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Coordination Chemistry Reviews.

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Citation for the published paper:

Daniel Lundberg and Ingmar Persson. (2016) The size of actinoid(III) ions –
structural analysis vs. common misinterpretations. *Coordination Chemistry
Reviews*. Volume: 318, Number: 1, pp 131-134.

<http://dx.doi.org/10.1016/j.ccr.2016.04.003>.

Access to the published version may require journal subscription.

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

Daniel Lundberg and Ingmar Persson*

Department of Chemistry and Biotechnology, P.O. Box 7015, Uppsala BioCenter,

Swedish University of Agricultural Sciences, SE-750 07 Uppsala, SWEDEN

e-mail address: daniel.lundberg@slu.se (corresponding author), ingmar.persson@slu.se

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Keywords: ionic radii, actinoid(III), lanthanoid(III), O-donor ligands, periodic trends

	57 La LANTHANUM	58 Ce CERIUM	59 Pr PRASEODYMIUM	60 Nd NEODYMIUM	61 Pm PROMETHIUM	62 Sm SAMARIUM	63 Eu EUROPIUM	64 Gd GADOLINIUM	65 Tb TERBIUM	66 Dy DYSPROSIUM	67 Ho HOLMIUM	68 Er ERBIUM	69 Tm THULIUM	70 Yb YTTERBIUM	71 Lu LUTETIUM
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Highlights

- Ionic radii for nine-coordinate actinoid(III) ions
- Suitable lanthanoid(III) ion substitutes for actinoid(III) ions are given
- The incline of the lanthanoid contraction is steeper than the actinoid contraction

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.

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 built upon data proposed by Landé [3], Wasastjerna [4], and Goldschmidt [5]. Since Pauling's set of ionic radii were 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 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 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. More appropriately, with accurately determined ionic radii from studies in solution, the foundation of ionic radii found in carefully selected solids will be further supplemented, 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 afterwards 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 has 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

The lanthanoids all 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 feature 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, $r_{\text{O}} = 1.34 \text{ \AA}$ [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, Figure 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 Figure 1 (bottom) and Table S3.

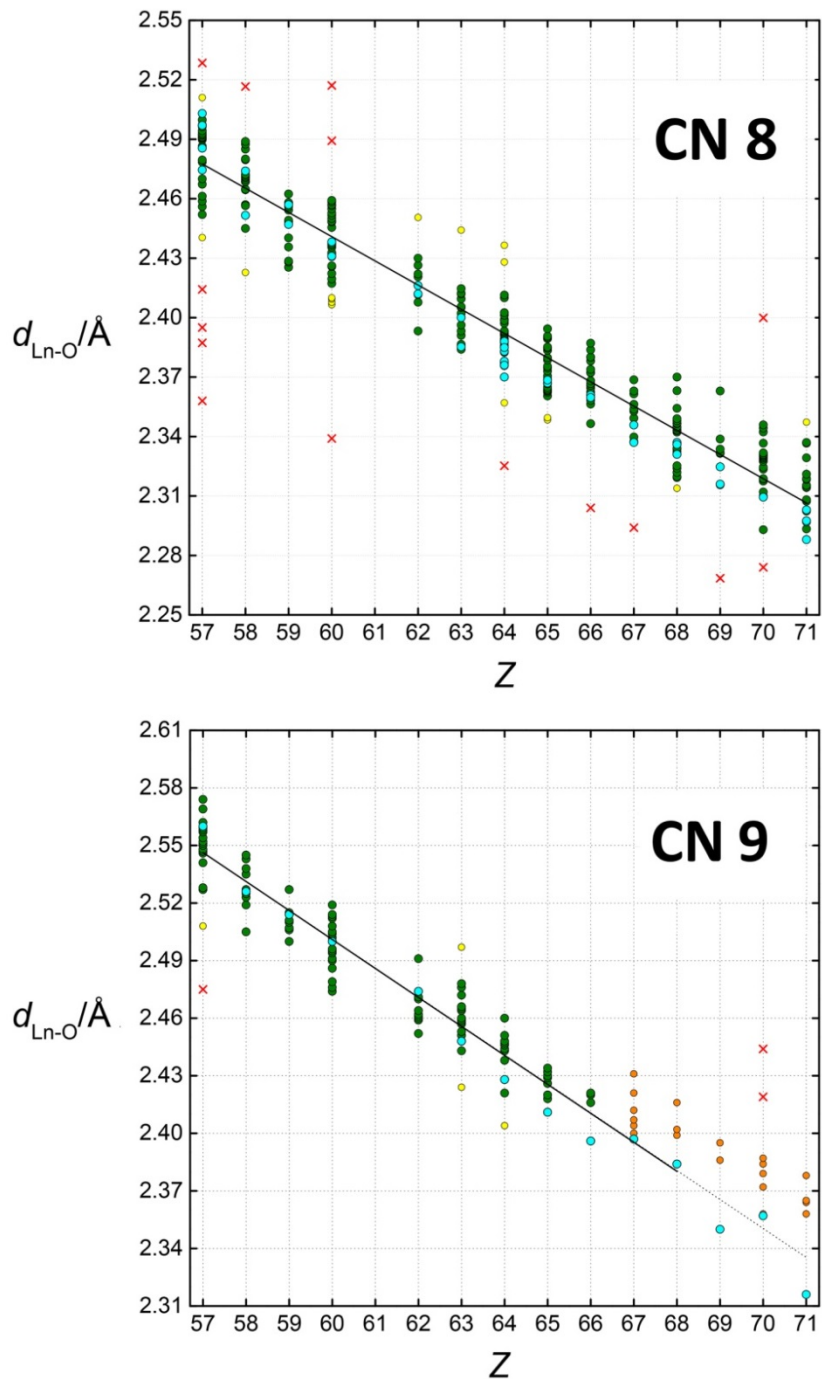


Figure 1. The mean Ln-O bond distances of all reported eight- (top) and nine-coordinate (bottom) lanthanoid(III) *O*-donor structures. The least-squares linear fits includes solution (cyan circles) and crystal data points (green circles). Outliers (red crosses) and data with deviating bond lengths (yellow) and/or mean coordination number (orange) were not included in the fit.

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 [34], 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 for different CNs have been obtained in different ways e.g. by combining the similarities in crystallographic structure with the Shannon radii for CN 6 to arrive at crystal radii for CN 8 [33] or by evaluating polynomial functions using thermodynamic properties [25]. Even today, there has been significantly fewer crystallographic studies with neutral donors carried out on the actinoids than the lanthanoids. In addition, from thorium to plutonium, other valence states are more stable than the trivalent one, limiting the available actinoid(III) data to only ten reported *O*-donor structures (all with CN 9) using the same selection criteria as previously given for the lanthanoid(III) ions, see Table S4. Individual studies of the nine-coordinate actinoid(III) ions in aqueous solution exist, using EXAFS as the investigation technique [35-44], but the data quality is generally low mainly due to low concentrations and/or the fact that the data treatment adversely affects the results by overestimating the contribution of the An-O bond distances from the ligands in trigonal prismatic positions and severely underestimating those in capping ones [23], Figure S1. This disqualifies these studies from inclusion in a mean bond length comparison. A selection of the data listed in these reports were recently re-evaluated and combined with MD simulations [45]. However, this study seemingly pre-supposed that the difference in ionic radius between two neighboring actinoid(III) ions is identical to that of two neighboring lanthanoid(III) ions by inaccurately using the “periodic positional correlation” mentioned earlier, and it also failed to correlate the results with analogous studies in the solid state, prohibiting the use of these re-examined results, Figure

S2. The only high quality data left for these ions thus stems from crystallographic determinations, Table S4.

For a reliable comparison, one needs a large enough spread over many elements, where the mean An-O bond distances can be correlated to the mean Ln-O bond distances in nine-coordinate lanthanoid(III) ions, thereby obtaining suitable actinoid(III) replacement ions for CN 9 and, by extension, for any CN. Coincidentally, such a spread is precisely what is currently available, as structures with *O*-donor solvated uranium(III) to californium(III) ions have been published [24, 35, 44, 46, 47]. Without any predetermined correlation, the resulting slope of the mean An-O bond distances is thus fitted to the calculated slope for the mean Ln-O bond distances for CN 9, setting the lanthanoid atomic number step length, Z_{Ln} , to unity. It becomes obvious that there is no straightforward 1:1 relationship between the two series, as the actinoid atomic number step length, Z_{An} , needs to be reduced by more than 30 % in addition to a downward parallel displacement from one to up to five elements, Figure 2. Using this method the Z_{Ln} values will, by necessity, be fractional for each of the actinoid, making it unlikely to find a perfect lanthanoid/actinoid match. On the other hand, using careful extrapolation of these values, it is possible to predict the best replacement ions even for actinoid(III) ions not yet studied, see Table 1.

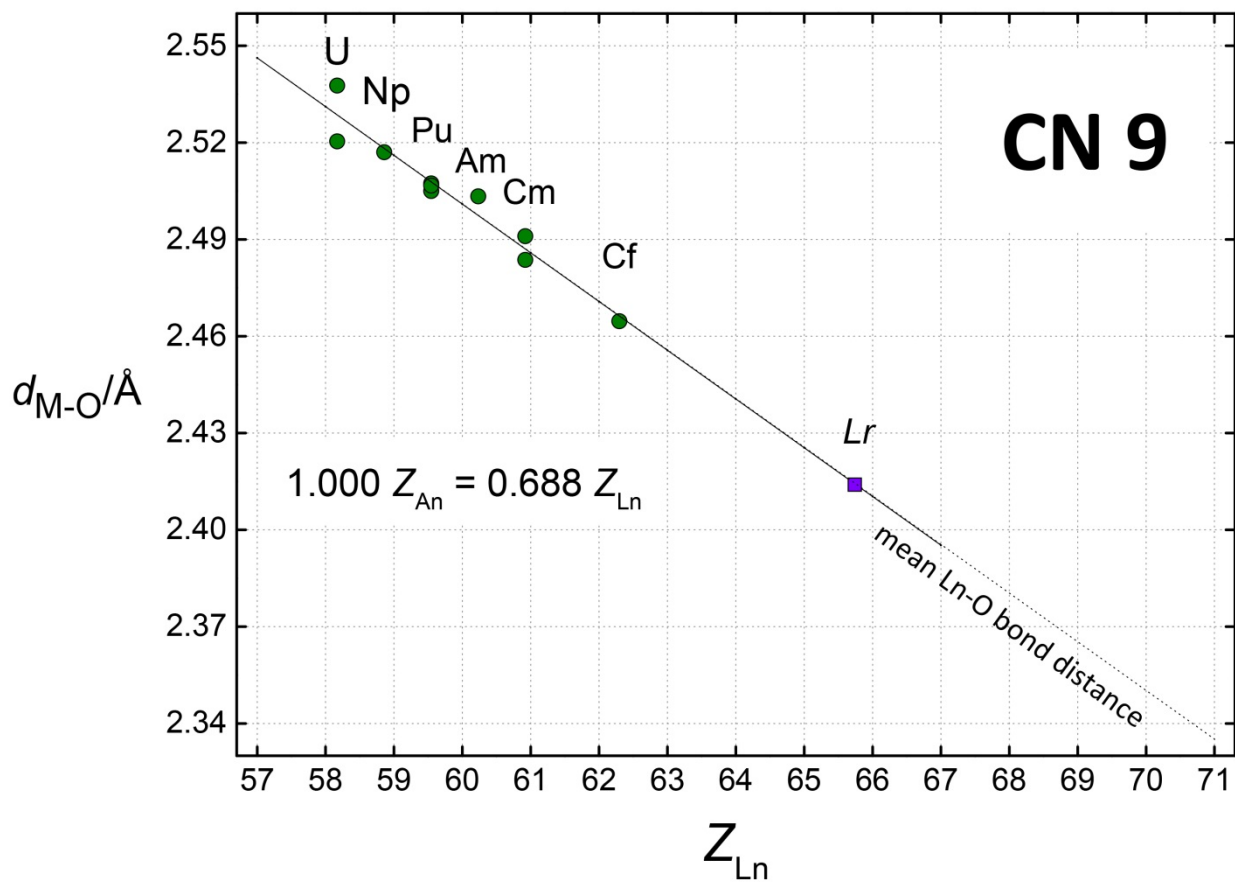


Figure 2. The mean An-O bond distance of all reported nine-coordinate actinoid(III) structures (green circles) following the selection criteria plotted with the same slope as the calculated slope in Figure 1 (bottom) for the nine-coordinate lanthanoid(III) structures (solid line to holmium; dotted line to lutetium). The resulting “atomic number step length” within the actinoid series, Z_{An} , corresponds to 68.8 % of one step in the lanthanoid series, Z_{Ln} . The predicted Z_{Ln} for the ultimate actinoid(III) ion, lawrencium, is 65.74 (purple square).

Table 1. List of replacement lanthanoid(III) ions for each of the actinoid(III) ions, based on their ionic radii in nine-coordination, $r_{\text{AnCN}9}$. The actinoid Z_{Ln} values are derived from matching the mean $d_{\text{An-O}}$ slope for CN 9 with the mean $d_{\text{Ln-O}}$ slope for CN 9, Figure 2. The ionic radii are calculated from the respective $d_{\text{An-O}}$ and $d_{\text{Ln-O}}$ slopes by subtracting 1.34 Å for the oxygen radius.

An ³⁺ ion	$r_{\text{AnCN}9}/\text{Å}$	Z_{Ln}	Best Ln ³⁺ ion	$r_{\text{LnCN}9}/\text{Å}$
Ac ³⁺	1.220 ^a	56.11	(La ³⁺) ^b	<i>v.i.</i>
Th ³⁺	1.209 ^a	56.79	La ³⁺	1.206
Pa ³⁺	1.199 ^a	57.48	La ³⁺ /Ce ³⁺	<i>v.s./v.i.</i>
U ³⁺	1.189	58.17	Ce ³⁺	1.191
Np ³⁺	1.178	58.86	Pr ³⁺	1.176
Pu ³⁺	1.168	59.55	Pr ³⁺ /Nd ³⁺	<i>v.s./v.i.</i>
Am ³⁺	1.157	60.23	Nd ³⁺	1.161
Cm ³⁺	1.147	60.92	Pm ³⁺	1.146 ^c
Bk ³⁺	1.137 ^c	61.61	Pm ³⁺ /Sm ³⁺	<i>v.s./v.i.</i>
Cf ³⁺	1.126	62.30	Sm ³⁺	1.131
Es ³⁺	1.116 ^a	62.98	Eu ³⁺	1.116
Fm ³⁺	1.105 ^a	63.67	Gd ³⁺	1.101
Md ³⁺	1.095 ^a	64.36	Gd ³⁺	<i>v.s.</i>
No ³⁺	1.085 ^a	65.05	Tb ³⁺	1.085
Lr ³⁺	1.074 ^a	65.74	Dy ³⁺ (Y ³⁺) ^d	1.070

^a extrapolated value; ^b even though the predicted Z_{Ln} lies markedly outside the lanthanoid(III) series, La³⁺ is still the best choice; ^c interpolated value; ^d possible “rare earth” ion with $r_{\text{CN}9} = 1.068$ Å, $Z_{\text{Ln}} = 66.15$; *v.i.* = vide infra, *v.s.* = vide supra.

4 Evaluation of the revised actinoid(III) radii

Based on the larger CN 9 radii of the actinoid(III) ions beyond californium(III), 1.126 Å, it seems very reasonable that they can accommodate nine water molecules throughout the remaining part of the series, as the lawrencium(III) ionic radius is extrapolated to be larger than that of dysprosium(III), an ion which shows no loss of capping water for CN 9, Figure 2 [23].

On the other end of the series, the actinium(III) ion is calculated to be 0.014 Å larger than lanthanum(III) one, thereby lacking a good replacement lanthanoid(III) ion, with the lanthanum(III) ion still being the best choice. The only non-halide, non-chalcogenide actinium(III) compound reported in the crystallographic databases [11-13], is a powder diffraction study on actinium oxalate decahydrate where only unit cell parameters were obtained [48]. The compound is said to be nine-coordinate and isostructural with lanthanum oxalate decahydrate, for which an accurate structural determination reports a mean La-O distance of 2.561(4) Å [49]. Combining the isostructurality and the cell parameters for the actinium counterpart, one obtains a very crude mean Ac-O distance of 2.615 Å, or 0.054 Å longer than the mean La-O distance. It is worth pointing out that these slightly longer mean bond distances include distances to bidentate oxalate anions and not exclusively monodentate, neutral ligands, and should therefore not be viewed as such.

Finally, regarding the widely held belief that the europium(III) ion is a suitable replacement for the americium(III) ion, a recently published structural study of the CyMe₄-BTBP solvation of these ions in a range of common co-solvents reveals that the americium(III) ion is large enough to allow inclusion of a counter ion (CN ≥ 9) whereas the europium(III) ion is not (CN 8) [50]. As seen in Table 1, the best replacement for an americium(III) ion is a neodymium(III) ion, in

addition to also being one of the two suitable replacement ions for plutonium(III) [51], while the europium(III) ion in fact is the spot-on replacement ion for the einsteinium(III) ion.

5 Conclusions

The study of ionic radii is as old as the coordination chemistry subject itself, as ionic radii directly or indirectly are responsible for the many of the properties we see in chemical structures. Through careful determination of the ionic radii for lanthanoid(III) ions from structural data in several different CNs, they can successfully be correlated to the experimentally much less studied actinoid(III) ions. This assessment of ionic radii can subsequently be applied to the study of any system, which should also be the basis of any study of a comparative nature. Any pair of actinoid(III) and lanthanoid(III) ions may be similar to one another, but from a structural point-of-view there is an optimal similarity possible to achieve as pointed out in this review. This is certainly also the case, even when the elements are aligned vertically in the periodic table of elements and both elements happen to be named after continents.

6 References

- [1] L. Pauling, J. Am. Chem. Soc., 49 (1927) 765-790.
- [2] L. Pauling, J. Am. Chem. Soc., 51 (1929) 1010-1026.
- [3] A. Landé, Z. Phys., 1 (1920) 191-197.
- [4] J.A. Wasastjerna, Comm. Phys-Math., Soc. Sci. Fenn., 38 (1923) 1-25.
- [5] V.M. Goldschmidt, Geochemische Verteilungsgesetze der Elemente, 1926.
- [6] W.H. Zachariasen, Phys. Rev., 73 (1948) 1104-1105.
- [7] R.D. Shannon, C.T. Prewitt, Acta Crystallogr., Sect. B, 25 (1969) 925-945.
- [8] R.D. Shannon, C.T. Prewitt, Acta Crystallogr., Sect. B, 26 (1970) 1046-1048.
- [9] R.D. Shannon, Acta Crystallogr., Sect. A, 32 (1976) 751-767.
- [10] I. Persson, D. Lundberg, P. D'Angelo, Inorg. Chem. *in preparation* 2016
- [11] F.H. Allen, Acta Crystallogr., Sect. B, 58 (2002) 380-388.
- [12] M. Hellenbrandt, Cryst. Rev., 10 (2004) 17-22.
- [13] S. Grazulis, D. Chateigner, R.T. Downs, A.F.T. Yokochi, M. Quirós, L. Lutterotti, E. Manakova, J. Butkus, P. Moeckg, A. Le Bailh, J. Appl. Cryst., 42 (2009) 726-729.
- [14] D. Lundberg, I. Persson, L. Eriksson, P. D'Angelo, S. De Panfilis, Inorg. Chem., 49 (2010) 4420-4432.
- [15] H.G.J. Moseley, Phil. Mag. (Sixth ser.), 27 (1914) 703-713.
- [16] J.A. Marinsky, L.E. Glendenin, C.D. Coryell, J. Am. Chem. Soc., 69 (1947) 2781-2785.
- [17] E. McMillan, P.H. Abelson, Phys. Rev., 57 (1940) 1185-1186.
- [18] G.T. Seaborg, Science, 104 (1946) 379-386.
- [19] M.J. Hudson, L.M. Harwood, D.M. Laventine, F.W. Lewis, Inorg. Chem., 52 (2013) 3414-3428.
- [20] B.J. Mincher, J.F. Wishart, Solvent Extr. Ion Exc., 32 (2014) 563-583.

- [21] Y. Wu, N. Liu, S. Ding, *Prog. Chem.*, 26 (2014) 1655-1664.
- [22] K.L. Nash, *Solvent Extr. Ion Exc.*, 33 (2015) 1-55.
- [23] I. Persson, P. D'Angelo, S. De Panfilis, M. Sandström, L. Eriksson, *Chem.-Eur. J.*, 14 (2008) 3056-3066.
- [24] C. Apostolidis, B. Schimmelpfennig, N. Magnani, P. Lindqvist-Reis, O. Walter, R. Sykora, A. Morgenstern, E. Colineau, R. Caciuffo, R. Klenze, R.G. Haire, J. Rebizant, F. Bruchertseifer, T. Fanghänel, *Angew. Chem.-Intl. Ed.*, 49 (2010) 6343-6347.
- [25] F.H. David, V. Vokhmin, *New J. Chem.*, 27 (2003) 1627-1632.
- [26] B.T. Kilbourn, *A lanthanide lanthology, Part 1, A-L, Second ed.*, Molycorp, Inc. Mountain Pass, CA, USA, Mountain Pass, CA, 1997.
- [27] N.N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, 2nd ed., Butterworth-Heinemann, Oxford, 1997.
- [28] B. Johansson, S. Li, *J. Alloy Compd.*, 444-445 (2007) 202-206.
- [29] R.G. Pearson, *J. Am. Chem. Soc.*, 85 (1963) 3533-3539.
- [30] O. Greis, T. Petzel, *Z. Anorg. Allg. Chem.*, 403 (1974) 1-22.
- [31] A. Abbasi, P. Lindqvist-Reis, L. Eriksson, D. Sandström, S. Lidin, I. Persson, M. Sandström, *Chem.-Eur. J.*, 11 (2005) 4065-4077.
- [32] J.K. Beattie, S.P. Best, B.W. Skelton, A.H. White, *J. Chem. Soc., Dalton Trans.*, (1981) 2105-2111.
- [33] F. David, *J. Less-Common Met.*, 121 (1986) 27-42.
- [34] J.H. Burns, R.D. Baybarz, *Inorg. Chem.*, 11 (1972) 2233-2237.
- [35] P. Lindqvist-Reis, C. Apostolidis, J. Rebizant, A. Morgenstern, R. Klenze, O. Walter, T. Fanghänel, R.G. Haire, *Angew. Chem.-Intl. Ed.*, 46 (2007) 919-922.
- [36] E. Galbis, J. Hernández-Cobos, C. den Auwer, C. Le Naour, D. Guillaumont, E. Simoni, R.R. Pappalardo, E. Sánchez Marcos, *Angew. Chem.-Intl. Ed.*, 49 (2010) 3811-3815.
- [37] B. Brendebach, N.L. Banik, C.M. Marquardt, J. Rothe, M.A. Denecke, H. Geckeis, *Radiochim. Acta*, 97 (2009) 701-708.

- [38] P.G. Allen, J.J. Bucher, D.K. Shuh, N.M. Edelstein, T. Reich, *Inorg. Chem.*, 36 (1997) 4676-4683.
- [39] P.G. Allen, J.J. Bucher, D.K. Shuh, N.M. Edelstein, I. Craig, *Inorg. Chem.*, 39 (2000) 595-601.
- [40] M.R. Antonio, L. Soderholm, C.W. Williams, J.-P. Blaudeau, B.E. Bursten, *Radiochim. Acta*, 89 (2001) 17-25.
- [41] M.R. Antonio, C.W. Williams, L. Soderholm, *Radiochim. Acta*, 90 (2002) 851-856.
- [42] S. Stumpf, T. Stumpf, K. Dardenne, C. Hennig, H. Foerstendorf, R. Klenze, T. Fanghänel, *Environ. Sci. Technol.*, 40 (2006) 3522-3528.
- [43] M. Weigl, M.A. Denecke, P.J. Panak, A. Geist, K. Gompper, *Dalton Trans.*, (2005) 1281-1286.
- [44] S. Skanthakumar, M.R. Antonio, R.E. Wilson, L. Soderholm, *Inorg. Chem.*, 46 (2007) 3485-3491.
- [45] P. D'Angelo, F. Martelli, R. Spezia, A. Filipponi, M.A. Denecke, *Inorg. Chem.*, 52 (2013) 10318-10324.
- [46] J.H. Matonic, B.L. Scott, M.P. Neu, *Inorg. Chem.*, 40 (2001) 2638-2639.
- [47] J.-C. Berthet, P. Thuéry, M. Ephritikhine, *Polyhedron*, 25 (2006) 1700-1706.
- [48] F. Weigel, H. Hauske, *J. Less-Common Met.*, 55 (1977) 243-247.
- [49] S.H. Huang, G.D. Zhou, T.C.W. Mak, *J. Cryst. Spectrosc.*, 21 (1991) 127-131.
- [50] C. Ekberg, E. Löfström-Engdahl, E. Aneheim, M.R.S. Foreman, A. Geist, D. Lundberg, M. Denecke, I. Persson, *Dalton Trans.*, 44 (2015) 18395-18402.
- [51] J.N. Cross, E.M. Villa, S.A. Wang, D.W. Juan, M.J. Polinski, T.E. Albrecht-Schmitt, *Inorg. Chem.*, 51 (2012) 8419-8424.

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

Supplementary information

Daniel Lundberg and Ingmar Persson*

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

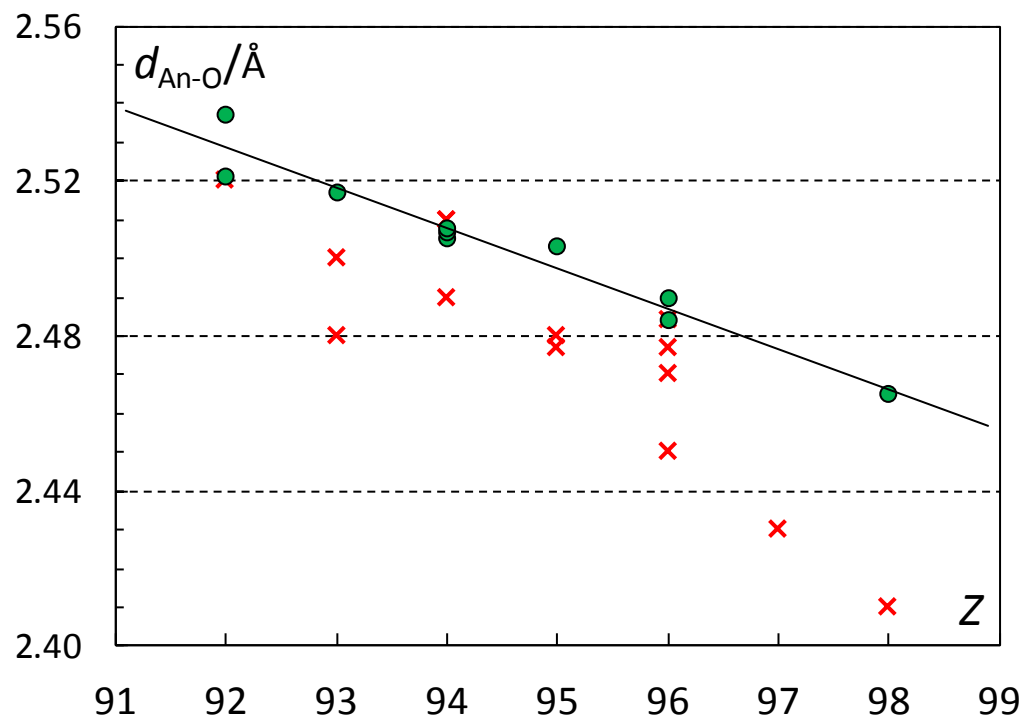


Figure S1. The reported mean An-O bond distance in all published nine-coordinate actinoid(III) structures following the selection criteria as given in the main text (green circles) and their least-squares linear fit, and the reported An-O distances from hydrated actinoid(III) ions from the EXAFS studies in refs. 35-44 (red crosses). The apparent deviation between the crystallographic data and the solution studies most likely originates from an overestimation of the contribution of the An-O distances in the trigonal prism.

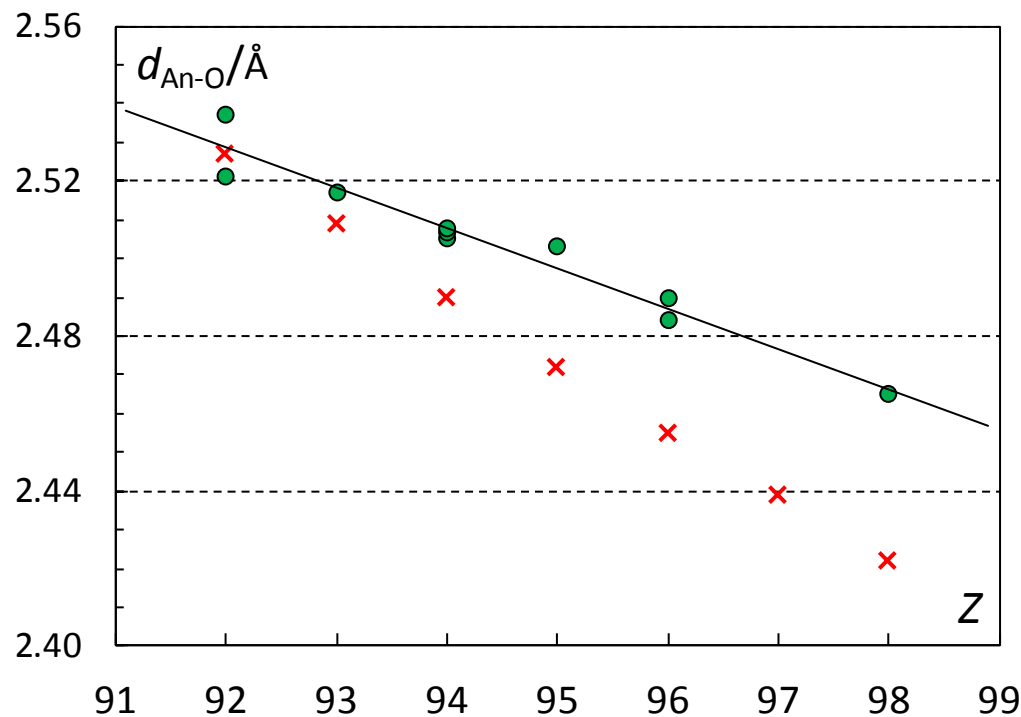


Figure S2. The reported mean An-O bond distance in all published nine-coordinate actinoid(III) structures following the selection criteria as given in the main text (green circles) and their least-squares linear fit, and the re-calculated An-O distances of hydrated actinoid(III) ions in ref. 45 (red crosses) based on a selection of previous results; see Figure S1. The apparent deviation between the crystallographic data and the solution studies most likely originates from an overestimation of the contribution of the An-O distances in the trigonal prism. Also, the actinoid(III) ion comparison with the lanthanoid series here erroneously pre-supposes a 1:1 atomic number step length ratio.

Table S1. Some suggested replacement or structurally analogous lanthanoid ions for selected actinoid(III) and actinoid(IV) ions and their placement in the periodic table. For a full description of the chosen selection criteria, please refer to the individual references.

Actinoid ion	Replacement ion(s)	“Structural analog”	Selected references
+III			
Np ³⁺	Nd ³⁺ , Er ³⁺		[52]*
Pu ³⁺	Sm ³⁺ , Ln ³⁺ , Y ³⁺	Nd ³⁺	[51], [52]*
Am ³⁺	Eu ³⁺ , Y ³⁺	Nd ³⁺	[51-53]
Cm ³⁺	Pm ³⁺	La ³⁺ , Dy ³⁺	[36], [44], [54]
Bk ³⁺	Gd ³⁺		[53]
Cf ³⁺		Nd ³⁺ , Sm ³⁺	[36], [55]
+IV			
Th ⁴⁺	Ce ³⁺ , Ce ⁴⁺ , Gd ³⁺		[52]
Pa ⁴⁺	<i>n/a</i>		
U ⁴⁺	Ce ⁴⁺ , Y ³⁺		[52]*
Np ⁴⁺	Nd ³⁺ , Er ³⁺		[52]*
Pu ⁴⁺	Nd ³⁺ , Eu ³⁺	Ce ⁴⁺	[52], [56]

Ln	⁵⁷ La	⁵⁸ Ce	⁵⁹ Pr	⁶⁰ Nd	⁶¹ Pm	⁶² Sm	⁶³ Eu	⁶⁴ Gd	⁶⁵ Tb	⁶⁶ Dy	⁶⁷ Ho	⁶⁸ Er	⁶⁹ Tm	⁷⁰ Yb	⁷¹ Lu
An	⁸⁹ Ac	⁹⁰ Th	⁹¹ Pa	⁹² U	⁹³ Np	⁹⁴ Pu	⁹⁵ Am	⁹⁶ Cm	⁹⁷ Bk	⁹⁸ Cf	⁹⁹ Es	¹⁰⁰ Fm	¹⁰¹ Md	¹⁰² No	¹⁰³ Lr

* The original reference refers only to Nd and Er for Np³⁺/Np⁴⁺, Ln and Y for Pu³⁺, and Y for U⁴⁺; the ionic charge has been added for clarity.

- [36] E. Galbis, J. Hernández-Cobos, C. Den Auwer, C. L. Naour, D. Guillaumont, E. Simoni, R.R. Pappalardo, E.S. Marcos, *Angew. Chem.-Intl. Ed.* 49 (2010), 3811-3815.
- [44] S. Skanthakumar, M.R. Antonio, R.E. Wilson, L. Soderholm, *Inorg. Chem.* 46 (2007), 3485-3491.
- [51] J.N. Cross, E.M. Villa, S. Wang, J. Diwu, M.J. Polinski, T.E. Albrecht-Schmitt, *Inorg. Chem.* 51 (2012), 8419-8424.
- [52] R. Villarreal, D. Spall. Selection of Actinide Chemical Analogues for WIPP Tests (Los Alamos National Laboratory, 1995).
- [53] H. Latrous, R. Besbes, N. Ouerfelli, *J. Mol. Liq.* 138 (2008), 51-54.
- [54] N.D. Priest, *Radiat. Res.* 168 (2007), 327-331.
- [55] R.E. Sykora, Z. Assefa, R.G. Haire, *Inorg. Chem.* 45 (2006), 475-477.
- [56] K. Raymond, G. Szigethy, G. in *Actinides 2008 - Basic Science, Applications and Technology Vol. 1104 Materials Research Society Symposium Proceedings* (eds D. K. Shuh et al.) 123-128 (2008).

Table S2. a) The reported mean bond distance, $d(\text{Ln-O})$, of all eight-coordinate lanthanoid(III) structures with neutral, *O*-donor ligands listed in the Cambridge Structural Database (CSD, ref. 11), the Inorganic Crystal Structure Database (ICSD, ref. 12), and Crystallography Open Database (COD, ref. 13; the CSD entries listed by their reference code and the ICSD ones by their code. Entries in red typeface were excluded on the fit based on a recursive Grubb's test (two-sided, 98 %); b) The reported mean bond distance, $d(\text{Ln-O})$, of all eight-coordinate lanthanoid(III) ions in solution with neutral, *O*-donor ligands as listed by given reference; c) summary of the recursive Grubb's test (two-sided, 98 %) performed on the 258 eight-coordinate lanthanoid(III) complexes listed in a) and b), element by element; parameter variables given as in F.E. Grubb, *Technometrics*, 11 (1969), 1-21. For the original analysis of this method, see ref. 14. Z = atomic number.

a)

Z	$d(\text{Ln-O})$	CSD code	ICSD code	note
57	2.358	LADLIM		
57	2.387	AYEGIV		
57	2.395	ZEQGEJ		
57	2.414	AZEBIQ	152162	
57	2.440	ZEQGIN		
57	2.452	KOBCIP		
57	2.456	KIKVIK		
57	2.459	KIKWIL		
57	2.461	HOXNIR		
57	2.467	DIQHUG		
57	2.470	KOBDAL		
57	2.479	VOGJOQ		
57	2.479	LADMPC10		
57	2.480	YIHPAG		
57	2.487	YIPKAK	249485	
57	2.490	LADPEN		
57	2.490			$[\text{La}(\text{dma})_8]^{3+}$, CODid=1512129
57	2.491	AFEYOB		

57	2.491	AFEYIV	
57	2.492	AFEYUH	
57	2.492	LITHOL	
57	2.493	FAQMOB	
57	2.494	KICFIN	
57	2.494	PYNOLA10	
57	2.496	YIPKAK01	249486
57	2.496	RUJYIF	
57	2.497	TUWSOT	
57	2.500	HOXNEN	
57	2.511	XIDZEQ	
57	2.529	AFEZAO	
<hr/>			
58	2.423	XILJIN	189675
58	2.445	KIKVOQ	
58	2.457	KICFOT	
58	2.457	KIKWOR	
58	2.465	QOVDAI00	
58	2.465	YASLEK	170711
58	2.469	YIPKEO	249487
58	2.469	UCAQIA	
58	2.470	XILHUX	189672
58	2.471	OGICOW	150811
58	2.471	XECHEU	
58	2.472	YEKMIL	
58	2.472	ROHQUC	
58	2.480	AFURUO	170720
58	2.480	ENESOF	
58	2.485	XIDZIU	
58	2.488	DIZPOS	
58	2.489	MIGHIU	
58	2.517	ITEFUI	CN=9?
<hr/>			
59	2.425	VIJNUY	
59	2.428	KOBDEM	
59	2.429	YIPKIS	249488
59	2.436	XILJEJ	189674
59	2.440	TEYJIQ	
59	2.448	XILJAF	189673
59	2.449	XILJOT	189676
59	2.449	XAWTAQ	
59	2.454	IBAVIR	
59	2.458	RUJYOL	
59	2.456	PODWIP	
59	2.458	AWIQUS	

1xCN=8, 2xCN=9

59	2.458	KIKWUX		
59	2.462	ENESUL		
60	2.339	WUNQUS		
60	2.407	PYOXND		
60	2.408	KIKVUW		
60	2.409	YEGHIC		
60	2.410	RIYZAA		
60	2.417	HOXNOX		
60	2.420	FETGIV01		
60	2.422	FUWDUW		
60	2.426	HIQMUQ	240959	
60	2.426	KOBDIQ		
60	2.431	FETGIV02		
60	2.432	YIPKOY01	249490	
60	2.433	TAQZIU		also listed as TAQZIU01
60	2.436	FETGIV		
60	2.437	YEKMOR		
60	2.437	AYEHIW		
60	2.446	SAZSIW		
60	2.448	YIGVUG		
60	2.449	ENETAS		
60	2.450	WUNSA A		
60	2.452	VOTKUK		
60	2.453	MIDDIM		
60	2.455	YEYSUQ		also listed as YEYSUQ01
60	2.457	YIPKOY	249489	
60	2.457	MONRUE		
60	2.458	MEWSIQ		Tb in CSD!?!
60	2.459	YIJIZ		
60	2.489	SIQYUM		
60	2.517	KANTEA		
62	2.393	TEZBUX		
62	2.408	TEZBOR		
62	2.412	YIPKUE	249491	
62	2.421	XAMBET	170109	
62	2.422	MUWFUF		
62	2.426	MIDCIL		
62	2.430	XIDZOA		
62	2.451	AZACOT		
63	2.384	KIKWAD		
63	2.386	UQAVAK		
63	2.387	FEZCOD		
63	2.391	NUCQUY		

63	2.393	AYEHOC	
63	2.396	AYEGOB	
63	2.402	TEYJOW	
63	2.405	HIDFEH	
63	2.406	MIDDOS	
63	2.409	VEPVOB	
63	2.412	XIFBAQ	
63	2.412	MONNAG	
63	2.415	ISOPIP	
63	2.444		87728
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64	2.325	LADPAJ	
64	2.357	KOBCOV	
64	2.376	IBILEL	
64	2.377	OGOJOJ	
64	2.377	DUHVIM	
64	2.383	JAFKOR	
64	2.386	FIBJIL	
64	2.387	IXOXOI	110488
64	2.389	RUJZAY	
64	2.389	YIPLAL	249492
64	2.391	RACNOA	
64	2.391	BUZWAV	
64	2.392	DAXNAT	
64	2.393	YIGVOA	
64	2.393	PEMDEQ	170010
64	2.397	SEYYIF	
64	2.399	RACNUG	
64	2.399	MIDDUY	
64	2.401	COKMOF	
64	2.403	BAXNIX	
64	2.410	POBGES	
64	2.411	FILVOL	
64	2.428	DAXMUM	
64	2.437	PITZIC	
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65	2.348	PARBUH	
65	2.350	RUQBIP	
65	2.361	RUNSOJ	
65	2.362	PARCOC	
65	2.363	PARTAF	
65	2.363	PARTIN	
65	2.363	IXOYAV	
65	2.364	PARBUH01	
65	2.365	RUNSAV	

65	2.367	PARCES
65	2.369	RUNSEZ
65	2.371	RUNSID
65	2.373	XUMKEV
65	2.375	RUJZEC
65	2.375	PARTEJ
65	2.379	HIDDUV
65	2.380	PARSUY
65	2.384	QAQGIZ
65	2.385	VUMQUQ
65	2.385	KIZGEG
65	2.389	MIDFAG
65	2.390	XIDZUG
65	2.391	NERJAX
65	2.394	YECSOO

66	2.304		248097
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66	2.347	XAXGOU	
66	2.356	KUXQUQ	also listed as KUXQUQ01
66	2.358	AYEHUI	
66	2.363	FALVUK	
66	2.365	AYEGUH	
66	2.366	TIWXIH	
66	2.367	MUQROG	
66	2.368	KIFSOJ	
66	2.372	YIPLEP	249493
66	2.372	VUMRAX	
66	2.374	QUTRON	
66	2.378	NIRGOM	
66	2.380	FIZKUU	
66	2.380	MIDFEK	
66	2.384	RINZIZ	
66	2.387	FOPNAZ	

67	2.294	WUNRAZ	
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67	2.337	IXOXUO	
67	2.338	VOJVEX	
67	2.340	AYEHAO	
67	2.349	VOJVAT	
67	2.353	BUZWEZ	
67	2.354	AYEJAQ	
67	2.356	MUQRUM	
67	2.362	VUMREB	
67	2.363	MIDFIO	
67	2.369		87629

68	2.314	LADNUB	
68	2.319	MITGOM	
68	2.320	DUHVOS	
68	2.322	JODBOU	
68	2.324	XAXGUA	
68	2.325	GEKVID	
68	2.332	LAZBIZ	
68	2.334	FEZCUJ	
68	2.334	BENDUV	
68	2.336		91458
68	2.342	MUQSAT	
68	2.343	KIWBAU	
68	2.343	BUZVUO	
68	2.344	VIJPAG	
68	2.345	GEKVOJ	
68	2.347	KIZGIK	
68	2.347	YIPLIT	249494
68	2.348	CICWUH	
68	2.349	VIMRIF	
68	2.354	QUTRIH	
68	2.363	YICCIW	
68	2.370	WUNRED	
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69	2.269	KOBCUB	
69	2.316	UCAQEW	
69	2.332	HIDDOP	
69	2.332	MUQSIB	
69	2.334	NERJEB	
69	2.339	VUMROL	
69	2.363	WUNRIH	
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70	2.274	WUNRON	
70	2.293	OMAYAD	
70	2.310	AHIRUF	
70	2.312		281540
70	2.318	AHISAM	
70	2.319	HOSFUQ	
70	2.319	BAQHAE	
70	2.324	PIFQOL	
70	2.325	YAVJEL	
70	2.328	IDIYEA	
70	2.329	YURFAT	
70	2.329	MONMUZ	
70	2.330	VUMRUR	
70	2.330	MEFMIU	

70	2.331	MONMOT	
70	2.331	MEFMOA	
70	2.331	HIDDIJ	
70	2.332	WUNRUT	
70	2.332	OMAXUW	
70	2.337	RANGET	
70	2.342	PIFQAX	
70	2.344	BAQHEI	
70	2.346	PUJCIG	
70	2.400	MIDFOU	
71	2.293	KIKWEH	
71	2.302	YIPLOZ	249495
71	2.307	KIKXAE	
71	2.308		91459
71	2.314	VALHUN	
71	2.314	HIDFAD	
71	2.315	GEKVUP	
71	2.315	AHISEQ	
71	2.318	YURFEX	
71	2.319		87630
71	2.321	VUMSAY	
71	2.329	GIPCOX	
71	2.337	FOPPOP	
71	2.337	GEKWAW	
71	2.347	FILVUR	

b)

Z	d(Ln-O)	Ref.	note
57	2.503	[57]	
57	2.497	[57]	
59	2.457	[57]	
60	2.431	[57]	
62	2.412	[57]	
63	2.400	[57]	
64	2.388	[57]	
64	2.388	[57]	
65	2.367	[57]	
66	2.361	[57]	
67	2.337	[57]	
68	2.331	[57]	

68	2.337	[57]	
69	2.316	[57]	
71	2.297	[57]	
71	2.288	[57]	
<hr/>			
64	2.378	[58]	dmf
64	2.383	[58]	dmf
64	2.376	[58]	dma
64	2.370	[58]	dmp
71	2.303	[58]	dmf
<hr/>			
57	2.486	[59]	
57	2.475	[59]	dma
58	2.474	[59]	
58	2.452	[59]	dma
59	2.447	[59]	
60	2.438	[59]	
62	2.416	[59]	
63	2.385	[59]	
64	2.385	[59]	
65	2.369	[59]	
66	2.360	[59]	
67	2.346	[59]	
68	2.336	[59]	
69	2.325	[59]	
70	2.309	[59]	
71	2.298	[59]	

[57] I. Persson, E. Damian Risberg, P. D'Angelo, S. De Panfilis, M. Sandström, A. Abbasi, *Inorg. Chem.*, 46 (2007), 7742–7748. [all in dmsol]

[58] A. Fuchs, D. Lundberg, D. Warminska, I. Persson, *J. Chem. Phys. B* 117 (2013), 8502–8511.

[59] S.-I. Ishiguro, K. Kato, R. Takahashi, S. Nakasone, *Rare Earths* 27 (1995), 61–77. [CN corrected; in dmf unless noted]

c)

Ln	N	N-2	t(N-2)	t ²	Y _{med}	s	Y _{min}	Y _{max}	G _{min}	G _{max}	G _{calc}	N-1	sqrt N	N-2	t(G _{98%})	
La	30	28	2.467	6.086	2.471	0.038	2.358	2.529	2.952	1.503	2.237	29	5.477	1	31.82	
	29	27	2.473	6.116	2.475	0.032	2.387	2.529	2.721	1.659	2.234	28	5.385	2	6.965	
	28	26	2.479	6.145	2.478	0.028	2.395	2.529	2.960	1.798	2.231	27	5.292	3	4.541	
	27	25	2.485	6.175	2.481	0.023	2.414	2.529	2.885	2.034	2.227	26	5.196	4	3.747	
	26	24	2.492	6.210	2.484	0.020	2.440	2.529	2.256	2.304	2.223	25	5.099	5	3.365	
	24	22	2.508	6.290	2.484	0.016	2.452	2.511	2.043	1.724	2.214	23	4.899	6	3.143	
Ce	19	17	2.567	6.589	2.471	0.019	2.423	2.517	2.507	2.417	2.183	18	4.359	7	2.998	
	17	15	2.602	6.770	2.471	0.012	2.445	2.489	2.243	1.578	2.164	16	4.123	8	2.896	
	16	14	2.624	6.885	2.472	0.010	2.457	2.489	1.569	1.706	2.153	15	4.000	9	2.821	
Pr	14	12	2.681	7.188	2.446	0.013	2.425	2.462	1.694	1.229	2.126	13	3.742	10	2.764	
Nd	29	27	2.473	6.116	2.437	0.031	2.339	2.517	3.203	2.606	2.234	28	5.385	11	2.718	
	27	25	2.485	6.175	2.438	0.020	2.407	2.489	1.553	2.578	2.227	26	5.196	12	2.681	
	26	24	2.492	6.210	2.436	0.017	2.407	2.459	1.666	1.337	2.223	25	5.099	13	2.650	
Pm	no data														14	2.624
Sm	8	6	3.143	9.878	2.420	0.017	2.393	2.451	1.609	1.814	1.952	7	2.828	15	2.602	
Eu	14	12	2.681	7.188	2.403	0.016	2.384	2.444	1.199	2.589	2.126	13	3.742	16	2.583	
	13	11	2.718	7.388	2.400	0.011	2.384	2.415	1.445	1.385	2.110	12	3.606	17	2.567	
Gd	24	22	2.508	6.290	2.391	0.022	2.325	2.437	3.053	2.107	2.214	23	4.899	18	2.552	
	23	21	2.518	6.340	2.394	0.017	2.357	2.437	2.197	2.535	2.209	22	4.796	19	2.539	
	22	20	2.528	6.391	2.392	0.014	2.357	2.428	2.430	2.469	2.203	21	4.690	20	2.528	
	20	18	2.552	6.513	2.392	0.010	2.376	2.411	1.623	1.886	2.190	19	4.472	21	2.518	
Tb	24	22	2.508	6.290	2.373	0.013	2.348	2.394	1.935	1.674	2.214	23	4.899	22	2.508	
Dy	17	15	2.602	6.770	2.366	0.019	2.304	2.387	3.239	1.105	2.164	16	4.123	23	2.500	
	16	14	2.624	6.885	2.370	0.011	2.347	2.387	2.094	1.588	2.153	15	4.000	24	2.492	
Ho	11	9	2.821	7.958	2.347	0.020	2.294	2.369	2.586	1.095	2.065	10	3.317	25	2.485	
	10	8	2.896	8.387	2.352	0.011	2.337	2.369	1.353	1.543	2.036	9	3.162	26	2.479	
Er	22	20	2.528	6.391	2.339	0.014	2.314	2.370	1.723	2.152	2.203	21	4.690	27	2.473	
Tm	7	5	3.365	11.323	2.326	0.029	2.269	2.363	1.965	1.269	1.889	6	2.646	28	2.467	
	6	4	3.747	14.040	2.336	0.015	2.316	2.363	1.277	1.765	1.801	5	2.449	29	2.462	
Yb	24	22	2.508	6.290	2.328	0.022	2.274	2.400	2.435	3.292	2.214	23	4.899	30	2.457	
	22	20	2.528	6.391	2.327	0.012	2.293	2.346	2.811	1.609	2.203	21	4.690	40	2.423	
	21	19	2.539	6.447	2.328	0.010	2.310	2.346	1.921	1.853	2.197	20	4.583	50	2.403	
Lu	15	13	2.650	7.023	2.319	0.014	2.293	2.347	1.810	2.010	2.141	14	3.873	60	2.390	
														80	2.374	
														100	2.364	
														120	2.358	
														inf.	2.326	

Table S3. The reported mean bond distance, $d(\text{Ln-O})$, of all nine-coordinate lanthanoid(III) structures with neutral, *O*-donor ligands listed in the Cambridge Structural Database (CSD; ref. 11) and the Inorganic Crystal Structure Database (ICSD; ref 12); the CSD entries listed by their reference code and the ICSD ones by their code. Entries in red typeface were excluded on the fit based on a recursive Grubb's test (two-sided, 98 %), see Table S2 c). Z = atomic number.

Z	$d(\text{Ln-O})$	CSD code	ICSD code
57	2.475		280944
57	2.508	REXGEI	
57	2.527	ZEQSIZ	
57	2.528	YEKMUX	
57	2.541	CEJFON	
57	2.546	FEZCIX	
57	2.547	BUVVIX	37206
57	2.548	BUVVIX01	91454
57	2.548	LUSMES	
57	2.550	ZZZAQP01	
57	2.551	ZILVIZ	
57	2.552	SUDDAW	
57	2.554	GIBTUH	
57	2.557	BOWGIF	
57	2.558	LUSNET	
57	2.559	COLHOB	
57	2.559	WUKJIX	
57	2.562	LAGGOQ	
57	2.562	VATHUV	
57	2.569	NUPDOS01	
57	2.574	WUKJOD	
58	2.505	YEKNAE	
58	2.519		421753
58	2.523	ITEFUI	
58	2.525	BUVWEU01	
58	2.527	CIBSAH	
58	2.535	SUDDEA	
58	2.538	COTPOR	
58	2.543		96528
58	2.545	BURSIR	
59	2.500		28147

59	2.500	XILJEJ	
59	2.506	BUVWIY01	
59	2.507	APRETS02	
59	2.510	GANMUF	262375
59	2.511	APRETS01	
59	2.515	COKMIZ	
59	2.527		170692
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60	2.474	JAXBAL02	
60	2.476	JAXBAL	
60	2.479	JAXBAL01	
60	2.486	WEXCOT	
60	2.490	BUVW0E01	61780
60	2.490	BUVW0E02	63668
60	2.491	SEYYAX	
60	2.494	SUDDIE	
60	2.495	ZZZAQS01	
60	2.495	BUVW0E05	
60	2.496	BUVW0E04	
60	2.496		240739
60	2.500	VESYUO	
60	2.502	BUVW0E03	63669
60	2.504	JEDLOU	
60	2.504	YAMYIV	
60	2.505	NABZEW	
60	2.508	SOZJAS	
60	2.512		170054
60	2.513	LAGGUW	
60	2.514	GOHTAY	
60	2.514	LUTHAJ	
60	2.519		23018
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62	2.452	SEYYEB	
62	2.452	NUHRIS	
62	2.459	YUBQUJ	
62	2.460	CEJFUT	
62	2.461		91456
62	2.462	BUVWOK02	
62	2.464	BUVWUK01	
62	2.470	ZZZAQV01	
62	2.471	DEYYIP	
62	2.474	COTNEF	
62	2.491		23757
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63	2.424	ZILVUL	
63	2.443	ZEFHUP	

63	2.448	UQAVAK	
63	2.451	BUVXAR01	
63	2.451	GEKZUT	
63	2.453	BUVXAR11	
63	2.457	BUVXAR12	
63	2.458	ZZZAQY01	
63	2.459	DAXCEM	
63	2.460	BAPGAB	
63	2.460	JEDLUA	
63	2.464	CUMDUK	
63	2.465	IBIBAX	
63	2.466	FEKGUY	
63	2.466	TAHDIQ	
63	2.472	NOMWIW	
63	2.476	NOMWES	
63	2.478		59282
63	2.497	JIMGES	
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64	2.404	OHAMEQ	
64	2.421	RACNOA	
64	2.428	AHADAP	
64	2.438		91457
64	2.443	BUVVOD02	
64	2.444	BUVVOD	37207
64	2.444	BUVVOD01	
64	2.446	ZZZARA01	
64	2.447	WEXCUZ	
64	2.448	OHAMOA	
64	2.451	CUJBUG00	
64	2.460	LUZXEK	
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65	2.418	PARTOT	
65	2.420		421756
65	2.426		300025
65	2.429	BUVXE01	
65	2.430	ZZZARD01	
65	2.432	BUVXE02	
65	2.434	BUVXE03	
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66	2.416	BUVXIZ01	
66	2.420	ZZZARG01	
66	2.421	GIKFOX	
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67	2.258	GELBAC	
67	2.400		62508
67	2.404		91455
67	2.407		62507

67	2.412	HOESUL02	
67	2.421		61781
67	2.421	BUVXOF01	
67	2.431	HOESUL	
68	2.260	GELBEG	
68	2.399	RAPYIR	
68	2.402	AERETS02	
68	2.416	AERETS	
69	2.386	RAPYEN	
69	2.395	ZZZARJ01	
70	2.358		28148
70	2.372	RAPYAJ	
70	2.379	BUVYEW01	
70	2.384	ESULYB01	
70	2.387	ESULYB	
70	2.419	PEJNUO	
70	2.444	GIKFIR	
71	2.358	RAPXUC	
71	2.364	BUVVUJ	37208
71	2.365	BUVVUJ01	
71	2.378	ZZZARM01	

Table A4. The reported mean bond distance, $d(\text{An-O})$, of all actinoid(III) structures with neutral, *O*-donor ligands listed in the Cambridge Structural Database (CSD; ref 11) and the Inorganic Crystal Structure Database (ICSD; ref 12); the CSD entries listed by their reference code and the ICSD ones by their code. Z = atomic number.

Z	$d(\text{An-O})$	CSD code	ICSD code
92	2.521	YEKNEI	
92	2.537	PUTQOL	
93	2.517	PUTQIF	
94	2.505	MOSBEB01	
94	2.507	MOSBEB02	
94	2.508	MOSBEB	280848
95	2.503	YEVRUN	240737
96	2.490	YEVROH01	249457
96	2.484	YEVROH	240738
98	2.465	PUTQEB	