Compounds with a ‘stuffed’ anti-bixbyite-type structure, analysed in terms of the Zintl–Klemm and coordination-defect concepts

Angel Vegas, Raymond L. Martin and D. J. M. Bevan


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Compounds with a ‘stuffed’ anti-bixbyite-type structure, analysed in terms of the Zintl–Klemm and coordination-defect concepts

The bixbyite structure (Mn₂O₃) (Ia₃) is often described as a distorted face-centered cubic (f.c.c.) array of Mn atoms, with O atoms occupying 3/4 of the tetrahedral holes. The empty M₄ tetrahedra are centred at 16c. In anti-bixbyite structures (Mg₃N₂), cation vacancies are centred in empty N₄ tetrahedra. If 16 hypothetical atoms were located at this site they would form the structure of γ-Si. This means that anti-bixbyite structures are ideally prepared to accommodate Si(Ge) atoms at these holes. Several compounds (Li₃AlN₂ and Li₃ScN₂) fully satisfy this expectation. They are really anti-bixbyites ‘stuffed’ with Al(Sc). The presence of these atoms in 16c is illuminated in the light of the extended Zintl–Klemm concept (EZKC) [Vegas & García-Baonza (2007). Acta Cryst. B63, 339–345], from which a compound would be the result of ‘multiple resonance’ pseudo-structures, emerging from electron transfers between any species pair (like or unlike atoms, cations or anions). The coordination-defect (CD) concept [Bevan & Martin (2008). J. Solid State Chem. 181, 2250–2259] is also consistent with the EZKC description of the pseudo-structures. A more profound insight into crystal structures is gained if one is not restricted to the contemplation of classical anions and cations in their conventional oxidation states.

1. Introduction

The mineral bixbyite (Mn₂O₃) and isostructural compounds like Sc₂O₃ and In₂O₃ (Zachariasen, 1928) are cubic. The space group of bixbyite is Ia₃, with Z = 16. The Mn atoms occupy two crystallographically independent sites, 8b and 24d, whereas all the O atoms are equivalent, located at 48e. The structure has often been described (Wells, 1975) as a slightly distorted f.c.c. array of Mn atoms, with the O atoms occupying 3/4 of the tetrahedral holes. Hence, bixbyite has also been regarded as an anion-deficient, fluorite-related structure, M₄O₆□₂, with the vacant site, designated □, located in the anion sublattice.

There are well known anti-bixbyite-type compounds such as N₂Mg₃ (von Stackelberg & Paulus, 1933): this example can be similarly regarded as a cation-deficient, anti-fluorite structure, N₂Mg₃□₂M, with the vacant site, □M, now located in the cation sublattice.

The similarity (topology and bond lengths) of cation arrays with the structures of the parent metals was also reported by Ramos-Gallardo & Vegas (1995), as an example of what have been called ‘real stuffed alloys’ (Martínez-Cruz et al., 1994; Vegas, 2000; Vegas & Jansen, 2002; Vegas et al., 2001). Very recently, Bevan & Martin (2008) have reported a crystal-chemical study in which their ‘coordination-defect theory’ of anion vacancies or voids was applied to analyse the structures of the anion-deficient, fluorite-related sesquioxide minerals bixbyite, braunite and parwelite.
In that paper, Bevan & Martin (2008) made an unusual observation, i.e. they noticed that in bixbyite the 16 vacancies (a quarter of the tetrahedral holes in the f.c.c. cation array) correspond to the positions of the 16c site of the space group Ia\(\overline{3}\), and that when an anion vacancy, \(\square\), is located at this site, the pattern represented in Fig. 1(b) is obtained. Looking at this array, we soon recognized that the pattern is coincident with that of the quenched high-pressure \(\gamma\) phases of Si and Ge (Wentorf & Kasper, 1963; Kasper & Richards, 1964; see Fig. 1a): these have not only the same space group (Ia\(\overline{3}\)) as bixbyite, but the Si(Ge) atoms occupy the same 16c sites as the bixbyite vacancies. Both structures are compared in Figs. 1(a) and (b).

At first glance, this feature could be considered as an accidental and unremarkable coincidence. However, encouraged by our intuition, and taking into account that many structures can be illuminated by the Zintl–Klemm concept (hereafter ZKC; Zintl, 1939; Klemm, 1958), we decided that this structural coincidence was worthy of a deeper analysis. This decision was based on two observed features. On the one hand, there was our previous experience of how the elemental structures were often preserved in the compounds (Vegas, 2000; Vegas & Jansen, 2002), and on the other because the presence of ‘foreign’ atoms can stabilize a given structure, as happens in the Zintl phases (Santamaría-Pérez & Vegas, 2003; Santamaría-Pérez et al., 2005; Vegas & García-Baonza, 2007). This feature occurs not only in alloys but also in oxides and can be considered as an extension of the Zintl–Klemm concept. Our first thought was that tetrahedral voids, \(\square_{M}\), in the cation sublattice of the anti-bixbyite structure should be the ideal sites to accommodate an atom such as Si or Ge: in other words, it would seem that the anti-bixbyite structure ‘is well prepared to accommodate Si(Ge) atoms that, when present, should necessarily be located in these holes’.

To test this hypothesis, we have undertaken the present study to ascertain whether ‘stuffed’ anti-bixbyite-type compounds of the general stoichiometry \(M_{n}SiX_{2}\), could exist, and also whether the Si (or indeed other) atoms would be located at the predicted positions.

Subsequently, we discovered the prior existence of a paper by Niewa et al. (2003) on the structure of Li\(_3\)ScN\(_2\), in which they reported thoughts very similar to ours. Their paper contains the following quote: ‘Focussing on the [Sc(N\(_3\))\(_{2}\)] framework, the Sc arrangement is topologically equivalent to the Si arrangement in \(\gamma\)-Si …

As the Li\(_3\)N\(_2\) substructure is isosstructural with that of Mg\(_3\)N\(_2\) and \(\alpha\)-Ca\(_3\)N\(_2\) (anti-bixbyite), the [Sc(N\(_3\))\(_{2}\)] framework consequently corresponds to the occupation of the unoccupied tetrahedral holes in the anti-bixbyite structure with Sc’.

**However, Sc is not Si(Ge)!** The electron configuration and stereochemical preferences of Sc usually differ substantially from those of Si and Ge.

**2. Results and discussion**

2.1. Extended Zintl–Klemm concept

If our hypothesis is valid, the existence of some compounds of the general formula \(M_{3}SiX_{2}\) would be expected. For such a compound, the sub-array \(M_{3}X_{2}\) should have the desired anti-bixbyite structure, and the foreign atom (Si, Ge) should be located at the 16c site of the space group Ia\(\overline{3}\). Considered as a whole, without any distinction between cations, the compound would be formulated as \(M_{3}X_{2}\), which corresponds to the stoichiometry of an anti-fluorite structure, \(i.e.\ M_{3}X\) (Mg\(_3\)Si, for example; Owen & Preston, 1924), rather than that of fluorite.

We now know of the existence of numerous ternary compounds with the same space group Ia\(\overline{3}\), such as, for example, Li\(_3\)AlN\(_2\), Li\(_3\)GaN\(_2\), Li\(_2\)(Ge\(_{0.67}\)Ga\(_{0.33}\))N\(_2\) and,
more recently, another such compound, Li₅ScN₂, as quoted above. Then there are other compounds of the general formula Li₅[(MIV)₀.₆₇Li₀.₃₃]N₂, with MIV = Si, Ti. In all of these, the cations of the [(MIV)₀.₆₇Li₀.₃₃] group are disordered.

Furthermore, there is also a group of compounds, Li₅MIVN₄ (MIV = Mn, V, Nb, Ta), which crystallize in the space group Pa₃, a sub-group of Ia₃ from which the body-centering operation has been lost. The formulae should more correctly be written as Li₅[MIVLi]N₂, by analogy with Li₅[(MIV)₀.₆₇Li₀.₃₃]N₂ (MIV = Ge), since the Li and MIV atoms in the square brackets are now ordered on two 8c sites of the space group, corresponding almost exactly with the 16c sites of Ia₃. All these compounds, as well as their references are summarized in Table 1.

In these various compounds, it is encouraging to see that the Al(Ga,Sc) atoms, the disordered sets [(MIV)₀.₆₇Li₀.₃₃] and the ordered sets [Li[MIV]] are all located in the relevant sites which give rise to the γ-Si framework. However, the crucial question is: why are the diverse atoms of these sets disposed in the tetrahedral network expected for Si(Ge)? The first impression is: why are the diverse atoms of these sets disposed in the electronic configuration and stereochemical properties (Santa-

<table>
<thead>
<tr>
<th>Compound</th>
<th>Stuffing cation</th>
<th>Space group</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₅AlN₄</td>
<td>Al</td>
<td>Ia₃</td>
<td>Juza &amp; Hund (1948)</td>
</tr>
<tr>
<td>Li₅GaN₄</td>
<td>Ga</td>
<td>Ia₃</td>
<td>Juza &amp; Hund (1948)</td>
</tr>
<tr>
<td>Li₅ScN₄</td>
<td>Sc</td>
<td>Ia₃</td>
<td>Niewa et al. (2003)</td>
</tr>
<tr>
<td>Li₅[Ge₀.₆₇Li₀.₃₃]N₂</td>
<td>Ge, Li</td>
<td>Ia₃</td>
<td>Juza et al. (1953)</td>
</tr>
<tr>
<td>Li₅[Si₀.₆₇Li₀.₃₃]N₂</td>
<td>Si, Li</td>
<td>Ia₃</td>
<td>Juza et al. (1953)</td>
</tr>
<tr>
<td>Li₅[Ti₀.₆₇Li₀.₃₃]N₂</td>
<td>Ti, Li</td>
<td>Ia₃</td>
<td>Juza et al. (1953)</td>
</tr>
<tr>
<td>Li₅[MnLi]N₄</td>
<td>Mn, Li</td>
<td>Pa₃</td>
<td>Niewa et al. (2001)</td>
</tr>
<tr>
<td>Li₅[VLi]N₄</td>
<td>V, Li</td>
<td>Pa₃</td>
<td>Niewa &amp; Kniep (2001)</td>
</tr>
<tr>
<td>Li₅[NbLi]N₄</td>
<td>Nb, Li</td>
<td>Pa₃</td>
<td>Vennos &amp; DiSalvo (1992)</td>
</tr>
<tr>
<td>Li₅[TaLi]N₄</td>
<td>Ta, Li</td>
<td>Pa₃</td>
<td>Wachsmann &amp; Jakobs (1992)</td>
</tr>
</tbody>
</table>

In the structures of the γ-Si(Ge) phases the four linkages are almost equal (Si—Si distances of 3 × 2.38 Å, 1 × 2.37 Å), whereas in Li₅AlN₃, the equivalent Al—Al distances show a somewhat greater difference (3 × 3.61 Å, 1 × 3.85 Å); in the case of Li₅ScN₂, these distances are 3 × 3.55 and 1 × 4.25. If the single longer linkage in each case were to be omitted, we would obtain the pattern represented in Fig. 1(c) for Li₅AlN₂. This consists of two infinite, interpenetrating subsets. These independent, three-connected Al networks simply interpenetrate, as shown in Figs. 1(c) and (d).

It should be remarked that this three-connected network is the one expected for the Group 15 elements (N, P, As etc.), and has been identified as the Al sub-array in Sr₅Al₂O₅Cl₂ (Santamaría-Pérez, 2006). This skeleton is represented in Fig. 1(e) and its structure can be interpreted in light of the ZKC. Here, the three Sr atoms act as donors. One of them transfers two electrons to the two Cl atoms. The two remaining Sr atoms transfer their four valence electrons to the Al atoms, converting them into (Ψ-P) and, consequently, the Al₂O₅ group becomes (Ψ-P₂O₅). Compare Figs. 1(d) and (e).

The structural behaviour of molecular N₂ illustrates this interpretation. At 115 GPa and 2600 K, nitrogen undergoes a phase transition adopting the three-connected structure represented in Fig. 1(f) (Eremets et al., 2004). The structure is also cubic, P2₁3, with a = 3.45 Å. The N atoms are located at 8a (x, x, x = 0.067), forming the same structure as the Al atoms (Ψ-P) in Sr₅Al₂O₅Cl₂ (Leib & Müller-Buschbaum, 1986). The important issue here is that the Al network, discovered in Sr₅Al₂O₅Cl₂ (Santamaría-Pérez & Vegas, 2003), is by no means a hypothetical structure for the Group 15 elements but it really exists as a stable phase for nitrogen! Compare Figs. 1(e) and 1(f). The similarity of this network with the Si skeleton (Ψ-P) in the Zintl phase SrSi₂ (Pringle, 1972), is also remarkable.

The structure is also related to the four-connected networks of β-BeO (Smith et al., 1965), CrB₄ (Andersson & Lundström, 1968), anorthite (CaAl₂Si₂O₈; Takeuchi et al., 1973) and the AIP sub-arrays of two polymorphs of AlPO₄·2H₂O (the minerals variscite and metavariscite; Kniep & Mootz, 1973; Kniep et al., 1977; Kniep, 1978). In all these structures, represented in Fig. 2, the involved atoms form puckerred layers of octagons and squares (the 4.8² nets), instead of the helices existing in the γ-Si(Ge) structure. Compare the structures drawn in Figs. 1 and 2.
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Table 2
Possible electron redistributions for species relevant to the present work.

The Zintl–Klemm notation describes the electron redistribution, so that, in the overall electron count for the elements concerned, the superscript \( -1 \) (rather than \(-1\)), for example, represents an excess electron on that atom; the superscript \(-1\) represents a one-electron loss. Thus, Li\(^{+1}\) is \((\Psi-\text{He})\), Al\(^{+3}\) and N\(^{-3}\) are \((\Psi-\text{Si})\) and \((\Psi-\text{O})\), respectively, and Al\(^{+3}\) is \((\Psi-\text{Ne})\).

<table>
<thead>
<tr>
<th>Electron donation</th>
<th>Electron acceptance</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>N(^{+3}) = (\Psi-\text{Be})</td>
<td>N(^{+2}) = (\Psi-\text{B})</td>
</tr>
<tr>
<td>Li(^{+2}) = (\Psi-\text{H})</td>
<td>Li(^{+1}) = (\Psi-\text{He})</td>
</tr>
<tr>
<td>Al(^{+3}) = (\Psi-\text{Ne})</td>
<td>Al(^{+2}) = (\Psi-\text{Na})</td>
</tr>
<tr>
<td>V(^{+3}) = (\Psi-\text{Ca})</td>
<td>V(^{+2}) = (\Psi-\text{Sc})</td>
</tr>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>N(^{-3}) = (\Psi-\text{O})</td>
<td>N(^{-2}) = (\Psi-\text{F})</td>
</tr>
<tr>
<td>Li(^{-2}) = (\Psi-\text{Be})</td>
<td>Li(^{-1}) = (\Psi-\text{Be})</td>
</tr>
<tr>
<td>Al(^{-3}) = (\Psi-\text{Si})</td>
<td>Al(^{-2}) = (\Psi-\text{P})</td>
</tr>
<tr>
<td>V(^{-3}) = (\Psi-\text{Cr})</td>
<td>V(^{-2}) = (\Psi-\text{Mn})</td>
</tr>
</tbody>
</table>

2.1.1. Li\(_3\)AlN\(_2\). The structure of Li\(_3\)AlN\(_2\) was reported exactly 60 years ago by Juza & Hund (1948). It can be analysed in the light of both the Zintl (1934) and Klemm (1958) concepts, in terms of which, various electron redistributions are allowed, provided that the overall electron count remains the same. Table 2 summarizes some of the possible redistributions for those species relevant to the present work.

**Case 1:** For example, if the formula Li\(_3\)AlN\(_2\) were to be expressed in the usual ionic form, it would be written as \((\text{Li}^{+1})_3[\text{AlN}_2]^{3-}\) (\(\text{Li}^{+1}\) is \((\Psi-\text{He})\)), \(\text{Al}^{+3}\) and \(\text{N}^{-3}\) are \((\Psi-\text{Si})\) and \((\Psi-\text{O})\), respectively, and \(\text{Al}^{+3}\) is \((\Psi-\text{Ne})\).

**Case 2:** The structure can accommodate a second interpretation (Table 2). If the Zintl–Klemm concept were applied in the opposite direction, the Al atom would transfer its three valence electrons to Li forming three \(\text{Li}^{-1}\) species which then become iso-electronic with three \((\Psi-\text{Be})\): this would leave an \([\text{AlN}_2]^{3-}\) component made up of \(\text{Al}^{+3}\) and \((\text{N}^{0})_2\). \(\text{Li}^{-1}\) is \((\Psi-\text{Be})\), \(\text{Al}^{+3}\) is \((\Psi-\text{Ne})\), and \((\text{N}^{0})_2\) remains as \(\text{N}\). The result is an \(\text{Al}^{+3}\)-stuffed \(\text{Li}_3\)N\(_2\) or a hypothetical \((\Psi-\text{Ne})\)-stuffed \((\Psi-\text{Be}_3)\)N\(_2\) with the anti-bixbyite structure, like the real Be\(_3\)N\(_2\) compound (von Stackelberg & Paulus, 1933). This description of bixbyite is illustrated in Fig. 3(a), where the \(\text{N}\) atoms (blue spheres) are arranged in an almost f.c.c. array. To see the deviation from the ideal f.c.c. array, we have represented in Fig. 4(a) a similar array of \(\text{O}\) atoms observed in BPO\(_4\) (Haines et al., 2003). Although the structures are not identical, they can be compared on the basis of the similar \(\text{O}\) subarray, and also because both compounds are formed by \(\text{XO}_4\) tetrahedra. In this compound (cristobalite-like), the \(\text{P}(\text{B})\text{O}_4\) tetrahedra rotate in a continuous way when pressure is applied. At 50 GPa, the \(\text{O}\) array collapses, as in the chalcopyrite structure (FeCu\(_2\)S\(_2\)), into an almost perfect f.c.c. arrangement, represented in Fig. 4(b) (Haines et al., 2003).

**Case 3:** Yet a third interpretation is possible (Table 2). This arises from the fact that the...
overall structure is essentially anti-fluorite, $N_2M_4$, with $NM_{8/4}$ cubes sharing edges, where $M_4 = Li_3Al$. A well known example is $Mg_2Si$ in which $SiMg_{8/4}$ cubes share edges (Owen & Preston, 1924).

If we assume the transfer of two electrons from the two $N$ atoms to the $[Li_3Al]$ array, the two $N$ atoms each become $N^{+1}$ or $(\Psi-C)$, while the $[Li_3Al]^{-2}$ array is electronically equivalent to $(\Psi-Li_3P)$ with its total of eight valence electrons for the four cations. This pseudo-compound $(\Psi-Li_3P)$ is then electronically equivalent to either $(\Psi-Mg_4)$ or $(\Psi-Be_4)$. Consequently, the compound $Li_3AlN_2$ would be formulated as the hypothetical $(\Psi-Li_3PC_2)$, electronically equivalent to $(\Psi-Mg_4Si_2)$ – the real anti-fluorite is $Mg_2Si$ (Owen & Preston, 1924). However, this structure is no longer a stuffed anti-bixbyite. On the other hand, the hypothetical $(\Psi-Li_3PC_2)$ compound could be described as a hypothetical, phosphorus-stuffed $Li_3C_2$ with the anti-bixbyite type structure.

The Zintl–Klemm concept can account for even more pseudo-structures derived from $Li_3AlN_2$.

**Case 4**: By assuming that two $Li$ atoms donate $2e^-$ to the third $Li$ atom to give $(Li^{+1})_2[Li^{2-}AlN_2]^{-2}$, $Li^{2-}$ would convert into $(\Psi-B)$, the anion becoming $(\Psi-BAlN_2)$. We must recall that both $AlN$ and $BN$ (III–V compounds) form blende-type structures (Wakatsuki et al., 1972) that are implicit in $Li_3AlN_2$, i.e. in its constituent nitrides $Li_3N$ and $AlN$ (see Fig. 5b). When all the $Li$ atoms (donors and acceptors) are drawn (Fig. 4b), the generated structure is a unit cell of a distorted fluorite, as was shown in Fig. 5. If four of the six $Li$ atoms (the donors) were eliminated, the blende-type pseudo-array, of the formula $(\Psi-Li_3AlN_2)$, would become evident, as seen in Fig. 6.

A final comment should be made on the $N$ array. It has been shown (Figs. 3 and 5) that $N$ atoms form a slightly distorted f.c.c. array, as do the indium atoms in $In_3O_3$ (Ramos-Gallardo & Vegas, 1995). If we assume that all 6 electrons from $[Li_3Al]$ are transferred from these cations to form two nitride $N^{3-}$ anions, the latter would behave as $(\Psi-Ne)$. The distorted f.c.c. unit cells of $N$ atoms have dimensions varying from 4.82 to 4.89 Å (mean 4.85 Å). This value is close to that of the unit cell of elemental Ne, also f.c.c., with $a \simeq 4.50$ Å. The $N-N$ distances, in the partial $LiAlN_2$ array, range from 3.11 to 3.14 Å, close to the $Ne-Ne$ distances (3.18 Å) in elemental $Ne$. Thus, the $Ne$ structure can also be recognized in $Li_3AlN_2$ (see Fig. 5).

This last compound provides a nice example of how the location of atoms in different structural sites is not only determined by their relative atomic sizes, but also by their pseudo-electronic configurations. It could be said that such compounds highlight the unequivocal relationship existing between composition and structure which was postulated by Vegas & García-Baonza (2007).
similar pattern. Here, the 16c site of space group $Ia\overline{3}$ is randomly occupied by $M^{IV}$ (Ge) and Li atoms, with reported population parameters of 0.67 and 0.33 for $M^{IV}$ and Li, respectively. The reader can readily recognize that this composition is equivalent to the presence of an atom with three valence electrons, like Al in Li$_3$AlN$_2$ (Juza & Hund, 1948). Thus, the fractional occupation factors are explained by the need for satisfying the four valence electrons of the 2/3 $M^{IV}$ plus 1/3 Li atoms located at 16c. Thus, two of the three Li atoms located at 48e transfer two electrons to the N atoms, converting them into two (Ψ-O). The third Li atom at 48e (16 Li atoms) donates its valence electron to the Li$_{0.33}$ located at 48c. This Li$_{0.33}$ is randomly occupied by a charge distribution of Li$_3$AlN$_2$. The need for satisfying the four valence electrons of the 2/3 $M^{IV}$ plus 1/3 Li atoms located at 16c, two of the three Li atoms located at 48e transfer two electrons to the N atoms, converting them into two (Ψ-O). The third Li atom at 48e (16 Li atoms) donates its valence electron to the Li$_{0.33}$ located at 48c to generate (Li$^{+1}$)$_3$(Li$^{-3}$)$_{0.33}$($M^{IV})_{0.67}$($N^{-1})_2$, with the electronically balanced charge distribution of Li$_3$AlN$_2$. This transfer of three electrons to the core Li atom converts it into (Ψ-C), hence forming, together with the $M^{IV}$ atoms, a four-connected net. Now we are able to explain two structural features: on the one hand, why the Li atoms occupy one third of the 16c site and not another position such as 8b. The reason is that this is the only way of achieving the observed four-connected network of γ-Ge. We can also explain why the $M^{IV}$ atoms are precisely located at that site and not partially occupying the alternative 48e positions: in this latter site, the Ge skeleton could not be formed.

2.1.3. Li$_6$[$M^{IV}$Li]$_4$ ($M^{IV}$ = V, Nb, Ta). Case 6: Like Li$_3$AlN$_2$ and Li$_3$[Li$_{0.33}$Ge$_{0.67}$]N$_2$, the EZKC, when applied to this compound, predicts that it also involves four-connected nets. For example, at one analytical level we can suppose that four Li atoms donate four electrons to the N atoms, converting them into (Ψ-O), and that the two remaining Li atoms transfer two additional electrons to the [M$^{IV}$Li] set, converting it into either (Ψ-[III–V]) or (Ψ-[II–VI]) pairs, forming four-connected nets. The [M$^{IV}$Li]$^{1/2}$ substructure is represented in Fig. 7. Here, the $M^{IV}$ and Li atoms are not distributed at random, as in the 16c site of $Ia\overline{3}$, but they are ordered into two sets on 8c sites of the subgroup $Pa\overline{3}$ from which the body-centering operation in $Ia\overline{3}$ has been dropped.

At a slightly deeper level, the outcome of these electron transfers (see Table 2) is the compound (Li$^{+1}$)$_3$(Li$^{-3}$)$_{0.5}$($M^{IV})_{0.5}$($N^{-1})_2$, which is isomorphous with the four-connected network of the tetrahedral pseudo-compound (Ψ-He)$_3$(Ψ-C$_{0.5}$Te$_{0.5})_2$ (Ψ-O) (assuming that $M^{IV}$ = V$^{+1}$), i.e. the hypothetical (Ψ-He)$_3$(Ψ-C$_{0.5}$Te$_{0.5})_2$O), a hypothetical ‘C/Ti-stuffed He$_3$O’.

The discussion about the different structures which co-exist in these stuffed bixbyite-type compounds can be extended to these compounds. The lack of isostructural compounds containing Group 15 elements (P, As, Sb and Bi) is noteworthy. However, we must recall the similar chemical and structural behaviors of vanadates and niobates on one hand, and phosphates and arsenates on the other. Moreover, if we assume that the [M$^{IV}$Li]$^{1/2}$ sub-array is formed by a (Ψ-[III–V]) pair, it must be strongly related to [AlP] substructures like those of AlPO$_4$, represented in Fig. 2. Compare Fig. 2(d) of variscite with Fig. 7. The remaining co-existing structures can be easily deduced, as with Li$_3$AlN$_2$.

Table 3 attempts to collect and summarize all the foregoing discussion of the Zintl–Klemm analyses.
The [VLi] skeleton in Li₆[V Li]N₄ similar to both the Al(Ψ-Si)-array in Li₃AlN₂ and the structure of γ-Si, represented in Fig. 1. Li and V atoms are ordered occupying different positions of the 8c site in the space group $P6_3$. Each atom connects to four unlike atoms. One of these bonds has been omitted to show the two interpenetrating three-connected subsets.

### Table 3
Summary of various electron redistributions discussed in the text.

<table>
<thead>
<tr>
<th>Case</th>
<th>Normal compound</th>
<th>Atomic species</th>
<th>Electron redistribution</th>
<th>Phase description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li₃AlN₂</td>
<td>(Li⁺)₂[Al⁺⁺(N⁻)₂]</td>
<td>(Ψ-He)₂(Ψ-Si)(Ψ-O)₂</td>
<td>‘Si-stuffed He₂O₂ anti-bixbyite’</td>
</tr>
<tr>
<td>2</td>
<td>Li₃AlN₂</td>
<td>(Li⁺)₂[Al⁺⁺(N⁻)₂]</td>
<td>(Ψ-He)₂(Ψ-Nc)(Ψ-O)₂</td>
<td>‘Ne-stuffed He₂N₂ anti-bixbyite’</td>
</tr>
<tr>
<td>3</td>
<td>Li₃AlN₂</td>
<td>[Li⁺⁺Al⁺⁺(N⁻)₂]</td>
<td>(Ψ-He)₂(Ψ-BAlN₂)</td>
<td>‘Blende’</td>
</tr>
<tr>
<td>4</td>
<td>Li₃AlN₂</td>
<td>(Li⁺)₂[Li⁺⁺Al⁺⁺(N⁻)₂]</td>
<td>(Ψ-He)₂(Ψ-BAlN₂)</td>
<td>‘Blende’</td>
</tr>
<tr>
<td>5</td>
<td>Li₃(Ge₁₋₀₇Li₀·₃₃₃)N₂</td>
<td>(Li⁺)₂<a href="N%E2%81%BB">(Li⁺⁺)₀·₃₃₃(Ge⁺⁺)₀·₃₃₃</a>₂</td>
<td>(Ψ-He)₂<a href="%CE%A8-O%E2%82%82">(Ψ-BLiₙ)(Ψ-BLiₙ)</a></td>
<td>‘Si/Ge-stuffed He₂O₂ anti-bixbyite’</td>
</tr>
<tr>
<td>6</td>
<td>Li₃(V⁺⁺)Li₃N₂</td>
<td>(Li⁺)₂<a href="N%E2%81%BB">(Li⁺⁺)₀·₃₃₃(M⁺⁺)₀·₃₃₃</a>₂</td>
<td>(Ψ-He)₂<a href="%CE%A8-O%E2%82%82">(Ψ-Cₙ)(Ψ-Cₙ)</a></td>
<td>‘Ti/C-stuffed He₂O₂ anti-bixbyite’</td>
</tr>
</tbody>
</table>

---

2.2. Coordination-defect (CD) approach

The CD theory was proposed originally by Martin (1974) to describe the structures of the many well known, anion-deficient, fluorite-related compounds, of which bixbyite is but one example. He proposed that the anion vacancies in such structures were not simply isolated point defects, randomly distributed throughout the lattice, but rather that each vacancy was strongly coordinated by its nearest and next-nearest neighbours, four cations and six anions, to generate an octahedral structural entity, the CD, of considerable thermodynamic and structural stability. Indeed this concept can be extended to other non-fluorite structures of different symmetry for it can be argued that the same principle would hold true for the presence of any atom different in kind from the predominant atomic species forming a lattice.

In the context of an anti-bixbyite structure (space group $Ia\overline{3}$) such as magnesium nitride (a cation-deficient, anti-fluorite-related compound of the general formula $M_3\square M_N_2$, where $\square$ is a vacancy in the cation sublattice), what we now might call an anti-CD is described as an octahedron of $MX_4$ tetrahedra sharing corners to enclose an empty tetrahedron $(\square_MX_4)$ or, alternatively, an empty tetrahedron, $(\square_MX_4)$, sharing all six edges with $MX_4$ tetrahedra, forming a $\square_M$-centred octahedron represented as $M_3\square_MX_4$. This is shown in Fig. 8, comprising a central tetrahedral core with six peripheral tetrahedra.

Incorporated into the anti-fluorite-type structure, and therefore taking account of the sharing of all tetrahedral edges such that every $X$ atom is common to eight tetrahedra, the anti-CD composition becomes $\square_MX_{4/8}(MX_{4/8})_0$ or $X_7M_{12}(\square_M)^2$. Moreover, analogous to the bixbyite case, each peripheral $MX_{4/8}$ tetrahedron of the anti-CD in the anti-bixbyite structure is common to another anti-CD, and the anti-bixbyite composition expressed in the anti-CD format is $\square_MX_{4/8}\square_MX_{4/8}$ or $M_3\square_MX_4$. The $\square_M$ site is the 16c site of $Ia\overline{3}$, which is also the site occupied by Si in $γ$-Si. If, now, this vacancy can accommodate a pseudo-Si atom, we obtain the compound $M_3(Ψ-Si)_X$ whose counterparts are Li₃AlN₂ and Li₃SeN₂, with a truly ‘stuffed’ anti-bixbyite structure, the Al...
and Sc atoms occupying respectively the tetrahedrally coordinated, vacant cation sites of the actual anti-bixbyite structure.

In the case of Li₃AlN₂, and assuming the normal ionic charge assignments, the anti-CD core becomes the [Al⁺₃(N³⁻)₄/₈]¹.₅⁺ tetrahedron, with Al occupying the anti-bixbyite cation vacancy, while each of the six peripheral anti-CD tetrahedra in the overall structure is ([Li⁺(N⁺)₄/₈]⁻¹.₅⁻)₂. In standard chemical usage, the overall anti-CD formula of Li₃AlN₂ is (AlN₄/₈)¹.₅⁺[(LiN₄/₈)⁶/₂]¹.₅⁻, i.e. (AlN₄/₈)-stuffed anti-bixbyite, in agreement with earlier. The resulting pseudo-CD representation for cases 1–3.

**Case 1:** We now apply the first of the above Zintl–Klemm interpretations of Li₃AlN₂, i.e. two Li atoms donate two valence electrons to the two N atoms converting them into (Ψ-O) atoms, the third Li atom transfers its electron to the Al atom, converting it into (Ψ-Si). The formal outcome is (Li⁺)₁Al⁻¹(N⁻)₂ in the Zintl–Klemm notation. Here, Li⁺ is (Ψ-He), Al⁻¹ and N⁻ are (Ψ-Si) and (Ψ-O), respectively. The anti-CD formulation of this becomes [Al⁻¹⁺(N⁻)₂]⁻¹.₅⁻ as the core, the peripheral tetrahedra being [Li⁺(N⁺)²]⁻⁰.₅⁻, with Al⁻¹⁻, i.e. (Ψ-Si), 'stuffing' the tetrahedral void, □₃₅, in the anti-CD core. Each of the six peripheral tetrahedra of the anti-CD, with the formula [Li⁺⁺(N⁺)²]⁻⁰.₅⁻ is common to another such anti-CD, and has Li⁺⁻, with the (Ψ-He) spherical electron configuration at its centre, coordinated by a tetrahedron of N⁻ atoms, i.e. (Ψ-O). The result is a pseudo-anti-CD representation of Li₃AlN₂ can now be written as [Al⁻¹⁺(N⁻)₂]⁻¹.₅⁻, [Li⁺⁺(N⁺)²]⁻⁰.₅⁻ or [(Ψ-Si)(Ψ-O)₄][(Ψ-He)(Ψ-O)₄]⁻⁰.₅⁻, i.e. overall (Ψ-SiO₂) + 3(Ψ-He) with the spherical eight-electron configuration. This is equivalent to (Ψ-He₂SiO₂), i.e. a hypothetical (Ψ-Si)-stuffed anti-bixbyite, in agreement with the conclusion reached in the previous section. In this CD description, we see that the CD core has an excess of electrons, while the core periphery has an equal electron deficit.

**Case 2:** The second interpretation applies the Zintl–Klemm concept in the opposite direction, with the Al atom transferring its three valence electrons to Li forming three Li⁺⁻ species, each of which is isostructural with (Ψ-Be) and an [Al⁺⁺(N⁺)²]⁻¹.₅⁻ sub-structure yielding a (Ψ-Ne)-stuffed (Ψ-Be₃N₂), with the anti-bixbyite structure as in real Be₃N₂ (von Stackelberg & Paulus,1933). With this second set of electronic assignments, Li₃AlN₂ can be formulated as the anti-CD, [Al⁺⁺(N⁺)²][Li⁺⁺(N⁺)²]⁻¹.₅⁻. The pseudo-anti-CD can now be written as [(Ψ-Ne)N₄][(Ψ-Be)N₄]⁻⁰.₅⁻, i.e. overall (Ψ-Be₃N₂) – a hypothetical, neon-stuffed (Ψ-Be₃N₂), as described earlier.

**Case 3:** The third interpretation involves the transfer of two electrons from the two N atoms to the Al so that the subarray becomes [Al⁻²⁺(N⁺)³]⁰, which is electronically equivalent to (Ψ-P)(Ψ-C)₂. The CD formulation becomes [Al⁻²⁺(N⁺)³]⁻¹.₅⁻[(Li⁺)(N⁺)⁴/₈]⁻¹.₅⁻, with the corresponding pseudo-CD being [(Ψ-P)(Ψ-C)₄][(Ψ-He)(Ψ-O)₄]⁻¹.₅⁻ or [(Ψ-Li₁PC)₂], i.e. a phospho-carbon stoichiometric analogue of Li₃AlN₂. Indeed it can be described as a hypothetical phosphorus-stuffed lithium carbide, Li₁₃PC₂ with the anti-bixbyite structure. These descriptions are summarized in Table 4.

**Table 5.**

<table>
<thead>
<tr>
<th>Case</th>
<th>Zintl–Klemm</th>
<th>Core tetrahedron</th>
<th>Peripheral tetrahedron</th>
<th>Overall formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(Li⁺)₁Al⁻¹(N⁻)₂</td>
<td>[Al⁻¹⁺(N⁻)₄]⁻¹.₅⁻</td>
<td>[Li⁺⁺(N⁺)²]⁻¹.₅⁻</td>
<td>[Al⁻¹⁺(N⁻)₂]⁻¹.₅⁻{[Li⁺⁺(N⁺)²]⁻¹.₅⁻}⁻²₀.₅⁻</td>
</tr>
<tr>
<td>2</td>
<td>(Li⁺)₁Al⁻¹(N⁻)²</td>
<td>[Al⁻¹⁺(N⁺)²]⁻¹.₅⁻</td>
<td>[Li⁺⁺(N⁺)²]⁻¹.₅⁻</td>
<td>[Al⁻¹⁺(N⁻)₂]⁻¹.₅⁻{[Li⁺⁺(N⁺)²]⁻¹.₅⁻}⁻²₀.₅⁻</td>
</tr>
<tr>
<td>3</td>
<td>Li⁺)Al⁻¹(N⁻)₂</td>
<td>[Al⁻¹⁺(N⁺)²]⁻¹.₅⁻</td>
<td>[Li⁺⁺(N⁺)²]⁻¹.₅⁻</td>
<td>[Al⁻¹⁺(N⁻)₂]⁻¹.₅⁻{[Li⁺⁺(N⁺)²]⁻¹.₅⁻}⁻²₀.₅⁻</td>
</tr>
</tbody>
</table>

For Li₃AlN₂ and assuming the normal ionic charge assignments, the anti-CD core becomes the [Al⁺⁺(N⁺)²]⁻¹.₅⁻ tetrahedron, with Al occupying the anti-bixbyite cation vacancy, while each of the six peripheral anti-CD tetrahedra in the overall structure is ([Li⁺⁺(N⁺)²]⁻¹.₅⁻)₂. In standard chemical usage, the overall anti-CD formula of Li₃AlN₂ is (AlN₄/₈)¹.₅⁺[(LiN₄/₈)⁶/₂]¹.₅⁻, i.e. (AlN₄/₈)-stuffed anti-bixbyite, in agreement with earlier. The resulting pseudo-CD representation for cases 1–3.

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form (very clearly how the Si atom is converted into Si$^-$).

This result is consistent with our earlier comment that the Li and Mg$^+$ atoms constituting the CD cores are highly ordered, thereby ensuring that the positive and negatively charged anti-CDs are appropriately disposed with respect to their opposed anionic and cationic charges. See Table 5.

### 3. Concluding remarks

#### 3.1. Need for EZKC approach

In this paper we have explored a new application of the Zintl–Klemm concept. It is well known that the classical Zintl–Klemm concept (ZKC) was enunciated to account for the so-called Zintl phases in which electron transfer, from very electronegative cations to atoms of the $p$-block elements, leads to the formation of Zintl polyanions. The structure of the compound NaSi, based on tetrahedral Si$_4$ groups, illustrates the Zintl–Klemm concept (ZKC) was enunciated to account for the so-called Zintl phases in which electron transfer, from very electronegative cations to atoms of the $p$-block elements, leads to the formation of Zintl polyanions. The structure of the compound NaSi, based on tetrahedral Si$_4$ groups, illustrates how the Si atom is converted into Si$^-$.

The novelty of the present contribution is that in the case of the anti-bixbyite-type compounds derived from lithium nitride, the nitrogen can also play a central role in the interpretation and rationalization of these structures. Thus, traditional anions and cations together can be involved in the charge-transfer process in order to produce a variety of possible structures. With the compounds discussed here it is clear that the application of this extended principle can now explain why several structure types – fluorite, the hypothetical blende AlBN$_2$ (i.e. the real blende AlN and BN), the real anti-bixbyite Mg$_3$N$_2$ (von Stackelberg & Paulus, 1933) and the real γ-Si (Kasper & Richards, 1964) – are all identifiable in Li$_3$AlN$_2$ and its isotypes. Thus, a novel conclusion of this study is that all these structure types are satisfied at the same time, the Zintl–Klemm concept being the universal key. In other words, a given compound might result from multiple resonance structures, which implies a partial delocalization of electrons. When these are distributed over all the atoms, the electron-count requirements for each structure are fulfilled. This would be a new convergence point between solid state and molecular chemistry.

In the case of the quaternary compounds Li$_3$(Ge$_{0.67}$Li$_{0.33}$)N$_2$ and Li$_3$(Ti$_{0.67}$Li$_{0.33}$)N$_2$ (Juza et al., 1953), we have provided arguments to demonstrate that both the relative amounts and the exact positioning of the Ge(Ti) and Li atoms inside the brackets are not just coincidental.

The correlation of Li$_3$AlN$_2$ with the tetrahedral blende structures necessitates an unusual and unsymmetrical charge transfer, [Li$^{0}_3$] $\rightarrow$ [[Li$^{+1}$]$_2$Li$^{-2}$], with two Li atoms donating one electron each to the third Li atom to give (Li$^{+1}$)$_2$[Li$^{-2}$AlN$_2$]. Li$^{-1}$ is (Ψ-He); Li$^{-2}$ is (Ψ-B), so that the anion becomes (Ψ-BAIN$_2$), providing the rationale for the presence of the blende-type anion in the pseudo compound (Ψ-He)(Ψ-BAIN$_2$) represented in Fig. 6. This could be viewed as a controversial proposal in the case of an electropositive element such as lithium: however, such unsymmetrical charge transfers are not particularly uncommon (Vegas & García-Baonza, 2007). For example, both Ca$_3$N$_2$ and Mg$_3$N$_2$ (von Stackelberg & Paulus, 1933) possess anti-bixbyite structures, and, in line with the arguments developed above, the identification of a blende structure in Mg$_3$N$_2$, for example, can be explained by assuming that one Mg atom transfers its two electrons to the other two Mg atoms so that Mg$_3$ in Mg$_3$N$_2$ becomes Mg$^{2+}$(Mg$^{1+}$)$_2$. Mg$^{2+}$ is (Ψ-Ne); Mg$^{1+}$ is (Ψ-AI), leading to the overall composition (Ψ-Ne)(Ψ-AI)$_2$N$_2$. The same description can be applied to Ca$_3$N$_2$, although the ternary, mixed-cation compounds, such as CaMg$_2$N$_2$ (Schulz-Coulon & Schnick, 1995) and BaMg$_2$P$_2$ (Klüfers & Mewis, 1984), no longer conform to this intra-cation transfer. Thinking in classical terms of structures dominated by ionic charge and size effects, and conventional coordination polyhedra, it might be expected that the three $M$ cations [CaMg$_2$, BaMg$_2$, Mg$_2$] would either randomly occupy the 48e site of Lu$_3$ or be ordered into a superstructure. However, the structure is in fact no longer anti-bixbyite, but one related to that of the Zintl phase Ca[Al$_3$Si$_2$] (Gladyshevskii et al., 1967), which is represented in Fig. 9.

The solution found by nature is quite elegant: because both Ca and Ba are more electropositive than Mg, they donate their two valence electrons to the two Mg atoms, converting each into (Ψ-AI), which, together with the N(P) atoms, form a four-connected (Ψ-AIN) (Ψ-AIP) network typical of the [Al$_3$Si$_2$]$^{2+}$ Zintl polyanion, and hence of the Group 14 elements. The
same solution was found for the compound ZrNCl (Vegas & Santamaría-Pérez, 2003) in which the \([\text{ZrN}]\) array transfers one electron to the Cl atom, giving rise to the polycation \([\text{ZrN}]^{+1}\), isoelectronic with \(\Psi\)-YN. This is a good example of how the electron transfer acts (in this case, in the opposite direction), to produce ‘Zintl polycations’.

### 3.2. Experimental justification

It is important to recall that such unexpected electron transfers are supported by NMR experiments that indicate the co-existence of entities such as \(K^+\) and \(K^-\) (e.g. potassides), even in the solid state (Tinkham & Dye, 1985; Nakayama et al., 1994; Terskikh et al., 2001), so it is quite conceivable that these ions might coexist in other compounds, regardless of the fact that such entities could not be identified in conventional diffraction experiments (Seiler & Dunitz, 1986).

In our opinion, the most remarkable finding of Niewa et al. (2003) was the coincidence of the \(\Psi\)-Si(Ge) structure with the Sc sub-array, and the consequent existence of the tetrahedral \(\text{ScN}_2\) skeleton, with covalent Sc—N bonds. Theoretical calculations, based on the electron localization function (ELF) and periodic nodal surfaces (PNS), indicated that \(\text{Li}_3\text{ScN}_2\) is formed by \(\text{Li}^{+}\) cations inserted in a three-dimensional skeletal of \([\text{ScN}_2]^2-\). The authors also mention the isostructural nitrides \(\text{Li}_3\text{AlN}_2\) and \(\text{Li}_3\text{GaN}_2\). It is noteworthy that this insight is only one of the many we have discovered in these stuffed bixbyites. From this point of view, the fact that the compound forms this type of structure remains unexplained. The coexistence of \(\text{Li}^{+}\) cations and the tetrahedral polyanion \([\text{ScN}_2]^2-\) could have been achieved with any of the many silica-like skeletons.

We have already mentioned that the isostructural compound \(\text{Li}_3(\text{Ge}_{0.66}\text{Li}_{0.33})\text{N}_2\) (Juza et al., 1953) is the key to understanding this family of compounds. However, this compound was overlooked by the authors (Niewa et al., 2003).

As explained above, this compound provokes two crucial questions:

(i) Is it possible to explain a \(\Psi\)-Ge-type substructure for the \((\text{Ge}_{0.66}\text{Li}_{0.33})\) set on the basis of the arguments given by Niewa et al. (2003)?

(ii) Why are the Ge atoms at the 16\(c\) positions and not distributed at random over the other possible Li positions as in \((\text{Li}_{2.33}\text{Ge}_{0.66})\text{LiN}_2\)?

In fact, in this latter case the anti-fluorite-type structure remains and the coordination number for all the atoms is the same. Our investigation began because we expected that a Ge(Si) atom must be at this 16\(c\) position, reproducing the structure of elemental Ge, and indeed the Ge atoms are there.

### 3.3. New perspectives

Inorganic solids should actually be regarded from a holistic perspective. One of the few models that can provide this holistic view is the Zintl-Klemm concept (ZKC) and its extension the EZKC. Until recently, this long-standing and illuminating concept has only been applied to the so-called Zintl phases. However, we have shown that this approach also applies successfully to the cation arrays in aluminates and silicates (Santamaría-Pérez & Vegas, 2003; Santamaría-Pérez et al., 2005), putting this multitude (thousands of compounds), for the first time, on a common and rational basis. In a more recent article, it has been shown that the ZKC can go even further (Vegas & García-Baonza, 2007) and provide a rational explanation of the many and varied structural types. Within this emerging pattern is where the novelty of this article resides. Here we provide a chemical reason for the experimental observation that the Sc sub-array in \(\text{Li}_3\text{ScN}_2\) resembles the tetrahedral structure of \(\Psi\)-Si(Ge). There is a huge conceptual difference between simply pointing out this topological similarity, and describing the structure by using the ZKC. The latter enables us to explore the structures of all the likely contributing resonance compounds discussed above. For example, we are able to give a rational explanation as to why the Sc atoms are tetrahedrally coordinated in \(\text{Li}_3\text{ScN}_2\), whereas they are octahedrally coordinated in the so-called interstitial nitride ScN? ZKC analysis leads us to \([\text{Sc}^{2+}\text{N}^2-]\), i.e.
the pseudo-compound (Ψ-KF) with the NaCl cubic close-packed structure.

In Li$_3$ScN$_2$, theoretical calculations, especially the periodic nodal surfaces, have led to the interpretation of the structure as composed of Li$^+$ cations and (ScN$_3$)$_3^{3–}$ polyanions. However, the question is how to account for the co-existence of other complementary arrangements which involve other structure types. The structures are there and must be explained! We encourage theoreticians to elaborate new models which can help us to understand all these features.

Our conclusion is that an important procedure for gaining insight into crystal structures is not to restrict the contemplation to anions and cations in their conventional oxidation states, but also to contemplate how selected pairs of atoms might accommodate their valence electrons to produce pseudo-structures characteristic of the elements of Group 14. If this is the driving force, the conventional oxidation states assigned to cations and anions lose some of their usefulness in accounting for crystal structures.

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