Bond-valence parameters of lanthanides

Agata Trzesowska,* Rafal Kruszynski and Tadeusz J. Bartczak

Department of X-ray Crystallography and Crystal Chemistry, Institute of General and Ecological Chemistry, Technical University of Lodz, Zeromskiego 116, 90-924 Lodz, Poland

Correspondence e-mail: agatat@p.lodz.pl

Ln—O and Ln—N bond-valence parameters have been computed in coordination complexes for lanthanides (Ln) at oxidation states other than +3 (Ce^{IV}, Sm^{II}, Eu^{II} and Yb^{II}). Moreover, Ln—Cl, Ln—S and Ln—C(π-bonded) bond-valence parameters are presented, as calculated for coordination compounds. In general, the bond-valence parameters decrease in the order Ln—O > Ln—C > Ln—N > Ln—Cl > Ln—S. It has been found that the values of bond-valence parameters decrease with increasing lanthanide atomic number for coordination compounds. As expected, the values of lanthanide–oxygen and lanthanide–nitrogen bond-valence parameters diminish with increasing lanthanide oxidation state. Several examples are given where the total valence of the lanthanide ion is apparently incorrectly assigned, as well as cases where bond-valence method calculations confirm the doubtful oxidation state assignment.

1. Introduction

If a compound can be obtained as a single crystal, X-ray diffraction is a routine method used to analyse it. The single-crystal technique allows the visualization of the structure of a compound, and provides information about bond lengths, the configuration of the molecule and the thermal motions of the atoms, but does not allow the identification of the oxidation state (exceptions are those compounds for which the electroneutrality rule can be used). Nevertheless, using the bond distances from diffraction experiments and employing the bond-valence method (BVM; Brown, 1977, 1992, 2002; Zachariasen, 1978; Hawthorne, 1994; Urusov, 1995; Urusov & Orlov, 1999; Mohri, 2003) one can establish the oxidation state without the necessity of carrying out other measurements, among which NMR spectroscopy (Evans & Hozbor, 1987) is the most popular.

Lanthanide chemistry at oxidation states other than +3 constantly develops. For many years, it was limited to four elements (Ce^{IV}, Sm^{II}, Eu^{II} and Yb^{II}). The first molecular complex of thulium(II) was isolated by Bochkarev et al. (1997). Subsequently, the compounds of divalent dysprosium, neodymium and holmium were synthesized. Divalent thulium and dysprosium compounds were found to be more powerful reducing agents than samarium(II) compounds (Evans & Allen, 2000; Evans et al., 2000; Fedushkin et al., 2001). Low-valent lanthanide compounds can be used in situ to accomplish dinitrogen reduction chemistry via organometallic intermediates (Evans et al., 2001; Evans, Allen et al., 2002 ; Evans et al., 2003). As the organometallic and coordination chemistry of lanthanides is not restricted to one oxidation state, the possibility exists that the total or partial reduction/oxidation of

Table 1
Bond-valence parameters for the $Ln^{II,IV}-O$ and $Ln^{II,IV}-N$ bonds (this work), the $Ln^{III}-O$ bonds (Trzesowska et al., 2004) and the $Ln^{III}-N$ bonds (Trzesowska et al., 2005).

CN: coordination number; n: No. of structures found; t: the size of the set used in the calculations (the number of lanthanide coordination centres forming bonds); s: bond-valence parameters calculated for compounds with ligands that cause the shortening of the $Ln-N$ bonds; r: bond-valence parameters calculated for all the remaining compounds.

	Ln—O bond-valence parameter [$R_{Ln^{II,IV}}-O$ (Å)]				Ln—N bond-valence parameter ($R_{Ln^{II,IV}}-N$ (Å))							
CN	Ce^{IV}	Sm^{II}	Eu^{II}	Yb^{II}	Ce^{IV}	Sm^{II}	Eu^{II}	$Eu^{II}r$	$Eu^{II}s$	Yb^{II}	$Yb^{II}r$	$Yb^{II}s$
4	–	–	–	1.983 (9)	–	2.318 (7)	–	–	–	2.168 (10)	2.168 (10)	–
n/t	0	0	0	6/6	0	2/3	0	0	0	9/11	9/11	0
5	–	2.126 (4)	2.105 (3)	1.991 (4)	–	2.316	2.291 (49)	2.291 (49)	–	2.107 (8)	2.107 (8)	–
n/t	0	6/6	2/3	7/7	0	1/1	1/2	1/2	0	2/2	2/2	0
6	2.069 (4)	2.132 (14)	2.105 (10)	1.989 (11)	2.148 (27)	2.238 (9)	2.218 (15)	2.232 (13)	2.143 (2)	2.098 (31)	2.098 (31)	–
n/t	11/15	5/7	3/4	11/13	2/2	7/7	10/12	9/10	1/2	11/11	11/11	0
7	2.071 (4)	2.087	2.098 (4)	–	2.224 (18)	–	–	–	–	2.088 (31)	2.141 (12)	2.035 (11)
n/t	2/5	1/1	2/5	0	2/2	0	0	0	0	3/4	1/2	2/2
8	2.076 (5)	–	–	1.978	2.179 (8)	–	2.105 (18)	2.186 (14)	2.065 (11)	2.014 (26)	2.106 (15)	1.948 (17)
n/t	26/36	0	0	1/1	11/11	0	8/12	3/4	5/8	11/12	5/5	6/7
9	2.080 (4)	2.111	2.093 (4)	2.009	2.166 (13)	–	2.015	–	2.015	–	–	–
n/t	3/3	1/1	2/2	1/1	2/2	0	1/1	0	1/1	0	0	0
10	2.078 (9)	2.130 (3)	2.111 (13)	–	2.182	–	–	–	–	–	–	–
n/t	6/6	3/4	2/2	0	1/1	0	0	0	0	0	0	0
Mean value	2.074 (4)	2.126 (7)	2.102 (6)	1.989 (8)	2.179 (11)	2.267 (8)	2.165 (61)	2.228 (18)	2.075 (8)	2.092 (24)	2.127 (14)	1.967 (16)

	Ce^{III}	Sm^{III}	Eu^{III}	Yb^{III}	Ce^{III}	Sm^{III}	Eu^{III}	Yb^{III}
Mean value	2.116	2.063	2.038	1.954	2.254	2.171	2.161	2.064

the central atom unexpectedly occurs under conditions used in the reaction.

Palenik (2003) and Roulhac & Palenik (2003) determined the $Ce^{IV}-O$ and $Sm^{II}-O$ bond parameters necessary to calculate the bond-valence sum (BVS). The aim of the present work was to establish the $Ln-O$ and $Ln-N$ bond-valence parameters for the coordination compounds of the four classical 'not trivalent' elements. Lanthanide–chlorine, lanthanide–sulfur and lanthanide–carbon (π-bonded) bond-valence parameters were also calculated. Two $Ln-S$ bond-valence parameter values (for Eu^{II} and La^{III}) have been given by Brown & Altermatt (1985). Brese & O'Keeffe (1991) provided the values of $Ln-S$ and $Ln-Cl$ bond-valence parameters calculated for the inorganic crystal structures of all rare-earth elements. Owing to the noticeable differences between the values of the bond-valence parameters for metal-organic and inorganic compounds, the previously determined bond-valence parameters should not be assumed to be applicable to metal-organic compounds.

2. Experimental

The bond lengths needed to calculate bond-valence parameters were obtained from the Cambridge Structural Database (CSD, Version 5.26, 2004; 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 lanthanides were considered, even those with high R-factor values,

because all deviations were averaged during the calculations. The oxidation state of the metal atom is not specified in many of the compounds available in the CSD [especially with regard to oxidation state +2, e.g. CSD refcode ZOGKOV (Abrahams et al., 1995), BEVXUW (Harder, 2004), XATWOE (Rabe et al., 2000), TEYVIC (Rogers, 1996), RADJIP (Hitchcock et al., 2000), CUWGEG (Evans, Grate et al., 1985)] or the oxidation state is incorrectly assigned. For example, in the CSD the central ion may be assigned as divalent, whereas in the original work it is correctly assigned as trivalent [CSD refcode SMNICD (Moore et al., 1972), KADKEG (Woodman et al., 2003), CUGPEZ (Deacon et al., 1984), EGIMUC (Chen et al., 2002)]. For one Sm^{III} compound in the original work the central atom is given as oxidation state +2 [CSD refcode RELNEB (Hou et al., 1996)]. Additionally, in one samarium compound the Sm is listed as having oxidation state +1 rather than +3 [DIGJEI (Evans, Hanusa & Levan, 1985)]. For these reasons, careful examination of the metal oxidation state was carried out for each structure. For each lanthanide atom, the coordination number was also taken into consideration. Bond-valence parameters were generally calculated for heteroleptic compounds, but the $Ln^{II,IV}-O$ bond-valence parameters were calculated for compounds containing only O-donor ligands because of the sufficient number of compounds having homoleptic coordination. The $Ln^{II,IV}-N$, $Ln-Cl$, $Ln-S$ and $Ln-C(\pi$-bonded) bond-valence parameters were calculated for compounds containing N, Cl, S, C(π-bonded) donors as well as for compounds containing both N,O, Cl,(O or N), S,(O or N) or C,O donor ligands around the lanthanide ion. Mixed Cl,O,N and S,O,N donors were used in the calculation of $Ln-$

Cl and Ln—S bond-valence parameters, respectively. The CSD reference codes of the lanthanide compounds and the calculated 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)

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

where V_i is the formal valence of the central atom i, d_{ij} is the distance between atoms i and j, and the summation is over all neighbours j that 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 ($j = $ N/Cl/S/C and O), (1) was modified to give

$$R_{ij} = b \ln\left(\left\{V_i - \sum \exp[(R_{iO} - d_{iO})/b]\right\}/\left[\sum \exp(-d_{ij}/b)\right]\right).$$

In order to allow for three different types of ligands ($j = $ Cl/S, O and N) (1) was modified to give

$$R_{ij} = b \ln\left[\left(V_i - \left\{\sum \exp[(R_{iO} - d_{iO})/b]\right.\right.\right.$$
$$\left.\left.\left. + \sum \exp[(R_{iN} - d_{iN})/b]\right\}\right)/\left[\sum \exp(-d_{ij}/b)\right]\right].$$

The contribution of Ln—O and/or Ln—N bonds to the valence of Ln is computed from the previously determined parameters $R_{\mathrm{Ln-O}}$ (Trzesowska et al., 2004), $R_{\mathrm{Ln-N}}$ (Trzesowska et al., 2005) and the known bond lengths. After subtraction of this amount from the formal valence, the remaining valence is used to compute $R_{\mathrm{Ln}-j}$. 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

3.1. Ln—O and Ln—N bond-valence parameters for lanthanides at oxidation states other than +3

Bond-valence parameters ($R_{\mathrm{Ln}^{\mathrm{II,IV}}}$—O, $R_{\mathrm{Ln}^{\mathrm{II,IV}}}$—N) for lanthanides at oxidation states other than +3 have been calculated as a function of the coordination number (CN) of Ln^{n+} and they are summarized in Table 1. It appears that they do not show an apparent dependence on the CN. Generally, a slight increase of $R_{\mathrm{Ln}-j}$ with increasing coordination number can be observed, although the variation is smaller than the standard uncertainties of $R_{\mathrm{Ln}-j}$ computed at a single coordination number. This implies that a single value of the bond-valence parameter can be used for the $\mathrm{Ln}^{\mathrm{II,IV}}$—O and $\mathrm{Ln}^{\mathrm{II,IV}}$—N bonds of each Ln, irrespective of the coordination number of Ln (bottom row of Table 1). The large standard

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: SN5037). Services for accessing these data are described at the back of the journal.

deviation values may be a result of the large spread of substituents connected to the lanthanide atom. It is worth noting that the relative contribution of Ln—N and Ln—O bonds does not greatly influence the value of the bond-valence parameter of $\mathrm{Ln}^{\mathrm{II,IV}}$—N, as has been previously observed for $\mathrm{Ln}^{\mathrm{III}}$—N bond-valence parameters (Trzesowska et al., 2005).

There are two publications in which bond-valence parameters for cerium(IV) (Roulhac & Palenik, 2003) and samarium(II) (Palenik, 2003) are given. The $R_{\mathrm{Ln}^{\mathrm{II,IV}}}$—O values presented in this paper (2.074 Å for Ce and 2.126 Å for Sm) and given in publications previously mentioned (2.068 Å for Ce and 2.116 Å for Sm) are similar despite the different assumptions concerning compound selection.

According to See et al. (1998) and Shields et al. (2000) two separate M—N bond-valence parameters should be established because of the different donor ability of the N ligand in different environments. The length of the bond depends not only on the bond valence but also on the ability of the N atom to form π bonds. The more π bonds the N atom forms, the stronger the M—N bond and the smaller the R_{M-N} value (Brown, 2002). Owing to the large standard deviations of $\mathrm{Eu}^{\mathrm{II}}$—N and $\mathrm{Yb}^{\mathrm{II}}$—N mean bond-valence parameter values (Table 1) the data were carefully examined. Different values of $R_{\mathrm{Ln}^{\mathrm{II,IV}}}$—N were established for $\mathrm{Eu}^{\mathrm{II}}$ (CN = 6, 8, 9) and $\mathrm{Yb}^{\mathrm{II}}$ (CN = 7, 8) according to the environment of the N atom. The $\mathrm{Ln}^{\mathrm{II}}s$—N bond-valence parameters were calculated for compounds in which the Ln—N bonds were shorter and the $\mathrm{Ln}^{\mathrm{II}}r$—N bond-valence parameters were calculated for all the remaining compounds. In the case of lanthanide compounds, one can distinguish three types of moieties that cause the shortening of the Ln—N bond length. Indeed, when the N atom forms a triple bond within its ligand (acetonitrile ligand), the Ln—N bond is much stronger and hence the Ln—N bond-valence parameter is significantly smaller [for example: JOYGUZ (Evans et al., 1998), HEFGOO (White et al., 1994), HEFGII (White et al., 1994)]. A similar effect was observed for the pyrazole ligand, but only when it acts as a bidentate ligand [GORJOM (Deacon et al., 1999), GORJUS (Deacon et al., 1999), JECKEH (Deacon et al., 1998)]. The pyrazole ligand, acting in a bridging fashion, does not shorten the bonds formed between the N atom and the metal. The smaller values of $R_{\mathrm{Ln}^{\mathrm{II}}}$—N were also noticed for complexes with ligands containing the triethanolatoamine moiety [WACBAE (Starynowicz & Gatner, 2003), XOXJUP (Starynowicz, 2001), XAGQIF (Burai et al., 2000), ULUCOT (Starynowicz, 2003)]. The O atoms of the pendant-arm ligands (Steed & Atwood, 2000) create bonds with the metal atom and force the tertiary N atom to be closer to the lanthanide atom. The strengthening of the Ln—N bond seems not to be related to the number of bonds which the N atom forms within its ligand, but rather to the electronic properties of the ligand. The $\mathrm{Ln}^{\mathrm{II}}s$—N bond-valence parameters should be used for the lanthanide(II) compounds containing such ligands as: acetonitrile, bidentate pyrazole and the triethanolatoamine moiety. For the $\mathrm{Eu}^{\mathrm{II}}$ and $\mathrm{Yb}^{\mathrm{II}}$ compounds containing other ligands, the $\mathrm{Ln}^{\mathrm{II}}r$—N bond-valence parameters should be used. The single $R_{\mathrm{Ln}^{\mathrm{II,IV}}}$—N values could have been calculated for $\mathrm{Ce}^{\mathrm{IV}}$ and $\mathrm{Sm}^{\mathrm{II}}$, but the

Table 2
Bond-valence parameters for $Ln^{III}-Cl$ bonds (this work) and $Ln^{III}-Cl$ bonds in inorganic compounds (IC; Brese & O'Keeffe, 1991).

CN: coordination number; n: No. of structures found; t: the size of the set used in the calculations (the number of lanthanide coordination centres forming bonds).

CN	Bond-valence parameter [R_{Ln-Cl} (Å)]													
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
4	–	–	–	2.595 (44)	2.614 (42)	2.545 (40)	2.569	2.527 (10)	2.506	2.498	2.516	–	2.506 (14)	–
n/t	0	0	0	3/3	3/3	2/3	1/1	2/2	1/1	1/1	1/1	0	3/4	0
5	–	2.585 (38)	2.578	2.539 (17)	2.503 (16)	2.518	2.521 (32)	–	–	2.442	2.388	–	2.475 (18)	2.564
n/t	0	2/2	1/1	4/5	7/8	1/1	2/2	0	0	1/1	1/1	0	7/7	1.1
6	2.520 (17)	2.500 (4)	2.507 (25)	2.527 (11)	2.497 (18)	2.434 (7)	2.427 (9)	2.409 (7)	2.388 (7)	2.375 (9)	2.376 (8)	2.352 (8)	2.357 (6)	2.373 (18)
n/t	3/4	2/2	7/7	18/30	11/15	5/5	8/9	11/13	8/9	2/2	12/15	2/2	32/40	5/5
7	2.504 (17)	2.512 (16)	2.511 (26)	2.474 (16)	2.447 (18)	2.436 (5)	2.437 (6)	2.410 (10)	2.401 (18)	2.381 (17)	2.386 (6)	2.383	2.348 (10)	2.328 (13)
n/t	8/11	7/8	6/6	12/13	13/14	9/10	8/8	4/4	5/5	5/5	11/11	1/1	18/18	9/9
8	2.532 (10)	2.504 (25)	2.514 (5)	2.511 (11)	2.451 (11)	2.441 (7)	2.418 (7)	2.407 (31)	2.464	2.394	2.379 (10)	2.399 (13)	2.382 (8)	2.382 (11)
n/t	15/16	2/3	12/14	14/15	9/10	7/8	4/8	3/4	1/1	1/1	2/2	3/3	2/2	2/2
9	2.554 (7)	2.547 (14)	2.540 (15)	2.500 (22)	2.466 (54)	2.497 (20)	2.511 (12)	2.526 (53)	2.428 (25)	–	–	–	2.397 (3)	–
n/t	18/20	8/8	10/10	12/12	2/2	7/9	7/9	2/2	2/2	0	0	0	1/2	0
10	2.639 (20)	2.756	–	2.549	–	2.651	–	2.665	–	–	–	–	–	–
n/t	5/6	1/1	0	1/1	0	1/1	0	1/1	0	0	0	0	0	0
Mean R_{Ln-Cl} value	2.545 (13)	2.538 (17)	2.521 (9)	2.512 (15)	2.481 (19)	2.468 (12)	2.457 (10)	2.437 (15)	2.407 (11)	2.399 (10)	2.385 (6)	2.381 (11)	2.376 (9)	2.361 (13)
R_{Ln-Cl} value (IC)	2.545	2.520	2.500	2.492	2.466	2.455	2.445	2.427	2.410	2.401	2.390	2.380	2.371	2.361

ligands that cause the shortening of the $M-N$ bonds were not observed among compounds of these elements. In spite of the relatively large weighted standard deviation values, these mean $Ln^{II,IV}-N$ bond-valence parameters can be used without any assumptions about the coordination number of the Ln atom. For example, for the seven-coordinate Ce^{IV} compound [JOWPIU (Hubert-Pfalzgraf et al., 1992)] and four-coordinate Sm^{II} compound [FUXSIA (Evans et al., 1988); the highest $R_{Ln^{II,IV}}-N$ values computed among coordination numbers] the BVS values are 3.92 and 1.84 v.u., respectively. For the nine-coordinate Ce^{IV} compound [NELLAR (Sailaja & Rajasekharan, 2001)] and six-coordinate and Sm^{II} compound [PIYVUO (Evans et al., 1994); the smallest $R_{Ln^{II,IV}}-N$ values computed among coordination numbers], the BVS values are 4.08 and 2.16 v.u., respectively. According to Palenik (2003) the difference between the calculated and predicted value of the total valence, 0.25–0.30 v.u., is acceptable.

Generally, the values of the $Ln-O$ and $Ln-N$ bond-valence parameters decrease with increasing oxidation state (Table 1). For the higher oxidation states, the bonds have larger valences and thus the bond lengths are shorter. A similar trend has been observed for Sb^{III} and Sb^{V} coordination compounds (Palenik et al., 2005). In the literature, examples of increasing R_{ij} values with increasing the oxidation state can be found, although the tendency of decreasing effective ionic radii (Shannon, 1976) is preserved [e.g. $Cu-L$ bond-valence parameters L = C, N, O, P, S, Se, Br, I (Shields et al., 2000); $Fe-L$ bond-valence parameters L = N, O, S (Liu & Thorp, 1993)]. There are also parameters which are strongly oxidation-state dependent, but not in a regular way (e.g. $Cr-O$ bond valence parameters; Wood et al., 2000). These results suggest that the R_{ij} value depends on the cation oxidation state in a distinct manner.

3.2. Ln—Cl bond-valence parameters

The $Ln-Cl$ bond-valence parameters (R_{Ln-Cl}) have been calculated as a function of the coordination number of Ln^{3+} and they are summarized in Table 2. It appears that they show a weaker than parabolic dependence on the CN. In general, the larger values of R_{Ln-Cl} can be observed for 4-, 5-, 10-coordinate lanthanide compounds. Owing to the large ligands acting in a tetradentate (or higher) fashion in the coordination sphere, the bonds are lengthened. This affects the standard deviation values, but does not significantly influence the bond-valence parameter value. The distributions of bond-valence parameters can be described by Gaussian curves. This implies that a single value of R_{Ln-Cl} can be used, irrespective of the coordination number of Ln (bottom row of Table 2).

The $Ln-Cl$ bond-valence parameters have been determined for the heteroleptic compounds. According to Brown (2002), parameters obtained in such a way can be less reliable. However, lanthanide compounds, in which the metal is bonded to one type of ligand, are unusual. The value of R_{Ln-Cl} calculated for heteroleptic compounds has universal character and can be used for mixed systems.

There are no lanthanide complexes with chloride ligands in which the central atom adopts a coordination number larger than 10, because of the large ionic radius of chlorine. For a given CN the number of coordinated chloride ions diminishes with increasing atomic number of the Ln. The complexes containing from one to four $Ln-Cl$ bonds are the most common. The maximum number of $Ln-Cl$ bonds, equal to 6, exists for La complexes.

All the weighted mean values of the bond-valence parameters diminish with an increase in the atomic number, which is in agreement with the lanthanide contraction (Fig. 1). The

Table 3
Bond-valence parameters for Ln^{III}−S bonds, the theoretical mean bond-valence parameters (T) (this paper) and the bond-valence parameters for Ln^{III}−S bonds in inorganic compounds (IC) (Brese & O'Keeffe, 1991).

CN: coordination number; n: No. of structures found; t: the size of the set used in the calculations (the number of lanthanides coordination centres forming bonds).
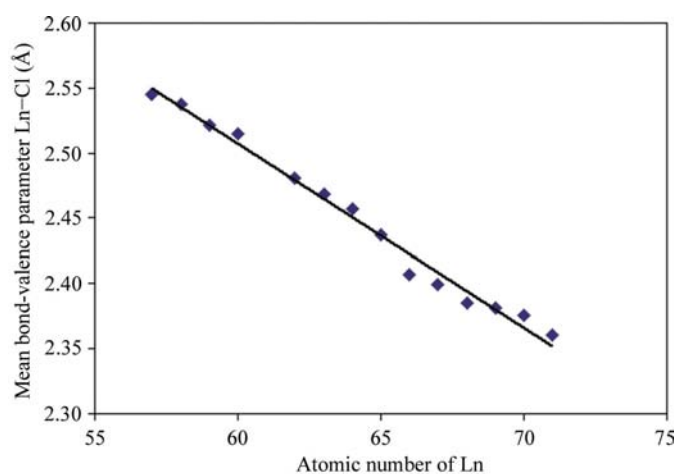
CN	Bond-valence parameter [R_{Ln-S} (Å)]													
	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
4	–	–	2.714	–	–	–	–	–	–	–	–	–	–	–
n/t	0	0	1/1	0	0	0	0	0	0	0	0	0	0	0
5	–	–	–	–	–	–	–	–	–	–	–	–	–	–
n/t	0	0	0	0	0	0	0	0	0	0	0	0	0	0
6	–	–	2.586	–	2.553 (9)	–	–	–	2.484	–	–	–	2.459 (11)	2.435
n/t	0	0	1/1	0	4/4	0	0	0	1/1	0	0	0	6/11	1/1
7	–	–	–	2.577 (65)	2.537 (11)	2.466	2.518	2.497 (4)	–	–	2.478 (24)	2.486	2.434	–
n/t	0	0	0	2/2	5/8	1/1	1/8	2/9	0	0	3/3	1/1	2/2	0
8	2.622 (5)	2.602 (10)	2.566 (17)	2.557 (3)	2.517 (60)	2.512 (4)	–	2.504	2.462	2.500	2.484 (8)	2.499	2.442 (17)	–
n/t	10/10	5/6	4/4	11/15	2/2	11/14	0	1/1	1/1	1/1	4/4	1/1	2/2	0
9	2.734	–	–	–	–	–	–	–	–	–	–	–	–	–
n/t	1/1	0	0	0	0	0	0	0	0	0	0	0	0	0
Mean R_{Ln-S} value	2.632 (11)	2.602 (10)	2.594 (26)	2.559 (6)	2.538 (9)	2.509 (5)	2.518 (0)	2.49 8(4)	2.473 (11)	2.500 (0)	2.475 (11)	2.493 (7)	2.453 (9)	2.435 (0)
R_{Ln-S} value (T)	2.619	2.593	2.569	2.561	2.531	2.517	2.507	2.489	2.475	2.461	2.449	2.437	2.423	2.414
R_{Ln-S} value (IC)	2.64	2.62	2.60	2.59	2.55	2.53	2.53	2.51	2.47	2.48	2.46	2.45	2.43	2.43

linear correlation between the average R_{Ln-Cl} and the atomic number of Ln (Z) can be described by the equation $R_{Ln-Cl} = 3.352\,(8) - 0.014\,(<1)Z$ (correlation coefficient $r2$ is equal to 0.986). Some small deviations from the linear dependence exist for neodymium and dysprosium.
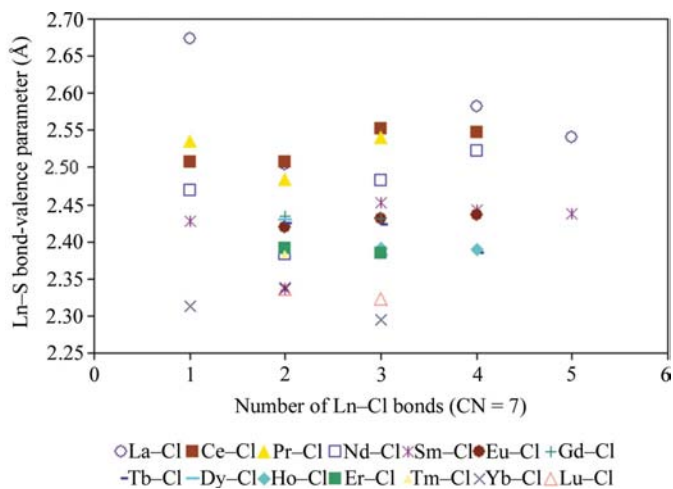
The relative contribution of Ln−Cl bonds does not greatly influence the value of the Ln−Cl bond-valence parameter (Fig. 2). However, slightly larger R_{ij} values can be observed for compounds containing one Cl atom in the lanthanide coordination sphere. Weakening of the Ln−Cl bond is probably caused by the presence of larger numbers of the more elec-

tronegative elements which alter the electronic distribution at the metal.

As was mentioned in §1 a systematic difference can be observed between the bond-valence parameters, based on the same equation, determined for coordination and inorganic compounds. For the Ln−Cl bond-valence parameter such a difference almost does not exist (Table 2). This probably results from the nature of the Cl atom acting as a ligand, which usually acts as a monodentate ligand (occasionally as a bridging ligand) regardless of the type of compound.

Figure 1
Average Ln−Cl bond-valence parameters plotted against the atomic number of lanthanide.
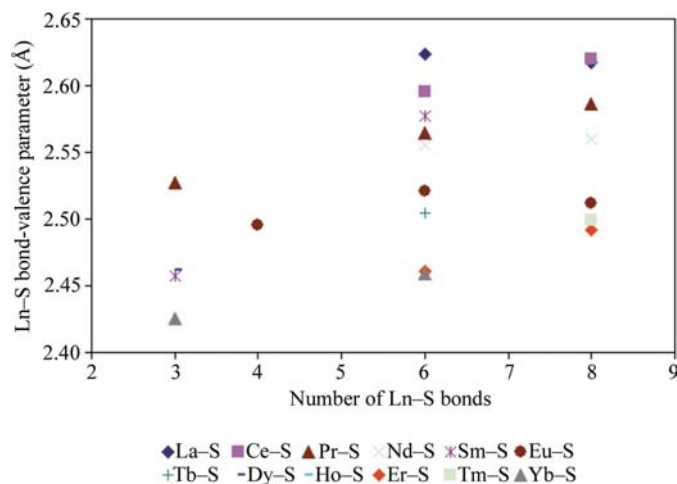

Figure 2
The influence of the relative contribution of the Ln−Cl bonds on the bond-valence parameter value for seven-coordination complexes.

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3.3. Ln—S bond-valence parameters

Establishing the values of Ln—S bond-valence parameters (R_{Ln-S}) seems useful because the Ln have a rich chemistry with S-donor ligands (thiolates, dithiocarbamates; Nief, 1998; Aspinall, 2001; Shen & Yao, 2002). Nevertheless, the number of molecular structures deposited in the Cambridge Structural Database is limited. The values of R_{Ln-S}, calculated as a function of the coordination number of Ln^{3+}, are summarized in Table 3. Owing to the large ionic radius of sulfur and its steric effect, the Ln form complexes with coordination numbers between 4 and 8. The distributions of bond-valence parameters can be described by Gaussian curves. This implies that a single value of R_{Ln-S} can be used, irrespective of the coordination number of Ln (mean values of R_{Ln-S}, Table 3). The complexes containing three, six and eight S atoms around the central atom are the most common (Fig. 3). It seems that the greater the number of Ln—S bonds, the greater the value of R_{Ln-S}.

In general, the weighted mean values of the bond-valence parameters decrease with increasing atomic number (Fig. 4). The correlation between the average R_{Ln-S} and the atomic number of Ln (Z) can be described by the equation $R_{Ln-S} = 3.307\,(18) - 0.012\,(1)Z$. Owing to the large deviations from the linear dependence (correlation coefficient equal to 0.92) and the relatively small number of molecular structures available, the theoretical values of the Ln—S bond-valence parameters have been calculated.

The difference between the R_{Ln-j} values and the effective ionic radii (IR; Shannon, 1976; CN = 6), described as $(IR_{Ln} + IR_j) - R_{Ln-j}$, is equal to 0.304 (10) Å for R_{Ln-O} (Trzesowska et al., 2004), 0.248 (15) Å for R_{Ln-N} (Trzesowska et al., 2005) and 0.299 (13) Å for R_{Ln-Cl}. The distinct value for R_{Ln-N} can result from the value of the effective radius of N (1.46 Å) used. In the literature other values of the N ionic radius can be found, whereas for O and Cl the values are almost invariable.
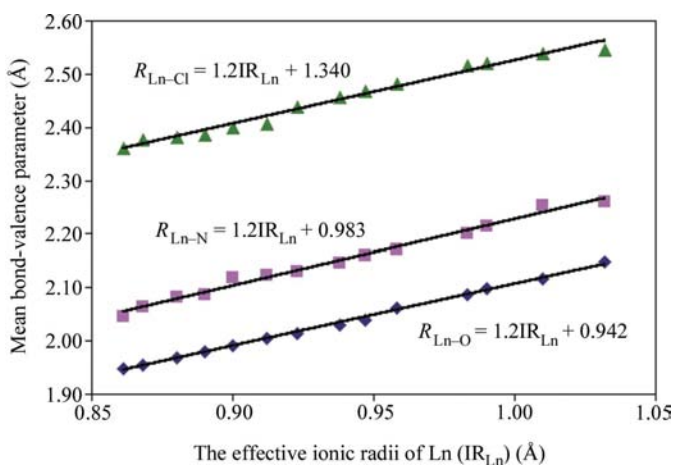
Theoretical R_{Ln-S} values can be established which rely on the assumption that the dependence of the Ln—S bond-valence parameter and the effective ionic radii of Ln is described by a linear function (regression coefficient equal to 1.2, Fig. 5), the difference between the sum of the effective ionic radii and R_{Ln-S} [$(IR_{Ln} + IR_S) - R_{Ln-S}$] is equal to 0.3 Å, and using the constant c (y intercept) from equations obtained for O [$c = 0.942\,(4)$] and Cl [$c = 1.340\,(11)$]. The dependence obtained is described by the equation $R_{Ln-S} = 1.2IR_{Ln} + 1.381$. The calculated theoretical Ln—S bond-valence parameters are summarized in Table 3.

Theoretical values and those determined from the crystal structures values of R_{Ln-S} are comparable (Fig. 4). Differences can be observed for heavier lanthanides: Ho (about
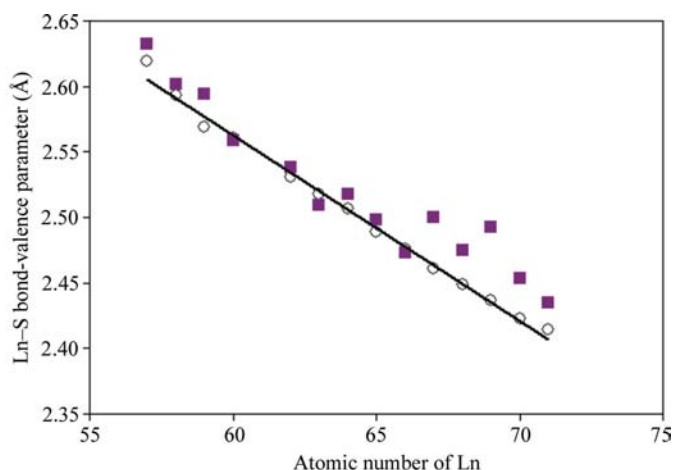
Figure 4
The theoretical Ln—S bond-valence parameters (circles) and Ln—S bond-valence parameters determined from crystal structures (squares) plotted against the atomic number of the lanthanide. The regression line [$R_{Ln-S} = 3.413\,(6) - 0.014\,(<1)Z$; correlation coefficient $r2$ is equal to 0.993] represents the relationship between the theoretical bond-valence parameters and the atomic number of the lanthanide.

Figure 3
The influence of the relative contribution of Ln—S bonds on the bond-valence parameter value for eight-coordination complexes.

Figure 5
Average Ln—O, Ln—N and Ln—Cl bond-valence parameters plotted against the effective ionic radii of the lanthanide.

Table 4
Ln^{III}—C(π-bonded) bond-valence parameters [R_{Ln-C} (Å)].

Ln: lanthanides; *n*: No. of structures found; *t*: the size of the set used in the calculations (the number of lanthanides forming bonds).

Ln	*n/t*	R_{Ln-C} (Å)
La	31/36	2.231 (7)
Ce	13/18	2.209 (10)
Pr	19/22	2.172 (5)
Nd	56/67	2.161 (9)
Sm	88/128	2.143 (4)
Eu	2/4	2.135 (41)
Gd	8/10	2.118 (14)
Tb	2/2	2.078 (42)
Dy	10/13	2.073 (12)
Ho	2/2	2.061 (12)
Er	7/9	2.058 (8)
Tm	4/6	2.047 (13)
Yb	43/78	2.008 (4)
Lu	15/20	1.999 (13)

0.039 Å), Er (about 0.026 Å), Tm (about 0.056 Å), Yb (about 0.030 Å) and Lu (about 0.021 Å). This may result from the small precision of the method used or from the specifics of the structures found. In complexes of these rare-earth elements, the central atom is coordinated by S atoms of ligands of relatively large rather than small ionic radii. Owing to the steric effect, the Ln—S bonds are longer than one would expect from the contraction of the lanthanides. The calculated theoretical Ln—S value can be verified only when a larger number of structures containing Ln—S bonds are available.

Since the sulfur has a larger ionic radius, the Ln—S bond-valence parameters are greater than the Ln—O, Ln—N and Ln—Cl bond-valence parameters. The R_{Ln-S} values calculated for coordination compounds and those for inorganic structures are different, as are R_{Ln-O} (Trzesowska *et al.*, 2004) and R_{Ln-N} (Trzesowska *et al.*, 2005). Compared with the work of Brese & O'Keeffe (1991) (Table 3), a systematic difference of ~ 0.018 (9) Å (excluding Dy) between bond-valence parameters can be found.

3.4. Ln—C(π-bonded) bond-valence parameters

The chemistry of the Ln—C bond is almost exclusively limited to complexes containing π-bonded ligands, *i.e.* mainly cyclopentadienyls and substituted derivatives (Schumann *et al.*, 1995; Hou & Wakatsuki, 2002; Zhou & Zhu, 2002). The homoleptic σ-bonded organolanthanide complexes are rare because of their sensitivity to oxygen and moisture (Aspinall, 2001). For this reason, the Ln—C bond-valence parameters have been calculated for complexes containing π-bonded ligands as well as for complexes containing mixed ligand, π-bonded and O-donor ligands. Each bond between the lanthanide ion and the C atom of the ligand was treated separately. The Ln—C bond-valence parameters were calculated on the basis of individual Ln—C bond lengths.

The bond-valence parameters (R_{Ln-C}) calculated are summarized in Table 4. The coordination numbers of Ln^{3+} were not taken into consideration. The distributions of the

bond-valence parameters can be described by Gaussian curves. The reliability of some of the bond-valence parameters might be questioned because there was only a few available structures, *e.g.* for europium, terbium, holmium and thulium, so there are not enough structures for reasonable statistics.

The mean bond-valence parameters diminish with increasing atomic number, which is in agreement with the lanthanide contraction. The linear correlation between the average R_{Ln-C} and the atomic number of Ln (Z) can be described by the equation $R_{Ln-C} = 3.103$ (11) $- 0.016$ (<1)Z (correlation coefficient $r2$ is equal to 0.979; Fig. 6). R_{Ln-C} are slightly larger for compounds with allyl and pentadienyl ligands. They show longer binding distances than other ligands, *e.g.* cyclooctatetraenyl ligands or substituted cyclopentadienyl derivatives.

The lanthanide–carbon(π-bonded) bond-valence parameters are larger than lanthanide–oxygen bond-valence parameters. In general, the bond-valence parameters for a given lanthanide decrease in the order: Ln—O > Ln–C(π-bonded) > Ln—N > Ln—Cl > Ln—S.

According to Brown (2002) the BVM should not be used for compounds containing aromatic systems or systems with odd-membered rings around the central ion unless the whole ligand is treated as a single atom. Apart from the large standard deviation values and a few questionable values, the bond-valence parameter values for a single Ln—C(π-bonded) bond proposed in this work make it possible to compute the total valence of the central atom.

3.5. Application of BVM

The organometallic and coordination chemistry of the lanthanides is not restricted to one oxidation state. The total or partial reduction/oxidation of the central atom can occur unexpectedly under the conditions used in the reaction. The oxidation state of the metal in a complex does not always remain the same as in the starting material.
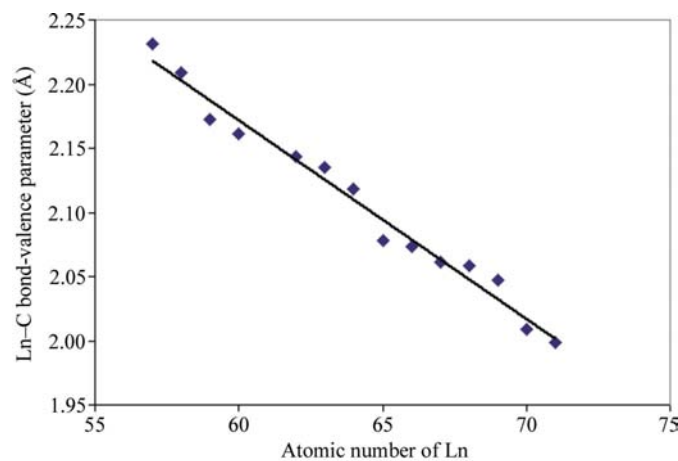
Figure 6
Average Ln—C bond-valence parameters plotted against the atomic number of the lanthanide.

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The crystal structure of hexakis(tetrahydrofurano)-ytterbium tetrakis(μ_3-selenido)tetrakis(phenylselenido)-tetrairon [CSD refcode IQASAU (Kornienko *et al.*, 2003)] was described by the authors as the first trivalent Yb complex that is stable as a thf solvate. The Yb oxidation state was established by comparing the Yb—O bond distances with bond distances in complexes containing $Yb(thf)_6^{2+}$. The total valence of Yb, calculated for $R_{Yb^{III}}$—O = 1.954 Å (Trzesowska *et al.*, 2004), is 1.91 v.u., whereas the total valence, calculated for $R_{Yb^{II}}$—O = 1.989 Å, is 2.10 v.u. These results suggest that the ytterbium ion in this compound is clearly divalent rather than trivalent.

In the case of 2,3,4-μ_3-chloro-l,2;1,2;2,3;2,4;3,4;3,5;4,5-heptakis(μ_2-chloro-2,5-bis(diethyl ether)-3,4,5-μ_3-oxo-1,1,3,-4,5-pentakis(η^5-pentamethylcyclopentadienyl)pentaytterbium [CSD refcode KASWEG (Zalkin & Berg, 1989)], the authors assume that the oxidation state of Yb is +3. This assumption is in poor agreement with the BVM calculations; BVS = 1.74 v.u. [for $R_{Yb^{III}}$—O = 1.954 Å (Trzesowska *et al.*, 2004) and $R_{Yb^{III}}$—Cl = 2.373 Å]. The BVS of 1.90 v.u. {calculated for $R_{Yb^{II}}$—O = 1.989 Å and for $R_{Yb^{II}}$—Cl = 2.405 Å [CSD refcode VUMKET (Bochkarev *et al.*, 1992)]} suggests that the ytterbium ion in this compound is divalent rather than trivalent.

A different situation exists for the compound reported by Chan *et al.* (1996; CSD refcode TINVOB). Those authors established the oxidation state of the Ce atom in a mixed (N- and O-donor) ligand complex on the basis of Ce—O and Ce—N bond lengths and *via* molecular mechanics calculations. The total valence of Ce, calculated for $R_{Ce^{IV}}$—O = 2.074 and $R_{Ce^{IV}}$—N = 2.179 Å, is 2.68 v.u., whereas the total valence, calculated for $R_{Ce^{III}}$—O = 2.116 Å (Trzesowska *et al.*, 2004) and $R_{Ce^{III}}$—N = 2.254 Å (Trzesowska *et al.*, 2005), is 3.08 v.u. These results suggest that the cerium ion in this compound is trivalent rather than tetravalent, which is possible because the ligand [2,4,6-tris-(4-*tert*-butyl-2-pyridyl)-1,3,5-triazine] can exist in the protonated form (Chan *et al.*, 1996).

In the compound presented by Evans, Giarikos *et al.* (2002; CSD refcode BAFVEK), BVS = 2.88 v.u. (for $R_{Eu^{III}}$—O = 2.038 Å; Trzesowska *et al.*, 2004). The authors confirmed the presence of trivalent europium by measuring the effective magnetic moment of the complex. The compound reported by Deacon *et al.* (2000; refcode XAZKAK) unexpectedly contains the Yb in the +3 oxidation state, which the authors established on the basis of $f \leftarrow f$ transitions in the electronic spectra. The BVS is equal to 2.93 v.u. [calculated for $R_{Yb^{III}}$—O = 1.954 Å (Trzesowska *et al.*, 2004) and for $R_{Yb^{III}}$—N = 2.064 Å (Trzesowska *et al.*, 2005)] supports that conclusion. The compound identified with the CSD reference code IFOPUO (Brouca-Cabarrecq *et al.*, 2002) was interesting since the mixed-valent Ce complex was obtained from the Ce^{III} compound as a starting material. The authors discussed the oxidation state problem in detail. The results of the BVS calculations [3.97 v.u. calculated for $R_{Ce^{IV}}$—O = 2.074 Å and $R_{Ce^{IV}}$—N = 2.179 Å, and 2.98 v.u. for $R_{Ce^{III}}$—O = 2.116 Å (Trzesowska *et al.*, 2004) and $R_{Ce^{III}}$—N = 2.254 Å (Trzesowska *et al.*, 2005)] are in agreement with the author based on the magnetic properties study.

4. Conclusions

Much progress has been made recently in the coordination chemistry of lanthanides. To date, many complexes of lanthanides with different ligands have been prepared and characterized by various physico-chemical methods. Although O- and N-donor ligands predominate, there are also compounds with P, S and halogen donors. Much interest in the organometallic chemistry has been driven by the application of organo-lanthanides in organic synthesis and catalysis. The bond-valence model can be treated as a method accompanying the single-crystal technique giving information about bond strength, the oxidation state of the central atom and the correctness of the structure solution. The bond-valence parameter values are prerequisites of the BVM usage. This was the reason for the calculation of the Ln—O and Ln—N bond-valence parameters of four classical 'not trivalent' elements and the Ln—Cl, Ln—S, Ln—C(π-bonded) bond-valence parameters

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