

A bond-valence investigation of two series of isostructural lanthanide compounds

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Motto: 'It is reasonable that any subject should be revisited from time to time, even age to age, and inspected with new ideas and techniques' (Dickey, 2007).

Since the days of Pauling it has been tacitly assumed that the valence, which is distributed between the bonds to neighbouring atoms, is the stoichiometric valence, $^{\text{stoich}}V$, which has integer values. It is shown here that this is not true. Instead, bond-valence sums (BVS) calculated for lanthanide (Ln) atoms of a series of garnet-type compounds $\text{Ln}_3^{\text{III}}\text{Te}_2^{\text{VI}}\text{Li}_3\text{O}_{12}$ deviate significantly from $^{\text{stoich}}V$. Values of $(\text{BVS})_{\text{Ln}}$ of this series, plotted *versus* the element number Z_{Ln} , show the same irregular sequence as: (i) the third ionization potentials of Ln atoms, (ii) the valence values previously calculated with quantum-chemical methods for lanthanide metals and sulfides, and (iii) the experimental efficiencies of the reactions between Ln^{I} and SF_6 in the gas phase. This indicates that in the $\text{Ln}_3\text{Te}_2\text{Li}_3\text{O}_{12}$ series the BVS values of the Ln atoms, which are 'rattling' in rather large and rigid voids of the structure, reflect the electronic structure of Ln. It is, therefore, concluded that BVS represent a non-integer valence, which is based on the electronic structure of bonded atoms, rather than $^{\text{stoich}}V$. For this non-integer valence the term 'structural valence' and the symbol $^{\text{struct}}V$ have been proposed. In another series of lanthanide chelates the $(\text{BVS})_{\text{Ln}}$ values deviate even more from $^{\text{stoich}}V_{\text{Ln}} = 3$ v.u. than in the garnet-type series. In the chelates the Ln atoms are 'squeezed' in rather small voids so that the electronic effects of Ln acting on $(\text{BVS})_{\text{Ln}}$ are overridden by stronger steric effects exerted by the organic ligands.

1. Introduction

Over the last few decades, lanthanide compounds have found increasing interest with regard to their valence states (Kaldis & Fritzler, 1982; Evans, 2007). In most lanthanide compounds the Ln atoms¹ have *stoichiometric valence*² values, *i.e.* a valence derived from the stoichiometry of the compound, $^{\text{stoich}}V_{\text{Ln}} = +3$ v.u. (valence units). In addition, several lanthanides are known to have $^{\text{stoich}}V_{\text{Ln}}$ values of +2 and +4 v.u. (*e.g.* Evans *et al.* 2002, 2003; Harder, 2004*a,b*; Edelman *et al.*, 2007*a,b*; Hitchcock *et al.*, 2008*a,b*). In the elemental state lanthanides have, like all other elements, $^{\text{stoich}}V_{\text{Ln}} = 0$ v.u. In Fig. 1 the known $^{\text{stoich}}V$ values for elements of the sixth period of the periodic system of elements (PSE) are shown. In contrast to these integer-number $^{\text{stoich}}V$ values, fractional-number valence values of lanthanides, which have been determined by spectroscopic measurements (*e.g.* Barla *et al.*, 2004; Dallera *et al.*, 2006), have been reported. The latter valence states are described as *mixed valences* and are asso-

¹Throughout this paper the term 'atom' is used regardless of cationic or anionic character. When necessary, the terms 'cationic atoms' and 'anionic atoms' are used instead of 'cations' and 'anions'.

²Where a term is introduced or defined in the text it is given in italics.

Table 1

Element numbers Z_{Ln} and ionic radii r_{Ln} of Ln^{III} atoms, which are eight-coordinated by oxygen atoms (Shannon, 1976), and calculated BVS values for the elements O, Li, Te and Ln (columns 4–7), which constitute the garnet-type compounds $Ln_3Te_2Li_3O_{12}$, and BVS values of Ln in the chelate series (column 8).

Lower part: appropriate values of $^{stoich}V$, coordination number CN and the values of the estimated mean errors, $^{estim}|\delta(BVS)_i|$. Bold-face BVS values deviate significantly from $^{stoich}V$. They are given as open circles in Figs. 2 and 3. Normal-face BVS values deviate insignificantly from $^{stoich}V$ and are given with filled symbols in Figs. 2 and 3.

1	2	3	Garnet-type series				8
			4	5	6	7	
Ln	Z	r_{Ln} (Å)	(BVS) _O (v.u.)	(BVS) _{Li} (v.u.)	(BVS) _{Te} (v.u.)	(BVS) _{Ln} (v.u.)	(BVS) _{Ln} (v.u.)
La	57	1.160	–	–	–	–	3.643
Ce	58	1.143	–	–	–	–	3.660
Pr	59	1.126	–2.002	1.123	5.777	3.031	3.656
Nd	60	1.109	–2.005	1.144	5.824	2.995	3.650
Sm	62	1.079	–2.013	1.208	5.824	2.962	3.594
Eu	63	1.066	–2.000	1.321	5.746	2.849	3.615
Gd	64	1.053	–1.991	1.303	5.473	3.011	3.626
Tb	65	1.040	–2.024	1.258	5.872	2.921	3.641
Dy	66	1.027	–2.036	1.292	5.903	2.915	3.583
Ho	67	1.015	–2.038	1.303	5.935	2.895	3.607
Er	68	1.004	–2.078	1.317	6.082	2.853	3.538
Tm	69	0.994	–2.056	1.303	6.148	2.909	3.533
Yb	70	0.985	–2.009	1.479	5.746	2.727	3.529
Lu	71	0.977	–2.012	1.368	5.903	2.744	3.360
$^{stoich}V$ (v.u.)	–	–	–2	1	6	3	3
CN	–	–	4	4	6	8	8 + 3
$^{estim} \delta(BVS)_i $ (v.u.)	–	–	0.04	0.038	0.186	0.080	0.080

ciated with the distribution of the valence electrons over hybridized atomic orbitals.

It is a general observation that inorganic structure types are rather flexible in accommodating atoms of different size, if cationic atoms of the upper periods of the PSE are considered. Consequently, for a given formula type $A_m A'_m A''_m X_n^3$ there are only a few structure types, each with a relatively large number of members. As the period number of the cationic atoms increases, structural flexibility decreases. Thus, a large series of strictly isotopic structures, so-called *isopointal structures*,⁴ divides. It forms several smaller series of crystal-chemically isotopic structures with subgroup–supergroup relationships and even different structure types. This is, for example, evident from a recent review of inorganic lanthanide compounds with complex anions (Wickleder, 2002). For instance, lanthanide silicates of the composition $Ln_2Si_2O_7$ are known to crystallize in at least six different structure types, $Ln_2[Si_2O_7]$, that contain $[Si_2O_7]$ double tetrahedra. Some of them have subgroup–supergroup relationships. In addition, three different structure types for $Ln_4[SiO_4][Si_3O_{10}]$ and one

³ In chemical formulae, the use of bold-face letters has been suggested for structure-site symbols to distinguish them from the usual element symbols, which are given as normal-face letters (Smith *et al.*, 1998). For example, **A** and **L** represent cations without regard to coordination and with lone electron pairs, respectively, and **X** represents monatomic anions.

⁴ Two structures are defined as isopointal if: (i) they have the same space-group type or belong to a pair of enantiomorphic space-group types, and (ii) the atomic positions occupied are the same in both structures (Lima-de-Faria *et al.*, 1990).

structure type for $Ln_6[SiO_4]_2[Si_4O_{13}]$ are known. They have the same bulk composition, but contain single and triple tetrahedra, and single and quadruple tetrahedra, respectively (Wickleder, 2002; Kahlenberg *et al.*, 2007; Müller-Bunz & Schleid, 2002; Fleet & Liu, 2004). Recently, however, two almost complete series of isopointal structures of lanthanide compounds have been synthesized and their structures determined (O’Callaghan *et al.*, 2006; Seitz, Oliver *et al.*, 2007; Seitz, Pluth *et al.*, 2007). This allows one to study the influence of the electronic structure of the Ln atoms on the crystal structure in such series. Therefore, we have analysed both series by application of the bond-valence concept.

Pauling (1929) postulated that the valence, V_i , of an atom in a compound is distributed between the bonds to its neighbouring atoms. Therefore, for each bond a *bond valence* s_{ij} is obtained via

$$V_i = \sum_j s_{ij}. \tag{1}$$

At present, the equation

$$V_i = \sum_j s_{ij} = \sum_j \exp[(r_0 - D_{ij})/b] = (BVS)_i, \tag{2}$$

which was introduced by Brown & Altermatt (1985) and where the term D_{ij} represents the experimentally determined bond lengths, is widely used to check the accuracy of a crystal structure or to determine the oxidation number of an atom. The bond-valence parameters r_0 and b are considered to be constant for a given type of **A–X** bond and for all **A–X** bond types, respectively; Brown, 2002).

Since the days of Pauling (1929), it has been tacitly assumed that the atomic valence V_i in (1) and (2) is the integer-number stoichiometric valence, $^{stoich}V$. It is shown here that this

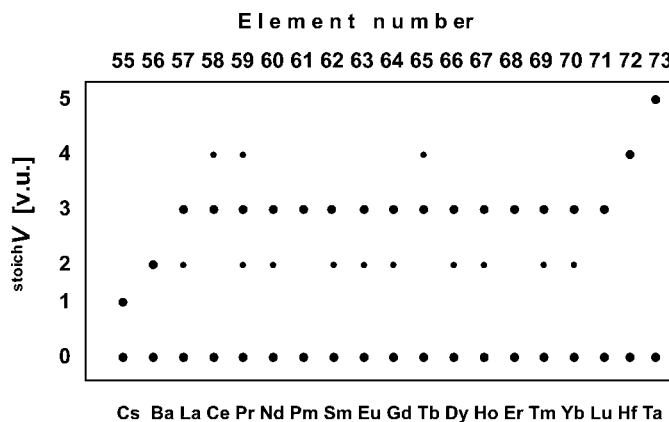
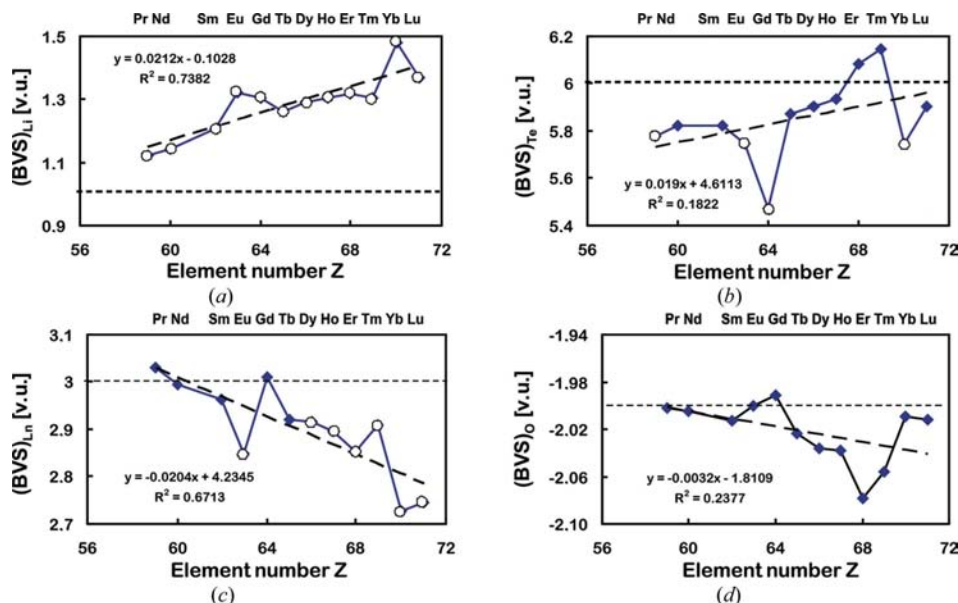


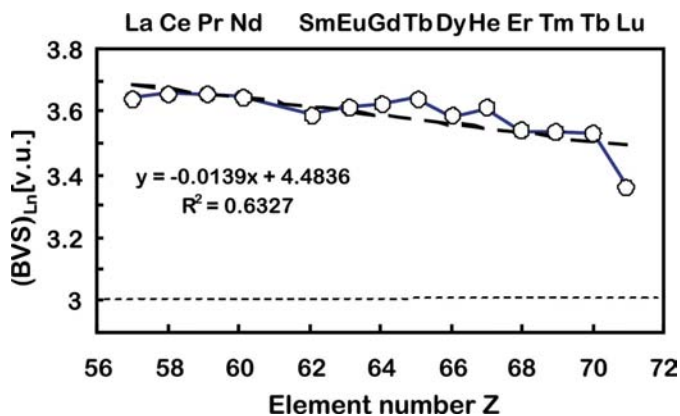
Figure 1
 $^{stoich}V$ values for elements of the sixth period of the periodic system of elements. Larger dots: more frequent $^{stoich}V$ values; smaller dots: less frequent $^{stoich}V$ values.


Figure 2

Calculated BVS values of atoms of the garnet-type phases $\text{Ln}_3\text{Te}_2\text{Li}_3\text{O}_{12}$ (O'Callaghan *et al.*, 2006) plotted versus the element number Z_{Ln} . The solid lines serve as an aid for the eye. The dashed lines are linear fits to the data. Thin dotted horizontal lines define the $^{\text{stoich}}V$ values. Open symbols: BVS values deviating significantly from $^{\text{stoich}}V_i$; filled symbols: BVS values deviating insignificantly from $^{\text{stoich}}V_i$. Note that the BVS scales of the four diagrams are not the same.

assumption is not correct. Instead, calculated BVS values for one of the two almost complete isopointal series of Ln compounds, the garnet-type phases of O'Callaghan *et al.* (2006), indicate that the BVS values:

- reflect the non-integer valence values for the Ln atoms, which were previously calculated using quantum-chemical methods (Strange *et al.*, 1999), and
- show the same irregular trend as the experimental efficiencies of gas-state reactions between Ln^1 and SF_6 (Cheng & Bohme, 2006).


Figure 3

Calculated $(\text{BVS})_{\text{Ln}}$ values plotted versus the element number Z_{Ln} for the chelate series of Seitz, Oliver *et al.* (2007) and Seitz, Pluth *et al.* (2007). Solid lines serve as an aid for the eye. The dashed line is a linear fit to the data. The horizontal dotted line indicates $^{\text{stoich}}V$.

Both the theoretically determined valence values and the experimental reaction efficiencies (for details see Cheng & Bohme, 2006) were interpreted to be a result of the electronic structures of the Ln atoms. This electronic structure is particularly expressed by the third ionization energies of the Ln elements (Lide, 2000). In the other almost complete series of isopointal chelate structures of Seitz, Oliver *et al.* (2007) and Seitz, Pluth *et al.* (2007), the influence of the electronic structure of the Ln atoms is partly concealed by steric influences exerted by the organic ligands.

2. Methods

2.1. Calculations of BVS values

BVS values were calculated using (2) and the bond-valence parameters, r_0 and b , tabulated by Brese & O'Keeffe (1991). For the

garnet-type series, the experimental bond length values, D_{ij} , were derived from the crystallographic data given in Table 1 of O'Callaghan *et al.* (2006). For the chelate series, the D_{ij} values used were those given in the supporting information to Seitz, Oliver *et al.* (2007) and Seitz, Pluth *et al.*, (2007), and, for the samarium chelate, in the CIF file kindly made available by the authors of Seitz, Oliver *et al.* (2007).

The calculated BVS values for all the atoms of the garnet-type series are presented in columns 4–7 and those for the Ln atoms of the chelate series in column 8 of Table 1. In Fig. 2 the calculated BVS values of all atoms for the garnet-type series are plotted versus the element number Z_{Ln} of the lanthanide element in question. A corresponding plot $(\text{BVS})_{\text{Ln}}$ versus Z_{Ln} of the chelate series is shown in Fig. 3.

2.2. Accuracies of calculated BVS values

In order to analyse the physical meaning of the calculated BVS values, their estimated errors have to be considered. If the error of the experimentally determined bond lengths, $|\delta(D_{ij})|$, is $\leq 0.01 \text{ \AA}$ – a value which in modern crystal structure analyses is usually not exceeded – error propagation rules (Mandel, 1964) lead to

$$\text{expect} |\delta(s_{ij})| \leq 0.038s_{ij} \quad (3)$$

and

$$\text{expect} |\delta(\text{BVS})_i| \leq 0.038s_{ij}(\text{CN})_i^{1/2} \quad (4)$$

for the expected mean errors of the calculated bond valences and BVS, respectively (Wang & Liebau, 2007). Since $\delta(D_{ij})$ is certainly not the only error in calculating BVS, the *estimated*

Table 2

Values of the estimated mean error, $^{\text{estim}}|\delta(\text{BVS})_i|$, and relative errors of $(\text{BVS})_i$ for the coordination polyhedra in the garnet-type compounds of O'Callaghan *et al.* (2006) and the chelate compounds of Seitz, Oliver *et al.* (2007) and Seitz, Pluth *et al.* (2007) of the lanthanides.

Polyhedron	stoich V_i (v.u.)	$^{\text{estim}} \delta(\text{BVS})_i $ (v.u.)	Relative error of $(\text{BVS})_i$ (%)
[LiO ₄]	1	0.038	3.8
[TeO ₆]	6	0.186	3.1
[LnO ₈]	3	0.081	2.7
[OA ₄]	-2	0.076	3.8
[LnO ₈ N ₃]	3	0.069	2.3

mean errors of s_{ij} and $(\text{BVS})_i$, $^{\text{estim}}|\delta(s_{ij})|$ and $^{\text{estim}}|\delta(\text{BVS})_i|$, may be higher than the expected mean errors of (3) and (4) by a factor of 2 (see Table 2). Therefore, whenever the difference between calculated bond-valence sums and the stoichiometric valence

$$\Delta V_i = |^{\text{calc}}(\text{BVS})_i - ^{\text{stoich}} V_i| \quad (5)$$

is greater than $^{\text{estim}}|\delta(\text{BVS})_i|$, the deviation is significant. Then ΔV_i cannot be ascribed to inaccuracies in the structure determination, but must have other chemical or physical reasons.

3. Results and discussion

3.1. The garnet-type series Ln₃Te₂Li₃O₁₂

In Ln₃Te₂Li₃O₁₂ garnets (O'Callaghan *et al.*, 2006), [Li^IO₄] tetrahedra and [Te^{VI}O₆] octahedra share corners to form a dense and rigid three-dimensional framework. Triangular dodecahedral cavities within the framework are occupied by Ln^{III} atoms.

The calculated BVS values for the oxygen atoms vary slightly between -1.99 and -2.08 v.u. (Table 1, column 4, and Fig. 2d). Their deviation from $^{\text{stoich}}V_{\text{O}} = -2$ v.u. is smaller than $^{\text{estim}}|\delta(\text{BVS})_i|$ and, therefore, insignificant. In comparison, the Li atoms are significantly 'overbonded', *i.e.* they are 'squeezed' in their tetrahedral voids. This overbonding of Li is jointly compensated by the Te^{VI} and Ln^{III} atoms. In fact, BVS values of Te vary between 5.47 and 6.15 v.u. with an average of 5.85 v.u., and those of Ln between 2.73 and 3.03 v.u. with an average of 2.90 v.u. (Table 1, columns 5-7, and Fig. 2a-c). This indicates that the Ln atoms are smaller than the rigid cavities formed by O atoms. That is, the Ln atoms are 'rattling' in their cavities and the smaller the Ln atoms, the more pronounced the misfit.

The regular variation of the Ln^{III} ionic radii as a function of the element number Z_{Ln} is included in the bond-valence parameters tabulated by Brese & O'Keeffe (1991), which are used to calculate the BVS values. Therefore, the calculated BVS values for all the Ln^{III} atoms are expected to be 3 v.u. with experimental errors that should be independent of Z_{Ln} . However, Fig. 2(c) shows that this is not the case. Indeed, the dashed line in this plot reflects the general trend of 'underbonding', which does not have to be linearly correlated with decreasing Ln size. However, the $(\text{BVS})_{\text{Ln}}$ values deviate

considerably and irregularly from this line. Since the Ln atoms are smaller than the cavities they occupy, the influence of the surrounding oxygen atoms on Ln will be small. Consequently, in this series of compounds the bond-valence sums of Ln are expected to reflect the electronic structure of the various lanthanide(III) atoms, which varies irregularly as a function of Z_{Ln} . Indeed, Fig. 2(c) shows a remarkable similarity to the variation pattern of the third ionization potentials of the Ln atoms (Fig. 4a; see Lide, 2000).

This conclusion is supported by a comparison of the present Fig. 2(c) with the plot of Fig. 4(b) that is reproduced from the work of Strange *et al.* (1999). These authors have calculated

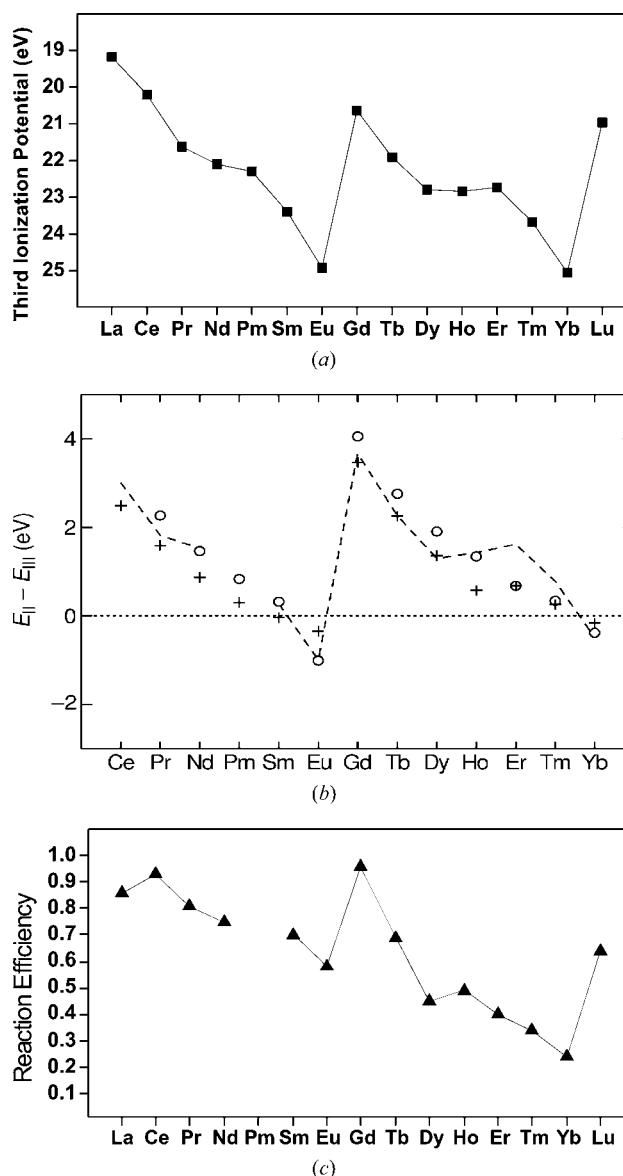


Figure 4 Diagrams showing the influence of the electronic structure of Ln atoms on: the third ionization potentials of Ln atoms (Lide, 2000), the valence of Ln calculated with quantum-chemical methods (open circles: Ln metals, crosses: Ln sulfides; Strange *et al.*, 1999), and the experimentally determined efficiency of the reactions between Ln^I and SF₆ (Cheng & Bohme, 2006). These three diagrams should be compared with the diagram of the calculated $(\text{BVS})_{\text{Ln}}$ values for the garnet-type compounds Ln₃Te₂Li₃O₁₂ (Fig. 2c).

with quantum-chemical methods the valence values for the Ln atoms in lanthanide metals and sulfides, taking into account the electronic structures of the Ln atoms, and plotted them *versus* Z_{Ln} . The striking similarity between Figs. 2(c) and 4(b) suggests that the bond-valence sums for the stoichiometrically trivalent Ln^{III} atoms in the garnet-type compounds are equivalent to the theoretically calculated valence values of stoichiometrically zerovalent Ln in metallic lanthanides, and to those of stoichiometrically divalent Ln^{II} atoms in LnS sulfides. It is, therefore, concluded that the BVS for Ln^{III} , calculated with (2) from structural data of the garnet-type lanthanide compounds, and the corresponding valence values, obtained through quantum-chemical calculations, are the same atomic property.

Our conclusion is further strengthened by a study of Cheng & Bohme (2006) involving reactions between Ln^{I} cations and SF_6 molecules, both in the gas state at 295 K. According to these authors, the experimental reaction efficiencies, which in Fig. 4(c) are plotted *versus* Z_{Ln} , correlate with the energy required to promote one $4f$ electron of Ln to a $5d^16s^1$ configuration. This makes two valence electrons available for bonding between Ln and F.

The similarity of the diagrams of the $(\text{BVS})_{\text{Ln}}$ values of the garnet-type series (Fig. 2c), the valence of Ln calculated with quantum-chemical methods (Fig. 4b) and the reaction efficiencies (Fig. 4c) indicate that the three effects have the same origin, namely the change of the electronic structure of Ln with Z_{Ln} shown in Fig. 4(a).

3.2. The chelate series $[\text{Ln}_3(\text{C}_{36}\text{H}_{32}\text{N}_7\text{O}_{10})\cdot\text{H}_2\text{O}]$

In the series of complexes studied by Seitz, Oliver *et al.* (2007) and Seitz, Pluth *et al.* (2007), each Ln^{III} atom forms three pairs of bidentate chelate bonds to the *para*-substituted O atoms of three isoquinoline systems, which are linked by amine bridges to form a large anionic ligand. The bond-valence values s_{ij} of these six bonds vary between 0.48 and 0.43 v.u. for the La chelate and decrease to 0.43 and 0.39 v.u. for the Lu chelate. The coordination of each Ln atom is supplemented by one O atom from a neighbouring complex and one O atom of a H_2O molecule. The s_{ij} values of these Ln–O bonds decrease from 0.40 to 0.38 v.u. and from 0.33 to 0.30 v.u. for the La and Lu chelates, respectively. For each of the Ln chelates, Ln has, in addition to these eight bonds, three N-atom neighbours, for which s_{ij} values between 0.07 and 0.06 v.u. are calculated.⁵ According to (4), these Ln–N interactions should be considered as very weak bonds, so the coordination sphere of Ln is $[\text{LnO}_8\text{N}_3]$. For more details of the structures see Seitz, Oliver *et al.* (2007) and Seitz, Pluth *et al.* (2007).

The calculated BVS values for the Ln atoms in these chelate compounds are listed in column 8 of Table 1 and plotted *versus* the element number Z_{Ln} in Fig. 3. The $(\text{BVS})_{\text{Ln}}$ values vary

between 3.66 and 3.36 v.u., and thus deviate much more from $\text{stoich}V_{\text{Ln}} = +3$ v.u. than the estimated error $^{\text{estim}}|\delta(\text{BVS})_i|$, which is 0.069 v.u. (Table 2). Consequently, all deviations are significant and cannot be explained by inaccuracies in the experimental determination of the crystal structures.

It strikes the eye that the calculated $(\text{BVS})_{\text{Ln}}$ values for the chelate series of Seitz, Oliver *et al.* (2007) are much larger than the corresponding values $(\text{BVS})_{\text{Ln}}$ in the garnet-type series. This is interpreted as being due to the fact that the three pairs of *para*-substituted O atoms of the ligand form six strained chelate bonds to Ln. Thus they exert strong steric effects on the Ln atom. The Ln atoms of the chelate series are ‘squeezed’ in their coordination spheres, whereas they ‘rattle’ in the larger cavities of the garnet-type compounds. The larger the Ln atoms the stronger the steric effect in the chelates and, therefore, the higher the calculated BVS values. As a consequence, strong steric effects in the chelate series ‘conceal’ the electronic effects, which are present in the garnet-type compounds. A comparison of Fig. 3 with Fig. 4, therefore, does not reveal the similarity seen between Fig. 2(c) and Fig. 4.

4. Conclusions

(i) Since in both series of isopointal Ln compounds there are a considerable number of values $\Delta V_i = |^{\text{calc}}(\text{BVS})_i - \text{stoich}V_i|$ that are significantly larger than $^{\text{estim}}|\delta(\text{BVS})_i|$, the $(\text{BVS})_i$ values cannot represent the integer-number stoichiometric valence, $\text{stoich}V_i$.

(ii) Usually, in inorganic structures, cationic atoms adapt to the anionic framework and *vice versa*. In the garnet-type series of Ln compounds (O’Callaghan *et al.*, 2006) the anionic framework is too rigid to adjust to Ln atoms of varying size. The Ln atoms occupy cavities in the framework that are larger than Ln^{III} . Under such conditions, the influence of the Ln electronic structure on the $(\text{BVS})_{\text{Ln}}$ values can be seen, because it is not hidden by other effects. A comparison of Fig. 2(c) with Figs. 4(b) and (c) strongly suggests that $(\text{BVS})_{\text{Ln}}$ values, quantum-chemically calculated valences of Ln (Strange *et al.*, 1999) and experimentally determined efficiencies of the reactions between gaseous Ln^{I} and SF_6 (Cheng & Bohme, 2006) represent the same valence property. This valence is different from $\text{stoich}V_{\text{Ln}}$. A comparison of Fig. 2(c) with Fig. 4(a), in addition, shows that in the garnet-type Ln compounds, $(\text{BVS})_{\text{Ln}}$ is determined by the third ionization energy of the Ln atoms.

(iii) It seems reasonable to assume that this interpretation of BVS applies not only to BVS values of lanthanide atoms, but also to BVS values in general.

(iv) Since BVS and $\text{stoich}V$ are two different valence properties, they should be described by different terms. For the valence property reflected by BVS the term ‘structural valence’ and the symbol $^{\text{struct}}V$ have been proposed (Liebau & Wang, 2005), because its property depends on the structure of a compound. In comparison, the ‘stoichiometric valence’, $\text{stoich}V$, is derived from the stoichiometry of a compound.

⁵ Supplementary data for this paper, including a complete list of bond-valence values, s_{ij} , for the chelate series, are available from the IUCr electronic archives (Reference: SN0041). Services for accessing these data are described at the back of the journal.

(v) In the series of Ln chelates of Seitz, Oliver *et al.* (2007) and Seitz, Pluth *et al.* (2007) the Ln atoms are 'squeezed' in small voids formed by the organic ligands. Therefore, the weak influence of the electronic structure of Ln on $(BVS)_{Ln}$ is overridden by stronger steric effects exerted by the ligands. Deviations of $(BVS)_{Ln}$ from $^{stoich}V$ (Fig. 3) are caused by both the electronic structure of the Ln and the dominating steric effects exerted by the anionic ligand.

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