New lanthanide–nitrogen bond-valence parameters

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The bond-valence parameters (R_{ij}), which connect bond valences and bond lengths, have been computed for lanthanide–nitrogen bonds. It has been found that values of bond-valence parameters decrease with increasing lanthanide atomic number in coordination compounds, and that they are smaller than the R_{ij} parameters of inorganic compounds. As expected, the lanthanide–nitrogen bond-valence parameters are larger than lanthanide–oxygen bond-valence parameters. There are no obvious dependencies between the number of N atoms in the coordination sphere and the bond-valence parameter value.

1. Introduction

The coordination chemistry of lanthanide complexes (Bagnall, 1975; Bailar *et al.*, 1973) is of great interest from both theoretical and practical viewpoints. In most compounds the lanthanide ions are in a trivalent state. However, some compounds contain lanthanide ions in a divalent or a tetravalent oxidation state. The large sizes of the lanthanide ions are responsible for the high coordination numbers (CN = 4–12) and coordination polyhedra that are often irregular. Low coordination numbers can be achieved with bulky ligands, whereas the highest coordination numbers can be achieved with chelating ligands, such as NO_3^- and $C_2O_4^{2-}$. The steric hindrance and the size of the ligand mainly determine the coordination geometry and the coordination number. Ligands pack around the metal ions in such a way as to minimize the ligand–ligand repulsions. Electrostatic effects dominate the lanthanide interactions with ligands. However, quantummechanical calculations have revealed the presence of a small degree of covalency in *f*-element bonds (Adamo & Maldivi, 1997; Chopin, 2002; Luo *et al.*, 2003).

Lanthanide ions as typical hard Lewis acids display strong affinities for first-row electron donors O and N. The N-donor ligands were thought for many years to be too soft to form complexes with rare earth elements, but in more recent years many lanthanide complexes with aromatic N donors such as pyridine, bipyridyl and terpyridyl have been synthesized and characterized by X-ray diffraction (Aspinall, 2001).

The aim of the present work was to establish the bond-valence parameters of the Ln—N bonds in coordination compounds of the lanthanides, Ln (Brown, 1977, 1992; Hawthorne, 1994; Urusov, 1995; Urusov & Orlov, 1999; Brown, 2002; Mohri, 2003). To our knowledge, the Ln—N bond-valence parameters have only been given in one publication (Brese & O'Keeffe, 1991). However, they were interpolated from correlations between bond-valence parameters

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Table 1
Bond-valence parameters for $Ln^{III}-N_{CN}$ 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 uncertainties are given in parentheses..

CN	Bond-valence parameter [R_{ij} (Å)]						
	La	Ce	Pr	Nd	Sm	Eu	Gd
6	2.303	2.255 (13)	2.256 (33)	2.227 (16)	2.201 (12)	2.161	2.139 (38)
n/t	3/3	2/2	5/6	11/11	11/12	1/1	5/5
7	2.243 (11)	2.206 (21)	2.199 (18)	2.201 (11)	2.158 (11)	2.066 (37)	2.154 (7)
n/t	7/8	3/3	4/4	9/11	23/26	5/5	5/6
8	2.222 (11)	2.236 (9)	2.184 (13)	2.185 (11)	2.160 (6)	2.144 (6)	2.115 (11)
n/t	27/28	13/17	19/19	40/44	26/33	51/65	48/51
9	2.261 (11)	2.244 (8)	2.224 (10)	2.177 (8)	2.161 (5)	2.165 (5)	2.160 (7)
n/t	51/59	22/24	28/30	32/36	18/19	88/111	66/80
10	2.260 (9)	2.240 (14)	2.218 (11)	2.221 (13)	2.178 (10)	2.197 (13)	2.174 (11)
n/t	43/52	11/12	18/20	29/30	12/12	28/28	18/18
11	2.303 (16)	2.266 (12)	2.225	2.331 (56)	2.246	–	–
n/t	15/17	4/4	1/1	2/2	1/1	0	0
12	2.316 (20)	2.321 (38)	2.246 (9)	2.297 (33)	2.262 (1)	2.258	–
n/t	7/7	3/3	3/3	3/4	2/4	1/1	0
Mean R_{ij} value	2.261 (13)	2.254 (13)	2.215 (9)	2.201 (22)	2.171 (16)	2.161 (24)	2.146 (8)

CN	Bond-valence parameter [R_{ij} (Å)]						
	Tb	Dy	Ho	Er	Tm	Yb	Lu
6	–	–	2.138	2.053 (8)	2.079	2.067 (10)	2.060 (17)
n/t	0	0	1/1	6/10	1/1	21/28	3/3
7	2.121 (20)	2.095	2.047 (38)	2.080 (18)	2.068	2.041 (4)	2.018 (14)
n/t	6/7	1/1	3/4	10/11	1/1	14/20	6/6
8	2.098 (18)	2.101 (14)	2.117 (16)	2.084 (11)	2.067 (13)	2.049 (7)	2.054 (6)
n/t	19/21	16/16	12/12	30/31	5/5	56/66	29/30
9	2.137 (8)	2.138 (13)	2.126 (12)	2.101 (16)	2.087 (10)	2.109 (9)	2.082 (7)
n/t	19/24	18/19	17/18	16/18	8/8	31/31	25/26
10	2.179 (8)	2.147 (12)	2.148 (9)	2.134 (13)	2.139	–	2.084 (18)
n/t	12/12	5/5	4/4	4/4	1/1	0	2/2
11	–	–	–	–	–	–	–
n/t	0	0	0	0	0	0	0
12	–	–	–	–	–	–	–
n/t	0	0	0	0	0	0	0
Mean R_{ij} value	2.130 (13)	2.124 (10)	2.118 (15)	2.086 (11)	2.082 (11)	2.064 (11)	2.046 (10)

for $Ln-X$ bonds involving the anions O, F, Cl, Br, I, P and N, and calculated for inorganic crystal structures. Owing to the noticeable differences between the values of bond-valence parameters for metal-organic and inorganic compounds, the bond-valence parameters determined by Brese & O'Keeffe (1991) should not be applied to metal-organic compounds.

Lanthanide compounds with ligands containing N atoms as electron-pair donors, such as polyaminopolycarboxylic acids, porphyrins, pyridines and calixarenes, have found applications in the separation of lanthanides (Öztekin & Erim, 2001; Dukov & Jordanov, 1999; Izatt et al., 1985) as contrast agents in magnetic resonance imaging (MRI; Peters et al., 1996; Wan et al., 1995; Zhang & Sherry, 2003) and as catalysts for the cleavage of RNA (Morrow et al., 1992; Chin & Morrow, 1994). Lanthanide complexes of ligands containing N atoms are of current research interest and thus establishing the bond-valence parameters for $Ln-N$ bond seems to be of importance.

2. Experimental

The bond lengths needed to calculate the bond-valence parameters were obtained from the Cambridge Structural Database (CSD), Version 5.25 (Allen, 2002). The metal coordination sphere was determined by the method implemented by Shields et al. (2000) and the results were in agreement with the default settings of the CSD search program QUEST3D. All the crystal structures of the trivalent lanthanides were included, even those with a high R factor, because all deviations were averaged during the calculations. The distributions of the bond-valence parameters can be described by Gaussian curves. Compounds with lanthanides in oxidation states other than +3 were excluded from the calculations. Thus, a few compounds were rejected. For example, five ytterbium compounds [CSD refcodes: HEFGUU (White et al., 1994), HEFGOO (White et al., 1994), HEFGII (White et al., 1994), GIWVOX (Hillier et al., 1998),

PIRLIL (Maunder *et al.*, 1994)], two samarium compounds [CSD refcodes: GIWVIR (Hillier *et al.*, 1998), ZURVEN (Minhas *et al.*, 1996)] were excluded. In all these cases the lanthanide ions were divalent, which was not marked in the CSD. The mixed-valence complex of Yb [CSD refcode: KEDVAQ (Deacon *et al.*, 1999)] was also omitted. Due to the bond discrepancies around the central atom, one compound of lanthanum [CSD refcode: HETALA (Fuller *et al.*, 1978)] was rejected. The coordination numbers (from 6 to 12) for each lanthanide atom were also taken into consideration. Bond-valence parameters were calculated for compounds containing N-donors as well as for compounds containing both N- and O-donor ligands around the lanthanide ion because of the small number of compounds containing only N-donor ligands. The CSD reference codes of the lanthanide compounds, used in the calculation of Ln—N bond-valence parameters, are available as supplementary material.[1]

Bond-valence parameters R_{ij} (bonds between the chemical elements i and j) can be computed by (Brese & O'Keeffe, 1991)

$$R_{ij} = b \ln[V_i / \Sigma \exp(-d_{ij}/b)], \qquad (1)$$

where V_i is the formal valence of the central atom i, d_{ij} is the distance between atom i and j, and the summation is over all neighbours j, which are assumed to be of the same chemical element; $b = 0.37$ is a universal constant (Brown & Altermatt, 1985). In order to allow for two different types of ligands (N and O in the present case) (1) was modified to give

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

The contribution of the Ln—O bonds to the valence of Ln is computed from the previously determined parameters R_{Ln-O} and the known bond lengths (Trzesowska *et al.*, 2004). After subtraction of this amount from the formal valence $V_{Ln} = 3$, the remaining valence is used to compute R_{Ln-N}. Results for different compounds of a single-element Ln were averaged. Once obtained, the bond-valence parameter is useful in a number of ways. It may be used to predict bond lengths from a given valence and for checking the correctness of a structure. All calculations were carried out using Microsoft *Excel* 97 (Microsoft Corporation, 1985–1997).

3. Results and discussion

Bond-valence parameters (R_{Ln-N}) have been calculated as a function of the coordination number of Ln^{3+} and they are summarized in Table 1. These results suggest an increase in R_{ij} with increasing coordination number, although the variation is smaller than the standard uncertainties in R_{ij} computed at a single coordination number, and a definite dependence cannot be discerned. This implies that a single value of the bond-valence parameter can be used for the Ln—N bond of each element Ln, irrespective of the coordination number of Ln (bottom row of Table 1). The large weighted standard devia-

tion values may be a result of very different substituents connected to the lanthanide atom, from small (*e.g.* nitrates, sulfates, water, acetonitrile) to bulky [*e.g.* calix(4)arene, porphyrin, crown ether, cryptand]. The large number of substituents may cause elongation of the bonds, which produces increasing standard deviation values for elements with large ionic radii. On the basis of the analysis of lanthanide compounds found in the CSD, it can be shown that the lanthanide ions mostly form the eight- and nine-coordinate compounds.

All values of average bond-valence parameters (R_{ij}) diminish with increasing atomic number, which is in agreement with the decreasing ionic radii and atomic radii from lanthanum to lutetium (Fig. 1). The linear correlation between the average R_{Ln-N} and the atomic number of Ln (Z) can be described by the equation $R_{Ln-N} = 3.093–0.015Z$. Cerium and holmium deviate somewhat from the straight line. Although
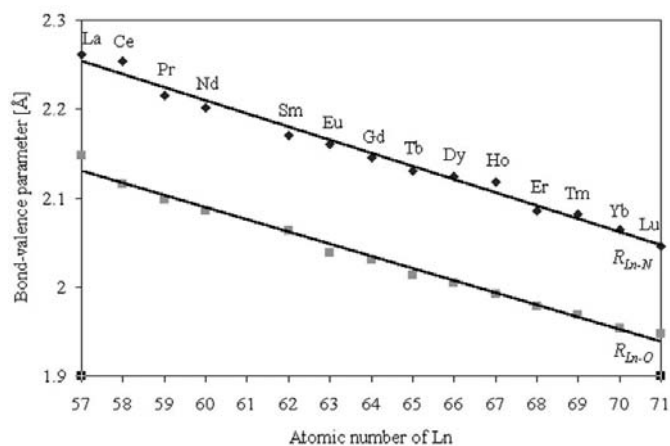
Figure 1
Average bond-valence parameters R_{ij} plotted against the atomic number of the lanthanide.
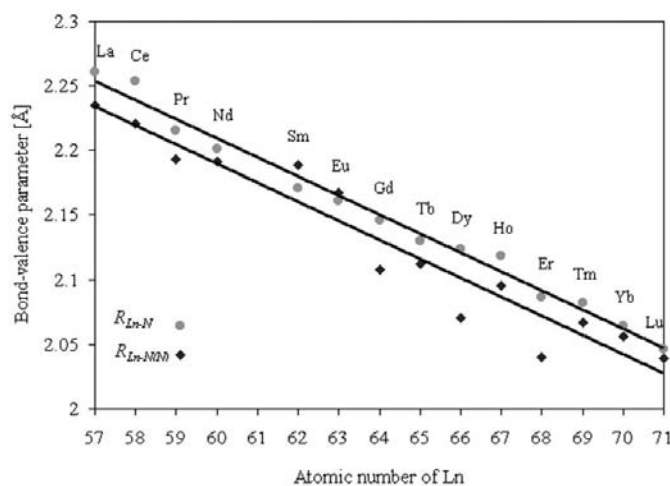
Figure 2
The $R_{Ln-N(N)}$ and R_{Ln-N} bond-valence parameters plotted against the atomic number of the lanthanide.

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[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: SN5018). Services for accessing these data are described at the back of the journal.

the values of the bond-valence parameter calculated for compounds containing only N-donor ligands ($R_{Ln-N(N)}$) vary from those calculated for compounds containing both N and O atoms around the lanthanide ion, they are located along the line which is parallel to the line formed by R_{Ln-N} (Fig. 2). The large data dispersion around the regression line in the case of $R_{Ln-N(N)}$ parameters is caused by the small number of available structures.

It is worth noting that the relative contribution of Ln—N and Ln—O bonds does not greatly influence the bond-valence parameter. However, slightly larger R_{ij} values can be observed for compounds containing one or two N atoms in the lanthanide coordination sphere, as shown in Fig. 3. The weakening of the Ln—N bond is probably caused by the presence of larger amounts of more electronegative elements changing the electron distribution at the metal.

Owing to the larger ionic radius of nitrogen, the metal–nitrogen bonds are longer than the lanthanide–oxygen bonds. However, the general trend of decreasing the average bond length along the lanthanide group and increasing the average bond length with increase of coordination number is preserved. This influences the linear correlation between the average Ln—N bond-valence parameter and the atomic number of Ln, which is almost parallel to the linear dependence of the average Ln—O bond-valence parameter calculated for metal-organic compounds (Fig. 1), as is the case for R_{ij} calculated for inorganic salts. The difference between R_{Ln-O} and R_{Ln-N} calculated for metal-organic compounds [0.116 (9) Å] is smaller than the difference determined for R_{ij} values calculated for inorganic compounds [0.157 (16) Å]. Brese & O'Keeffe (1991) described the correlation between bond-valence parameters for oxides and nitrides as $R_{iN} = -0.027 + 1.090R_{iO}$.

Bond-valence parameters calculated for metal-organic compounds and those for inorganic structures are different, thus the latter should not be used for metal-coordination complexes. For example, R_{ij} for the Ti—N bond (Palenik, 1997) in metal-organic compounds is obtained as 1.906 Å, but it is calculated as 1.93 Å for inorganic compounds (Brese & O'Keeffe, 1991). R_{ij} for the Sn—N bond (Palenik, 2001) in metal-organic compounds is 2.058 Å, but it is equal to 2.14 Å for inorganic compounds (Brese & O'Keeffe, 1991). For the Cu—N bond R_{ij} is smaller for inorganic salts; the bond-valence parameter is 1.657 Å for metal-organic complexes (Shields et al., 2000) and 1.61 Å for inorganic compounds (Brese & O'Keeffe, 1991). Compared with the work of Brese & O'Keeffe (1991), we find a systematic difference of ca 0.077 Å between bond-valence parameters determined from organic and inorganic structures. The same tendencies can also be observed for the bond-valence parameters calculated for lanthanide–oxygen bonds (Trzesowska et al., 2004) and other metal–oxygen bonds (Wood & Palenik, 1998; Wood et al., 2000; Kanowitz & Palenik, 1998).

According to Adams (2001) weak interactions with atoms of the second coordination shell significantly contribute to the valence sum and they should not be neglected in the case of inorganic compounds. The importance of bonds outside the

first coordination sphere has also been suggested by Wang & Liebau (1996a,b) in a study of the influence of lone-electron pairs of cations on the bond-valence parameters, and by Liebau (2000) in a study of the conduction paths of semiconducting electrons, as well as by Preiser et al. (1999) in a study of the connection between the bond-valence approach and long-range Coulomb interactions. There are no additional intermolecular interactions between the central atom and atoms of the second coordination sphere in lanthanide coordination compounds of higher coordination number (Dobler et al., 2003; Luo et al., 2003; Ionova et al., 2002; Rogachev et al., 2004), probably due to the electronic effects and steric hindrance. It can be stated on the basis of quantum-mechanical calculation results, especially the natural bond orbital (NBO) analysis and second-order perturbation analysis (Foster & Weinhold, 1980; Reed & Weinhold, 1985; Reed et al., 1988), which show interactions between both close-shell fragments including all intermolecular interactions, such as hydrogen bonds (Sosa et al., 2002), donor–acceptor (Lewis acid–base; Kempe et al., 2001) and any other attractive interactions between atoms and molecules (Ebrahimi et al., 2003). However, secondary bonding interactions can take place in lanthanide compounds of lower coordination number. On the basis of density functional theory (DFT) calculations, agostic interactions in the lanthanide silyl complexes and their analogues (Clark et al., 2002; Maron & Eisenstein, 2001; Eisenstein & Maron; 2002) have been found. The bond-valence method with the newly determined Ln—N bond-valence parameters allows the analysis of these types of interactions. As an example, consider the samarium compound $Sm[N(SiMe_3)_2]_3$ (Brady et al., 2003). Although in this compound disorder of the central atom exists, the distances are determined precisely and they agree with those obtained from quantum-mechanical calculations, thus this compound can be used as a model compound. The short $Sm\cdots C$ distances (3.003 Å) suggest the presence of additional
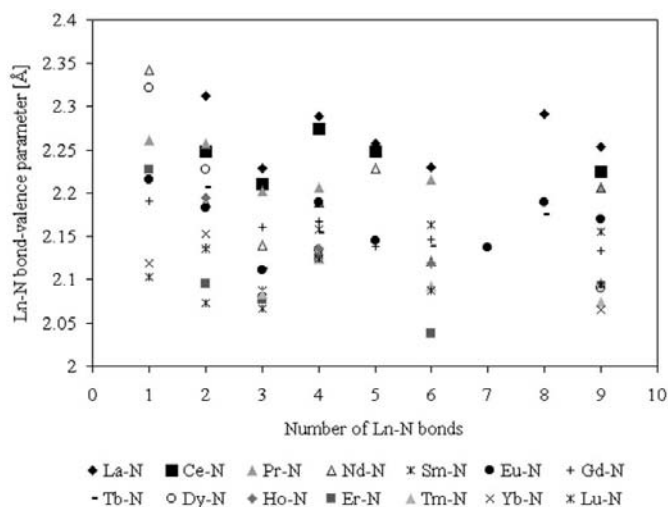
Figure 3
The influence of the relative contributions of Ln—N and Ln—O bonds on the bond-valence parameter value for nine-coordination complexes.

agostic interactions with one β-Si—C bond of each amido ligand. The total valence of samarium, calculated for R_{ij} = 2.171 Å and a mean Sm—N bond length of 2.284 Å, is 2.21 v.u. According to Palenik (2003), the difference between the calculated and predicted value of the total valence which is larger than 0.25–0.30 v.u. may indicate that some bonding interactions have been overlooked, or that extreme steric crowding has lengthened bonds. This is a reasonable guide to those structural studies that should be examined in more detail because of possible errors. Thus, it can be stated that in Sm[N(SiMe$_3$)$_2$]$_3$ there is space for other attractive interactions. If we include Sm···(Si—C) agostic interactions the total valence of samarium is 2.80 v.u. The Sm—C bond-valence parameter value of 2.401 (19) Å was calculated for seven samarium compounds with C-donor and mixed C-, N-, O-donor ligands (CSD refcodes: JAHMUA, Hitchcock $et\ al.$, 1989; MIMPIH, Giesbrecht $et\ al.$, 2002; MOQYOG, Gordon $et\ al.$, 2002; QISLUZ, Lin $et\ al.$, 2000; UMOJUB, Hou $et\ al.$, 2003; UMOKAI, Hou $et\ al.$, 2003; UMOKEM, Hou $et\ al.$, 2003). The compounds with silyl ligands (—SiR$_3$) were rejected because of the non-direct character of the bonding. Owing to the small size of the data set used in the calculations, the R_{Sm-C} value can be inaccurate but it was accurate enough to estimate the formal oxidation state. The results of DFT calculations (Klooster $et\ al.$, 1999; Clark $et\ al.$, 2002), structural studies (Tilley $et\ al.$, 1982) and bond-valence sum calculations exclude the possibility of Sm—(γ-C—H) attractive interactions. The total valence of samarium in Sm[N(SiMe$_3$)$_2$)]$_3$ is 3.40 v.u., provided that the six C—H···Ln agostic interactions (Brady $et\ al.$, 2003) are included in the calculation. Although accurate positions of the H atoms are not available from the X-ray study, the Sm—H bond-valence parameter value of 2.224 (87) Å was calculated approximately for four samarium compounds with H-, N- and O-donor ligands (CSD refcodes: JAQNOE, Onishi $et\ al.$, 1998; QAPBAK, Xie $et\ al.$, 1999; QAPBOY, Xie $et\ al.$, 1999; RUPJAN, Xie $et\ al.$, 1997). According to Hieringer $et\ al.$ (2000), the Ln···(Si—H) β-agostic interactions exist in the rare-earth disilylamide complexes. It is difficult to verify the presence of this interaction from the bond-valence method because the compounds under study possess ligands which are interacting with the metal by π-electrons. The lanthanide···π-donor ligand bond-valence parameters have not yet been determined.

4. Conclusions

The analysis of bond-valence parameters provides evidence for the necessity of calculating new parameters for metal-organic compounds. Lanthanide–oxygen and lanthanide–nitrogen bond-valence parameters have been found to be different for metal-organic compounds and inorganic structures. There is no obvious correlation between the number of N atoms in the coordination sphere and the value of the bond-valence parameter. The bond-valence method can be a useful tool in proving the presence of agostic interactions, as was shown in the example of a samarium silyl complex.

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