addenda and errata

New bond-valence parameters for lanthanides. Addendum

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Recently, we have been informed that the part of our work [Trzesowska *et al.* (2004), *Acta Cryst.* B**60**, 174–178] concerning the linear correlation between the average bond-valence parameters and atomic number of a lanthanide is in agreement with the results of Chen & Hu (2002).

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Trzesowska, A., Kruszynski, R. & Bartczak, T. J. (2004). *Acta Cryst.* B**60**, 174–178.

New bond-valence parameters for lanthanides

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The bond-valence method, especially the valence-sum rule, is very useful for checking if the structures formed by trivalent lanthanides are correct. In this work bond-valence parameters (R_{ij}), which connect bond valences and bond lengths, have been computed for a large number of bonds taken from the Cambridge Structural Database, Version 5.24 (2002) [Allen (2002). *Acta Cryst.* B**58**, 380–388]. The calculated values of bond-valence parameters for metal-organic compounds decrease with an increase in lanthanide atomic number; the R_{ij} values are also smaller than bond-valence parameters calculated for inorganic compounds. A summary of bond-valence sums calculated for R_{ij} given in this work and reported in the literature, and a functional correlation between lanthanide–oxygen distances and coordination number are presented.

1. Introduction

The chemistry of lanthanides (Ln) has not been well understood until recently. Today, because of their huge and versatile applications, lanthanides attract more and more interest. Lanthanide compounds exhibit interesting chemical, biological and catalytic properties. For example, they are used as NMR contrast agents (Calabi *et al.*, 2002; Feng *et al.*, 2002; Sherry, 1997; Wenzel *et al.*, 2001; Zhang & Sherry, 2003), biological markers (Gudgin Dickson *et al.*, 1995; Hemmila, 1995; Ulusoy & Whitley, 1999), bond-coupling and homogeneous catalysts (Carmona *et al.*, 2000; Collin & Giuseppone, 1998; Epstein *et al.*, 2000; Imanishi & Naga, 2001; Jacobsen *et al.*, 1999; Mikami *et al.*, 2002; Morrow *et al.*, 1992) and in photodynamic therapy (Kostenich *et al.*, 1997; Sessler & Miller, 2000; Sessler *et al.*, 1997),

The lanthanides which act as coordination centers have large ionic radii, which decrease continually as the element atomic number increases ('lanthanide contraction; Bagnall, 1975; Bailar *et al.*, 1973). Rare-earth elements form complexes in which higher coordination numbers (7–12) appear to dominate. The most common ligands in these compounds contain an O atom; for example, nitrates, phosphates, sulfates, oxalates, carboxylate groups, alcohols, crown ethers, Schiff bases and water molecules (Boucher *et al.*, 2002; Cotton & Raithby, 1999; Eriksson *et al.*, 1980; Jiang *et al.*, 2002; Lees *et al.*, 2001; Wang *et al.*, 1995; Zalewicz & Bartczak, 1993). The rich coordination chemistry of lanthanides offers potential applications in the design of intelligent complexes, but also creates problems relevant to solving structures by X-ray

Table 1
Statistics for the lanthanide compounds taken from the Cambridge Structural Database, Version 5.24 (2002) (Allen, 2002).

Ln: lanthanide; n: the number of structures used; Avg.: the average R value (residual factor: crystallographic agreement index) found for all the structures used; R is the R value range.

Ln	n	Avg.	R
La	163	5.59	2.0–13.3
Ce	62	4.99	1.8–11.5
Pr	85	5.22	1.04–13.3
Nd	163	5.14	1.3–15.0
Sm	68	4.89	1.4–13.0
Eu	132	5.39	1.8–14.9
Gd	120	4.45	1.2–10.88
Tb	44	4.31	1.85–8.80
Dy	43	4.40	1.8–7.73
Ho	36	4.77	1.5–14.66
Er	91	5.09	1.58–12.64
Tm	19	4.25	2.3–8.3
Yb	76	5.63	1.76–15.0
Lu	38	5.17	2.0–13.0

crystallography methods. One of the factors which can be used to verify the structure of the coordination sphere is the valence. There are some publications in which Ln—X (X = O, F, Cl, Br, I, S, Se, Te, N, P, As, H) bond-valence parameters are given, but they are calculated for inorganic crystal structures (Brese & O'Keeffe, 1991; Brown & Altermatt, 1985; Brown & Wu, 1976). The aim of this work was to establish the values of the Ln—O bond-valence parameters for metal-organic complexes, which the rare-earth elements form mostly.

The bond-valence method is well known and documented (Brown, 1992; Hawthorne, 1994; Urusov, 1995; Urusov & Orlov, 1999) and this is the reason why only the main features of this method are summarized here. It is a powerful tool for predicting the bond distances in crystals (Brown, 1977), the analysis of the geometric strains in the crystals, the estimation of the oxidation states of atoms (Jensen et al., 2001), checking structure solution correctness and identifying the light atoms, e.g. in proteins (Müller et al., 2003). Two expressions are commonly used in bond-valence analysis. One describes the relationship between the bond length between nearest-neighbouring atoms $i - j$ (d_{ij}) and the bond valence (v_{ij})

$$v_{ij} = \exp[(R_{ij} - d_{ij})/b].$$

The second expression allows the calculation of the total atom valence V_i

$$\sum_j v_{ij} = V_i$$

and, according to the valence-sum rule (Brown, 1992), it must be equal to the formal oxidation state. The value of the constant b was established by Brown & Altermatt (1985) and the accepted value is 0.37 Å. R_{ij} is known as the bond-valence parameter. Once obtained, this parameter is useful in a number of ways. It may be used in predicting bond lengths from a given valence and for checking the correctness of the structure determination.

2. Experimental

We focus our research on complexes having O atoms around the central atom because of the strong hydrolytic properties of Ln^{3+}. The coordination numbers (from 6 to 12) for each lanthanide atom were also taken into account. The bond lengths needed to calculate bond-valence sums were obtained from the Cambridge Structural Database (CSD), Version 5.24 (Allen, 2002), which contains information on the crystal structures of over 272 000 organic and metal-organic compounds. All the crystal structures of trivalent lanthanides were included, even those with disorder, partial occupancy and a high R value because of the small number of available structures of some lanthanides and the fact that all deviations were averaged during calculations. Since some lanthanides can exist in different stable oxidation states, it is sometimes difficult to determine them. Thus, some compounds were rejected. For example, nine compounds of cerium [refcodes: AFOKEL (Gun'ko et al., 2002), CURQEL (Hubert-Pfalzgraf et al., 1999), GAQVEZ (Hubert-Pfalzgraf et al., 1998), GUPCCE (Voliotis et al., 1975), GUPCCE01 (Marsh & Herbstein, 1988), GUOCCE10 (Butman et al., 1976), NOJTEL (Becht et al., 1996), RUGQIT (Sirio et al., 1997), YAWVEX (Troyanow et al., 1992)] were excluded. In all these cases the cerium ion was tetravalent, which was not marked in the CSD. Two compounds of europium [refcodes: WIGYEQ and WIHBAQ (Evans et al., 2000)] were omitted because the first one is the mixed-valence complex containing a 3:1 Eu^{II}:Eu^{III} mixture and in the second one the Eu atoms are all divalent. Some statistical data are presented in Table 1. Since 1140 structures were considered, their enumeration and references are not included.

In order to calculate the bond-valence parameters for lanthanide–oxygen bonds, the following equation was used (Brese & O'Keeffe, 1991)

$$R_{ij} = b \ln[V_i / \Sigma \exp(-d_{ij}/b)].$$

For each structure formed by trivalent lanthanide atoms (with the same coordination numbers) the bond-valence parameters, using the bond lengths from the Cambridge Structural Database and a value of constant b of 0.37 Å (Brown & Altermatt, 1985), were calculated and averaged. The various calculations were carried out using Microsoft® Excel (Microsoft Corporation, 1985–1997).

3. Results and discussion

All the bond-valence parameters calculated as a function of coordination number are collected in Table 2. It appears that they do not show a dependence on the CN. The R_{ij} values are generally larger for lanthanides forming 11- and 12-coordinate structures. The large number of substituents may cause an elongation of the bonds. This produces an increase in the standard deviations for elements with large ionic radii: lanthanum, cerium, praseodymium, samarium and europium. The reliability of some of the bond-valence parameters might be questioned because there was only one or two available

Table 2
Bond-valence parameters for Ln—O_{CN} bonds.

CN: coordination number; n: No. of structures found; t: the size of the set used in the calculations (the number of lanthanides forming bonds). Standard deviations are given in parentheses.

CN	Bond-valence parameter [R_{ij} (Å)]													
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
6	2.151 (34)	2.016	2.094 (14)	2.094 (9)	2.052 (17)	2.045 (14)	2.037 (10)	2.006 (24)	2.006	–	1.981 (31)	–	1.944 (26)	1.937 (6)
n/t	4/4	1/1	2/2	7/12	7/10	5/7	2/6	5/7	1/1	0	10/18	0	13/17	4/4
7	2.130 (46)	2.143	2.094 (26)	2.093 (20)	2.057 (17)	2.024 (9)	2.034 (17)	2.016	2.010 (24)	1.986 (12)	1.970 (8)	1.963 (19)	1.947 (15)	1.933 (38)
n/t	6/9	1/1	8/9	8/11	6/6	7/8	10/15	1/1	4/5	4/5	8/8	2/2	11/14	2/2
8	2.134 (21)	2.116 (27)	2.094 (16)	2.079 (21)	2.050 (26)	2.036 (30)	2.029 (16)	2.013 (20)	2.000 (21)	1.990 (9)	1.978 (17)	1.963 (14)	1.956 (21)	1.945 (23)
n/t	33/34	10/11	21/23	44/52	17/27	60/71	57/66	18/24	18/20	14/15	41/56	8/11	34/38	15/21
9	2.138 (21)	2.109 (16)	2.098 (13)	2.085 (18)	2.055 (18)	2.039 (14)	2.029 (18)	2.016 (15)	2.009 (12)	1.995 (16)	1.981 (14)	1.974 (10)	1.962 (15)	1.954 (14)
n/t	44/45	25/28	31/34	65/72	22/22	46/50	37/38	20/20	17/17	18/19	31/35	9/10	16/16	16/18
10	2.146 (22)	2.121 (17)	2.092 (45)	2.089 (18)	2.059 (10)	2.045 (14)	2.039 (15)	–	2.000 (16)	–	1.982	–	1.967 (18)	1.944
n/t	47/61	19/22	16/21	26/32	8/8	10/14	13/14	0	3/3	0	1/1	0	2/2	1/1
11	2.188 (10)	2.145 (19)	2.121 (9)	2.100 (16)	2.056 (18)	–	–	–	–	–	–	–	–	–
n/t	16/18	2/2	5/6	6/6	1/1	3/3	0	0	0	0	0	0	0	0
12	2.187 (15)	2.136 (20)	2.150 (8)	2.098 (21)	2.166 (20)	2.080	2.057	–	–	–	–	–	–	–
n/t	13/15	4/4	2/2	7/7	7/7	1/1	1/1	0	0	0	0	0	0	0
Mean R_{ij} value	2.148 (24)	2.116 (46)	2.098 (22)	2.086 (7)	2.063 (42)	2.038 (18)	2.031 (10)	2.013 (5)	2.005 (5)	1.992 (5)	1.979 (5)	1.968 (6)	1.954 (10)	1.947 (8)

structures, for example, cerium (CN = 6, 7) or ytterbium (CN = 10), so there are not enough structures for reasonable statistics. The number of compounds found confirms that lanthanides create mostly eight- and nine-coordinate complexes.

The last line of Table 2 includes the weighted averages of the bond-valence parameters for the trivalent lanthanides. All the average R_{ij}-factor values decrease on increasing the atomic number, which is in agreement with decreasing the ionic and atomic radii in the lanthanide series from lanthanum to lutetium (Fig. 1). There are some deviations from the linear dependence for lanthanum and europium that also occur when we consider the mean bond lengths for different coordination numbers. It could be expected that the average bond lengths decrease along the lanthanide group. The lanthanide contraction results in a narrowing of the coordination sphere and an increase in strength of the Ln–ligands interaction. For each linear correlation (Fig. 2) between metal–donor-atom mean distance and coordination number, the correlation coefficient was computed and these values are greater than 0.9. Almost all curves are parallel, which is validated by the slope of a straight line. Only for lanthanum, cerium, neodymium, gadolinium and erbium are these coefficients different and the lines inclined at a lower angle.

Two publications exist in which the bond-valence parameters for cerium (Roulhac & Palenik, 2003) and samarium (Palenik, 2003) are reported. The R_{ij} values presented in this paper (2.116 Å for Ce and 2.063 Å for Sm) and given in these publications (2.121 Å for Ce and 2.055 Å for Sm) are similar, despite different assumptions made regarding the compound selection. This indicates that the method of calculation is accurate and the selection scheme is proper.
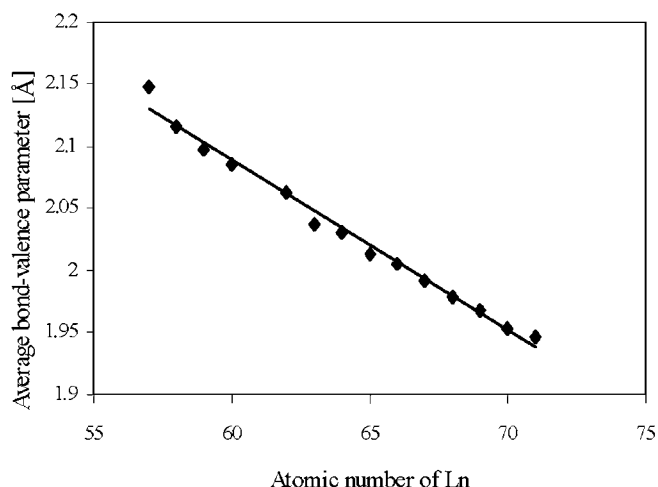

Figure 1
Average bond-valence parameters R_{ij} plotted against the atomic number of lanthanide.
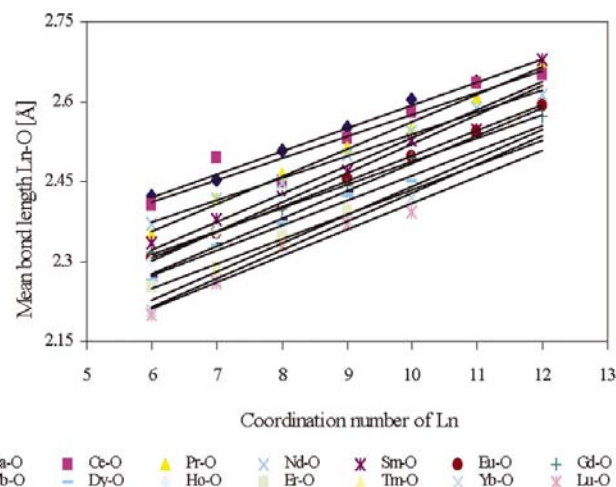

Figure 2
Mean Ln—O bond length as a function of coordination number.

Table 3
The lanthanide bond-valence parameters reported in the literature.

Ln: lanthanide; $R_{ij}1$: the bond-valence parameters according to Brown & Wu (1976); $R_{ij}2$: the bond-valence parameters taken from Brown & Altermatt (1985); $R_{ij}3$: the bond-valence parameters taken from Brese & O'Keeffe (1991); $R_{ij}4$: the calculated mean bond-valence parameters (this paper).

Ln	$R_{ij}1$	$R_{ij}2$	$R_{ij}3$	$R_{ij}4$
La	2.167	2.172	2.172	2.148
Ce	2.160	–	2.151	2.116
Pr	2.150	2.138	2.135	2.098
Nd	2.137	2.105	2.117	2.086
Sm	2.107	–	2.088	2.063
Eu	2.090	2.074	2.076	2.038
Gd	2.077	–	2.065	2.031
Tb	2.065	2.032	2.049	2.013
Dy	2.053	2.001	2.036	2.005
Ho	2.041	2.025	2.023	1.992
Er	2.029	1.988	2.010	1.979
Tm	2.020	–	2.000	1.968
Yb	2.012	1.965	1.985	1.954
Lu	2.004	–	1.971	1.947

Table 4
Bond-valence sums calculated for lanthanide compounds.

Ln: lanthanide; V_i1: the mean bond-valence sums calculated for the bond-valence parameters (this work); V_i2: the mean bond-valence sums calculated for the bond-valence parameters from Brese & O'Keeffe (1991).

Ln	t	V_i1	V_i2
La	186	3.01 ± 23	3.21 ± 25
Ce	69	2.98 ± 16	3.28 ± 17
Pr	97	3.01 ± 25	3.24 ± 28
Nd	192	3.00 ± 15	3.27 ± 17
Sm	81	3.01 ± 28	3.22 ± 30
Eu	154	3.00 ± 18	3.33 ± 19
Gd	140	3.00 ± 13	3.29 ± 15
Tb	52	3.00 ± 15	3.31 ± 17
Dy	46	3.01 ± 14	3.27 ± 16
Ho	39	3.00 ± 11	3.27 ± 12
Er	118	3.01 ± 15	3.27 ± 16
Tm	23	3.00 ± 11	3.27 ± 12
Yb	87	3.01 ± 17	3.27 ± 19
Lu	46	3.00 ± 16	3.20 ± 17

As was mentioned in §1, many different bond-valence parameters for lanthanide–oxygen bonds have been reported in the literature. All these parameters were calculated (Brese & O'Keeffe, 1991; Brown & Altermatt, 1985) or interpolated between the well determined R_{ij} values (Brown & Wu, 1976) for inorganic compounds. All these values are presented in Table 3 (the $R_{ij}1$ values were obtained from a different expression, see Brown & Shannon, 1973). There is a systematic difference of *ca* 0.028 Å between bond-valence parameters, based on the same equation, determined from metal-organic and inorganic structures. This can originate from electronic character differences between coordination and ionic bonds. The R_{ij} value can be viewed as a bond length of unit valence. Bond length depends on the size of the bonded atoms, the bond order and the nature of two atoms. In inorganic compounds, lanthanides form ionic bonds (the bonds are non-directional and electrostatic forces attract the ions). In coordination compounds the coordinate covalent Ln—O bonds are shorter and hence the bond-valence parameters are smaller for metal-organic compounds.

Smaller bond-valence parameters can also be observed for other transition metal atoms bonded to O atoms: Co (Wood & Palenik, 1998), Cr (Wood *et al.*, 2000), Fe (Kanowitz & Palenik, 1998), Mn (Palenik, 1997*b*) and Ti (Palenik, 1997*a*). For example, the R_{ij} value calculated for the Fe^{II}—O bond in metal-organic compounds is equal to 1.713 Å, but is calculated as 1.734 Å for inorganic compounds (Brese & O'Keeffe, 1991). The R_{ij} value calculated for the Co^{III}—O bond in metal-organic compounds is 1.637 Å, but is equal to 1.70 Å for inorganic compounds (Brese & O'Keeffe, 1991) . The differences between the calculated values of bond-valence parameters for metal-organic and inorganic compounds are noticeable and they may occur for all elements.

Bond-valence sums calculated for the average bond-valence parameters from this work and those from Brese & O'Keeffe (1991) are given in Table 4. The bond-valence sums calculated for 1140 lanthanide complexes with CN from 6 to 12 have 135 examples where the difference between the observed and expected value is equal to 0.25 v.u. or more. According to Palenik (2003), a difference larger than 0.25–0.30 v.u. is a reasonable guide to those structural studies that should be examined in more detail because of possible errors.

4. Conclusions and recommendations

The bond-valence method is a relatively simple tool that can give a strong indication to the nature of a lanthanide cation, not only in inorganic structures. One goal of our studies was to demonstrate that this method also allows the oxidation state of a rare-earth ion to be calculated for a metal-organic complex. The R_{ij} values for Ln—O bonds proposed in this work make it possible to compute the valence of the central atom. This value can be a good guide to verifying the accuracy of the structure solution. In those cases where the oxidation state values are not as expected, there may be problems with the structure determination that often happen because of the rich and largely unknown coordination chemistry of the lanthanides, and because of the high frequency of disorders seen in these types of structures.

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