Inorg. Chem. **2002**, *41*, 167–169

Inorganic Chemistry
Communication

Lanthanide Contraction over the 4f Series Follows a Quadratic Decay

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Received August 29, 2001

An analysis of the structural data available for isotypical series of rare earth compounds shows that the contraction of X-ray determined Ln–O bond distances over the f block is at least quadratic. Such quadratic decay is observed also for Ln(III) ionic radii, calculated bond distances, and lanthanide atomic orbital expectation values.

Lanthanide elements (Ln) are experiencing an upsurge of experimental[1] and theoretical work,[2] because of their technological and catalytic importance and recent significant progress in computational techniques. Concurrently, the well-known phenomenon of *lanthanide contraction*,[3] that is, the monotonic shrinking of observables (e.g., bond distances, $d(\text{Ln}-\text{X})$) over the 4f series, is attracting a renewed interest.[1g,h,2a−f] Nevertheless, there is a lack of a general formula that describes such a trend satisfactorily. This work aims at proposing an adequate formula for this phenomenon, by revisiting experimental and theoretical data available in the literature.

Regarding the interpolation of experimental data, a linear relationship between bond distances and the ionic radius of the metal, R, or the number of f electrons of the metal, n ($n = 0$ for La^{3+}; $n = 14$ for Lu^{3+}), is commonly reported or implied.[1h,3g−i] A few studies mention a deviation from linearity,[2c,3e−g] but further investigations of the matter do not appear to be available. In the recent literature addressing the evaluation of the lanthanide contraction through quantomechanical calculations, explicit references to a linear extrapolation between $d(\text{Ln}-\text{X})$ and the electronic configuration of the metal can be found.[2b−e,h] Furthermore, the use of the single parameter $\Delta_{\text{lanthanide}}$ commonly employed[2a−c] to define the overall lanthanide contraction (eq 1) implies, at best, a first-order polynomial of n (eq 2).

$$\Delta_{\text{lanthanide}} = d(\text{La}-\text{X}) - d(\text{Lu}-\text{X}) \tag{1}$$

$$d(\text{Ln}-\text{X}) = d(\text{La}-\text{X}) - \frac{\Delta_{\text{lanthanide}}}{14}n \tag{2}$$

Hereafter, the need to adopt a second-order treatment will become evident.

Work from these laboratories has recently pointed out how X-ray structural studies on *isotypical* compounds can provide a direct experimental assessment of the lanthanide contraction.[1i] The isotypicity condition ensures that no parameters other than the nature of the metal change along the series, therefore facilitating the study of the phenomenon. A subsequent scrutiny of the available structural data[4] has shown that a most appropriate series for such an investigation is given by the isotypical compounds $[\text{Ln}(\text{OH}_2)_9][\text{EtOSO}_3]_3$[3g] because (i) the series extends over the whole lanthanide series (Ln = La−Lu, except Pm), (ii) the quality of the diffractometric data allows a good analysis of the fitting curves, and (iii) the presence of a single type of ligand in the coordination sphere of the lanthanide simplifies the analysis of the data.

The cation displays a tricapped trigonal prism geometry (C_{3h} symmetry) that leads to two sets of independent bond

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10.1021/ic015580v CCC: $22.00

Table 1. Results of the Quadratic Fit [$A_0 - A_1 n + A_2 n^2$] of Parameters Displaying Lanthanide Contraction (See Text), the Associated Errors in Brackets and the Correlation Factor R^2

parameter	group considered	A_0 (Å)	$A_1\,10^2$ (Å)	$A_2\,10^4$ (Å)	R^2 (%)
X-ray Ln−O bond distances in isotypical series	$[Ln(OH_2)_9][EtOSO_3]_3$[3g]				
	bond-type a	2.613(18)	1.48(6)	4.7(4)	99.6
	bond-type b	2.513(19)	1.84(7)	3.2(5)	99.7
	$[Ln(OH_2)_9][CF_3SO_3]$[3f]				
	bond-type a	2.611(2)	1.66(9)	7.7(7)	99.0
	bond-type *b*	2. 507 (3)	1.77(10)	1.7(8)	99.6
	$[Ln(O_2CN^iPr_2)_3]_4$[1i,5]				
	bond-type a_1	2.53(3)	2.0(7)	4.3(3)	98.4
	bond-type a_2	2.39(2)	1.9(4)	3.9(2)	99.3
	bond-type b	2.486(6)	2.04(13)	5.3(7)	99.9
	bond-type c	2.384(11)	1.4(2)	2(1)	99.7
Ln^{3+} ionic radii[3a]	CN				
	6	1.026(2)	1.43(8)	1.8(5)	99.7
	7	1.093(4)	1.51(1)	2(1)	99.2
	8	1.160(4)	1.774(15)	3.29(10)	99.9
	9	1.214(2)	1.77(3)	3.5(2)	99.9
calcd Ln−N bond distances[2a]	$Ln(NH_2)_3$	2.306(2)	1.67(8)	3.0(6)	99.8
expectation value $\langle r \rangle$	molecular orbitals ($LnCl_3$) [2e]				
	a_1'	0.434(5)	2.5(1)	9.0(10)	99.3
	a_2'	0.421(4)	2.2(1)	8(1)	99.2
	e''	0.323(4)	1.6(1)	5.5(8)	99.0
	e'	0.285(2)	1.39(8)	4.3(6)	99.4
	a_2''	0.266(3)	1.28(10)	3.9(7)	99.0
	atomic orbitals[2c]				
	6s*	1.243(3)	3.1(9)	4.5 (6)	99.9
	5p	0.976(3)	2.0(10)	4.5(7)	99.9
	4f	0.563(3)	2.5(11)	7.8(7)	99.9

types, hereafter referred to as type a for the three equatorial bonds and type b for the six prismatic ones. A weighted polynomial regression has been performed on the experimentally determined Ln−O bond distances. The weight on each datum was the reciprocal of the error associated with the bond distance. The two sets of independent Ln−O bonds have been treated separately. The polynomial fit over the experimental data, with A_0, A_1, and A_2 as the constant, linear, and quadratic optimized parameter of the regression, respectively, showed that a suitable expression for the lanthanide contraction is given by

$$d(\mathrm{Ln{-}X}) = A_0 - A_1 n + A_2 n^2 \qquad (3)$$

The relevant data are reported in Figure 1 and Table 1.

The analysis of the residues between the experimental type a bond distances and the best linear or quadratic fits (see Figure 1b) leads to two considerations: (i) a first-order approximation is insufficient, the difference between the experimental data and the calculated ones being as large as five standard deviations; (ii) the highest significant polynomial fit acceptable is parabolic (viz., when a cubic fit is performed, the error on the cubic term is larger than the term itself). Analogous conclusions can be drawn for type b Ln−O bonds.

Similar analyses were performed on the two series of Ln−O bond distances present in the closely related isotypical $[Ln(OH_2)_9][CF_3SO_3]_3$ (Ln = La−Nd, Sm−Dy, Yb, and Lu)[3f] and on the four series of Ln−O bond distances[1i] present in the previously reported isotypical $[Ln(O_2CN^iPr_2)_3]_4$ (Ln= Nd, Gd, Ho, Yb,[5] Lu[5]). All the fitting curves show the same trend, although the smaller extension of these series leads to larger errors on the regression parameters (Table 1). In all eight cases, the best fitting parabola displayed a constant term of about 2.5 Å,[6] a negative linear term 2 orders of magnitude smaller, and a positive quadratic term 2 orders of magnitude smaller than the slope. The 4 orders of magnitude decrease from the constant to the quadratic term entails quite large relative errors on the parabolic terms (as large as 50%), but

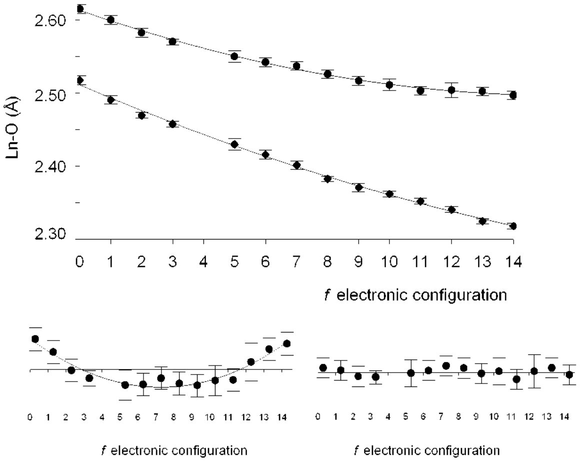

Figure 1. (a) Lanthanide(III)−oxygen bond distances (Å) vs f electronic configuration in the series of isotypical compounds $[Ln(H_2O)_9][EtOSO_3]_3$ and the relative best fit parabola (above, bond-type a; below, bond-type b). (b) Residuals from the experimental error obtained with linear (left) and quadratic (right) fits of type a Ln−O bond distances in $[Ln(H_2O)_9][EtOSO_3]_3$ (error bars are calculated at a 95% confidence level).

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(5) A more accurate structural analysis of the previously reported $[Yb(O_2CN^iPr_2)_3]_4$ and the novel structure of $[Lu(O_2CN^iPr_2)_3]_4$ are now available: Belli Dell'Amico, D.; Calderazzo, F.; Marchetti, F.; Baish, U. Manuscript in preparation.

(6) Because A_0 is the extrapolated value of $d(\mathrm{La{-}X})$ (see eq 3, for $n = 0$), the physical meaning of the corrected constant $A_0' = A_0 - R(\mathrm{X})$ obtained by subtracting the radius of the element [e.g., $R(O^{2-}) = 1.35$ Å][3a] is an estimate of the lanthanum radius. Experimentally, the range 1.03−1.36 Å for $R(La^{3+})$ is reported in the literature,[3a] which correlates satisfactorily with the corrected constants obtained here ($A_0' = 1.04-1.26$).

nevertheless, the error is always smaller that the term itself, making it significant in all cases. Furthermore, the numerical dispersion of each parameter is relatively narrow (see Table 1), although bonds with presumably different degrees of covalency are considered. Preliminary work suggests that similar results may be obtained for other bond types, such as Ln−Cl, Ln−O, and Ln−C in the series of isotypical compounds $CpLnCl_2(THF)_3$[7] (Ln= Nd,[7a] Sm,[7b] Eu,[7c] Gd,[7d] Ho,[7e] Er,[7f] and Yb[7g]). Systematic work in this field is currently in progress.

In an attempt to test the scope of the fitting procedure beyond strictly isotypical series, some literature data have been revisited. In 1976, Shannon[3a] published a set of self-consistent ionic radii, still in use nowadays, based on 900 X-ray-determined nonisotypical M−E (E = O or F) bond distances. A quadratic fit [$R(La^{3+}) = A_0 + A_1n + A_2n^2$] performed on such Ln^{3+} ionic radii with different coordination number (6−9) proved satisfactory, with parameters numerically close to the ones reported here for the isotypical series (Table 1).[8,9] The same fitting procedure has been successfully applied to the Ln−N bond distances obtained from energy optimization DFT calculations carried out by Maron and Eisenstein[2a] on model compounds $Ln(NH_2)_3$ (Ln = La−Lu), see Table 1.[10] Moreover, it has been shown that the lanthanide contraction can be estimated from the contraction of atomic orbital expectation values, $\langle r \rangle$.[2b,h] Along these lines, the quadratic fitting of $\langle r \rangle$ values available in the literature[2c,e] was performed. The variation of the expectation value in the molecular plane for the respective 4f orbitals in the series of lanthanide trichlorides $LnCl_3$ calculated ab initio follows a quadratic decay (see Table 1). Similarly, the expectation value of 4f, 5p, and 6s atomic orbitals of the lanthanide atoms is satisfactorily fit by a parabola (see Table 1).

In summary, a similar parabolic decay of the lanthanide contraction throughout the 4f series has been found for the different set of data considered.

In light of the present evidence, eq 3 may be proposed as a good description of the lanthanide contraction over the series. In particular, considering the definition of lanthanide contraction presented in eq 1, and the fitting equation proposed in eq 3, we propose to calculate the extent of lanthanide contraction using both equations:

$$\Delta_{\mathrm{lanthanide}} = d(\mathrm{La-X}) - d(\mathrm{Lu-X}) = 14A_1 - 14^2A_2 \quad (4)$$

In conclusion, the data presented here suggest that a suitable phenomenological expression of the lanthanide contraction is a quadratic equation. Further work is in progress aimed at investigating the scope of the quadratic fit.

Acknowledgment. Funding from the Università di Pisa for a postdoctoral fellowship and from the Ministero dell'Università e della Ricerca Scientifica (MURST), Programmi di Ricerca Scientifica di Rilevante Interesse Nazionale, Co-finanziamanento MURST 2000-2001, is gratefully acknowledged. The author is indebted to Prof. F. Calderazzo for constant support and insightful comments and to Prof. F. Marchetti and Dr. V. Passarelli for helpful discussions.

IC015580V

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[8] Unlike the cases discussed previously,[6] the physical meaning of the constant term obtained by fitting the ionic radii is a direct estimate of $R(La^{3+})$, and it correlates well with the experimental data (vide supra).

[9] A direct implication of such a finding is that a quadratic dependence between the electronic configuration and the cell volume can be found. For example, a quadratic fit of the cell volume against the electronic configuration in the recently reported[1h] series of new oxides $Ln_4Cu_3MoO_{12}$ is satisfactory.

[10] The calculated Ce, Eu, and Yb data were disregarded because the computation predicts the anomalous configuration for Ce(IV), Eu(II), and Yb(II). This anomaly is disregarded also because it is at odds with experimental values, showing that the Ln−N distances in the isotypical species $[Ln(N(SiMe_3)_2)_2(thf)(\mu\text{-}Cl)]_2$ (Ln = Sm,[10a] Gd,[10b] Yb[10b]) decrease monotonically. (a) Karl, M.; Seybert, G.; Massa, W.; Agarwal, S.; Greiner, A.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1405. (b) Aspinall, H. C.; Bradley, D. C.; Hursthouse, M. B.; Sales, K. D.; Walker, N. P. C.; Hussain, B. *J. Chem. Soc., Dalton Trans.* **1989**, 623.