the acceptance of the modern atom model. The common way to describe the size of an ion is to determine its radius, defined as one of a pair of radii adding up to the bond distance between the centers of two nuclei. There are numerous factors that influence the ionic radius of a metal ion, where both valence and coordination number are essential when explaining reactivity, complexation, and chemical behavior. The similarity in ionic radii and chemical behavior between the elements in the lanthanoid and actinoid series is well-known and frequently used, making members of the former safe substitutes to avoid hazardous experiments with the radioactive actinoids. This review establishes reliable ionic radii for the nine-coordinate actinoid(III) ions, based on reported structural data, shedding light upon common misconceptions and clarifying the relationship between the ionic radii in the lanthanoid and actinoid series.

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1. Introduction

1.1. Ionic radii

The first widely accepted list of ionic radii was published by Pauling in the late 1920s [1,2], though he was not the first one to compile such a list as his work was built upon data proposed by Landé [3], Wasastjerna [4], and Goldschmidt [5]. Since Pauling's set of ionic radii was published they have been expanded and refined both in part and as a whole, including Zachariasen's actinoid radii in 1948 [6]. The standard reference work today has its origin in the citation classic published by Shannon and Prewitt in 1969 [7] with a correction published in 1970 [8], and later singlehandedly revised and updated by Shannon in 1976 [9]. In these papers, using

crystallographic data from oxides and fluorides and calculated values from various isostructural compounds, Shannon was able to show the strong correlation between ionic radius and coordination number (CN) within each valence state of every ion. This resulted in new or improved ionic radii for most CNs of nearly all elements structurally studied at that time. The list of so-called *Shannon radii* is exhaustive and perhaps also intimidating and as such often abridged with generalized radii regardless of CN thereby missing the central point: for every configuration and CN, most ions have a well-defined ionic radius; among the exceptions one finds the $d^{10}s^2$ metal ions [10].

The method to elucidate radii from highly symmetric systems, which is often the case in oxides and fluorides, has proven to stand the test of time quite well. However, there are situations when favorable lattice energy levels in such highly symmetric systems can overrule the configuration of an ion in solution where no such energy gain is available. Also, when Shannon made his compilation of ionic radii, a very limited number of structure investigations were performed in solution. Even today, structural studies are much more prevalent in the solid state than in solution, but there is nonetheless

* Corresponding author. Tel.: +46 18 67 15 49; fax: +46 18 67 28 50.

E-mail addresses: daniel.lundberg@slu.se (D. Lundberg), ingmar.persson@slu.se (I. Persson).

a significant amount of solution data available. Furthermore, the Shannon radii were tediously tabulated before the advent of computer-aided databases [11–13] which can access (nearly) all crystallographic structures ever reported in a matter of seconds, which means that the statistical material available today is enormous compared to that in 1976. This means that any comparison using Shannon radii as starting point will be limited to the data set available at that time. Instead, more appropriately, with accurately determined ionic radii from studies in solution, the foundation of ionic radii found in carefully selected solids will be further augmented, achieving a significantly better, statistically-based correlation between ionic radii and CNs, minimizing possible influence from lattice energies. Such correlations would also provide theoretical chemists with appropriate values for dynamic systems commonly featuring a mixture of different CNs.

1.2. Discovery and modern use of the lanthanoids and actinoids

Similar to the development of ionic radii, the history of the lanthanoids is a walk through the history of chemistry. During their primary years of discovery, the lanthanoids and other so-called “rare earths” were noted for being notoriously difficult to chemically separate from each other using fundamental separation techniques [14]. The question of how many lanthanoids actually existed was not settled until 1914 when Moseley completed his studies in X-ray emission spectroscopy, clearly showing that, at the time, three elements between aluminum and gold were missing, namely $Z = 43$ (technetium), $Z = 61$ (promethium), and $Z = 75$ (rhenium) [15], where the lanthanoid promethium was not discovered until the Manhattan Project [16]. Around the same time as promethium was discovered, McMillan and Abelson synthesized neptunium [17], proving that additional chemical elements existed beyond uranium. However, in the dawn of nuclear chemistry few scientists had any real ideas of what these elements could be used for given their scarcity and radioactivity, except the frightening concept of atomic weapons [18].

Separation of lanthanoids and actinoids is still a challenge and many on-going research projects exist in this field [19–22]. The main obstacle for any actinoid study is still the level of radiation, though reasonably controllable early in the series, it becomes very hazardous in the latter half. This has led to a less developed experimental understanding and to higher acceptance of theoretical calculations as basis for their ionic radii. While theoretical work may be advantageous from a safety point-of-view, it is also heavily reliant on correct interpretation of physico-chemical data. For instance, the so-called “gadolinium break”, a proposed mid-series change from nine- to eight-fold coordination for hydrated lanthanoid(III) ions, was disproven through careful examination of structural data in both the solid state and aqueous solution [23], but was in essence afterward also applied to the actinoid(III) ions [24,25]. Regardless of the level of apparent similarity, there are different chemical criteria in addition to ionic radii, including natural occurrence [26], oxidation states [27], and electron configuration [28], that needs to be taken into consideration when forming the basis for suitable chemical analogues. However, the bonding properties of the trivalent lanthanoid and actinoid ions, being hard acids or *class (a)* following Pearson’s HSAB classification [29], means that they primarily form electrostatic interactions, reducing the impact from many other physical properties. Ultimately, depending on the area of study, one may thus end up with different ion selection criteria when replacing radioactive actinoid(III) ions for stable lanthanoid(III) ones, which may explain why there has not been any real consensus for the use of a particular replacement ion for any given actinoid ion (Table S1). All these different interpretations have led to the misapprehension that *any* lanthanoid is a good representation of *any* actinoid, although, in many studies, the lanthanoid (ion) situated above the actinoid (ion) of interest in the periodic table is chosen

for comparisons, based on nothing but a “periodic positional correlation”, i.e. the number of *f* electrons; the most common pair studied is without any doubt the vertical pair americium/europium.

The purpose of this review is to get a deeper insight and understanding of the ionic radii of the actinoid(III) ions, using the radii of the lanthanoid(III) ions, to serve as a guide for a proper choice of an actinoid substitute whenever experiments including highly radioactive elements are not possible or suitable. With its basis on available structural data, the review thus attempts to correct the misconceptions regarding the similarities between the two series.

2. The radii of lanthanoid(III) ions based on complexes with O-donor ligands

All lanthanoids feature a stable trivalent state, though a few of them can exist as divalent or tetravalent ions under certain conditions [27]. As hard Lewis acids, the lanthanoid(III) ions exhibit CNs that are largely limited to geometric restrictions, which is reflected in the different CNs related to the spatial demands of the coordinated ligands. Shannon lists ionic radii for the lanthanoid(III) ions for CNs 6, 8, and 9, using radii-unit cell volume (r^3 vs. V) plots for isostructural compounds [9], adjusting the ionic radii given by Greis and Petzel for CNs 8 and 9 [30]. Additionally, for CN 7, the list is incomplete both in terms of values and quality comments. The much larger amount of data available today has allowed improvement of the Shannon radii, as they feature all these CNs: 9 (primarily hydrates; tricapped trigonal prismatic), 8 (most other O-donor solvates; square antiprismatic), 7 (space-demanding solvates in solution), and 6 (space-demanding solvates in solids; octahedral), respectively [14]. The hydrates of the heavier lanthanoid(III) ions show water deficit in the capping positions, which means the actual CN of the lanthanoid(III) ions, starting from holmium, deviates more and more from 9 with increasing atomic number [31], leaving this CN without proper examples in the end of the series. By combining structural data from lanthanoid(III) complexes with monodentate, neutral ligand molecules in solution and solid state, preferably compounds crystallizing in space groups with low symmetry [11–13], a detailed picture of the ionic radii of the lanthanoid(III) ions has previously been obtained [14]. The basis for this comparison was the proven fact that the radius of any neutral oxygen donor atom, except ethers, is similar enough to the one generally accepted for coordinated water oxygen, $r_O = 1.34 \text{ \AA}$ [32].

The fairly large number of reported lanthanoid(III) structures since our most recent paper in this field [14] warrants for a re-calculation using the same method, using CN 8 as it allows for best statistical treatment. In addition to several studies in solution, more than 250 eight-coordinate lanthanoid(III) O-donor crystal structures have been published to date (see Table S2). After removing 15 gross outliers, a statistical treatment was performed, where an additional 16 data points (5.7 %) significantly deviate from the assumed linear trend, an effect of the *lanthanoid contraction*, translating to a difference of more than $\pm 0.03 \text{ \AA}$ (see Supplementary Information for a full statistical analysis). The resulting slope from a least-squares fit on the remaining structures, Fig. 1 (top), yields the expected Ln–O bond length for any eight-coordinate lanthanoid(III) ion from which it is possible to calculate the corresponding lanthanoid(III) ionic radii. The same rationale was applied to CN 9 (see Fig. 1 (bottom) and Table S3).

3. The radii of actinoid(III) ions based on complexes with O-donor ligands

Except for a value for the eight-coordinate americium(III) ion, stemming from an americium sulfate study by Burns and Baybarz [33], Shannon only lists data for six-coordinate actinoid(III) ions and only up to californium, $Z = 98$, most of them extracted from r^3 vs. V plots [9]. To tackle this lack of actinoid(III) data, estimated values

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