An alternative approach to rationalizing the structures of the cyclotrisilicates: $\text{Rb}_{10}[\text{Si}_6\text{O}_{17}]$, $\text{Cs}_8[\text{Si}_6\text{O}_{16}]$ and $\text{Na}_3\text{Y}[\text{Si}_6\text{O}_{15}]$ by viewing them in light of the extended Zintl–Klemm concept

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The structures of the three dimeric cyclotrisilicate anions $[\text{Si}_6\text{O}_{17}]^{10-}$, $[\text{Si}_6\text{O}_{16}]^{8-}$ and $[\text{Si}_6\text{O}_{15}]^{6-}$ forming part of the compounds $\text{Rb}_{10}[\text{Si}_6\text{O}_{17}]$ or $\text{Rb}_{14}[\text{Si}_4][\text{Si}_6\text{O}_{17}]$, $\text{Cs}_8[\text{Si}_6\text{O}_{16}]$ and $\text{Na}_3\text{Y}[\text{Si}_6\text{O}_{15}]$, respectively, have been described as different ways of condensing the more elemental cyclotrisilicate anions $[\text{Si}_3\text{O}_9]^{6-}$ [Hlukhyy & Fässler (2013). *Z. Anorg. Allg. Chem.* **639**, 231–233]. Such a description prevents a rational explanation of the connectivity between the Si atoms. So, in this article the Si skeletons of the above silicate anions are put on a common basis in light of the extended Zintl–Klemm concept. Their connectivity is directly related to the ratio $\Psi\text{-S}/\Psi\text{-P}$ resulting from the number of electrons transferred from the electropositive Na, Y, Rb and Cs atoms, offering a new example of the fact that there exists a univocal link between chemical composition (in terms of pseudo-atoms) and structure: the generalized Zintl–Klemm concept. The three skeletons fit the connectivity of hypothetical Zintl polyanions of composition $[\Psi\text{-S}_4\text{P}_2]^{10-}$, $[\Psi\text{-S}_2\text{P}_4]^{8-}$ and $[\Psi\text{-P}_6]^{6-}$ respectively.

1. Discussion

Recently, Hlukhyy & Fässler (2013) reported the synthesis of a new silicate, $\text{Cs}_8[\text{Si}_6\text{O}_{16}]$, containing discrete dimeric cyclotrisilicate anions $[\text{Si}_6\text{O}_{16}]^{8-}$. These polyanions are formed by two $[\text{Si}_3\text{O}_9]$ rings double linked by two Si–O–Si bonds (see Fig. 1*d*) in which the Si skeleton consists of a pair of Si_3 triangles connected by a common Si_4 square. As seen in Fig. 1(*d*), the two $[\text{Si}_3\text{O}_9]$ rings are in a *trans* position with respect to the central Si_4 square.

Considering the skeletons of silicates which are formed by the condensation of smaller units, the $[\text{Si}_6\text{O}_{16}]^{8-}$ anion of Fig. 1(*d*), they should be formed by the dimerization of two $[\text{Si}_3\text{O}_9]^{6-}$ units like that given in Fig. 1(*a*). This type of skeleton, as predicted by Liebau (1985), represents one of three ways of condensing two such units yielding the unbranched cyclotrisilicate $\{\mathbf{uB}, 2\mathbf{r}\}$ anions. Two other ways of condensing two $[\text{Si}_3\text{O}_9]^{6-}$ units have been described in the study of the $[\text{Si}_6\text{O}_{17}]^{10-}$ anion of $\text{Rb}_{10}[\text{Si}_6\text{O}_{17}]$ (see Fig. 1*c*; Hoffmann & Fässler, 2006) or in $\text{Rb}_{14}[\text{Si}_4][\text{Si}_6\text{O}_{17}]$ (Hoffmann *et al.*, 2001) and the $[\text{Si}_6\text{O}_{15}]^{6-}$ anion present in the compounds $[\text{Ni}(\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—NH}_2)_3]_3[\text{Si}_6\text{O}_{15}]\cdot 26\text{H}_2\text{O}$ (Smolin, 1970) and $\text{Na}_3\text{Y}[\text{Si}_6\text{O}_{15}]$ (Haile *et al.*, 1995; see Fig. 1*e*). These three related anions are represented in Figs. 1(*c*)–(*e*). It should be remarked that in $\text{Rb}_{14}[\text{Si}_4][\text{Si}_6\text{O}_{17}]$ (Hoffmann *et al.*, 2001) the silicate polyanions coexist with the Zintl $[\text{Si}_4]^{4-}$ polyanions, as shown in Fig. 1(*c*).

This way of looking at the silicate structures is currently in vogue and is offered as a means of classifying the structures. Liebau's comprehensive book (Liebau, 1985) represents a

good example of the enormous effort expended by crystal chemists to sort the vast variety of skeletons found in these compounds. It should be emphasized, however, that neither classification nor mere description necessarily lead to an *understanding* of the structures of the skeletons which should be the ultimate goal.

In this context the extension of the Zintl–Klemm concept (Zintl, 1939; Klemm, 1958) to the polyanions of aluminates and silicates has successfully provided a means of placing all these structures on a common basis. Beginning with the attempts of Parthé & Engel (1986) and Parthé & Chabot (1990) and extending to the works devoted to aluminates and silicates by Santamaría-Pérez & Vegas (2003) and Santamaría-Pérez *et al.* (2005), the polyanions of these *p*-block elements can be rationalized when they are regarded as being true Zintl polyanions. Thus, in silicates such as $\text{Cs}_8[\text{Si}_6\text{O}_{16}]$, if the O atoms are neglected, then the cation array Cs_8Si_6 is, in fact, a Zintl phase in which the atoms forming the Zintl polyanion (in this case $[\text{Si}_6]^{8-}$) obey the generalized 8-*N* rule. This rule establishes that each atom forms 8-*N* directed bonds, *N* being the number of valence electrons.

The combination of Zintl's original concept (Zintl, 1939) and Klemm's pseudo-atom description (Klemm, 1958) is referred to here as the Zintl–Klemm concept in which a pseudo-atom is denoted by the prefix Ψ . We shall use this notation throughout this article. It is now possible to show how the application of this extended Zintl–Klemm concept (EZKC) can easily account for the structure of the three dimeric cyclotrisilicate anions, thus providing the electronic reason why the $[\text{Si}_3\text{O}_9]^{6-}$ units are singly, doubly and triply

linked in $[\text{Si}_6\text{O}_{17}]^{10-}$, $[\text{Si}_6\text{O}_{16}]^{8-}$ and $[\text{Si}_6\text{O}_{15}]^{6-}$, respectively (see Fig. 1).

The elemental anion $[\text{Si}_3\text{O}_9]^{6-}$ has a ring periodicity $P^R = 3$ (Liebau, 1985). It was firstly reported in $\text{K}_6[\text{Si}_3\text{O}_9]$ (Werthmann & Hoppe, 1981) and is represented in Fig. 1(a). Its interpretation is straightforward in terms of the Zintl–Klemm concept: the transfer takes place of six e^- from K atoms to the three Si atoms, each Si atom accepting two electrons so being converted into Si^{2-} anions, which – being electronically equivalent to S atoms – also convert structurally into pseudo- $\Psi\text{-S}_3$ molecules. Similarly, the structure of the anion $[\text{Si}_3\text{O}_9]^{6-} \equiv \Psi\text{-S}_3\text{O}_9$ is coincident with that of the real S_3O_9 molecule (Pascard & Pascard-Billy, 1965; McDonald & Cruickshank, 1967), as shown in Fig. 1(b).

As the (*M*)/Si ratio decreases across a series of silicates, the number of electrons transferred to the Si atoms will be reduced, thus accordingly not all the Si atoms can convert into $\Psi\text{-S}$ and therefore some of them are forced to remain as $\Psi\text{-P}$. Thus, in $\text{Rb}_{14}[\text{Si}_4][\text{Si}_6\text{O}_{17}]$ (Hoffmann *et al.*, 2001), four of the 14 e^- of the Rb atoms transform the $[\text{Si}_4]$ groups into tetrahedral $[\Psi\text{-P}_4]$ molecules (see Fig. 1c), whereas the remaining 10 e^- form the $[\text{Si}_6\text{O}_{17}]^{10-}$ anion. Within the oxoanion, the 10 e^- transform four Si atoms into $\Psi\text{-S}$ (terminal) and the other two into $\Psi\text{-P}$ (bridging atom), as shown in Fig. 1(c). In $\text{Cs}_8[\text{Si}_6\text{O}_{16}]$ (Hlukhyy & Fässler, 2013), four e^- of the eight Cs atoms convert four Si atoms into $\Psi\text{-P}$ (bridging atoms), while the remaining 4 e^- transform the other two Si atoms into $\Psi\text{-S}$ (terminal; see Fig. 1d). Finally, in $\text{Na}_3\text{Y}[\text{Si}_6\text{O}_{15}]$ (Haile *et al.*, 1995), both the Na and Y atoms transfer 6 e^- to the six Si atoms converting them into $\Psi\text{-P}$ and so forming the $[\text{Si}_6\text{O}_{15}]^{6-}$ anion, as represented in Fig. 1(e).

Following the Zintl–Klemm concept, the number of electrons transferred to the Si atoms explains their connectivity. Thus, in $[\text{Si}_6\text{O}_{17}]^{10-}$ (Fig. 1c), the four terminal Si atoms ($\Psi\text{-S}$) are two-connected as expected for Group 16 elements, following the 8-*N* rule. On the other hand, the two bridging Si atoms ($\Psi\text{-P}$) are three-connected according to the 8-*N* rule for the Group 15 elements. In the same way, in $[\text{Si}_6\text{O}_{16}]^{8-}$ (Fig. 1d) the two terminal Si atoms ($\Psi\text{-S}$) are two-connected, whereas the four bridging Si atoms ($\Psi\text{-P}$) are three-connected. Finally, in the $[\text{Si}_6\text{O}_{15}]^{6-}$ anion the six Si atoms ($\Psi\text{-P}$) are three-connected, as expected for the Group 15 elements (see Fig. 1e).

The EZKC is further able to explain other geometrical features such as why the two 3-rings are not coplanar (see Figs. 1c and d) and also why they should be in a *trans*

Figure 1

Structures of the isolated dimeric cyclotrisilicate anions: (a) $[\text{Si}_3\text{O}_9]^{6-}$ in $\text{K}_6[\text{Si}_3\text{O}_9]$. (b) The structure of the isoelectronic $[\text{S}_3\text{O}_9]$ molecule. (c) $[\text{Si}_6\text{O}_{17}]^{10-}$ in $\text{Rb}_{10}[\text{Si}_6\text{O}_{17}]$ (Hoffmann & Fässler, 2006) or in $\text{Rb}_{14}[\text{Si}_4][\text{Si}_6\text{O}_{17}]$ (Hoffmann *et al.*, 2001). Note the presence of the $[\text{Si}_4]^{4-}$ Zintl polyanion, coexisting with the silicate anion. (d) $[\text{Si}_6\text{O}_{16}]^{8-}$ in $\text{Cs}_8[\text{Si}_6\text{O}_{16}]$ (Hlukhyy & Fässler, 2013). (e) $[\text{Si}_6\text{O}_{15}]^{6-}$ in $\text{Na}_3\text{Y}[\text{Si}_6\text{O}_{15}]$ (Haile *et al.*, 1995). Si: grey-blue; O: red. The Si skeleton is marked with dark yellow lines. All Si atoms are labeled according to their Zintl–Klemm pseudo-atom character.

position to one another. The apparently striking *trans* conformation of the 3-rings satisfies a double requirement: the first one is the pyramidal geometry of the two bridging Ψ -P forming the central line in $[\text{Si}_6\text{O}_{17}]^{10-}$ (Fig. 1*c*) and those forming the central square in $[\text{Si}_6\text{O}_{16}]^{8-}$ (Fig. 1*d*). Note that the average Si—Si—Si angles, at the two bridging (Ψ -P) atoms of Fig. 1(*c*), are around 99° . The second requirement arises so as to avoid collision of the terminal O atoms with each other.

Despite the fact that P_6/N_6 molecules have not yet been isolated, an analogous N_6 skeleton is stabilized in the N_6S_5 molecule (Chivers & Proctor, 1979) and would also be formed by the isoelectronic molecule of prismane C_6H_6 (Katz & Acton, 1973; see also Santamaría-Pérez, 2005). Note that here each C—H group is equivalent to an N atom not only because they are isoelectronic but also because the six C—H bonds are mimicking the six lone pairs of the trigonal N_6 , as has recently been reported (Vegas *et al.*, 2013). Both molecules N_6S_5 and C_6H_6 are represented in Fig. 2, which can be compared with Fig. 1(*e*).

Our conclusion is that the simple, conventional description of silicate anions is now outdated since it does not adequately account for the connectivity which is found in SiO_4 tetrahedra. Only when the EZKC concept is applied to the Si skeletons can a rational and logical explanation be obtained. The vast amount of similarities which are now demonstrable between the Si skeletons and the structures of either elements or true Zintl phases means that our new approach continues to gain credibility and is poised to advance the current way of viewing crystal structures in the interest of making sense of their complex geometries.

In this work, as well as in other previous articles, the application of the EZKC has been challenged by some reviewers arguing that the structures of silicates are 'easily understood in terms of the normal rules for bonding and valence'. Their arguments are solely supported by the charge counts of the silicate polyanions and how they are balanced by positive alkali metal cations. Although such arguments have previously been rebutted (Santamaría-Pérez *et al.*, 2005;

Santamaría-Pérez, 2005), it should be emphasized that these criticisms can only explain the *first* coordination sphere (in this case tetrahedral) of the Si atoms by four O atoms, but they cannot, by any means, account for both the connectivity and stereochemistry of the whole silicate polyanion.

It is here where the EZKC offers a rational and universal explanation, as does the classical Zintl–Klemm concept with the connectivity and structure of Zintl polyanions. If not, how can the co-existence of both tetrahedrally and octahedrally coordinated Si atoms in a compound synthesized at ambient pressure, $\text{Ce}_{16}\text{Si}[\text{Si}_{14}\text{O}_6\text{N}_{32}]$, when $[\text{SiO}_6]$ octahedra are anticipated only to exist at elevated pressures, as in stishovite (SiO_2 ; see the final part of the article by Santamaría-Pérez *et al.*, 2005), be explained? Despite the fact that many examples have been previously reported (Santamaría-Pérez & Vegas, 2003; Santamaría-Pérez *et al.*, 2005; Santamaría-Pérez, 2005), for the sake of clarity it seems appropriate to illustrate, using some examples, both the validity and usefulness of the EZKC.

A first example is provided by the compounds of general stoichiometry $M^L\text{XO}_3$ ($X = \text{Al, Si, P}$). In most of these reported compounds, *i.e.* ($M^{\text{III}}\text{AlO}_3$), ($M^{\text{IV}}\text{SiO}_3$) or ($M^{\text{V}}\text{PO}_3$), each MO_4 tetrahedron shares two corners, thus giving rise to either infinite chains (*catena*-silicates) or to cycles (ring-silicates). Consequently, their respective Al/Si/P skeletons form either chains or rings (fibrous sulfur, $\Psi\text{-S}_3$, $\Psi\text{-S}_6$, $\Psi\text{-S}_8$, $\Psi\text{-S}_{12}$), which are characteristic of elements of Group 16. The reason is that the M atoms transfer the electrons needed to convert the Al/Si/P atoms into $\Psi\text{-S}$, thus producing two-connected skeletons which obey the 8- N rule.

Only in three compounds, $\text{K}_6(\text{Al}_2\text{O}_6)$, $\text{Rb}_6(\text{Al}_2\text{O}_6)$ (Schläger & Hoppe, 1994) and $\text{Cs}_6(\text{Al}_2\text{O}_6)$ (Hoppe & Müller, 1990), do the $M = \text{Al}$ atoms form a pair of edge-sharing AlO_4 tetrahedra. However, also in this case the Al_2 pairs can be regarded as diatomic $\Psi\text{-S}_2$ molecules whose double $\text{S}=\text{S}$ bond serves to attract two O atoms that in turn form the shared edge (Santamaría-Pérez & Vegas, 2003). Such isolated disulfur molecules are *real entities* that have been observed in the gas phase and also found sorbed in type A zeolites, with a S—S distance of 2.13 Å (Heo *et al.*, 1998).

At this point it is important to stress that the anion $[\text{Al}_2\text{O}_6]^{6-}$ formed by two edge-sharing AlO_4 tetrahedra cannot be explained as being formed by the condensation of corner-sharing AlO_4 tetrahedra, as occurs in most of the aluminates and silicates. Why else does the stoichiometry of XO_3 not conform to the stereochemistry of corner-sharing tetrahedra as in the *catena*- or ring-silicates ($X = \text{Al, Si, P}$) also having the general formula $M_x\text{XO}_3$ or $M'_x\text{AlO}_3$? This apparent conflict easily disappears if the different polyanions are contemplated as being derived from the diverse geometries adopted by the $\Psi\text{-S}$ molecules, including the S_2 molecule.

A second example – that of the silicophosphate $\text{In}_4[\text{Si}_2\text{P}_6\text{O}_{25}]$ – supplies structural features of great interest because it is formed by the condensation of both SiO_4 and PO_4 tetrahedra. In the $[\text{Si}_2\text{P}_6\text{O}_{25}]^{12-}$ polyanion, as represented in Fig. 3, each Si atom (grey sphere) is linked to the other Si atom and to three P atoms, resulting in four-connected Si atoms and the single-connected P atoms. The fourfold connectivity of the

Figure 2
(*a*) The molecular structure of N_6S_5 showing the N_6 trigonal prism. The lateral edges and the trigonal faces are capped by S atoms. N: blue; S: yellow. (*b*) The structure of prismane C_6H_6 showing its similarity with the Si atoms ($\Psi\text{-P}$) in $\text{Na}_3\text{Y}[\text{Si}_6\text{O}_{15}]$ represented in Fig. 1(*c*). C: black; H: white.

Si atoms is, according to the 8-*N* rule, characteristic of Group 14 elements ($8 - 4 = 4$ bonds), thus the Si atoms behave as real Si atoms. On the other hand, the terminal P atoms are singly connected to their respective Si atom, a connectivity that is characteristically found in the halogen diatomic molecules ($8 - 7 = 1$ bond).

The important question which then arises here is as follows: If the compound were formed by the condensation of single XO_4 tetrahedra or, in other words, if the structure is to be explained by only the first coordination sphere around either Si or P, any of these atoms could center any of the XO_4 tetrahedra. Thus, the classical valence rules *are incapable* of explaining why the SiO_4 and the PO_4 tetrahedra are where they are. If the $[Si_2P_6O_{25}]^{12-}$ polyanion were formed by the condensation of individual SiO_4 and PO_4 tetrahedra, then they would likely be arranged randomly at any position in the Si_2P_6 skeleton. Only when the EZKC is invoked can the spatial distribution of both Si and P atoms become physically meaningful. Thus, if we assume that the four In atoms transfer $12 e^-$ to the six P atoms (the most electronegative atom), they would convert into Ψ -Cl just the atomic species which show the observed single connectivity. In support of this interpretation one can cite the similarity of the Si_2P_6 skeleton (Ψ - Si_2Cl_6) with that of the real Si_2I_6 molecule (Si_2Cl_6 has not been reported so far in the solid state).

Our third example is provided by the compound $VO[SiP_2O_8]$, whose $[SiP_2O_8]^{2-}$ anion is drawn in Fig. 4. According to the EZKC, if the vanadyl group (VO) transfers $2 e^-$ to the SiP_2 skeleton, the conversion $SiP_2 \rightarrow \Psi$ - SiS_2 takes place. Once again the electrons are transferred onto the most electronegative P atoms, thus converting them into Ψ -S and consequently the skeleton must have four-connected Si atoms (grey spheres) and two-connected S atoms, in accordance with the 8-*N* rule ($8 - 6 = 2$ bonds). Again, were the structure determined by the condensation of independent XO_4 tetrahedra ($X = Si, P$) then the P atoms might occupy *any* of the positions of the Si atoms. However, following EZKC, all the Si

atoms assume the right positions and all the P atoms are found at positions fitting their Ψ -S character. The structure is then identical to the real SiS_2 compound, as shown in Fig. 4. The Si atoms appear at the same position in both structures. Similarly, both S and P(Ψ -S) atoms are also coincident; in other words, the P atoms are two-connected because they are behaving as Ψ -S atoms.

The stereochemistries as exhibited by these silicates are thus understood when they are regarded in light of Klemm's pseudoatom concept. In the absence of employment of this concept and/or relying solely on the classical valence rules their structure would remain unexplained! The reality is that they have both been unexplained and misunderstood for more than 80 years, as was clearly demonstrated by O'Keeffe & Hyde (1985).

Perhaps it is pertinent at this point in this paper to refer back to the three compounds discussed at the beginning of this article and as represented in Fig. 1, *i.e.* $Rb_{10}[Si_6O_{17}]$ (Hoffmann & Fässler, 2006), $Cs_8[Si_6O_{16}]$ (Hlukhy & Fässler, 2013) and $Na_3Y[Si_6O_{15}]$ (Haile *et al.*, 1995). An aspect specially stressed by Hoffmann & Fässler (2006) and by Hlukhy & Fässler (2013) is the condensation process of smaller units yielding these anions. Reaction (1) has been proposed for the formation of the $[Si_6O_{17}]^{10-}$ anion, implying the release of Rb_2O (Hoffmann & Fässler, 2006).

Other such condensation processes like the formation of cyclotrisilicate anions $M_6[Si_3O_9]$ from disilicate anions $M_6[Si_2O_7]$ ($M = Rb, Cs$) have been observed experimentally by Schartau (1974). However, acknowledging the importance of the reaction path, we believe that the explanation of the skeletons formed in terms of universal concepts must be a priority. This explanation is especially important when one

Figure 3

(a) The structure of the $[Si_2P_6O_{25}]^{12-}$ polyanion in $In_4[Si_2P_6O_{25}]$ formed by corner-sharing SiO_4 and PO_4 tetrahedra. The Si_2P_6 skeleton is highlighted with black lines to show the four-connectivity of the Si atoms and the singly linked P atoms. According to the Zintl–Klemm concept, such connectivity is consistent with the pseudo-formula Ψ - P_2Cl_6 . (b) The existing related P_2I_6 molecule for comparison. Si: dark grey; P: purple; O: red; I: green.

Figure 4

(a) The structure of the infinite double chains in the polyanion $[SiP_2O_8]^{2-}$ in which each Si atom is connected to four P atoms, whereas the P atoms (Ψ -S) are connected to two Si atoms. (b) The equivalent structure of real SiS_2 showing the similarity with the SiP_2 skeleton of the oxide. Si: dark grey; P: purple; O: red; S: yellow.

considers that silicates can also be synthesized using alkali carbonates and SiO_2 as starting products, and that in this case the reaction proceeds by breaking down the quartz structure into smaller fragments, as, for example, in the previously mentioned cyclotrisilicate anion $[\text{Si}_3\text{O}_9]^{6-}$.

Since different reaction paths can yield the same structure, the important issue here is to identify the driving force leading to the formation of a given skeleton or at least to explain its structure on the basis of general principles. As recognized by Hoffmann & Fässler (2006) the release of Rb_2O in reaction (1) is difficult to detect due to the presence of impurities of RbSi and elemental Rb .

On the contrary, if we proceed in the opposite direction, that is we start from $\text{Na}_3\text{Y}[\text{Si}_6\text{O}_{15}]$ and add stepwise 1 mol of $M_2\text{O}$ (M = alkali metal) to the resulting products, the following reaction sequence is given.

The structures of the three Si_6 skeletons can then be placed on a common basis by applying the EZKC and a mechanistic process can be inferred from the drawings represented in Fig. 5. Thus, if one $M_2\text{O}$ unit is inserted into $\text{Na}_3\text{Y}[\text{Si}_6\text{O}_{15}]$, the two M (alkali) atoms transfer two additional electrons to the

$[\text{Si}_6\text{O}_{15}]^{6-}$ anion which, according to reaction (2), then transforms into $[\text{Si}_6\text{O}_{16}]^{8-}$ by adding the new O atom. The result is that the Si_6 skeleton of Fig. 5(a) – that is in fact $(\Psi\text{-P})_6$ – becomes $(\Psi\text{-P}_4\text{S}_2)$ involving the breaking of one of the Si–Si bonds, as shown in Fig. 5(b). Note that the Si1–O bond has also been broken to indicate that the new O atoms would be bonded to that *precise* Si1 atom (Fig. 5b). This would provoke a repulsion between Si1 and Si2 so that the upper Si_3 triangle of Fig. 5(b) would rotate up, as indicated by the arrow in Fig. 5(b), to reach the position of Si(11) in Fig. 5(c) which is the *real* structure of the new anion $[\text{Si}_6\text{O}_{16}]^{8-}$ in $\text{Cs}_8[\text{Si}_6\text{O}_{16}]$.

A similar situation occurs when an additional $M_2\text{O}$ group is inserted into the $[\text{Si}_6\text{O}_{16}]^{8-}$ anion according to reaction (3) and Figs. 5(c)–(e). The $(\Psi\text{-P}_4\text{S}_2)$ skeleton becomes $(\Psi\text{-P}_2\text{S}_2)$ and consequently another Si–Si bond is broken, as shown in Fig. 5(d). Note that the Si1–O bond has also been broken to indicate that the new O atoms will be bonded to Si1 thus forming the $[\text{Si}_6\text{O}_{17}]^{10-}$ anion (Fig. 5e). This is achieved by rotating the upper Si_3 group around the unique Si–Si bond up to the Si1 atom position in Fig. 5(d) which reaches a position similar to that of Si11 in Fig. 5(e) which is the real structure of $[\text{Si}_6\text{O}_{17}]^{10-}$ in $\text{Rb}_{10}[\text{Si}_6\text{O}_{17}]$ (see Fig. 1c). The reader can easily deduce that a new insertion of the $M_2\text{O}$ group [equation (4)] would break the third Si–Si bond in the $[\text{Si}_6\text{O}_{17}]^{10-}$ anion (Fig. 5e) and the insertion of an additional O atom would give rise to two $[\text{Si}_3\text{O}_9]^{6-}$ anions with the Si atoms being converted into $\Psi\text{-S}$ atoms.

Figure 5

(a) The structure of the anion $[\text{Si}_6\text{O}_{15}]^{6-}$ in $\text{Na}_3\text{Y}[\text{Si}_6\text{O}_{15}]$ already represented in Fig. 1(e). (b) The hypothetical structure obtained after adding one $M_2\text{O}$ group that breaks the Si1–Si2 bond. The additional O atom has not been represented. The bent arrow indicates the movement of the upper Si_3 triangle which must rotate 180° up to form the structure of the $[\text{Si}_6\text{O}_{16}]^{8-}$ anion in $\text{Cs}_8[\text{Si}_6\text{O}_{16}]$ represented in (c). The arrow indicates how the displacement of the Si1 atom in (b) reaches the position of the Si11 in (c). (d) When an additional $M_2\text{O}$ group is added to $\text{Cs}_8[\text{Si}_6\text{O}_{16}]$ in (c), the Si1–Si2 bond is broken forming the structure of $[\text{Si}_6\text{O}_{17}]^{10-}$ in $\text{Rb}_{10}[\text{Si}_6\text{O}_{17}]$ represented in (e). The bonding of the additional O atom to Si1 in the upper Si_3 triangle would rotate up to the Si1 atom in (d) occupying the position of the Si11 atom in (e).

Such an approach has been demonstrated in the comprehensive work on silicates reported by Santamaría-Pérez *et al.* (2005). This view of things was latterly also supported by Professor Liebau by co-authoring the above article. ‘In it’, we wrote, referring to his own book, ‘the structures are classified and described following a criterion of increasing complexity of the silicate polyanions but it should be pointed out that *the reasons* why these polyanions adopt a given structure are *far from being explained*’. Clearly Liebau recognized the inevitable limitations of current thinking and was ready to embrace new ideas as being likely to herald a fuller rationalization of these complex observations. Such a process is inevitable, good for science, enabling it to progress.

Detractors might be inclined to cling to the view that the aluminate, silicate or phosphate skeletons depend on the type and number of surrounding cations. We firmly believe, however, that such a diffuse and incomplete argument cannot

account for the connectivity and structure of these oxopolyanions. We have reported elsewhere (Vegas & García-Baonza, 2007; Vegas, 2011) that there exists a univocal link between chemical composition (in terms of pseudo-atoms) and structure: the generalized Zintl–Klemm concept. Our future papers will continue to develop this clarifying approach which offers insight beyond current horizons.

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