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LnO_n coordination polyhedra (Ln = La–Lu) in crystal structures

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Voronoi–Dirichlet (VD) polyhedra and the method of intersecting spheres were used to analyze the crystal structures of 2917 compounds containing 3903 crystallographically non-equivalent types of LnO_n polyhedra (Ln = La–Lu). It was established that Ln coordination numbers (CN) vary from 3 to 12, and 20 types of coordination polyhedra are present in the structures. Despite the great diversity of CN and types of coordination polyhedra, the volume of the VD polyhedron was found to depend only on the identity of the Ln atom and its oxidation state.

1. Introduction

During prior decades, the crystal structures of a relatively large number of oxygen-containing lanthanide compounds containing LnO_n (Ln = La–Lu) coordination polyhedra have been determined. A large amount of work is being devoted to the investigation of the interrelationship between the identity of lanthanides and the properties of their compounds. It was established (Sinha, 1975; Kiselev, 1994) that the Ce–Lu series can be divided into four segments. The borders of these segments are the following: (1) La–Nd, (2) Pm–Gd, (3) Tb–Ho and (4) Er–Lu. Within a segment, the properties vary smoothly, and near the borders, a sharp property change is possible [the 'inclined W' or tetrad effect in the terminology of, respectively, Sinha (1975) and Peppard *et al.* (1969)]. Attempts to generalize the crystal structure data accumulated to date resulted in the conclusion that the LnO_n polyhedra are 'nonrigid' and easily deformable (Bandurkin & Dzhurinskii, 1998), so that the coordination numbers (CNs) of the Ln atoms and the shapes of the coordination polyhedra formed are fairly diverse. This work has been undertaken in order to demonstrate the potential of new methods of crystal-chemical analysis (Serezhkin *et al.*, 1997), based on the use of characteristics of the Voronoi–Dirichlet (VD) polyhedra of Ln atoms in crystal structures.

2. Experimental

All reported crystal structures containing Ln atoms surrounded by oxygen were the object of the investigation. The primary crystal structure information was selected from structural databases of inorganic [Inorganic Crystal Structure Database (ICSD); FIZ Karlsruhe/NIST, 2004] and coordination [Cambridge Structural Database (CSD); November 2004 Release; Allen, 2002] compounds. The data were taken into account provided that, in the crystal structure containing the LnO_n (Ln = La–Lu) coordination polyhedron, the Ln or O atoms were not statistically disordered and the structure had been determined to $R < 0.1$. These conditions were met for

Table 1
Examples of calculation of the CN of Nd and Ce atoms by the method of Serezhkin *et al.* (1997).

VD polyhedron of the central atom A			Intersection volume (Å^3) of two spheres with radii†				Type of intersection§
Y‡	$A-Y$ (Å)§	$\Omega(A-Y)$ (%)§	r_Sr_S	r_SR_{SD}	$R_{SD}r_S$	$R_{SD}R_{SD}$	
Nd_2CuO_4 {86753}, central atom Nd1, CN = 10							
O1	2.293 (×4)	11.08 (×4)	0.033	1.497	0	0.384	I_3 (×4)
O2	2.631 (×4)	10.39 (×4)	0	1.506	0	0.329	I_2 (×4)
Nd1	2.802	2.04	2.152	0.592	0.592	0.019	I_4
O2	2.815	11.33	0	0.902	0	0.090	I_2
#Cu1	2.924 (×4)	0.19 (×4)	0	0	0	0	#I_0 (×4)
Bis[(μ_2-*tert*-butoxo)bis(tri-*tert*-butylmethoxy)cerium(III)] {SOZLUO}, central atom Ce1, CN = 4							
O3	2.158	18.01	0.109	2.478	0	1.138	I_3
O2	2.161	19.35	0.107	2.452	0	1.122	I_3
O1	2.423	16.44	0.001	1.916	0	0.739	I_3
O1	2.430	14.00	0.001	1.885	0	0.720	I_3
H50	2.812	8.29	0	0.326	0	0	$I_1^{\text{agost.}}$
H63	2.828	5.93	0	0.323	0	0	$I_1^{\text{agost.}}$
H61	2.876	5.59	0	0.249	0	0	$I_1^{\text{agost.}}$
H17	3.005	5.48	0	0.056	0	0	$I_1^{\text{agost.}}$
H29	3.221	3.96	0	0	0	0	I_0
#H10	3.655	0.92	0	0	0	0	#I_0
#H5	3.718	0.20	0	0	0	0	#I_0
#H8	3.787	1.29	0	0	0	0	#I_0
#H4	3.791	0.17	0	0	0	0	#I_0
#H38	3.799	0.00	0	0	0	0	#I_0
#H41	3.833	0.25	0	0	0	0	#I_0
#H21	3.920	0.08	0	0	0	0	#I_0
#H29	4.253	0.03	0	0	0	0	#I_0

† In all the products, r_s is the Slater radius and R_{SD} is the radius of the sphere whose volume is equal to the A or Y VD polyhedron volume; the first radius in each term is that of the central atom A and the second that of the Y atom. ‡ The # sign marks the atoms for which the mid-point of the A–Y segment does not lie on the VD polyhedron surface of the central atom. The atoms of the #Y type are so-called non-essential neighbors. § The number of symmetrically equivalent $A-Y$ interatomic distances, corresponding solid angles (Ω) of the VD polyhedron faces and types of pair intersections are given in parentheses. The Ce···H agostic contacts (see also §3.1.2) are marked by superscripts.

2917 compounds containing 3903 crystallographically non-equivalent Ln atoms. The compounds involved contain not only Ln^{III} atoms but also Ce^{IV}, Pr^{IV}, Tb^{IV}, Sm^{II}, Eu^{II} and Yb^{II} (95, 29, 22, 4, 18 and 21 types of atom, respectively). In 734 compounds, all or some of the H atoms were not located during the structure determination. Accordingly, at the first investigation stage the coordinates of the missing H atoms were calculated using the *HSite* program (Blatova *et al.*, 2001) included in the *TOPOS* package (Blatov *et al.*, 2000; http://www.topos.ssu.samara.ru).

Provided that complexing atom A in the crystal structure is a soft, easily deformed sphere of constant volume (Serezhkin *et al.*, 1997), the VD polyhedron of atom A becomes the atom's geometrical image. The VD polyhedron of atom A surrounded by $\{Y_i\}$ atoms is a convex polyhedron formed by planes that are drawn perpendicular to $A-Y_i$ contacts at their midpoints. In the general case, the VD polyhedron of atom A has the composition AX_nZ_m, where X are chemically bonded atoms and n is the CN of the A atoms. The VD polyhedra of the Z atoms share faces with the VD polyhedron of the A atom, but these contacts are not chemical bonds; the sum $n + m$ is equal to the total number of the VD polyhedron faces (N_f).

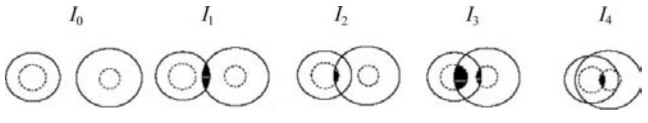


Figure 1
Schematic representation of the major types of two-sphere atom intersection. For each atom whose nucleus is at the center of two spheres, the sphere of radius r_S is shown with a solid line and the sphere of radius R_{SD} is shown with a dashed line. Only the case for $R_{SD} < r_S$ is depicted. The shaded regions correspond to the intersections of the spheres of neighboring atoms.

The method of intersecting spheres (Serezhkin *et al.*, 1997), based on usage of VD polyhedra characteristics, makes it possible to classify all interatomic interactions of atom A into valence $A-X$ and nonvalence $A\cdots Z$ interactions. Within this method, each atom in the crystal structure is approximated by two spheres with radii r_S and R_{SD} and a common center in the atom's core. The first sphere is a characteristic of the isolated (not bonded chemically) atom, so its radius (r_S) is equal to the Slater (1964) radius of the atom. The second (with radius R_{SD}) corresponds to the chemically bonded atom and has a volume equal to the VD polyhedron volume. Provided that in a crystal structure there are no intersections (I_0) between spheres corresponding to atoms A and Z or only their exterior spheres intersect (I_1), one can say that a nonvalence contact $A\cdots Z$ exists that should not be taken into account for the CN(A) calculation. The criterion for a strong chemical bond $A\cdots X$ (covalent, ionic or metal) as defined by Serezhkin *et al.* (1997) is the simultaneous existence of two (I_2), three (I_3) or four (I_4) possible intersections between spheres corresponding to atoms A and X. The main merit of the method is that no information is needed about the nature of the chemical bond or its existence. Some types of intersection are depicted in Fig. 1.

As an example, Table 1 presents the results of calculations by this method (Serezhkin *et al.*, 1997) of the CNs of Nd and Ce atoms in the structures of Nd_2CuO_4 {86753} and $Ce_2(C_4H_9O)_2(C_{13}H_{27}O)_4$ {SOZLUO}. Fig. 2 shows the Ln VD polyhedra in these compounds. Here and below, the characters in braces are the digit or letter code under which the compound is registered in the ICSD or CSD, respectively.

3. Results and discussion

The analysis has shown that 2917 compounds contain Ln atoms with a CN of 3–12 (Table 2), whereas the number of VD

Table 2
Characteristics of the VD polyhedra of Ln atoms in LnO_n complexes (Ln = La–Lu).

CN is the coordination number of Ln atoms with respect to oxygen; $N_{compounds}$ is the number of compounds; N_{Ln} is the number of symmetry-independent Ln atoms; N_f is the average number of VD polyhedron faces; V_{VDP} is the VD polyhedron volume; R_{SD} is the radius of a sphere whose volume is equal to V_{VDP}; D_A is the displacement of the Ln atom from the geometric center of gravity of its VD polyhedron; G_3 is a dimensionless value of the second moment of inertia of a VD polyhedron; r(Ln—O) is the average Ln—O bond length in the classical coordination polyhedron at a given CN; and μ is the overall number of these bonds. The r.m.s. deviations are given in parentheses.

Atom	CN	$N_{compounds}$	N_{Ln}	N_f	V_{VDP} (Å^3)	R_{SD} (Å)	D_A (Å)	G_3	Average r(Ln—O) (Å)	μ
La^{III}	4–12	553	762	13 (3)	13.9 (7)	1.490 (23)	0.04 (4)	0.081 (2)	2.59 (13)	6625
Ce^{IV}	6–10, 12	76	95	10 (2)	11.1 (3)	1.382 (14)	0.02 (3)	0.082 (2)	2.36 (12)	770
Ce^{III}	4, 6–12	147	211	11 (2)	13.2 (6)	1.466 (21)	0.04 (4)	0.081 (1)	2.55 (11)	1863
Pr^{IV}	5–9	17	29	9 (2)	11.8 (7)	1.412 (25)	0.03 (2)	0.084 (3)	2.35 (14)	204
Pr^{III}	5–12	221	302	11 (2)	13.0 (6)	1.458 (22)	0.04 (3)	0.081 (2)	2.52 (11)	2556
Nd^{III}	4–12	306	417	12 (3)	13.0 (8)	1.458 (28)	0.05 (4)	0.082 (2)	2.50 (13)	3375
Sm^{III}	4–12	129	151	12 (4)	12.7 (8)	1.442 (27)	0.03 (3)	0.082 (2)	2.44 (12)	1174
Sm^{II}	5, 7, 9	4	4	17 (5)	15.5 (8)	1.553 (27)	0.04 (2)	0.082 (2)	2.57 (12)	26
Eu^{III}	6–12	113	143	11 (2)	12.1 (7)	1.425 (25)	0.04 (3)	0.081 (2)	2.43 (9)	1187
Eu^{II}	6–12	14	18	15 (4)	16 (1)	1.555 (36)	0.06 (7)	0.082 (2)	2.71 (19)	150
Gd^{III}	5–12	164	225	11 (3)	12.0 (6)	1.420 (22)	0.04 (4)	0.082 (2)	2.42 (10)	1798
Tb^{IV}	6	19	22	11 (3)	10.0 (3)	1.337 (15)	0.01 (1)	0.083 (1)	2.16 (4)	132
Tb^{III}	6–10, 12	146	173	11 (3)	11.8 (6)	1.411 (23)	0.03 (3)	0.082 (2)	2.16 (4)	1356
Dy^{III}	6–10	146	191	12 (3)	11.6 (6)	1.405 (23)	0.03 (3)	0.082 (2)	2.38 (9)	1482
Ho^{III}	6–9	145	184	12 (4)	11.5 (6)	1.401 (22)	0.03 (3)	0.082 (2)	2.36 (9)	1405
Er^{III}	4–10	289	393	11 (4)	11.3 (6)	1.393 (25)	0.03 (3)	0.082 (2)	2.35 (9)	2994
Tm^{III}	6–10	67	91	11 (1)	11.4 (6)	1.394 (24)	0.03 (3)	0.083 (2)	2.33 (9)	673
Yb^{III}	4–10	229	306	11 (3)	11.2 (6)	1.386 (26)	0.03 (3)	0.083 (2)	2.30 (9)	2176
Yb^{II}	3–6, 8, 9	19	21	15 (4)	13.8 (8)	1.489 (28)	0.04 (4)	0.085 (3)	2.36 (14)	111
Lu^{III}	5–10	125	165	10 (3)	10.9 (5)	1.375 (22)	0.03 (3)	0.083 (2)	2.30 (10)	1191

polyhedron faces varies from 6 to 27. The smallest CN, equal to 3, was found only for Yb^{II}. The most common CN for Ln atoms was found to be 8, which is in a good agreement with the results of Bandurkin & Dzhurinskii (1998). At the same time, as we go from left to right across the lanthanide series, the maximum CN and the CN values that are more common for Ln atoms fall. For example, a CN equal to 12 is found only for atoms from La to Tb, and for the following Ln the CN does not exceed 10. The most common CN in the segment La–Gd is 9, for Tb–Tm it is 8, whereas for Yb and Lu it is 6. As can be seen from Fig. 3, with an increase in the CN for ErO_n polyhedra, the mean Er—O bond length increases. The same conclusion can be drawn for the rest of the lanthanides.

3.1. Method of intersecting spheres and some types of chemical bond

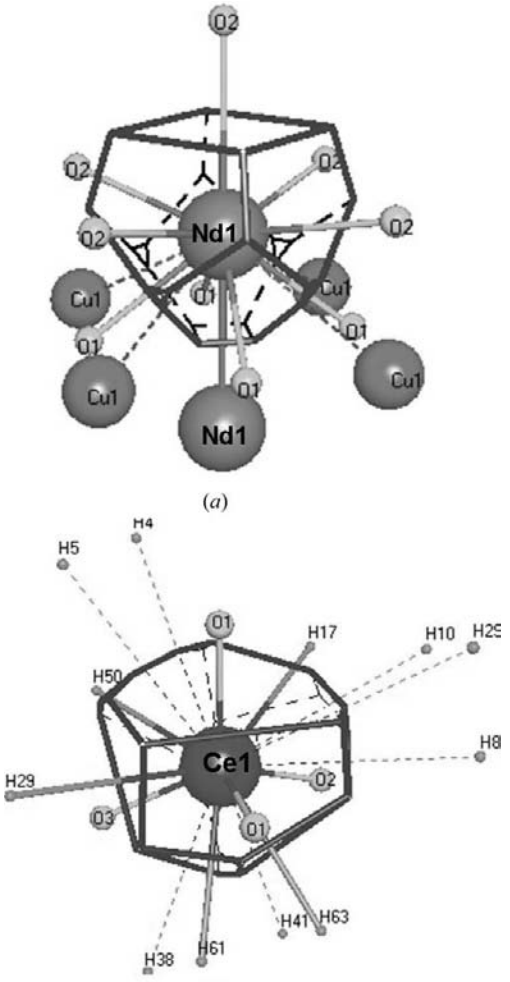
It should be noted that bis(μ_2-2,6-di-*tert*-butyl-4-methylphenolato)bis(2,6-di-*tert*-butyl-4-methylphenolato)-diytterbium(II) [$Yb_2(C_{15}H_{23}O)_4$] {PIZBOP} is the only example of an oxygen-containing lanthanide compound studied to date in which the CN of Ln is equal to 3. The crystals of this compound contain Yb_2O_4 dimers consisting of two YbO_3 triangles sharing an edge. The distance between the Yb atoms in this dimer (3.54 Å) is 0.3 Å shorter than the shortest r(Yb—Yb) (= 3.85 Å) distance in ytterbium metal with a body-centered cubic lattice. However, the method of intersecting spheres (Serezhkin *et al.*, 1997) indicates a lack of direct contacts between the Yb atoms, because their VD polyhedra have no common faces. Note also that the structure of $Yb_2(C_{15}H_{23}O)_4$ {PIZBOP} contains abnormally long (1.91 Å) C—C bonds in one *tert*-butyl group and a nonvalence Yb—H contact with an interatomic distance of 2.18 Å, *i.e.* shorter than the Yb—H bonds (2.25 Å) in YbH_2 {56195} and YbH_3 {56196} crystals. In addition, the structure of $Yb_2(C_{15}H_{23}O)_4$ {PIZBOP} was refined in the isotropic approximation for all atoms except Yb, because, as noted previously by the authors of the X-ray experiment (Van den Hende *et al.*, 1995), structure refinement in the anisotropic approximation for all non-H atoms gives results having no physical meaning. Therefore, in this work, we did not take into account the coordinates of H atoms in $Yb_2(C_{15}H_{23}O)_4$ {PIZBOP} when calculating the VD polyhedra characteristics.

3.1.1. Bonds between two metals. In the structures of the compounds in question, the VD polyhedra of 3903 Ln atoms form 45 065 faces. Of the 35 329 faces corresponding to lanthanide–oxygen contacts, the method of intersecting spheres (Serezhkin *et al.*, 1997) distinguished 31248 faces classified as Ln—O chemical bonds. Ln—O bonds are characterized by solid angles Ω (subtended by the face at the central atom of the VD polyhedron, expressed in percent of 4π steradian) ranging from 5.0 to 23.9%. In addition, 137 more faces equivalent to Ln—Q contacts (Q = Be, Ba, Co, Cu, Li, Mn, Nd, Ni and Zn) were found in the structures of 72 compounds. These metal–metal bonds are characterized by solid angles from 0.8 to 4.6% and interatomic distances not exceeding the sum of the atomic, orbital or Slater radii of the elements. The Ln—Q bonds are described by the I_4, I_3 or, most often, I_2 intersection types and, in a vast majority of cases, by binuclear island fragments formed by the Ln and Q atoms. Only in the structure of Nd_2CuO_4 {86753} has the valence contact Ln–Ln been determined (Table 1 and Fig. 2) by means of the method of intersecting spheres (Serezhkin *et al.*, 1997). Probably, the reason for this discrepancy is the high pressure

(21.5 GPa) required for the synthesis of Nd_2CuO_4 {86753}. Therefore, the method of intersecting spheres makes it possible to determine chemical bonds from an identical position for both large (as for Ln—O) and small (for Ln—Q) differences between the electronegativities of interacting atoms. Since the presence of the Ln—Q bonds has little influence on the characteristics of the lanthanide's VD polyhedra, only the CNs with respect to O atoms were taken into account in all calculations.

3.1.2. Agostic contacts. The presence of 13 680 Ln$\cdots Z$ nonvalence contacts with I_1 and I_0 types of intersection explains the inequality $N_f \geq$ CN (Table 2). Note that the greatest number of nonvalence contacts corresponds to the O and H atoms (respectively, 4081 and 3088 faces). Some of the Ln$\cdots$H contacts are agostic (Brookhart & Green, 1983) interactions caused by redistribution of electron density between the coordinatively unsaturated Ln atom and partially negatively charged H atom of a ligand. According to the definition of Blatova *et al.* (2001), among all the Ln$\cdots$H contacts with interatomic distances r(Ln$\cdots$H) of 2.42–4.77 Å and solid angles of up to 10.1%, only 50 faces with $\Omega > 5\%$ belong to agostic contacts. They all occur in the structure of 34 coordination compounds containing Ln atoms with low CNs (not higher than 6).

For example, in the structure of bis[(μ_2-*tert*-butoxo)bis(tri-*tert*-butylmethoxy)cerium(III)] {SOZLUO} these interactions are Ce$\cdots$H50, Ce$\cdots$H61, Ce$\cdots$H63 and Ce$\cdots$H17 (Table 1). The presence in the lanthanide compounds with low CNs and bulky ligands (such as di- and tri-*tert*-butylmethoxo, *tert*-butoxo and isopropylphenoxo) leads to their mutual repulsion upon coordination to one metal atom. As a result, the Ln—O bonds account only for 66.7–88.8% of the full solid angle of the Ln atom (for {SOZLUO}, Table 1, this value is 67.8%). Therefore, Ln atoms with low CN are coordinatively unsaturated and can be involved in the formation of numerous intramolecular nonbonded contacts.



(*a*)

(*b*)

Figure 2
The Ln VD polyhedra in the structures of (*a*) Nd_2CuO_4 {86753} and (*b*) $Ce_2(C_4H_9O)_2(C_{13}H_{27}O)_4$ {SOZLUO}. The atom numbering coincides with that in Table 1.

3.2. Shape of the LnO$_n$ polyhedron

When determining the geometric type of the coordination polyhedron, we considered 'simplified' VD polyhedra in which the number of faces coincides with the CN of the Ln atoms calculated by the method of intersecting spheres (Serezhkin *et al.*, 1997). The small faces corresponding to nonvalence Ln$\cdots Z$ contacts were removed and all the short edges of the metal VD polyhedron were pulled to a single point. The compounds under discussion were found to contain 20 types of LnO_n coordination polyhedra of different shapes. For CN equal to 8 the number of polyhedron types is the largest; in the structures of the compounds under discussion, the following LnO_8 polyhedra can be found: bicapped trigonal prism, square antiprism, trigonal dodecahedron and cube.

3.3. The degree of LnO$_n$ polyhedron distortion

In most cases the LnO_n coordination polyhedra are distorted to a greater or lesser extent, as indicated by the low site symmetry of the lanthanide atoms in these crystals. Although this distortion depends on the compound composition and structure, the Ln atoms occupy 25 positions differing in symmetry, with the asymmetric C_1 position being found most often (53% of cases). Lanthanide atoms with C_s and C_2

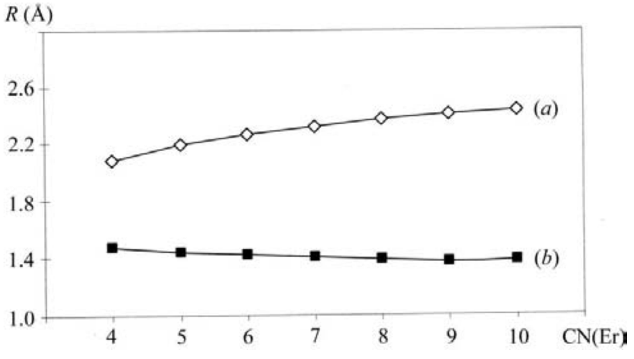


Figure 3
Dependence of (*a*) mean interatomic distances r(Er—O) and (*b*) the R_{SD} value for ErO_n polyhedra on the CN of Er atoms.

Table 3
Some examples of Ce-atom oxidation state determination.

Reference code	CN(Ce)	z†	R_{SD} (Å)	Mean R_{SD} for this CN (Å)	Oxidation state ‡
SOZKUN	4	2.57	1.581	1.49 (6)	III
SOZLUO	4	2.69	1.523	1.49 (6)	III
KIPLEA	4	2.84	1.552	1.49 (6)	III
SOZMAV	7	3.76	1.426	1.40 (1)	IV
VIXMEU	6 and 7	3.88 and 3.60	1.410 and 1.455	1.39 (1) and 1.49 (3)	IV and III
JAXDUH	8	2.51	1.494	1.47 (2)	III
ACACCE01	8	4.07	1.359	1.37 (1)	IV
GUPCCE	8	3.59	1.387	1.37 (1)	IV
CECATI	8	3.64	1.380	1.37 (1)	IV
TINVUH	11 and 11	2.69	1.450 and 1.452	1.46 (1)	III and III
CILKOX	12	2.88	1.463	1.46 (1)	III

† The bond-valence sums of Ce atoms (z) were determined by Roulhac & Palenik (2003). ‡ The resulting oxidation state was estimated using R_{SD} values.

site symmetry are also rather abundant (14 and 8%). However, the shift of the Ln atoms from the center of gravity of their VD polyhedra (D_A) is equal to zero within 2 s.u. (Table 2). This fact, together with the pattern of (r, φ) (Serezhkin & Buslaev, 1997) distributions (in which the points corresponding to Ln—O bonds form contact curves shaped like semicircles), attests to a quasi-spherical distribution of the electron density around the Ln atoms. Fig. 4 shows the (r, φ) distribution for 165 symmetry-independent Lu atoms; the plots for other lanthanides are similar. The dimensionless G_3 (Blatov *et al.*, 1995) value is yet another parameter that characterizes the uniformity of the Ln-atom coordination. In the structures of the compounds considered here, G_3 ranges from 0.079 to 0.094 (for a sphere, $G_3 = 0.077$). With an increase in the CN, the parameter G_3 decreases regularly, *i.e.* the uniformity of the Ln coordination in the structure increases. Since for all lanthanides at CN ≥ 8 the average $G_3 \leq 0.082$ then, according to the criterion of Blatov *et al.* (1995), the major contribution to the formation of the Ln coordination sphere in the crystals is made by nondirected (ionic) Ln—O interatomic contacts.

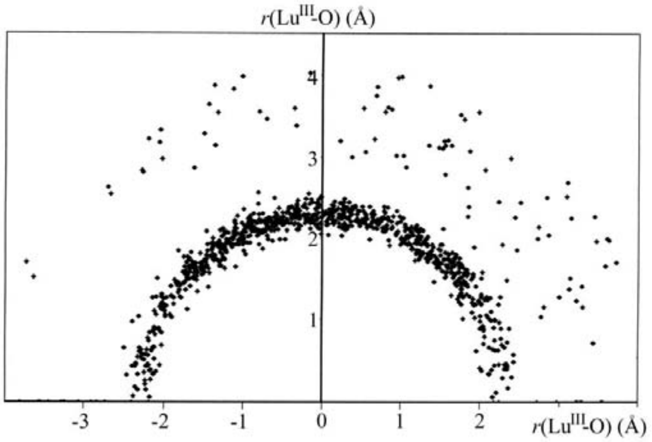


Figure 4
Distribution (r, φ) for 1324 Lu^{III}—O contacts. The position of each point is determined by the r(Lu—O) interatomic distance and the polar angle φ between the Lu—O bond and the D_A vector of the Lu VD polyhedron, directed from the origin of coordinates (where all the lutetium nuclei are located) to the right along the horizontal axis.

3.4. Lanthanides contraction rule

Note that the set we consider contains compounds studied in the temperature (T) range 1.5–1673 K and at pressures of up to 3.3 GPa. Analysis of compounds studied at temperatures in the ranges $5 < T \leq 250$ K and $350 \leq T < 1700$ K has shown that the change in the temperature over this broad range does not actually influence the R_{SD} values, which are nearly equal to the average value for all La atoms to within the determination error. An increase in the R_{SD}(Ln) value becomes noticeable only at temperatures above 1000 K. An increase in the pressure to 1.6 and then to 3.3 GPa in the case of $LaNbO_4$ {61012–61014} (Mariathasan *et al.*, 1985) decreases R_{SD}(La) only from 1.471 to 1.468 and 1.461 Å, respectively.

According to the data obtained, a great diversity of CNs and shapes of the coordination polyhedra and an increase in r(Ln—O) following an increase in the CN were found for the Ln atoms. Nevertheless, the VD polyhedron volume of a lanthanide remains constant within the error of the X-ray diffraction experiment, being dependent only on the identity and the oxidation state of the metal atom (Table 2). This fact allows one to consider the radius of a sphere (R_{SD}) with a volume equal to the VD polyhedron volume as a one-dimensional characteristic of Ln atoms (Ln = La–Lu) in the oxygen environment. The approximate invariability of the lanthanide VD volume supports the standpoint according to which the complexing atom in the crystal structure should be considered as a soft, easily deformed sphere of constant volume.

Fig. 5(a) represents the dependence of the R_{SD} values of Ln^{III} atoms in the oxygen environment on the lanthanide atomic number (for La $Z^* = 1$ and for Lu $Z^* = 15$). According to the least-squares calculations, with an increase of Z^* in the series La^{III}–Lu^{III} a decrease of the R_{SD}(Ln) values is observed that can be described by the common linear dependence

$$R_{SD}(LnO_n) = 1.485 - 0.008Z^*, \qquad (1)$$

with a correlation coefficient equal to −0.985. As there is no information about compounds containing PmO_n polyhedra, by means of (1) the R_{SD}(Pm) value of 1.45 Å in the oxygen environment may be obtained.

Although the R_{SD}(Ln) values in the La^{III}–Lu^{III} series obey the lanthanide contraction rule (Cotton, 1991), for some lanthanides the experimental R_{SD} value differs from the regression line (Fig. 5a). Let, for any Ln, ΔR_{SD} be a model of the difference between the experimental R_{SD} value and that calculated from (1). As can be seen from Fig. 5(b), ΔR_{SD} changes non-monotonically and obeys the 'inclined W' effect.

Table 4
Oxidation state of the Pr atoms in the structures of some oxides.

Complex	Central atom	Position multiplicity	Average r(Pr—O) (Å)	R_{SD} (Å)	ζ†	Oxidation state of Pr determined from R_{SD}
Pr_2O_3 {61179, 75481}	Pr1, CN = 7	2	2.49	1.51	III	III
Pr_9O_{16} {80308}	Pr1, CN = 6	1	2.23	1.41	IV	IV
	Pr2, CN = 7	2	2.41	1.47	3.67	III
	Pr3, CN = 7	2	2.33	1.41	3.67	IV
	Pr4, CN = 7	2	2.33	1.41	3.67	IV
	Pr5, CN = 8	2	2.50	1.47	III	III
$Pr_{10}O_{18}$ {80309}	Pr1, CN = 7	4	2.30	1.39	3.83	IV
	Pr2, CN = 7	4	2.33	1.41	3.83	IV
	Pr3, CN = 6	4	2.22	1.41	IV	IV
	Pr4, CN = 7	4	2.33	1.41	3.83	IV
	Pr5, CN = 7	4	2.31	1.40	3.83	IV
	Pr6, CN = 8	4	2.48	1.46	III	III
	Pr7, CN = 7	4	2.32	1.41	3.83	IV
	Pr8, CN = 7	4	2.43	1.48	3.83	III
	Pr9, CN = 8	4	2.49	1.47	III	III
	Pr10, CN = 8	4	2.49	1.47	III	III
$Pr_{12}O_{22}$ {82107}	Pr1, CN = 7	4	2.31	1.40	IV	IV
	Pr2, CN = 7	4	2.31	1.40	IV	IV
	Pr3, CN = 7	4	2.32	1.41	IV	IV
	Pr4, CN = 7	4	2.31	1.40	IV	IV
	Pr5, CN = 8	4	2.47	1.46	III	III
	Pr6, CN = 8	4	2.47	1.46	III	III
PrO_2 {28786}	Pr1, CN = 8	4	2.34	1.38	IV	IV

† Zhang *et al.* (1995*a*,*b*, 1996) determined the oxidation states of Pr atoms by comparing the average interatomic distances r(Pr—O) with the sum (Σ) of the corresponding Shannon (1976) radii. For Pr^{III} with CN 6, 7 and 8, Σ = 2.37, 2.44 and 2.51 Å, respectively. For Pr^{IV} with CN 6, 7 and 8, Σ = 2.23, 2.29 and 2.34 Å, respectively.

3.5. VD polyhedron characteristics and classical methods of crystal analysis

The increase in the R_{SD} value upon a decrease in the Ln oxidation state indicates a decrease in the electron density transfer from the metal valence orbitals. It is worth noting that, on the basis of the R_{SD} value, the oxidation state of Ln can be determined even in cases when the bond-valence sum method or radii systems cannot solve the problem. Table 3 contains the results of valence-state determination of some Ce atoms by means of the bond-valence sum method (Roulhac & Palenik, 2003) and by means of the corresponding R_{SD} values. As can be seen from Table 3, for low CN both bond-valence sums (z_i) and R_{SD} are poor criteria for oxidation state calculation. We agree with Roulhac & Palenik (2003) that the main reason is that Ce atoms with CN = 4 are coordinatively unsaturated and are involved in numerous specific contacts.

Let us consider the structure of $[Ce_4O(C_3H_7O)_{13}(C_3H_8O)]$ {VIXMEU}, which contains two types of Ce atoms, and $(CN_3H_6)_6[Ce(CO_3)_5]\cdot 4H_2O$ {1986}. According to Roulhac & Palenik (2003), the bond-valence sums for the Ce atoms in these compounds are 3.88 and 3.60 in the former case and 3.59 in the latter (the CNs of the Ce atoms are 6, 7 and 10, respectively). Inasmuch as the principle of electroneutrality calls for different oxidation states of the Ce atoms in $[Ce_4O(C_3H_7O)_{13}(C_3H_8O)]$ {VIXMEU}, it was stated by Roulhac & Palenik (2003) that the atom with a lower z_i value (3.60) is in the oxidation state +3. At the same time, even though the bond-valence sum for $(CN_3H_6)_6[Ce(CO_3)_5]\cdot 4H_2O$ {1986} (z_i = 3.59) is lower than in the former case, the oxidation state of cerium is taken as being +4 (Roulhac & Palenik, 2003). The discrepancy between the calculated and expected oxidation states is explained by the low quality of the X-ray crystallographic experiment (R = 0.072). Our findings show that, for the Ce atoms with z_i = 3.88, 3.69 and 3.59 in this compound, which were identified as Ce^{IV}, Ce^{III} and Ce^{IV}, respectively, the R_{SD} values are 1.41, 1.46 and 1.39 Å and coincide, within 2σ, with the average R_{SD} value (Table 2).

As another example, let us consider some representatives of fluorite-like praseodymium oxides constituting the homologous series Pr_nO_{2n-2}, which are intermediate between Pr_2O_3 and PrO_2. The oxidation states of the Pr atoms in Pr_9O_{16} {80308}, $Pr_{10}O_{18}$ {80309} and $Pr_{12}O_{22}$ {82107} (Table 4) were estimated by comparing the average experimental interatomic distances r(Pr—O) with the sum of the corresponding Shannon (1976) radii. Note that the fractional oxidation states were assigned by Zhang *et al.* (1995*a*,*b*) to some praseodymium atoms in Pr_9O_{16} and $Pr_{10}O_{18}$

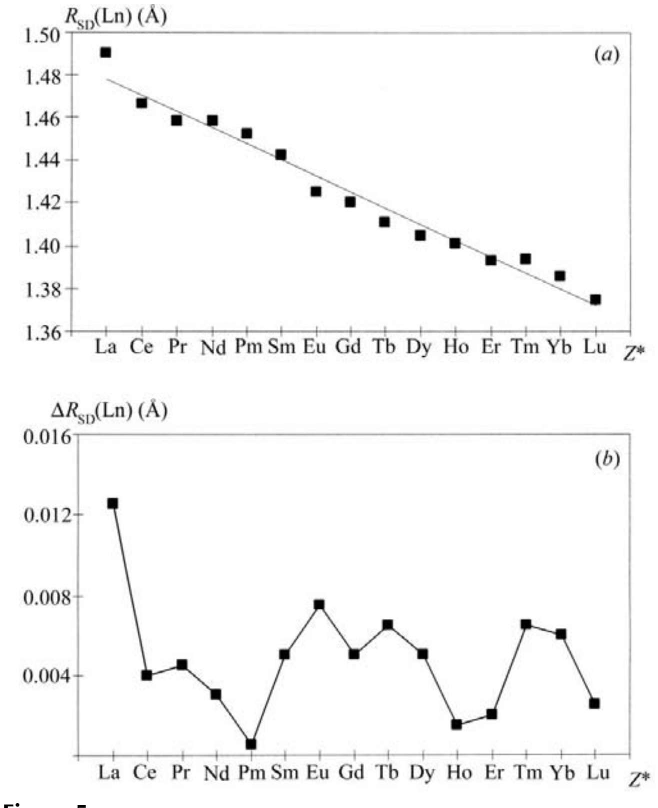


Figure 5
Dependence of (*a*) the R_{SD} and (*b*) the ΔR_{SD} values on the identity of the Ln^{III} atoms.

(Table 4). However, according to an X-ray absorption study (Karnatak *et al.*, 1987), the structures of cerium, praseodymium and terbium oxides contain no lanthanides in non-integer oxidation states. Our calculations showed that Pr atoms in the structures Pr_nO_{2n-2} can be distinctly divided, regardless of their CNs and the variety of their average Pr—O distances, into two groups with R_{SD} = 1.39–1.41 and 1.46–1.48 Å, respectively (Table 4). Considering the average R_{SD} values (Table 2), one can state that the metal atoms in the former group are Pr^{IV} and those in the latter group are Pr^{III}. Therefore, with allowance made for the Wyckoff positions occupied by the Pr atoms, the formulae of oxides Pr_9O_{16}, $Pr_{10}O_{18}$ and $Pr_{12}O_{22}$ (Table 4) may be written as $Pr_5^{4+}Pr_4^{3+}O_{16}$, $Pr_6^{4+}Pr_4^{3+}O_{18}$ and $Pr_8^{4+}Pr_4^{3+}O_{22}$, respectively.

4. Conclusions

It has been stated that the VD polyhedron volume of lanthanides remains constant, being dependent only on the identity and the oxidation state of the metal atom. The results of this investigation support the standpoint according to which Ln atoms surrounded by O atoms in a crystal structure should be approximated by soft, easily deformed spheres of a constant volume. On the basis of the radii of these spheres (Table 2), the oxidation state of Ln coordinated by oxygen in crystals can be determined even in cases when the bond-valence sum method or other radii systems cannot solve the problem.

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