

than in the experimental investigation, and they are located much closer to the central atom (0.35 versus 0.82 Å). This is again due to the thermal smearing of the experimental densities, and similar differences have been seen in many other studies. Qualitatively the two investigations do, however, compare reasonably well as far as bonds, lone pairs and the non-bonding  $d$  orbital are concerned. The dense positive peak found close to the central atom in the experiment is not matched by the theoretical results; it is probably caused by experimental errors and series-termination effects. There is a peak in the direction of the axial water ligand, but it is questionable whether this can account for the experimental peak. The negative region on the vanadyl V—O bond close to vanadium is, on the other hand, well reproduced.

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## Classification of Structures with Anionic Tetrahedron Complexes using Valence-Electron Criteria

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### Abstract

A classification is proposed for the structures of  $C_m C'_m A_n$  compounds which contain anionic tetrahedron complexes formed with all the  $C'$  and  $A$  atoms, the  $C'$  atoms centering the tetrahedra, and with the  $C$  atoms outside the complex. The classification is based on the observation that compounds with these structures can be considered as general valence compounds, which permits the use of the generalized  $(8-N)$  rule. The parameters considered are: (a)  $VEC_A$ , the partial valence-electron concentration with respect to the anion  $A$ , calculated from the position of the elements in the Periodic Table; (b)  $AA(n/m')$  or  $C'C'$  (this depends on the  $VEC_A$  value) which correspond to the average number of electrons

per tetrahedron available for bonds between anions or between central atoms (and/or for electron lone pairs on the central atom), respectively; and finally (c)  $C'AC'$  which expresses the average number of  $C'-A-C'$  links originating from a tetrahedron. Using simple rules it is possible to calculate the most probable value for  $C'AC'$  without knowing the structure. Based on these parameters, classification codes are proposed, written as  $^{AA(n/m')}VEC_A/C'AC'$ ,  $^{08/C'AC'}$  or  $^{C'C'}VEC_A/C'AC'$  depending on the  $VEC_A$  value. Each of these codes expresses an average of the heteronuclear and homonuclear bonds in the anionic tetrahedron complex. Base tetrahedra can be defined for particular sets of  $VEC_A$ ,  $C'AC'$  and  $AA(n/m')$  or  $C'C'$  values. All tetrahedron complexes are interpreted as a linkage of one or more

kinds of these base tetrahedra. The classification is applied to some 290 structure types with anionic or neutral tetrahedron complexes.

### Introduction

Anionic tetrahedron complexes are found in many ionic-covalent compounds such as silicates, phosphates and their analogues, but also in semi-metallic 'Zintl phases'. By grouping the elements according to their functions in the structure, the general formula of these compounds can be expressed as  $C_m C'_m A_n$  with electronegativity values of the corresponding elements increasing from left to right. The elementary unit of an anionic tetrahedron complex consists of a  $C'$  (central atom)-centered  $A_4$  (anions) tetrahedron. This may be linked in different ways with one or more other tetrahedron ( $a$ ) by sharing anion corners and/or edges thus forming  $C'-A-C'$  links, ( $b$ ) by interpenetration with a second tetrahedron and replacement of a  $C'-A$  bond by a  $C'-C'$  bond or ( $c$ ) by the formation of  $A-A$  bonds between different tetrahedra. The  $C'$  atom may also have an electron lone pair in place of a tetrahedral anion neighbour, the corresponding defect tetrahedron being called a  $\psi$  tetrahedron. The  $C$  atoms (cations) do not participate in the tetrahedral anion complex.

There is no general method available for classifying these kinds of structures. Liebau (1985) has developed an elaborate classification system for silicates and phosphates; however, in these compounds neither  $A-A$  nor  $C'-C'$  bonds nor electron lone pairs occur on the central atoms. Further, to commence the classification one has to know the structure first. We thought it worthwhile to develop a primary classification system to ( $a$ ) relate the composition of the compound to the valence electrons of the participating atoms and ( $b$ ) evaluate the average number of  $C'-A$ ,  $A-A$  or  $C'-C'$  bonds (and/or electron lone pairs on  $C'$ ) and the number of  $C'-A-C'$  links originating from a tetrahedron which characterize the anionic tetrahedron complex. As will be seen, in many cases it will be possible to predict important bonding features of the anionic tetrahedron complex and to classify the structure with only the knowledge of the compound formula and the valence electrons of the participating elements.

### The model behind the classification scheme

The proposed classification requires the multicomponent compounds to satisfy the generalized  $(8-N)$  rule, also called the Mooser-Pearson rule (Hulliger & Mooser, 1963; Pearson, 1964; Hulliger, 1968; Kjekshus & Rakke, 1974), which as far as the subdivision of polyanionic compounds is concerned is

also known under the name of the Zintl-Klemm-Busmann (ZKB) concept (Schäfer, Eisenmann & Müller, 1973; Klemm & Busmann, 1963). The generalized  $(8-N)$  rule was originally only applied to semiconductors; however, Zintl has demonstrated that the valence concept can also be used with certain intermetallic compounds.\*

In a formal approach, we consider these compounds as 'ionic compounds' with the  $C$  atoms contributing all their valence electrons to the complex made up of the  $A$  and  $C'$  atoms. This electron transfer allows the  $A$  atoms (but also the  $C'$  atoms by electron sharing and/or electron lone pairs, if any) to obtain completely filled octets. Thus, the model assumes heteropolar bonding between the  $C$  atoms and the anionic complex, and covalent two-electron bonds within the complex. In this sense, these compounds agree with the ZKB concept established for binary compounds such as NaI or NaSi, which states that the non-noble atoms transfer their electrons to the more noble component, the 'anion former'. With the resulting outer-electron configuration, an 'anion partial structure' is constructed (whose atomic arrangement corresponds to the element having the same number of valence electrons). In the case of the  $C_m C'_m A_n$  compounds considered here, a binary anionic tetrahedron complex is formed with, now, heteronuclear  $C'-A$  bonds and also, if necessary, with  $A-A$  or  $C'-C'$  homonuclear bonds. In the strict definition of the ZKB concept, the  $C'$  atoms should also be considered as anions. However, to conserve the notation used with the generalized  $(8-N)$  rule, we will treat the  $C'$  atoms as 'cations *ex-officio*' and only the  $A$  atoms as anions. Thus, we will speak below about *polycationic* valence compounds (with covalent  $C'-A$  and  $C'-C'$  bonds and/or lone pairs on  $C'$ ), *polyanionic* valence compounds (with  $C'-A$  and  $A-A$  bonds) and *normal* valence compounds (with  $C'-A$  bonds only).

According to the definition given above for the anionic tetrahedron complex, *all* the anions  $A$  share covalent two-electron bonds with the  $C'$  atoms and *all* the valence electrons of the compound are assumed to be transferred to the  $C'_m A_n$  tetrahedron complex. However, the total electron transfer is only a model. For many multicomponent compounds it might be argued that the  $A$  atoms also share covalent bonds with the  $C$  cations and even that  $C$ -centered  $A_4$  tetrahedra are formed. In this latter case one could alternatively include the  $C$  atoms in the tetra-

\*According to the definition given by Schäfer (1985a,b) the term 'Zintl phases' is applied today to semimetallic or even metallic compounds where the underlying ionic and covalent bonds play such an important role that chemically based valence rules, normally reserved for semi- or nonconducting compounds, can be used to account for the stoichiometry and the observed structural features.

hedron complex and describe the complete structure as a tetrahedral structure. The possibility of describing a structure in this way does not interfere with the possibility of also using the ionic-covalent model.

Another limiting case occurs with compounds of composition  $C'_m A_n$  which have no  $C$  cations. Here, the number of valence electrons provided by the central atoms  $C'$  is just sufficient to complete the octets of the  $A$  atoms. These  $C'_m A_n$  compounds also have tetrahedral structures for which valence-electron rules have been given before (Parthé, 1972).

From the generalized  $(8-N)$  rule we shall calculate the average number of electrons per  $A$  or  $C'$  atom which are used for the formation of  $A-A$  or  $C'-C'$  bonds (and/or lone pairs on the  $C'$  atoms). We shall also calculate from the stoichiometry of the compound a parameter labelled  $C'AC'$ , which expresses the average number of  $C'-A-C'$  links originating from one tetrahedron. This parameter corresponds in the case of normal-valence compounds to the tetrahedron-sharing coefficient  $TT$  (Parthé & Engel, 1986; Engel, 1986). As we shall see, the values for  $C'AC'$  cannot be calculated with certainty because this parameter does not depend on the composition alone. However, from simple empirical rules, it is possible to obtain the correct  $C'AC'$  value of a given structure type with a probability of 95%. This makes  $C'AC'$  another interesting parameter to be considered for the proposed classification.

#### The generalized $(8-N)$ rule applied to ternary compounds with binary anionic tetrahedron complexes

For an application of the generalized  $(8-N)$  rule to a compound  $C'_m C'_m A_n$  with an anionic tetrahedron complex of composition  $C'_m A_n$ , we shall proceed as described below.

First, following a formulation proposed by Parthé (1973), we shall express the electronic quantities by the *partial valence-electron concentration with respect to the anion*,  $VEC_A$ , defined as:

$$VEC_A = (m e_C + m' e_{C'} + n e_A) / n \quad \text{for } C'_m C'_m A_n \quad (1)$$

where  $e_C$ ,  $e_{C'}$  and  $e_A$  are the numbers of valence electrons of the neutral atoms, and  $m$ ,  $m'$  and  $n$  are composition parameters. The value of  $VEC_A$  can be easily calculated from the composition of a given compound and from the positions of its component elements in the Periodic Table (for exceptions and the contribution of the transition elements see Table 2).

Next, concerning the structural features, we make the assumption that, if there are electrons left which are not needed by the anions, they are retained by the central atoms  $C'$  and are used either for  $C'-C'$  bonds or for lone pairs (LP). In this case the

generalized  $(8-N)$  rule, as reformulated by Parthé (1972, 1973), can be written in the modified form:

$$VEC_A = 8 + (m'/n)C'C' - AA \quad (2)$$

where  $C'C'$  is the average number of electrons per central atom for  $C'-C'$  bonds and/or for lone pairs on the  $C'$  atoms. If there are only  $C'-C'$  bonds, the  $C'C'$  value corresponds to the average number of  $C'-C'$  bonds per  $C'$  atom.  $AA$  is the average number of electrons per anion for  $A-A$  bonds. The  $AA$  value corresponds to the average number of  $A-A$  bonds per  $A$  atom.

It can be concluded from observations that  $A-A$  and  $C'-C'$  bonds (or LP on  $C'$ ) do not coexist in a structure except for very rare cases. Consequently, the  $VEC_A$  value allows the differentiation between three kinds of valence compounds:

(a) *Normal-valence compounds* for which  $C'C' = AA = 0$  and thus:

$$VEC_A = 8.$$

The great majority of the compounds with anionic tetrahedron complexes are normal-valence compounds (silicates in particular) where there are neither  $A-A$  bonds, nor  $C'-C'$  bonds or lone pairs associated with the central atoms.

(b) *Polyanionic valence compounds* with  $AA > 0$ ,  $C'C' = 0$  and then:

$$VEC_A < 8 \rightarrow AA = 8 - VEC_A. \quad (3)$$

The polyanionic valence compounds are characterized by homonuclear  $A-A$  bonds between anions belonging to different tetrahedra. Since, in a compound of composition  $C'_m C'_m A_n$ , the average number of anions per tetrahedron of the anionic tetrahedron complex is  $n/m'$ , the average number of  $A-A$  bonds per tetrahedron is  $AA(n/m')$ . This quantity applies to the bonds between different tetrahedra.

(c) *Polycationic valence compounds* with  $C'C' > 0$ ,  $AA = 0$  and thus:

$$VEC_A > 8 \rightarrow C'C' = (n/m')(VEC_A - 8). \quad (4)$$

The polycationic valence compounds are characterized by homonuclear  $C'-C'$  bonds between the central atoms and/or lone pairs (non-bonding orbitals) attached to the central atoms. Since each tetrahedron of the anionic tetrahedron complex has one  $C'$  central atom, the  $C'C'$  value corresponds to the number of electrons which, on the average, are available for  $C'-C'$  bonds and/or lone pairs per tetrahedron. We retain here the conventional term 'polycationic' valence compound although some of the elements corresponding to the central atoms, such as P, S, or Se, are normally not considered as cations.

Equation (4) allows the total number of valence electrons which rest with a central atom to be

obtained. For our purposes, it is necessary to indicate how many of these are used for a  $C'-C'$  bond (one electron per central atom) or for an electron lone pair (two electrons per central atom). We introduce a parameter, called  $x$ , which relates the average number of  $C'-C'$  bonds ( $N_{C'-C'}$ ) to the number of lone pairs ( $N_{LP}$ ) per central atom as follows:

$$x = N_{C'-C'}/(N_{C'-C'} + 2N_{LP}) = N_{C'-C'}/C'C'. \quad (5)$$

An analysis of the 109 structure types of polycationic valence compounds listed in Table 2 allows the formulation of a simple empirical rule to predict when  $C'-C'$  bonds or lone pairs are expected:

(a) when  $C'C' = 1$  then  $x = 1$ : this means that all  $C'$  atoms participate in  $C'-C'$  bonds (93% of 42 structure types);

(b) when  $C'C' = 2$  then  $x = 0$ : this means that all  $C'$  atoms have a lone pair (98% of 44 structure types);

(c) when  $C'C' = 3$  then  $x = \frac{1}{3}$ : this means that all  $C'$  atoms have one lone pair and one  $C'-C'$  bond (5 of 5 structure types).

We have found too few polycationic valence compounds with  $C'C'$  values different from 1, 2 or 3 to formulate an empirical rule concerning their most probable value of  $x$ .

### The general tetrahedral structure equation applied to ternary compounds with binary anionic tetrahedron complexes

Ternary compounds with a binary anionic tetrahedron complex may be treated as compounds with a tetrahedral anion partial structure. The general tetrahedral structure equation as given by Parthé (1972, 1973) can be applied to the charged anionic tetrahedron complex, assuming that the cations  $C$  have transferred all their valence electrons to the complex.

Using a total valence-electron concentration value referred to the charged complex given by:

$$VEC' = (me_C + m'e_C + ne_A)/(m' + n) \quad (6)$$

one can write the general tetrahedral structure equation as:

$$VEC' = 4 + N_{NBO} \quad (7)$$

where  $N_{NBO}$  is the number of non-bonding orbitals per atom of the charged anionic tetrahedron complex. For example, an isolated charged tetrahedron has 12 non-bonding orbitals, that means  $N_{NBO} = 12/5$  and consequently,  $VEC' = 32/5$ .

A special case occurs when  $VEC' > 6$  and when the anionic tetrahedron complex consists of one or more *non-cyclic* molecular tetrahedron groupings with a *finite* number of linked tetrahedron. By tetrahedron grouping we understand (besides the limiting

case of the isolated tetrahedron) tetrahedra linked by  $A-A$  bonds or by  $C'-C'$  bonds and/or  $C'-A-C'$  links. The tetrahedra can only be corner-linked, not edge-linked (this would correspond to a cycle of bonds). A derivative formula of the general tetrahedral structure equation allows the calculation of the average number of atoms in the molecular tetrahedron grouping, labelled  $N'_{A/M}$ , according to:

$$N'_{A/M} = 2/(VEC' - 6) \quad \text{for } VEC' > 6. \quad (8)$$

For example, in the case of  $KSO_4$  with  $VEC' = 31/5$  it is found that  $N'_{A/M} = 10$ , which corresponds to the observed number of atoms in the anionic tetrahedron complex. More examples can be found in Fig. 5.

### The $C'AC'$ parameter for different kinds of valence compounds

The  $C'AC'$  parameter, which denotes the average number of  $C'-A-C'$  links per tetrahedron, depends on the number of  $C'-A$  bonds of a central atom and on the ratio  $n/m'$ . The number of  $C'-A$  bonds of a central atom, denoted  $N_{C'-A}$ , is four in the case of normal or polyanionic valence compounds but less than four in the case of polycationic valence compounds. It should be noted that a  $C'-C'$  bond replaces two anions (one each on two tetrahedra), but an electron lone pair only one. It follows that:

$$N_{C'-A} = 4 - [(1 + x)C'C']/2 \quad (9)$$

where  $x$  is the fraction of the number of valence electrons used for  $C'-C'$  bonds over the total number of valence electrons which rest with the  $C'$  atoms to form  $C'-C'$  bonds and/or lone pairs as defined by (5).

All possible  $C'AC'$  versus  $n/m'$  equations can be derived by combining the following three equations:

$$N_{C'-A} = N_0 + N_1 + N_2 + N_3 \quad (10)$$

$$n/m' = N_0 + \frac{1}{2}N_1 + \frac{1}{3}N_2 + \frac{1}{4}N_3 \quad (11)$$

$$C'AC' = N_1 + 2N_2 + 3N_3 \quad (12)$$

where  $N_0$  is the mean number of 'unshared' anions per tetrahedron (they do not participate in  $C'-A-C'$  links to other tetrahedra),  $N_1$  is the mean number of shared anions per tetrahedron which participate in one  $C'-A-C'$  link to one other tetrahedron,  $N_2$  is the mean number of shared anions per tetrahedron which participate in two  $C'-A-C'$  links to two other tetrahedra, and  $N_3$  is the mean number of shared anions per tetrahedron which participate in three  $C'-A-C'$  links to three other tetrahedra. To derive an equation for  $C'AC'$  as a function of  $n/m'$  it is necessary to specify first which of the  $N_0$  to  $N_3$  values will be zero for the particular case of interest and then to eliminate the remaining non-zero values of  $N$  by combining the three equations.

In the common case (98% of 293 structure types) there is an *equipartition* of the  $C'-A-C'$  links over the tetrahedron corners occupied by the  $A$  anions. Equipartition means that there is either none or only a difference of one in the number of  $C'-A-C'$  links which pass through the different anion corners of a tetrahedron; this corresponds to a minimization of  $C'AC'$  for a given  $n/m'$  value. An equivalent definition of the equipartition (Zoltaï, 1960) is that the difference between the smallest and the largest number of tetrahedra participating in the sharing of a tetrahedral corner in a structure cannot be more than one.

For the general case of *equipartition* the different anions of one tetrahedron participate only in, say,  $k$  or  $k-1$   $C'-A-C'$  links to other tetrahedra. Thus, in (10), (11) and (12), only the parameters  $N_k$  and  $N_{k-1}$  have values different from zero. This leads to:

$$C'AC' = k[2N_{C'-A} - (k+1)(n/m')], \quad (13)$$

with  $(1/k)N_{C'-A} \geq n/m' \geq [1/(k+1)]N_{C'-A}$ . The integer  $k$ , which corresponds to the number (or if there are two to the larger number) of  $C'-A-C'$  links in which the different anions of a tetrahedron participate, can be obtained from

$$k < [N_{C'-A}/(n/m')] \leq k + 1.$$

Equation (13) is a modified form of Zoltaï's expression for the sharing coefficient (Zoltaï, 1960) which is also extended here to include compounds with  $C'-C'$  bonds and/or lone pairs.

The three solutions of (13) for  $k = 1, 2$ , or  $3$  are:

(a) For unshared anions or anions participating in one  $C'-A-C'$  link to another tetrahedron ( $k = 1$ ):

$$C'AC' = 2[N_{C'-A} - (n/m')] \quad \text{for } N_{C'-A} \geq n/m' \geq \frac{1}{2}N_{C'-A} \quad (13a)$$

and thus  $0 \leq C'AC' \leq N_{C'-A}$ .

(b) For anions participating in one or two  $C'-A-C'$  links to other tetrahedra ( $k = 2$ ):

$$C'AC' = 6[\frac{2}{3}N_{C'-A} - (n/m')] \quad \text{for } \frac{1}{2}N_{C'-A} \geq n/m' \geq \frac{1}{3}N_{C'-A} \quad (13b)$$

and thus  $N_{C'-A} \leq C'AC' \leq 2N_{C'-A}$ .

(c) For anions participating in two or three  $C'-A-C'$  links to other tetrahedra ( $k = 3$ ):

$$C'AC' = 12[\frac{1}{3}N_{C'-A} - (n/m')] \quad \text{for } \frac{1}{3}N_{C'-A} \geq n/m' \geq \frac{1}{4}N_{C'-A} \quad (13c)$$

and thus  $2N_{C'-A} \leq C'AC' \leq 3N_{C'-A}$ .

Of the different imaginable possibilities for *non-equipartition*, we want to consider only the case where the anions participate in  $k$  or  $k-2$  links to other tetrahedra. The resulting equation obtained from (10), (11) and (12), assuming that  $N_k$  and  $N_{k-2}$  are non-zero, is:

$$C'AC' = (2k-1)N_{C'-A} - (k^2-1)(n/m'), \quad (14)$$

with  $N_{C'-A}/(k-1) \geq n/m' \geq N_{C'-A}/(k+1)$ . For the evaluation of  $k$ , the inequality can be rewritten as:

$$k-1 < [N_{C'-A}/(n/m')] \leq k+1.$$

*Normal-valence compounds* ( $VEC_A = 8$  and  $N_{C'-A} = 4$ )

In the case of normal-valence compounds the parameter  $C'AC'$  is identical to the tetrahedron-sharing coefficient  $TT$ , discussed by Parthé & Engel (1986) and Engel (1986).

(a) To calculate  $C'AC'$  for normal-valence compounds with equipartition of the  $C'-A-C'$  links (167 of 172 types) we use (13) with  $N_{C'-A} = 4$ . The resulting equation becomes similar to the one derived by Engel (1986; see equation III.19). The three particular solutions for  $k = 1, 2$  and  $3$ , already given by Parthé & Engel (1986), are:

(i) For unshared anions or anions participating in one  $C'-A-C'$  link to another tetrahedron ( $k = 1$ ):

$$C'AC' = 2[4 - (n/m')] \quad \text{for } 4 \geq n/m' \geq 2. \quad (15a)$$

(ii) For anions participating either in one or two  $C'-A-C'$  links to other tetrahedra ( $k = 2$ ):

$$C'AC' = 6[\frac{2}{3} - (n/m')] \quad \text{for } 2 \geq n/m' \geq \frac{4}{3}. \quad (15b)$$

(iii) For anions participating either in two or three  $C'-A-C'$  links to other tetrahedra ( $k = 3$ ):

$$C'AC' = 12[2 - (n/m')] \quad \text{for } 4/3 \geq n/m' \geq 1. \quad (15c)$$

The  $n/m'$  ranges of these three equations, together with symbolic drawings indicating the different numbers of  $C'-A-C'$  links which may pass through a tetrahedron corner corresponding to different  $k$  values, are given on the bottom line of Fig. 1 ( $N_{C'-A} = 4$  which corresponds to  $C'C' = 0$ ). Only (15a) is shown in the diagram.

(b) For the rare cases (5 of 172 types) where there is no equipartition of the  $C'-A-C'$  links one uses (14) with  $N_{C'-A}$  replaced by 4. Two solutions are of interest:

(i) for anions either unshared or participating in two  $C'-A-C'$  links to other tetrahedra ( $k = 2$ ):

$$C'AC' = 3[4 - (n/m')] \quad \text{for } 4 \geq n/m' \geq \frac{4}{3}; \quad (16a)$$

(ii) for anions participating either in one or in three  $C'-A-C'$  links to other tetrahedra ( $k = 3$ ):

$$C'AC' = 8[\frac{5}{2} - (n/m')] \quad \text{for } 2 \geq n/m' \geq 1. \quad (16b)$$

*Polyanionic valence compounds* ( $VEC_A < 8$  and  $N_{C'-A} = 4$ )

The calculation of  $C'AC'$  is not affected by the presence of extra  $A-A$  bonds between the tetrahedra. Equations (15a) and (15b) can be applied here without any change. Structures of polyanionic valence compounds with  $C'-A-C'$  links corresponding to (15c), (16a) or (16b) are not known so far.

*Polycationic valence compounds* ( $VEC_A > 8$  and  $N_{C-A} = 4 - [(1+x)C'C']/2$ )

For the general case of an equipartition of the  $C'-A-C'$  links (99% of 109 structure types),  $C'AC'$  is calculated from (13) using the  $N_{C-A}$  value obtained from (9). Thus, for the polycationic valence compounds, different  $n/m'$  ranges apply for (13), depending on the  $C'C'$  and  $x$  values. They can be read from Fig. 1 which shows a diagram for  $C'AC'$  as a function of  $[(1+x)C'C']/2$  and  $n/m'$ . Thick inclined lines separate the three regions where, from right to left, (13a), (13b) and (13c) are valid. The ordinate corresponds to the number of  $C'-A$  bonds lost by the central atom of a  $C'_4A$  tetrahedron when  $C'-C'$  bonds are formed and/or when there are lone pairs on  $C'$ . The solutions of (13a) for  $N_{C-A} = 4, 3$  and 2, that is  $[(1+x)C'C']/2 = 0, 1$  and 2, are shown in the diagram.

Each  $C'AC'$  equation used in this work was obtained from the combination of (10), (11) and (12). All of them contain the parameter  $N_y$ , the subscript of which may take integral values between 0 and 3. When  $y = 3$ , according to the definition given above, the anion participates in four two-electron  $A-C'$  bonds. This case corresponds to the maximum possible number of  $A-C'$  covalent bonds which allows

the anion to complete its octet shell by electron sharing. Compounds with anionic tetrahedron complexes are known, however, where the anions may participate in more than four bonds to central atoms and which, thus, do not correspond to our model of valence compounds. It is still possible, in such a case, to derive  $C'AC'$  equations as a function of  $n/m'$  from (10), (11) and (12) extended by  $N_y$  terms with  $y > 3$ . For example, in metallic  $KCu_4S_3$  (Brown, Zubieta, Vella, Wroblewski, Watt, Hatfield & Day, 1980), there are  $CuS_4$  tetrahedra which are linked in such a way that two anions participate in three  $C'-A-C'$  links and two in seven  $C'-A-C'$  links. Thus, with  $4 = N_3 + N_7$  from (10),  $n/m' = \frac{1}{4}N_3 + \frac{1}{8}N_7$  from (11) and  $C'AC' = 3N_3 + 7N_7$  from (12), one finds  $C'AC' = 4[11 - 8(n/m')]$ . For  $KCu_4S_3$  the calculated  $C'AC'$  is 20, which is the correct value.

A final remark can be added that (10), (11) and (12) can be easily modified to obtain a relation between the average number of  $C'-A-C'$  links and the  $n/m'$  ratio assuming that the anion complex is built up of polyhedra different from tetrahedra [this possibility has already been noted by Engel, (1986)]. The digit 4 in (9) has to be replaced by a value which corresponds to the number of corners of the new polyhedron and all parameters have to be related to the new kind of polyhedron.

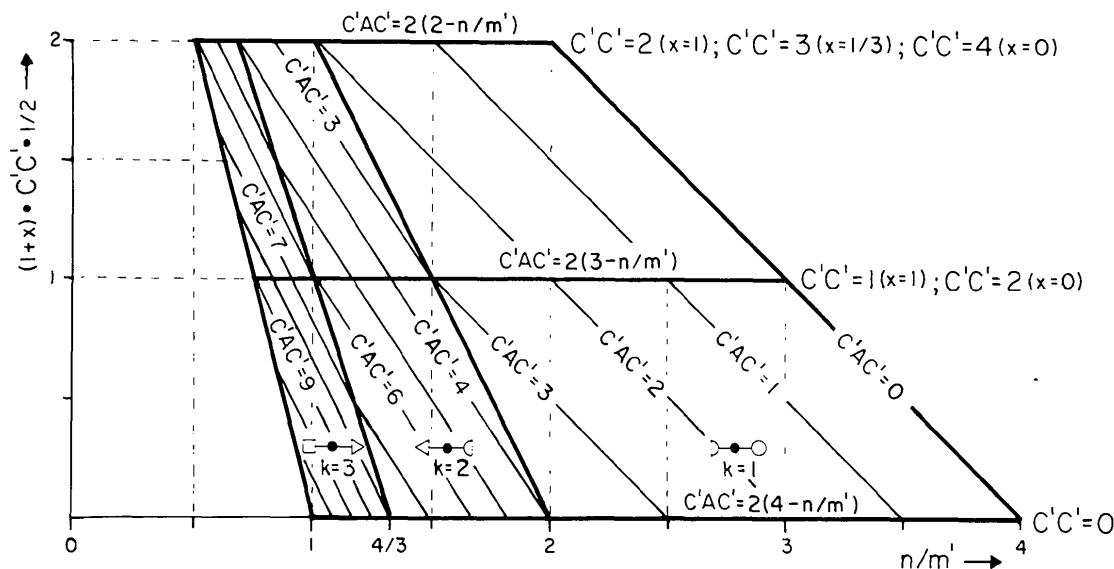


Fig. 1.  $C'AC'$  diagram as a function of  $[(1+x)C'C']/2$  and  $n/m'$  for the case of equipartition of the  $C'-A-C'$  links. Thick inclined lines separate the three domains which differ in the way the anions are shared and for which, from right to left, the equations (13a), (13b) and (13c) are valid. Anion sharing is represented by a symbolic drawing in each of these domains. A small black circle corresponds to a central atom, the blank symbols represent the anions. A complete blank circle corresponds to an anion which belongs to only one tetrahedron (no  $C'-A-C'$  link), a half circle to an anion which is shared with one other tetrahedron (it participates in one  $C'-A-C'$  link), a triangle to an anion shared with two other tetrahedra (two  $C'-A-C'$  links) and a square corresponds to an anion shared with three other tetrahedra (three  $C'-A-C'$  links). Within the range of a  $C'AC' - n/m'$  equation, the number of  $C'-A-C'$  links of a tetrahedron varies from one limiting case where all the anions have links (as shown by the blank symbol on the right) to the other limiting case (represented by the blank symbol on the left of the black circle). The number of anion neighbours of a central atom is  $N_{C-A} = 4 - [(1+x)C'C']/2$ . The composition of a single tetrahedron depends, however, on the number of  $C'-A-C'$  links in which its anions participate (half circles, triangles and squares count, respectively, for one half, one third and one quarter of an anion.)

**Prediction of the most probable base tetrahedron(a)  
from the chemical formula of the compound**

We consider as base tetrahedra the isolated  $C'A_4$  tetrahedron but also the tetrahedra which share anions, those in which each anion may extend one bond to an anion of another tetrahedron and finally, the tetrahedra which have a  $C'-C'$  bond or a lone pair instead of a  $C'-A$  bond.

In Fig. 2 graphs are shown of the 32 possible base tetrahedra subject to the restriction that a central atom has no less than two anion neighbours and that an anion is either unshared or shared with only one other tetrahedron. Note that the planar graph presentation suggests a certain order of the ligands

which is however irrelevant, all four ligands of a central atom in a tetrahedron being geometrically equivalent with respect to each other. The  $C'AC'$  value of each base tetrahedron in Fig. 2 can be calculated by counting the half-circles, the  $AA(n/m')$  value by counting the number of indicated  $A-A$  bonds per tetrahedron and the  $C'C'$  value by adding twice the number of non-bonding orbitals to the number of  $C'-C'$  bonds. Inserting the values for  $AA$  or  $C'C'$  and  $n/m'$  into (2) one can calculate a  $VEC_A$  value for each base tetrahedron. This value should correspond to the  $VEC_A$  value of a valence compound with an anionic tetrahedron complex built up only with this particular base tetrahedron. The base tetrahedra in Fig. 2 are arranged according to their

$n/m'$	AA • (n/m')				AA=C'C'=	C'C'					
	4	3	2	1	0	1 (x=1)	2 (x=0)	2 (x=1)	3 (x=1/3)	4 (x=0)	
4:1	 <sup>4</sup> 7/0	 <sup>3</sup> 7.25/0	 <sup>2</sup> 7.5/0	 <sup>1</sup> 7.75/0	 <sup>0</sup> 8/0						
7:2		 <sup>3</sup> 7.143/1	 <sup>2</sup> 7.429/1	 <sup>1</sup> 7.714/1	 <sup>0</sup> 8/1						
3:1			 <sup>2</sup> 7.333/2	 <sup>1</sup> 7.667/2	 <sup>0</sup> 8/2	 <sup>1</sup> 8.333/0	 <sup>2</sup> 8.667/0				
5:2				 <sup>1</sup> 7.6/3	 <sup>0</sup> 8/3	 <sup>1</sup> 8.4/1	 <sup>2</sup> 8.8/1				
2:1					 <sup>0</sup> 8/4	 <sup>1</sup> 8.5/2	 <sup>2</sup> 9/2	 <sup>3</sup> 9/0	 <sup>3</sup> 9.5/0	 <sup>4</sup> 10/0	
3:2						 <sup>1</sup> 8.667/3	 <sup>2</sup> 9.333/3	 <sup>2</sup> 9.333/1	 <sup>3</sup> 10/1	 <sup>4</sup> 10.667/1	
1:1								 <sup>2</sup> 10/2	 <sup>3</sup> 11/2	 <sup>4</sup> 12/2	

Fig. 2. Graphs of the 32 possible base tetrahedra where each central atom has at least two anion neighbours and where each anion is either unshared or shared with only one other tetrahedron ( $0 \leq C'AC' \leq N_{C'-A}$ ,  $k = 1$ ). The base tetrahedra are arranged according to their  $n/m'$ ,  $AA(n/m')$  or  $C'C'$  values and in the last case also their  $x$  value. Assuming an equipartition of the  $C'-A-C'$  links and of the  $A-A$  links over the corners of the tetrahedron, each base tetrahedron is unambiguously identified by means of the  $AA(n/m')VEC_A/C'AC'$  code (when  $VEC_A < 8$ ), the  ${}^08/C'AC'$  code (when  $VEC_A = 8$ ) or the  ${}^{C'}VEC_A/C'AC'$  code (when  $VEC_A > 8$ ). The value of  $AA(n/m')$  corresponds to the average number of  $A-A$  bonds per tetrahedron and  $C'C'$  to the average number of  $C'-C'$  bonds and/or the number of electrons used for lone pairs on the central atom per tetrahedron. The  $A-A$  bonds and  $C'-C'$  bonds are indicated by short heavy lines extending from the blank symbol and the filled circle, respectively. A lone pair is shown as a heavy bar on a filled circle.

$n/m'$  and their  $AA(n/m')$  or  $C'C'$  values and in the latter case also the  $x$  value. To classify the base tetrahedra we use the parameters  $AA(n/m')$  or  $C'C'$ ,  $VEC_A$  and  $C'AC'$  written in the form  $^{AA(n/m')}VEC_A/C'AC'$ ,  $^{\circ 8}/C'AC'$  or  $^{C'C'}VEC_A/C'AC'$ . When  $VEC_A < 8$ , then the superscript corresponds to the  $AA(n/m')$  value. For  $VEC_A = 8$  the superscript is 0. When  $VEC_A > 8$ , then the superscript expresses the  $C'C'$  value. In the case of  $^{AA(n/m')}VEC_A/C'AC'$ , the  $AA$  parameter is simply the difference from 8 of the  $VEC_A$  value. In the case of  $^{C'C'}VEC_A/C'AC'$ , however, the relation between  $C'C'$  and  $VEC_A$  also depends, according to (4), on the  $n/m'$  ratio. The proposed codes allow unambiguous characterization of the base tetrahedra provided there is an equipartition of the  $C'-A-C'$  links and  $A-A$  bonds over the corners of the tetrahedron.

In Fig. 3 base tetrahedra are shown where one or more anions participate on more than one  $C'-A-C'$  link. The list does not include all the possibilities; however, all the base tetrahedra found in the crystal structures in Table 2 are presented. In the three base tetrahedra at the bottom of Fig. 3 there is no equipartition of the  $C'-A-C'$  links. To distinguish these exceptional base tetrahedra their codes are surrounded by square brackets.

An observed anionic tetrahedron complex either corresponds directly to a base tetrahedron or can be interpreted as a linkage of different base tetrahedra. Inversely, using the equations given above, it is possible to express the expected structural features of a compound in terms of the most probable base tetrahedron(a): one first calculates the  $AA$  or  $C'C'$  value and next, the most probable  $C'AC'$  value

#### Base tetrahedra with equipartition of $C'-A-C'$ links

$n/m'$	3/2					
$VEC_A < 8$						
	1/27·667/7					
$n/m'$	11/6	5/3	3/2	4/3	5/4	1/1
$VEC_A = 8$						
	$^{\circ 8}/5$	$^{\circ 8}/6$	$^{\circ 8}/7$	$^{\circ 8}/8$	$^{\circ 8}/9$	$^{\circ 8}/12$
$n/m'$	4/3	7/6	1/1	3/4	$x = 1$	
$VEC_A > 8$					$x = 1$	
	$^1 8 \cdot 75/4$	$^1 8 \cdot 857/5$	$^1 9/6$	$^1 9 \cdot 333/9$	$x = 1$	
$n/m'$	2/1	3/2	5/3	$x = 0$		
$VEC_A > 8$				$x = 0$		
	$^2 9 \cdot 5/4$	$^2 9 \cdot 714/5$	$^2 10/6$	$x = 0$		

#### Base tetrahedra with non-equipartition of $C'-A-C'$ links

$n/m'$	2/1	3/2	5/3
$VEC_A > 8$			
	[ $^{\circ 8}/6$ ]	[ $^{\circ 8}/8$ ]	[ $^2 9 \cdot 2/4$ ]
	$x = 0$		

Fig. 3. Graphs of the base tetrahedra which occur in the structures listed in Table 2 and where one or more anions participate on more than one  $C'-A-C'$  link ( $k > 1$ ). For the meaning of the filled and blank symbols, see the legend to Fig. 1. Note that, in the base tetrahedron on the top, a shared anion (half circle) has a bond to another anion. Thus there is one half of an  $A-A$  bond for 3/2 anions and the  $AA$  value is consequently 1/3 and  $AA(n/m') = 1/2$ .



(assuming that there is an equipartition of the  $C'-A-C'$  links and that, for  $C'C' > 0$ , the partitioning of the electrons between  $C'-C'$  bonds and lone pairs on  $C'$  follows the rule given above). In this way the most probable  $^{AA(n/m')}VEC_A/C'AC'$ ,  $^08/C'AC'$  or  $^{C'C'}VEC_A/C'AC'$  code for the compound can be established.

Depending on the code, two cases have to be distinguished to find the most probable base tetrahedron(a):

(a) The most probable code of the compound is identical with the code of a base tetrahedron (260 of 293 types).

Here, one expects the tetrahedron complex to be built up with only this single base tetrahedron (this is verified in 242 of 260 types). Examples are to be found in Fig. 4 where the predicted most probable single base tetrahedra of five compounds with composition  $CC'A_3$  can be compared with the observed tetrahedron complexes. The  $VEC_A$  values vary from 7.333 to 8.667 and, consequently, the predicted base tetrahedra are all different. In the case of  $BaTeS_3$ , the predicted base tetrahedron ( $^28.667/0$ ) is identical to the observed isolated  $\psi$ -tetrahedron. For the four other compounds the anionic tetrahedron complex can be obtained by linking the corresponding single base tetrahedron with itself.

In 18 of 260 types of this category the tetrahedron complex is built up from more than one kind of base tetrahedron. As an example one may study the schematic drawings of the observed tetrahedron complexes found in particular (alkali)-sulfur(selenium)-oxygen compounds shown in Fig. 5. The predicted most probable single-base tetrahedra are not shown

here; however, using the observed  $n/m'$  ratios and the listed codes of the anionic tetrahedron complexes, the drawings of the base tetrahedra can be easily found in Fig. 2. It can be noted that each observed tetrahedron complex is built up with one kind of base tetrahedron in all compounds except for  $Se_2O_5$  (most probable code  $^18.4/1$ ) and  $K_2S_2O_5$  ( $^28.8/1$ ). To construct the observed tetrahedron complex two different kinds of base tetrahedra are needed for both compounds ( $^08/2$  plus  $^29/2$  for  $Se_2O_5$  and  $^18.333/0$  plus  $^39.5/0$  for  $K_2S_2O_5$ ). The reason why two different base tetrahedra are necessary in these two S or Se compounds seems to lie in the splitting of the oxidation states of the pairs of chalcogen atoms into 4 and 6 instead of 5.

(b) The most probable code of the compound is not identical with the code of a base tetrahedron (33 of 293 types).

Normally, whenever the  $C'AC'$  and/or the  $C'C'$  and/or the  $AA(n/m')$  values of a compound code are not integers, the tetrahedron complex is built up from more than one single base tetrahedron (one exception can be found in Fig. 3). As an example, one may consider the compound  $Zn_2P_3S_9$  for which the most probable calculated code is  $^{1/3}8.111/1.333$ , assuming  $x = 1$ . No base tetrahedron with this code is possible. Restricting the search to base tetrahedra with the same  $n/m'$  value, the two most probable ones with codes close to the code of the compound are  $^08/2$  and  $^18.333/0$ . There must be twice as many of the first kind in order to obtain the correct  $C'C'$  and  $C'AC'$  values. The predictions are in full agreement with the observed anionic tetrahedron complex in  $Zn_2P_3S_9$ : one finds one isolated con-

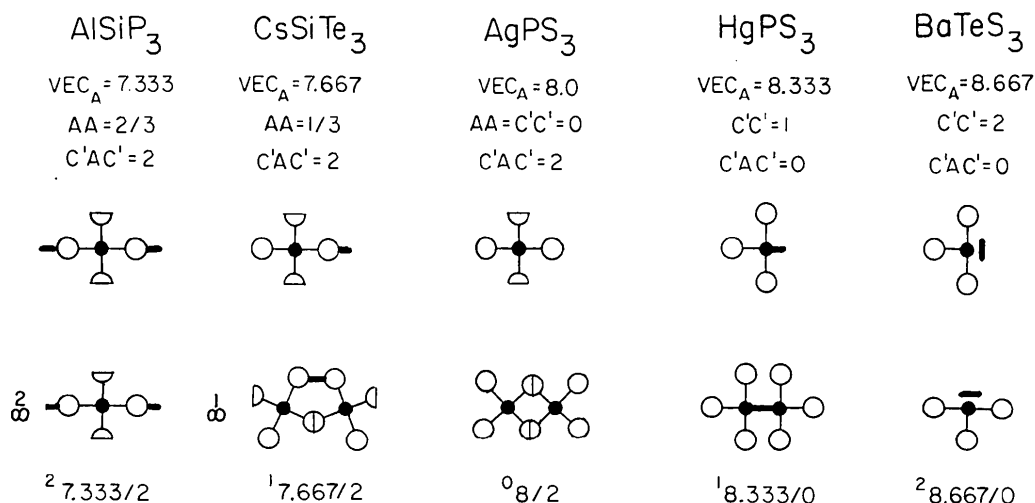


Fig. 4. Graphs of the predicted most probable single-base tetrahedra (upper drawings) and of the observed tetrahedron linkages of the anion complexes (lower drawings) in five compounds with composition  $CC'A_3$ , where  $VEC_A$  varies from 7.33 to 8.667. The classification code is given for each anionic tetrahedron complex.

densed double tetrahedron, as in  $\text{HgPS}_3$ , together with two isolated edge-linked double tetrahedra, as in  $\text{AgPS}_3$  (see Fig. 4).

The average code of a structure built up of different base tetrahedra and the overall composition of the anionic complex can be obtained from the following equations:

$$\begin{aligned} AA(n/m') &= \langle AA(n/m') \rangle \text{ or } C'C' = \langle C'C' \rangle \\ VEC_A &= \langle VEC_A(n/m') \rangle / \langle n/m' \rangle \\ C'AC' &= \langle C'AC' \rangle \end{aligned} \quad (17)$$

where  $n/m' = \langle n/m' \rangle$  and where the angled brackets indicate that the enclosed data are the average values of the base tetrahedra involved. Note also that  $x = \langle xC'C' \rangle / \langle C'C' \rangle$ .

To find the most probable base tetrahedra of a compound whose code is not identical with a code of a base tetrahedron, it is helpful to use the following guidelines:

(i) For a normal-valence compound one expects two base tetrahedra, of the type  ${}^0_8/C'AC'$ , with their  $n/m'$  values closest to the  $n/m'$  value of the compound. Their proportions are chosen so that the average  $n/m'$  value is equal to the  $n/m'$  value of the compound.

(ii) For polycationic compounds the following cases are considered:

—If the  $n/m'$  ratio of the compound is the same as that of listed base tetrahedra, two base tetrahedra with different  $C'C'$  values are selected from that group.

—If base tetrahedra exist with the same  $C'C'$  value as for the compound, two with different  $n/m'$  values are selected.

—For more complicated cases there is no simple rule. However, the pairs of  $C'C'$  and  $n/m'$  values are expected to be not too different between tetrahedra.

Application of (17) permits the verification that the chosen base tetrahedra and their proportions

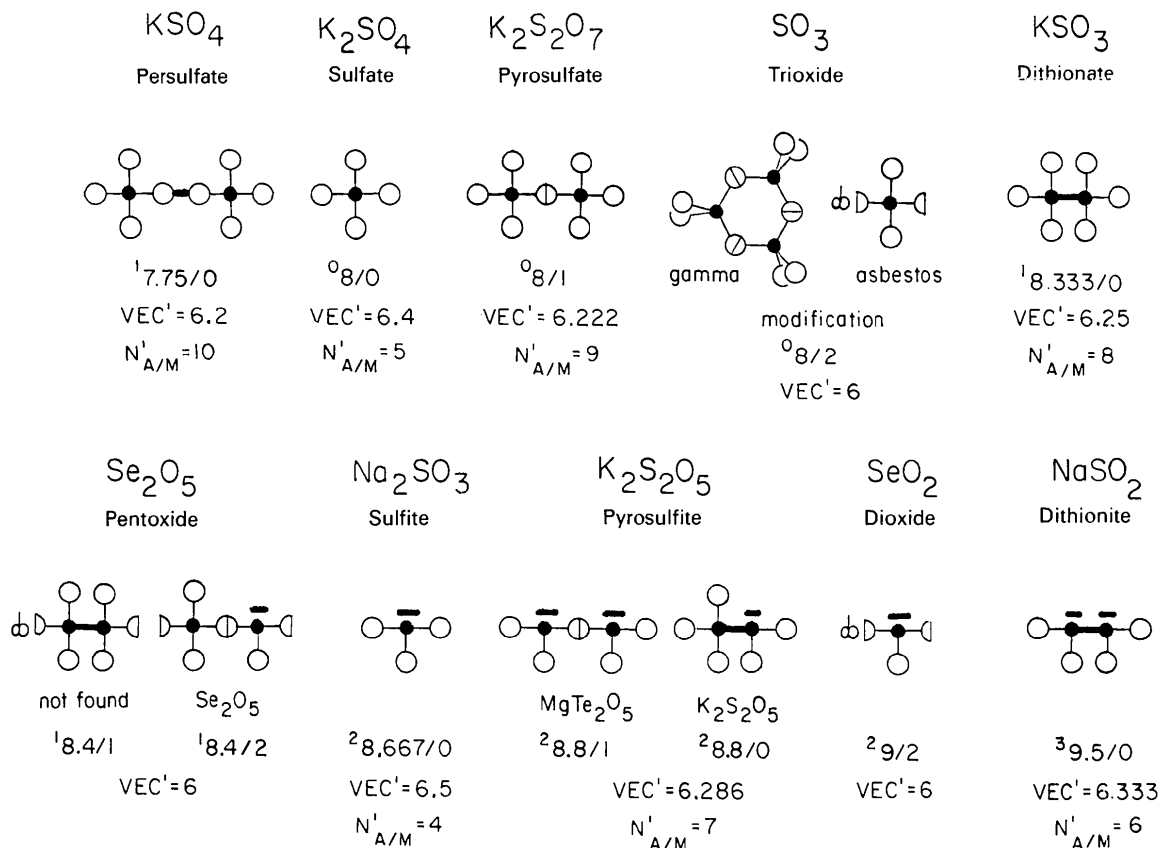


Fig. 5. Schematic presentation of the observed tetrahedron complexes in different (alkali-)sulfur(selenium)-oxygen compounds. Filled circles: S or Se; blank or half-circles: O. The classification code and its  $VEC'$  (equation 6) and  $N'_{A/M}$  (equation 8) values are given for each anionic tetrahedron complex. With the exception of  $\text{Se}_2\text{O}_5$  and  $\text{K}_2\text{S}_2\text{O}_5$  each observed tetrahedron complex can be constructed with a base tetrahedron which can be predicted from the calculated  $VEC_A$ ,  $AA$  or  $C'C'$  and most probable  $C'AC'$  values. In the case of  $\text{Se}_2\text{O}_5$  and  $\text{K}_2\text{S}_2\text{O}_5$  two drawings are given, those on the left corresponding to the expected tetrahedron complexes, and those on the right to the ones observed with the compounds. They are constructed from two different base tetrahedra (for their codes see text). The single base tetrahedron which is expected for  $\text{K}_2\text{S}_2\text{O}_5$  is found with  $\text{MgTe}_2\text{O}_5$ .

Table 1. The 55 classification codes  $^{AA(n/m')}VEC_A/C'AC'$ ,  ${}^08/C'AC'$  and  ${}^{C'C}VEC_A/C'AC'$  of  $C_mC'_m A_n$  compounds arranged according to their  $n/m'$ ,  $AA(n/m')$  and  $C'C'$  values

A code within square brackets indicates that there is no equipartition of the  $C-A-C'$  links over the apices of the tetrahedron. The number within parentheses below each code indicates how many different structure types with this code are listed in Table 2.

$n/m'$	Polyanionic valence compounds				Normal-valence compounds	Polycationic valence compounds									
	$AA(n/m')$ values					$C'C'$ values									
	4	2	1	1/2		1/3	1/2	2/3	1	4/3	3/2	2	5/2	3	7/2
4	<sup>4</sup> 7/0 (1)	<sup>2</sup> 7-5/0 (1)	<sup>1</sup> 7-75/0 (3)		<sup>0</sup> 8/0 (54)										
15/4					<sup>0</sup> 8/0-5 (1)										
11/3					<sup>0</sup> 8/0-67 (2)										
7/2			<sup>1</sup> 7-71/1 (1)		<sup>0</sup> 8/1 (11)										
10/3					<sup>0</sup> 8/1-33 (2)										
13/4					<sup>0</sup> 8/1-5 (1)										
16/5					<sup>0</sup> 8/1-6 (1)										
3		<sup>2</sup> 7-33/2 (1)	<sup>1</sup> 7-67/2 (3)		<sup>0</sup> 8/2 (31)	<sup>1</sup> 28-11/1-33 (1)			<sup>1</sup> 8-33/0 (20)			<sup>2</sup> 8-67/0 (12)			
14/5					<sup>0</sup> 8/2-4 (1)										
11/4					<sup>0</sup> 8/2-5 (1)										
8/3										<sup>4</sup> 18-5/0 (1)					
5/2			<sup>1</sup> 7-6/3 (1)		<sup>0</sup> 8/3 (11)				<sup>1</sup> 8-4/1 (4)			<sup>2</sup> 8-8/0 (1)			
									<sup>1</sup> 8-4/2 (1)			<sup>2</sup> 8-8/1 (5)			
7/3					<sup>0</sup> 8/3-33 (2)										
9/4							<sup>1</sup> 28-22/3 (2)								
2					<sup>0</sup> 8/4 (31)				<sup>1</sup> 8-5/2 (4)			<sup>2</sup> 9/2 (16)		<sup>3</sup> 9-5/0 (2)	
					[ <sup>0</sup> 8/6] (4)				<sup>1</sup> 8-5/3 (1)						
7/4					<sup>0</sup> 8/5-5 (3)							<sup>3</sup> 28-86/2-5 (2)			
												<sup>3</sup> 28-86/3 (1)			
5/3									<sup>1</sup> 8-6/3-33 (1)			<sup>2</sup> 9-2/2-67 (1)			
13/8												<sup>2</sup> 9-23/2-75 (2)			
3/2				<sup>1</sup> 27-67/7 (1)	<sup>0</sup> 8/7 (7)				<sup>1</sup> 8-67/3 (3)			<sup>2</sup> 9-33/3 (4)			
					[ <sup>0</sup> 8/8] (1)							[ <sup>2</sup> 9-33/4] (1)			
4/3					<sup>0</sup> 8/8 (3)										
5/4														<sup>5</sup> 210/2 (2)	
														<sup>5</sup> 210/2-5 (2)	
1					<sup>0</sup> 8/12 (5)			<sup>2</sup> 18-67/8 (1)	<sup>1</sup> 9/6 (8)			<sup>2</sup> 10/6 (2)		<sup>3</sup> 11/2 (5)	
3/4														<sup>2</sup> 12-67/1-5 (4)	

agree with the most probable code of the compound. There are cases, however, where different combinations of different base tetrahedra lead to the same code for the compound.

#### Classification of structures with anionic tetrahedron complexes

The structures with anionic tetrahedron complexes are characterized by their  $VEC_A$ ,  $AA(n/m')$  or  $C'C'$  and  $C'AC'$  values. We have proposed writing these

parameters in the coded forms  $^{AA(n/m')}VEC_A/C'AC'$ ,  ${}^08/C'AC'$  or  ${}^{C'C}VEC_A/C'AC'$ .

The advantage of using these parameters as codes for the compounds is that they combine observable structural features with the number of available valence electrons. We have seen above how the most probable code and the most probable base tetrahedron(a) of a compound can be derived from its chemical formula. Inversely, one can state what the value of the valence-electron concentration of a compound would have to be in order that a structure

Table 2. Classification codes of structure types with anionic tetrahedron complexes and the codes of their base tetrahedra

Codes enclosed by square brackets correspond to tetrahedron complexes where the equipartition of the  $C'-A-C'$  links is not respected. The formal charge is indicated as a superscript for each element where the number of valence electrons cannot be predicted from its position in the Periodic Table. Type formulae which are preceded by a hyphen correspond to an uncharged tetrahedron complex where there are no cations  $C'$  present. References were taken mainly from *Strukturberichte* (SB) or from *Structure Reports* (SR). Note that the number of atoms in the Pearson code of rhombohedral structures applies to the triple hexagonal cell; in addition, in the case of hydrates and ammonium cations, the H atoms have been ignored for the atom count in the unit cell.

I. Polyanionic valence compounds:  $VEC_A < 8$ ,  $AA > 0$  and  $C'C' = 0$ 

Structure types are arranged in groups of same  $VEC_A$  and  $AA(n/m')$  values. These groups (separated by dashed lines) are ordered according to increasing  $VEC_A$  and then according to decreasing  $AA(n/m')$  values. In each group, the structures are ordered first according to increasing  $n/m'$ , next according to the number of atoms in the unit cell (see Pearson code) and then according to increasing space-group number.

Classification code	Type formula	Pearson code	Space-group number	Code(s) of base tetrahedron(a)	Ref.
$^{47/0}$	$Cd_2GeAs_4$	<i>oP28</i> (62)		$^{7/0}$ *	SR40A,15
$^{27-333/2}$	$AlSiP_3$	<i>oP20</i> (62)		$^{27-333/2}$	SR45A,9
$^{27-5/0}$	$K_2GeTe_4$	<i>mP28</i> (14)		$^{27-5/0}$	SR51A,54
$^{17-6/3}$	$Na_7Al_5Sb_5$	<i>mP28</i> (11)		$^{17-6/3}$	SR51A,6
$^{17-667/2}$	$CsSiTe_3$	<i>mS40</i> (9)		$^{17-667/2}$	SR52A,26
$^{17-667/2}$	$Ca_3Ga_2As_6$	<i>oP26</i> (55)		$^{17-667/2}$	SR42A,27
$^{17-667/2}$	$Ca_3Al_2Bi_6$	<i>oP26</i> (55)		$^{17-667/2}$	SR51A,4
$^{127-667/7}$	$Na_3Al_2Sb_3$	<i>mP56</i> (14)		$^{127-667/7}$	SR51A,6
$^{17-714/1}$	$Cs_3Sn_2Te_7$	<i>mS52</i> (15)		$^{17-714/1}$	SR52A,86
$^{17-75/0}$	$KSO_4$	<i>aP12</i> (2)		$^{17-75/0}$	SB3,138
$^{17-75/0}$	$(NH_4)^+SO_4$	<i>mP24</i> (14)		$^{17-75/0}$	SR41A,427
$^{17-75/0}$	$Na_3SiSe_4$	<i>mP64</i> (14)		$^{17-75/0}$	SR52A,89

\* For the polyanionic base tetrahedra shown in Fig. 2 an equipartition is assumed of the  $A-A$  bonds over the four anions of a tetrahedron. This is not the case in  $Cd_2GeAs_4$  where one As has two homonuclear bonds, two As one and the fourth As no bonds.

II. Normal-valence compounds:  $VEC_A = 8$ ,  $AA = 0$  and  $C'C' = 0$ 

Structure types are arranged in groups of same  $n/m'$  values. These groups (separated by dashed lines) are ordered according to decreasing  $n/m'$  values. In each group, the ordering of the structures is the same as in I.

Classification code	Type formula	Pearson code	Space-group number	Code(s) of base tetrahedron(a)	Ref.
$^{8/0}$	$-SiF_4$	<i>cI10</i> (217)		$^{8/0}$	SR18,353
$^{8/0}$	$AlPS_4$	<i>oP12</i> (16)		$^{8/0}$	SR24,405
$^{8/0}$	$BPS_4$ LT	<i>oI12</i> (23)		$^{8/0}$	SR28,153
$^{8/0}$	$InPS_4$	<i>tI12</i> (82)		$^{8/0}$	SR44A,71
$^{8/0}$	$Cu^2+PS_4$	<i>mS24</i> (5)		$^{8/0}$	SR43A,48
$^{8/0}$	$GaPS_4$	<i>mP24</i> (14)		$^{8/0}$	SR39A,61
$^{8/0}$	$LiAlCl_4$	<i>mP24</i> (14)		$^{8/0}$	PSR82
$^{8/0}$	$NaAlCl_4$	<i>oP24</i> (19)		$^{8/0}$	PSR82
$^{8/0}$	$ZrSiO_4$	<i>tI24</i> (141)		$^{8/0}$	SR22,314
$^{8/0}$	$Bi^{3+}PS_4$	<i>oI96</i> (73)		$^{8/0}$	SR41A,35
$^{8/0}$	$PrPS_4$	<i>tI96</i> (142)		$^{8/0}$	SR51A,77
$^{8/0}$	$La_4Ge_3S_{12}$	<i>hR114</i> (161)		$^{8/0}$	SR41A,63
$^{8/0}$	$Pd_3^{2+}P_2S_8$	<i>hP13</i> (164)		$^{8/0}$	SR38A,135
$^{8/0}$	$Ba_3As_2S_8 \cdot 7H_2O$	<i>mP80</i> (14)		$^{8/0}$	SR52A,249
$^{8/0}$	$Eu_2^{2+}GeS_4$	<i>mP14</i> (4)		$^{8/0}$	SR45A,69
$^{8/0}$	$Sr_2GeS_4$	<i>mP14</i> (11)		$^{8/0}$	SR38A,100
$^{8/0}$	$Cu_2HgI_4 \beta$	<i>tI14</i> (121)		$^{8/0}$	SR19,337
$^{8/0}$	$Ba_2SnS_4 \alpha$	<i>mP28</i> (14)		$^{8/0}$	SR41A,29
$^{8/0}$	$Pb_2^{2+}GeS_4$	<i>mP28</i> (14)		$^{8/0}$	SR37A,25
$^{8/0}$	$Pb_2^{2+}SiS_4$	<i>mP28</i> (14)		$^{8/0}$	SR39A,80
$^{8/0}$	$Pb_2^{2+}SiSe_4$	<i>mP28</i> (14)		$^{8/0}$	SR39A,80
$^{8/0}$	$K_2SO_4 \beta$	<i>oP28</i> (62)		$^{8/0}$	SR22,447
$^{8/0}$	$MgFe^{2+}SiO_4$	<i>oP28</i> (62)		$^{8/0}$	SR28,245
$^{8/0}$	$Ba_2SnS_4 \beta$	<i>oP56</i> (33)		$^{8/0}$	SR37A,26
$^{8/0}$	$LiGaSiO_4 \alpha$	<i>hR126</i> (146)		$^{8/0}$	SR51A,17
$^{8/0}$	$Ba_3Ga_2S_8$	<i>oS120</i> (64)		$^{8/0}$	SR51A,17

Classification code	Type formula	Pearson code	Space-group number	Code(s) of base tetrahedron(a)	Ref.
$^{8/0}$	$Tl_3^+SbS_4$	<i>aP16</i> (1)		$^{8/0}$	SR48A,15
$^{8/0}$	$Na_2ZnSiO_4$	<i>mP16</i> (7)		$^{8/0}$	JLBP69
$^{8/0}$	$Cu_3AsS_4$	<i>oP16</i> (31)		$^{8/0}$	SR35A,19
$^{8/0}$	$Cu_2CdGeS_4$	<i>oP16</i> (31)		$^{8/0}$	SR34A,47
$^{8/0}$	$Cu_3SbS_4$	<i>tI16</i> (121)		$^{8/0}$	SR21,349
$^{8/0}$	$Cu_2Fe^{2+}SnS_4$	<i>tI16</i> (121)		$^{8/0}$	SR44A,56
$^{8/0}$	$(NH_4)_3^+SbS_4$	<i>cI16</i> (217)		$^{8/0}$	SR41A,421
$^{8/0}$	$Cu_2SrSnS_4$	<i>hP24</i> (144)		$^{8/0}$	SR42A,77
$^{8/0}$	$Na_2MgSiO_4$	<i>mP32</i> (7)		$^{8/0}$	SR48A,337
$^{8/0}$	$Tl_2^+Pb^{2+}GeS_4$	<i>mP32</i> (14)		$^{8/0}$	SR46A,82
$^{8/0}$	$Li_2Co^{2+}SiO_4 \beta$	<i>oP32</i> (33)		$^{8/0}$	SR45A,364
$^{8/0}$	$K_3AsS_4$	<i>oP32</i> (33)		$^{8/0}$	SR40A,22
$^{8/0}$	$(NH_4)_3^+AsS_4$	<i>oP32</i> (62)		$^{8/0}$	SR42A,302
$^{8/0}$	$Cs_3TaSe_4$	<i>oP32</i> (62)		$^{8/0}$	YR188
$^{8/0}$	$K_3PS_4 \cdot H_2O$	<i>oP36</i> (18)		$^{8/0}$	SR45A,275
$^{8/0}$	$Na_4SnS_4$	<i>tP18</i> (114)		$^{8/0}$	SR41A,29
$^{8/0}$	$Tl_4^+GeS_4$	<i>mS36</i> (9)		$^{8/0}$	SR44A,66
$^{8/0}$	$Tl_4^+SnS_4$	<i>mP36</i> (14)		$^{8/0}$	SR51A,86
$^{8/0}$	$Na_4SnTe_4$	<i>oP36</i> (19)		$^{8/0}$	SR50A,62
$^{8/0}$	$Na_4GeSe_4 \cdot 14H_2O$	<i>mS46</i> (5)		$^{8/0}$	SR42A,301
$^{8/0}$	$Ba_4SiAs_4$	<i>cP72</i> (218)		$^{8/0}$	SR48A,17
$^{8/0}$	$Na_4SnS_4 \cdot 14H_2O$	<i>mS96-4</i> (15)		$^{8/0}$	SR39A,259
$^{8/0}$	$Na_3Fe^{3+}S_4$	<i>oP80</i> (61)		$^{8/0}$	SR53A,57
$^{8/0}$	$Na_4ZnO_4$	<i>hP22</i> (186)		$^{8/0}$	SR40A,214
$^{8/0}$	$Na_8SnSb_4$	<i>cF104</i> (227)		$^{8/0}$	EK88
$^{8/0-5}$	$Na_2Ba_4Si_4O_{15}$	<i>mP54</i> (14)		$^{8/0} + ^{8/1}$	TMS87
$^{8/0-667}$	$Ag_7P_3S_{11}$	<i>mS224-56</i> (15)		$^{8/0} + (^{8/1})_2$	TKR82
$^{8/0-667}$	$Ag_{10}Si_3S_{11}$	<i>aP50-2</i> (2)		$^{8/0} + (^{8/1})_2$	SR42A,124
$^{8/1}$	$Hg_2P_2S_7$	<i>mS22</i> (5)		$^{8/1}$	SR44A,80
$^{8/1}$	$K_2S_2O_7$	<i>mS44</i> (15)		$^{8/1}$	SR24,378
$^{8/1}$	$Ba_3Sn_2S_7$	<i>mP48</i> (14)		$^{8/1}$	SR37A,28
$^{8/1}$	$Ca_3Si_2O_7$	<i>mP48</i> (14)		$^{8/1}$	SR40A,314
$^{8/1}$	$Ca_3Si_2O_7$	<i>oP96</i> (46)		$^{8/0} + (^{8/1})_2 + ^{8/2}$	SR37A,336
$^{8/1}$	$Ba_4Ga_4S_7$	<i>mP26</i> (11)		$^{8/1}$	EJS84
$^{8/1}$	$Ag_4P_2S_7$	<i>mS52</i> (15)		$^{8/1}$	SR43A,92
$^{8/1}$	$Cu_4Ni^{2+}Si_2S_7$	<i>mS28</i> (5)		$^{8/1}$	SR46A,64
$^{8/1}$	$Cu_4^{2+}Si_2S_7$	<i>mS56</i> (9)		$^{8/1}$	DJR82
$^{8/1}$	$Na_6Sn_2S_7$	<i>mS60</i> (15)		$^{8/1}$	SR39A,95
$^{8/1}$	$Na_6Ge_2Se_7$	<i>mS60</i> (15)		$^{8/1}$	EHS86
$^{8/1-333}$	$NaBa_3Nd_3Si_6O_{20}$	<i>oS132</i> (40)		$^{(8/1)}_3 + ^{8/3}$	MBB83
$^{8/1-333}$	$Na_3P_3O_{10}$ LT	<i>mS72</i> (15)		$^{(8/1)}_2 + ^{8/2}$	SR22,402
$^{8/1-5}$	$Pb_3^{2+}P_4O_{13}$	<i>aP40</i> (2)		$^{8/1} + ^{8/2}$	AD87
$^{8/1-6}$	$Na_3Mg_2P_3O_{16}$	<i>mP52</i> (13)		$^{(8/1)}_2 + (^{8/2})_3$	SR45A,316
$^{8/2}$	$-AlBr_3$	<i>mP16</i> (14)		$^{8/2}$	SR10,104
$^{8/2}$	$-SO_3$	<i>mP16</i> (14)		$^{8/2}$	SR18,367
$^{8/2}$	$-SO_3$	<i>oP48</i> (33)		$^{8/2}$	SR8,148
$^{8/2}$	$AgPS_3$	<i>mS20</i> (12)		$^{8/2}$	SR44A,89
$^{8/2}$	$Pb^{2+}GeS_3$	<i>mP20</i> (14)		$^{8/2}$	SR40A,72
$^{8/2}$	$TaCuS_3$	<i>oP20</i> (62)		$^{8/2}$	SR29,46
$^{8/2}$	$Tl^{1+}PS_3$	<i>oP20</i> (71)		$^{8/2}$	SR50A,55
$^{8/2}$	$Eu^{2+}GeS_3$	<i>aP30</i> (2)		$^{8/2}$	SR44A,59
$^{8/2}$	$InGaS_3$	<i>hP30</i> (169)		$^{8/2}$	GAKM87
$^{8/2}$	$LaGaS_3$	<i>mP60</i> (14)		$^{8/1} + ^{8/2} + ^{8/3}$	JJD82
$^{8/2}$	$Ba_3Ga_3S_6$	<i>mS44</i> (15)		$^{8/2}$	EJS84
$^{8/2}$	$Tl_2^+GeS_3$	<i>aP12</i> (2)		$^{8/2}$	SR44A,66
$^{8/2}$	$Cu_2GeSe_3$	<i>oI12</i> (44)		$^{8/2}$	SR37A,73
$^{8/2}$	$Tl_2^+SnS_3$	<i>mS24</i> (12)		$^{8/2}$	SR51A,85
$^{8/2}$	$Na_2GeS_3$	<i>mP24</i> (14)		$^{8/2}$	SR38A,100
$^{8/2}$	$Li_3SiO_3$	<i>oS24</i> (36)		$^{8/2}$	SR48A,335
$^{8/2}$	$K_2AgI_3$	<i>oP24</i> (62)		$^{8/2}$	SR16,204

Table 2 (cont.)

Classification code			Type formula	Pearson code group		Code(s) of base tetrahedron(a)		Ref.	Classification code			Type formula	Pearson code group		Code(s) of base tetrahedron(a)		Ref.
$^{\circ}8/C'AC'$	$n/m'$	$n/m'$		code	number	$^{\circ}8/C'AC'$	$n/m'$		code	number	$^{\circ}8/C'AC'$		$n/m'$	code	number	$^{\circ}8/C'AC'$	
$^{\circ}8/2$	3		$K_2CuCl_4$	<i>oP24</i>	(62)	$^{\circ}8/2$	SR12,188		$^{\circ}8/4$	2	$CaAl_2Se_4$	<i>oS36-8</i>	(66)	$^{\circ}8/4$		SR45A,5	
$^{\circ}8/2$	3		$Eu_2^{3+}CuS_4$	<i>oP24</i>	(62)	$^{\circ}8/2$	SR53A,46		$^{\circ}8/4$	2	$BaAl_2Se_4$	<i>tP30-2</i>	(126)	$^{\circ}8/4$		SR48A,5	
$^{\circ}8/2$	3		$Na_2GeS_5 \cdot 7H_2O$	<i>aP26</i>	(2)	$^{\circ}8/2$	SR38A,291		$^{\circ}8/4$	2	$BaGa_2S_4$	<i>cP84</i>	(205)	$^{\circ}8/4$		EJS82b	
$^{\circ}8/2$	3		$K_2SnS_5 \cdot 2H_2O$	<i>oP40</i>	(62)	$^{\circ}8/2$	SR41A,278		$^{\circ}8/4$	2	$BaIn_2Se_4$	<i>oF224</i>	(70)	$^{\circ}8/4$		SR46A,25	
$^{\circ}8/2$	3		$Rb_2TiO_5$	<i>oS48</i>	(64)	$^{\circ}8/2$	SR40A,185		$^{\circ}8/4$	2	$NaNdGa_4S_8$	<i>oF224</i>	(70)	$^{\circ}8/4$		IGGF88	
$^{\circ}8/2$	3		$Ca_3Sn_2As_6$	<i>oP26</i>	(55)	$^{\circ}8/2$	SR52A,13		$^{\circ}8/4$	2	$SrGa_2Se_4$	<i>oS756</i>	(6)	$^{\circ}8/4$		SR50A,36	
$^{\circ}8/2$	3		$Rb_3InS_3$	<i>mS28</i>	(12)	$^{\circ}8/2$	SR46A,87		[ $^{\circ}8/6$ ]	2	$ScCuS_2$	<i>hP4</i>	(156)	[ $^{\circ}8/6$ ]		SR37A,75	
$^{\circ}8/2$	3		$Na_3Fe^{3+}S_3$	<i>mP28</i>	(14)	$^{\circ}8/2$	SR45A,89		$^{\circ}8/4$	2	$BaZnO_2$	<i>hP12</i>	(152)	$^{\circ}8/4$		SR24,254	
$^{\circ}8/2$	3		$Cs_3GaSe_3$	<i>mP28</i>	(14)	$^{\circ}8/2$	SR50A,18		$^{\circ}8/4$	2	$Tl^{1+}Fe^{3+}Se_2$	<i>mS16</i>	(12)	$^{\circ}8/4$		SR45A,88	
$^{\circ}8/2$	3		$Ca_3AlAs_3$	<i>oP28</i>	(62)	$^{\circ}8/2$	CSS2		[ $^{\circ}8/6$ ]	2	$LaCuS_2$	<i>mP16</i>	(14)	[ $^{\circ}8/6$ ]		SR48A,45	
$^{\circ}8/2$	3		$Sr_3GaSb_3$	<i>mP56</i>	(14)	$^{\circ}8/2$	CSS87		$^{\circ}8/4$	2	$KFe^{3+}S_2$	<i>mS16</i>	(15)	$^{\circ}8/4$		SR10,123	
$^{\circ}8/2$	3		$Ba_3GaSb_3$	<i>oP56</i>	(62)	$^{\circ}8/2$	SR52A,6		$^{\circ}8/4$	2	$ErAgSe_2$	<i>oP16</i>	(19)	$^{\circ}8/4$		SR43A,58	
$^{\circ}8/2$	3		$Ba_3AlSb_3$	<i>oS56</i>	(64)	$^{\circ}8/2$	CSS82		$^{\circ}8/4$	2	$NaFe^{3+}O_2\beta$	<i>oP16</i>	(33)	$^{\circ}8/4$		SR18,422	
$^{\circ}8/2$	3		$Na_3GeP_3$	<i>mP36</i>	(14)	$^{\circ}8/2$	SR52A,76		$^{\circ}8/4$	2	$SrZnO_2$	<i>oP16</i>	(62)	$^{\circ}8/4$		SR26,396	
$^{\circ}8/2-4$	14/5		$NdP_2O_{14}$	<i>mP80</i>	(14)	$(^{\circ}8/2)_3 + (^{\circ}8/3)_2$	SR40A,257		$^{\circ}8/4$	2	$CsFe^{3+}S_2$	<i>oI16</i>	(71)	$^{\circ}8/4$		SR46A,46	
$^{\circ}8/2-5$	11/4		$CaP_2O_{11}$	<i>mP64</i>	(14)	$^{\circ}8/2 + ^{\circ}8/3$	SR40A,256		$^{\circ}8/4$	2	$CuFe^{3+}S_2$	<i>iI16</i>	(122)	$^{\circ}8/4$		SR39A,51	
$^{\circ}8/3$	5/2		$-P_2S_5$	<i>aP28</i>	(2)	$^{\circ}8/3$	SR30A,353		$^{\circ}8/4$	2	$NaInTe_2$	<i>iI16</i>	(140)	$^{\circ}8/4$		SR39A,100	
$^{\circ}8/3$	5/2		$-P_2O_5$	<i>hR84</i>	(161)	$^{\circ}8/3$	SR29,360		$^{\circ}8/4$	2	$Tl^{1+}GaSe_2$	<i>mS64</i>	(9)	$^{\circ}8/4$		SR44A,64	
$^{\circ}8/3$	5/2		$BaGe_2S_3$	<i>cF128</i>	(203)	$^{\circ}8/3$	SR39A,22		$^{\circ}8/4$	2	$Sr_3In_2P_4$	<i>oP18</i>	(58)	$^{\circ}8/4$		SR53A,38	
$^{\circ}8/3$	5/2		$Na_3Ge_2Se_5$	<i>oP36</i>	(33)	$^{\circ}8/3$	SR51A,55		$^{\circ}8/4$	2	$Ca_3Al_2As_4$	<i>mS36</i>	(15)	$^{\circ}8/4$		SR48A,3	
$^{\circ}8/3$	5/2		$Tl_3^{3+}Ge_2S_5$	<i>mS72</i>	(15)	$^{\circ}8/3$	SR42A,92		$^{\circ}8/4$	2	$K_2SiP_2$	<i>oI20</i>	(72)	$^{\circ}8/4$		SR51A,77	
$^{\circ}8/3$	5/2		$K_3Si_2Te_5$	<i>oP80-8</i>	(62)	$^{\circ}8/3$	ES82b		$^{\circ}8/4$	2	$K_2ZnO_2$	<i>oI20</i>	(72)	$^{\circ}8/4$		SR33A,325	
$^{\circ}8/3$	5/2		$Na_3Ge_2S_5$	<i>oS72</i>	(63)	$^{\circ}8/3$	SR37A,93		[ $^{\circ}8/6$ ]	2	$Tl_3^{3+}AgTe_2$	<i>mP24</i>	(14)	[ $^{\circ}8/6$ ]		SR53A,57	
$^{\circ}8/3$	5/2		$Pb_3^{2+}B_3S_5$	<i>tP72</i>	(92)	$^{\circ}8/3$	SR33A,363		$^{\circ}8/5-5$	7/4	$BaAl_4S_7$	<i>oP24</i>	(31)	$^{\circ}8/5 + ^{\circ}8/6$		SR50A,4	
$^{\circ}8/3$	5/2		$Cs_3Ge_2S_{10} \cdot 3H_2O$	<i>mS92-8</i>	(9)	$^{\circ}8/3$	SR42A,300		$^{\circ}8/5-5$	7/4	$SrB_4O_7$	<i>oP24</i>	(31)	$^{\circ}8/5 + ^{\circ}8/6$		SR31A,169	
$^{\circ}8/3$	5/2		$Cs_3Ga_2Se_5$	<i>aP22</i>	(2)	$^{\circ}8/2 + ^{\circ}8/4$	SR51A,27		$^{\circ}8/5-5$	7/4	$CaAl_4O_7$	<i>mS48</i>	(15)	$^{\circ}8/5 + ^{\circ}8/6$		SR40A,302	
$^{\circ}8/3$	5/2		$Rb_4In_2S_5$	<i>aP22</i>	(2)	$^{\circ}8/3$	SR46A,87		$^{\circ}8/7$	3/2	$-Ga_2S_3\alpha$	<i>mS20</i>	(9)	$^{\circ}8/7$		SR42A,86	
$^{\circ}8/3-333$	7/3		$Ba_3Fe_3^{3+}S_{14}$	<i>mS108</i>	(15)	$(^{\circ}8/3)_2 + ^{\circ}8/4$	SR37A,17		$^{\circ}8/7$	3/2	$-Ga_2S_3\beta$	<i>mS20</i>	(9)	$^{\circ}8/7$		SR50A,35	
$^{\circ}8/3-333$	7/3		$Cs_3Ga_3Se_7$	<i>mS60</i>	(12)	$^{\circ}8/2 + (^{\circ}8/4)_2$	SR51A,27		$^{\circ}8/7$	3/2	$-B_2O_3$ II HP	<i>oS20</i>	(36)	$^{\circ}8/7$		SR33A,259	
$^{\circ}8/4$	2		$-SiO_2$ quartz	<i>hP9</i>	(152)	$^{\circ}8/4$	DL78		$^{\circ}8/7$	3/2	$-Al_2S_3\alpha$	<i>hP30</i>	(169)	$^{\circ}8/7$		HF55	
$^{\circ}8/4$	2		$-SiS_2$	<i>oI12</i>	(72)	$^{\circ}8/4$	SR30A,55		$^{\circ}8/7$	3/2	$CuFe_2^{2+}S_3$ LT	<i>oP24</i>	(62)	$^{\circ}8/7$		SR40A,56	
$^{\circ}8/4$	2		$-GeS_2$ II HP	<i>iI12</i>	(122)	$^{\circ}8/4$	SR42A,91		$^{\circ}8/7$	3/2	$Na_2Mn_2^{2+}S_3$	<i>mS56</i>	(15)	$^{\circ}8/7$		SR50A,48	
$^{\circ}8/4$	2		$-GeS_2$ LT	<i>mP36</i>	(7)	$^{\circ}8/4$	SR41A,72		[ $^{\circ}8/8$ ]	3/2	$K_3Al_2As_3$	<i>mP16</i>	(11)	[ $^{\circ}8/8$ ]		SR52A,3	
$^{\circ}8/4$	2		$-GeS_2$ HT	<i>mP48</i>	(14)	$^{\circ}8/4$	SR46A,79		$^{\circ}8/7$	3/2	$Ca_3Al_2Ge_3$	<i>oP32</i>	(62)	$^{\circ}8/7$		CS82	
[ $^{\circ}8/6$ ]	2		$Fe^{2+}Ga_2S_4$ LT	<i>hP7</i>	(164)	[ $^{\circ}8/6$ ]	EJS82a		$^{\circ}8/8$	4/3	$-Si_3N_4\beta$	<i>hP14</i>	(176)	$^{\circ}8/8$		SR26,292	
$^{\circ}8/4$	2		$BaAl_3Te_4$ II	<i>tP14</i>	(125)	$^{\circ}8/4$	SR45A,32		$^{\circ}8/8$	4/3	$-Si_3N_4\alpha$	<i>hP28</i>	(159)	$^{\circ}8/8$		SR26,292	
$^{\circ}8/4$	2		$BaFe_2^{2+}S_4\beta$	<i>iI16-2</i>	(87)	$^{\circ}8/4$	SR39A,100		$^{\circ}8/8$	4/3	$Cs_2Zn_3S_4$	<i>oI36</i>	(72)	$^{\circ}8/8$		SR48A,38	
$^{\circ}8/4$	2		$SrFe_2^{2+}S_4$	<i>tP16-2</i>	(117)	$^{\circ}8/4$	SR45A,32		$^{\circ}8/12$	1	$-ZnS$ wurtzite	<i>hP4</i>	(186)	$^{\circ}8/12$		SB1,78	
$^{\circ}8/4$	2		$SrAl_3Te_4$	<i>iI16-2</i>	(140)	$^{\circ}8/4$	SR45A,32		$^{\circ}8/12$	1	$-ZnS$ zinc blende	<i>cF8</i>	(216)	$^{\circ}8/12$		SB1,76	
$^{\circ}8/4$	2		$BaFe_2^{2+}S_4\alpha$	<i>iI16-2</i>	(140)	$^{\circ}8/4$	SR45A,32		$^{\circ}8/12$	1	$CaAl_2Si_2$	<i>hP5</i>	(164)	$^{\circ}8/12$		SR32A,5	
$^{\circ}8/4$	2		$SrAl_3Se_4$	<i>oS28</i>	(66)	$^{\circ}8/4$	SR45A,5		$^{\circ}8/12$	1	$BaZn_2P_2$	<i>tI10</i>	(139)	$^{\circ}8/12$		SR44A,18	
$^{\circ}8/4$	2					$^{\circ}8/4$	SR45A,5		$^{\circ}8/12$	1	$BaCu_2S_2$	<i>oP20</i>	(62)	$^{\circ}8/12$		SR40A,31	

III. Polycationic valence compounds:  $VEC_A > 8$ ,  $AA = 0$  and  $C'C > 0$ .

Structure types are arranged in groups with the same  $VEC_A$  and  $C'C$  values. These groups (separated with dashed lines) are ordered first according to increasing  $VEC_A$  values and then according to increasing  $C'C$  values. In each group, the ordering of the structures is the same as in I.

Classification code	$n/m'$	$x$	Type formula	Pearson code	Space-group number	Code(s) of base tetrahedron(a)	Ref.
$^{12}8-111/1-33$	3	1	$Zn_2P_3S_9$	<i>mS56</i>	(12)	$(^{\circ}8/2)_2 + ^{\circ}8-333/0$	SR44A,90
$^{12}8-222/3$	9/4	0	$-P_4O_9$	<i>hR156</i>	(167)	$(^{\circ}8/3)_3 + ^{\circ}9-333/3$	SR32A,252
$^{12}8-222/3$	9/4	0	$-P_4S_9$ II	<i>cI208</i>	(206)	$(^{\circ}8/3)_3 + ^{\circ}9-333/3$	SR34A,118
$^{24}8-667/8$	1	1	$Na_2Ga_3Sb_3$	<i>oP32</i>	(62)	$^{\circ}8/9 + ^{\circ}9/6 + ^{\circ}9-333/9$	SR53A,14
$^{\circ}8-333/0$	3	1	$-CCl_3$	<i>oP32</i>	(62)	$^{\circ}8-333/0$	SR23,520
$^{\circ}8-333/0$	3	1	$TiP_2S_6$	<i>oF72</i>	(43)	$^{\circ}8-333/0$	SR46A,109
$^{\circ}8-333/0$	3	1	$In_2P_3S_9$	<i>mP56</i>	(14)	$^{\circ}8-333/0$	SR44A,71
$^{\circ}8-333/0$	3	1	$HgPS_3$	<i>aP10</i>	(2)	$^{\circ}8-333/0$	SR44A,79
$^{\circ}8-333/0$	3	1	$Sn^{2+}PS_3$	<i>mP20</i>	(7)	$^{\circ}8-333/0$	SR40A,94
$^{\circ}8-333/0$	3	1	$LiGaBr_3$	<i>mP20</i>	(11)	$^{\circ}8-333/0$	SR53A,103
$^{\circ}8-333/0$	3	1	$Fe^{2+}PS_3$	<i>mS20</i>	(12)	$^{\circ}8-333/0$	SR39A,76
$^{\circ}8-333/0$	3	1	$Pb^{2+}PSe_3$	<i>mP20</i>	(14)	$^{\circ}8-333/0$	SR54A,65
$^{\circ}8-333/0$	3	1	$CsSO_3$	<i>hP20</i>	(186)	$^{\circ}8-333/0$	SR46A,364
$^{\circ}8-333/0$	3	1	$Fe^{2+}PSe_3$	<i>hR30</i>	(146)	$^{\circ}8-333/0$	SR39A,76
$^{\circ}8-333/0$	3	1	$Cr^{3+}SiTe_3$	<i>hR30</i>	(148)	$^{\circ}8-333/0$	M88
$^{\circ}8-333/0$	3	1	$KSO_3$	<i>hP30</i>	(150)	$^{\circ}8-333/0$	SR20,336
$^{\circ}8-333/0$	3	1	$HgPSe_3$	<i>mS40</i>	(15)	$^{\circ}8-333/0$	SR44A,79
$^{\circ}8-333/0$	3	1	$CuCr^{3+}P_2S_6$	<i>mS52-12</i>	(15)	$^{\circ}8-333/0$	CLDR82

Table 2 (cont.)

Classification code <i>CC</i> <i>VEC</i> <sub>λ</sub> / <i>C'</i> <i>AC'</i>	<i>n/m'</i>	<i>x</i>	Type formula	Pearson code	Space-group number	Code(s) of base tetrahedron(a)	Ref.
<sup>1</sup> 8-333/0	3	1	Mn <sup>3+</sup> Si <sub>2</sub> Te <sub>6</sub>	<i>hP22</i>	(163)	<sup>1</sup> 8-333/0	SR53A,58
<sup>1</sup> 8-333/0	3	1	Tl <sup>3+</sup> PSe <sub>3</sub>	<i>mP48</i>	(14)	<sup>1</sup> 8-333/0	SR53A,57
<sup>1</sup> 8-333/0	3	1	Ag <sub>3</sub> PS <sub>3</sub>	<i>mP72</i>	(14)	<sup>1</sup> 8-333/0	TMKR82
<sup>1</sup> 8-333/0	3	1	K <sub>3</sub> SiTe <sub>3</sub>	<i>mS28</i>	(12)	<sup>1</sup> 8-333/0	SR44A,94
<sup>1</sup> 8-333/0	3	1	K <sub>3</sub> SnTe <sub>3</sub>	<i>mP28</i>	(14)	<sup>1</sup> 8-333/0	SR45A,75
<sup>1</sup> 8-333/0	3	1	K <sub>3</sub> GeTe <sub>3</sub>	<i>mS56</i>	(15)	<sup>1</sup> 8-333/0	SR45A,75
<sup>1</sup> 8-4/1	5/2	1	Ba <sub>3</sub> Ge <sub>2</sub> Te <sub>5</sub>	<i>oP36</i>	(33)	<sup>1</sup> 8-4/1	SR51A,17
<sup>1</sup> 8-4/1	5/2	1	Na <sub>4</sub> Ge <sub>2</sub> Se <sub>5</sub> II	<i>aP22</i>	(2)	<sup>1</sup> 8-4/1	SR52A,49
<sup>1</sup> 8-4/1	5/2	1	Na <sub>4</sub> Ge <sub>2</sub> Te <sub>5</sub> II	<i>aP22</i>	(2)	<sup>1</sup> 8-4/1	SR50A,41
<sup>1</sup> 8-4/1	5/2	1	Na <sub>4</sub> Ge <sub>2</sub> Te <sub>5</sub> I	<i>mP88</i>	(14)	<sup>1</sup> 8-333/0 + ( <sup>1</sup> 8-4/1) <sub>2</sub> + <sup>1</sup> 8-5/2	SR50A,41
<sup>1</sup> 8-4/2	5/2	0	-Se <sub>2</sub> O <sub>5</sub>	<i>mP28</i>	(14)	<sup>0</sup> 8/2 + <sup>2</sup> 9/2	SR46A,230
<sup>1</sup> 8-5/2	2	1	LiGeTe <sub>2</sub>	<i>aP24</i>	(2)	<sup>1</sup> 8-4/1 + <sup>1</sup> 8-667/3	SR50A,39
<sup>1</sup> 8-5/2	2	1	Ba <sub>3</sub> Sn <sub>2</sub> P <sub>4</sub>	<i>mP36</i>	(4)	<sup>1</sup> 8-4/1 + <sup>1</sup> 8-667/3	SR53A,34
<sup>1</sup> 8-5/2	2	1	Ca <sub>3</sub> Si <sub>2</sub> As <sub>4</sub>	<i>mP36</i>	(14)	<sup>1</sup> 8-4/1 + <sup>1</sup> 8-667/3	ES82a
<sup>1</sup> 8-5/2	2	1	Sr <sub>3</sub> Si <sub>2</sub> As <sub>4</sub>	<i>mS36</i>	(15)	<sup>1</sup> 8-5/2	ES82a
<sup>1</sup> 8-5/3	2	0	-PO <sub>2</sub>	<i>mS48</i>	(15)	<sup>0</sup> 8/3 + <sup>2</sup> 9-333/3	SR34A,240
<sup>1</sup> 8-6/3-333	5/3	1/3	K <sub>4</sub> Sn <sub>3</sub> As <sub>5</sub>	<i>oP56</i>	(59)	<sup>0</sup> 8/4 + <sup>1</sup> 8-667/3 + <sup>2</sup> 9-333/3	KE88
<sup>1</sup> 8-667/3	3/2	1	-Si <sub>3</sub> Te <sub>3</sub>	<i>hP40-20</i>	(163)	<sup>1</sup> 8-667/3	SR42A,125
<sup>1</sup> 8-667/3	3/2	1	Ba <sub>3</sub> Si <sub>4</sub> P <sub>6</sub>	<i>mP26</i>	(11)	<sup>0</sup> 8/4 + <sup>2</sup> 10/2	SR51A,18
<sup>1</sup> 8-667/3	3/2	1	Na <sub>2</sub> Ga <sub>2</sub> Se <sub>3</sub>	<i>hR18-4</i>	(166)	<sup>1</sup> 8-667/3	SR42A,85
<sup>1</sup> 9/6	1	1	-InSe HP	<i>mP8</i>	(10)	<sup>1</sup> 9/6	WIKN82
<sup>1</sup> 9/6	1	1	-InS	<i>oP8</i>	(58)	<sup>1</sup> 9/6	SR18,176
<sup>1</sup> 9/6	1	1	-GaSe 2H	<i>hP8</i>	(187)	<sup>1</sup> 9/6	SR17,166
<sup>1</sup> 9/6	1	1	-GaS 2H	<i>hP8</i>	(194)	<sup>1</sup> 9/6	SR42A,86
<sup>1</sup> 9/6	1	1	-GaSe 3R	<i>hR12</i>	(160)	<sup>1</sup> 9/6	SR17,167
<sup>1</sup> 9/6	1	1	-GaSe 4H	<i>hP16</i>	(186)	<sup>1</sup> 9/6	SR24,128
<sup>1</sup> 9/6	1	1	-GaTe	<i>mS24</i>	(12)	<sup>1</sup> 9/6	SR45A,73
<sup>1</sup> 9/6	1	1	-SiP	<i>mS48</i>	(36)	<sup>1</sup> 9/6	SR41A,101
<sup>4</sup> 8-5/0	8/3	1	Na <sub>3</sub> P <sub>3</sub> O <sub>9</sub> ·14H <sub>2</sub> O	<i>aP60</i>	(2)	( <sup>1</sup> 8-333/0) <sub>2</sub> + <sup>2</sup> 9/0	SR34A,321
<sup>3</sup> 28-857/2-5	7/4	1/3	-P <sub>4</sub> S <sub>7</sub> α	<i>mP44</i>	(14)	<sup>0</sup> 8/3 + <sup>3</sup> 11/2	SR30A,353
<sup>3</sup> 28-857/2-5	7/4	1/3	-P <sub>4</sub> S <sub>7</sub> β	<i>oP44</i>	(60)	<sup>0</sup> 8/3 + <sup>3</sup> 11/2	SR30A,354
<sup>3</sup> 28-857/3	7/4	0	-P <sub>4</sub> O <sub>7</sub>	<i>mP44</i>	(13)	<sup>0</sup> 8/3 + ( <sup>2</sup> 9-333/3) <sub>3</sub>	SR48A,193
<sup>2</sup> 8-667/0	3	0	-AsBr <sub>3</sub>	<i>oP16</i>	(19)	<sup>2</sup> 8-667/0	SR30A,285
<sup>2</sup> 8-667/0	3	0	BaTeS <sub>3</sub>	<i>oP20</i>	(62)	<sup>2</sup> 8-667/0	SR42A,43
<sup>2</sup> 8-667/0	3	0	Na <sub>2</sub> SO <sub>3</sub>	<i>hP12</i>	(147)	<sup>2</sup> 8-667/0	SR41A,426
<sup>2</sup> 8-667/0	3	0	AgHgAsS <sub>3</sub>	<i>mS24</i>	(9)	<sup>2</sup> 8-667/0	NA83
<sup>2</sup> 8-667/0	3	0	AgPb <sup>2+</sup> AsS <sub>3</sub>	<i>mP24</i>	(14)	<sup>2</sup> 8-667/0	SR32A,229
<sup>2</sup> 8-667/0	3	0	K <sub>2</sub> TeSe <sub>3</sub>	<i>mP24</i>	(14)	<sup>2</sup> 8-667/0	ZE88
<sup>2</sup> 8-667/0	3	0	CuPb <sup>2+</sup> AsS <sub>3</sub>	<i>oP24</i>	(31)	<sup>2</sup> 8-667/0	SR20,30
<sup>2</sup> 8-667/0	3	0	Na <sub>2</sub> TeSe <sub>3</sub>	<i>mS48</i>	(15)	<sup>2</sup> 8-667/0	ZE88
<sup>2</sup> 8-667/0	3	0	KHgSbS <sub>3</sub>	<i>mS48</i>	(15)	<sup>2</sup> 8-667/0	SR53A,48
<sup>2</sup> 8-667/0	3	0	Ag <sub>4</sub> Mn <sup>2+</sup> Sb <sub>2</sub> S <sub>6</sub>	<i>mP26</i>	(14)	<sup>2</sup> 8-667/0	SR40A,13
<sup>2</sup> 8-667/0	3	0	Na <sub>3</sub> AsS <sub>3</sub>	<i>cP28</i>	(198)	<sup>2</sup> 8-667/0	SR42A,30
<sup>2</sup> 8-667/0	3	0	Ag <sub>3</sub> AsS <sub>3</sub>	<i>mS56</i>	(15)	<sup>2</sup> 8-667/0	SR33A,37
<sup>2</sup> 8-8/0	5/2	1/2	K <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	<i>mP18</i>	(11)	<sup>1</sup> 8-333/0 + <sup>2</sup> 9-5/0	SR21,371
<sup>2</sup> 8-8/1	5/2	0	MgTe <sub>2</sub> O <sub>5</sub>	<i>oP32</i>	(60)	<sup>2</sup> 8-8/1	SR41A,360
<sup>2</sup> 8-8/1	5/2	0	Ba <sub>2</sub> As <sub>2</sub> Se <sub>5</sub>	<i>mP36</i>	(4)	<sup>2</sup> 8-667/0 + <sup>2</sup> 9/2	CSS85
<sup>2</sup> 8-8/1	5/2	0	Ca <sub>2</sub> Sb <sub>2</sub> S <sub>5</sub>	<i>mP36</i>	(14)	<sup>2</sup> 8-667/0 + <sup>2</sup> 9/2	SR48A,11
<sup>2</sup> 8-8/1	5/2	0	Ba <sub>2</sub> As <sub>2</sub> S <sub>5</sub>	<i>oP72</i>	(29)	<sup>2</sup> 8-667/0 + <sup>2</sup> 9/2	SR50A,9
<sup>2</sup> 8-8/1	5/2	0	Sr <sub>2</sub> Sb <sub>2</sub> S <sub>5</sub> ·15H <sub>2</sub> O	<i>mS96</i>	(15)	<sup>2</sup> 8-8-1	CSS85
<sup>2</sup> 9/2	2	0	-SeO <sub>2</sub>	<i>tP24</i>	(135)	<sup>2</sup> 9/2	SBS,4
<sup>2</sup> 9/2	2	0	Tl <sup>1+</sup> HgAs <sub>3</sub> S <sub>6</sub>	<i>mP44</i>	(14)	<sup>2</sup> 9/2	ENBS82
<sup>2</sup> 9/2	2	0	AgPb <sup>2+</sup> Sb <sub>3</sub> S <sub>6</sub>	<i>oP44</i>	(33)	<sup>2</sup> 9/2	SKHT87
<sup>2</sup> 9/2	2	0	Tl <sup>4+</sup> Hg <sub>3</sub> (As <sub>3</sub> Sb <sub>2</sub> ) <sub>2</sub> S <sub>20</sub>	<i>oS148</i>	(41)	( <sup>2</sup> 8-8/1) <sub>2</sub> + <sup>2</sup> 9/2 + ( <sup>2</sup> 9-333/3) <sub>2</sub>	SR38A,9
<sup>2</sup> 9/2	2	0	KAsSe <sub>2</sub>	<i>aP16</i>	(1)	<sup>2</sup> 9/2	SH88
<sup>2</sup> 9/2	2	0	(NH <sub>4</sub> ) <sup>1+</sup> SbS <sub>2</sub>	<i>aP16</i>	(2)	<sup>2</sup> 9/2	SR45A,275
<sup>2</sup> 9/2	2	0	NaAsS <sub>2</sub>	<i>mP16</i>	(14)	<sup>2</sup> 9/2	SR44A,27
<sup>2</sup> 9/2	2	0	BaSnS <sub>2</sub>	<i>mP16</i>	(14)	<sup>2</sup> 9/2	SR39A,26
<sup>2</sup> 9/2	2	0	CsSbS <sub>2</sub>	<i>mP16</i>	(14)	<sup>2</sup> 9/2	SR46A,10
<sup>2</sup> 9/2	2	0	AgSbS <sub>2</sub>	<i>mS32</i>	(9)	<sup>2</sup> 9/2	SR29,21
<sup>2</sup> 9/2	2	0	Tl <sup>1+</sup> AsS <sub>2</sub>	<i>mP32</i>	(14)	<sup>2</sup> 9/2	SR23,42
<sup>2</sup> 9/2	2	0	CsSbSe <sub>2</sub>	<i>mP32</i>	(14)	<sup>2</sup> 9/2	SR48A,11
<sup>2</sup> 9/2	2	0	CsAsSe <sub>2</sub>	<i>oP32</i>	(61)	<sup>2</sup> 9/2	SH88

Table 2 (cont.)

Classification code ${}^c c VEC_A C' AC'$	$n/m'$	$x$	Type formula	Pearson code	Space-group number	Code(s) of base tetrahedron(a)	Ref.
${}^9/2$	2	0	RbAsSe <sub>2</sub>	<i>m</i> 564	(15)	${}^9/2$	SH88
${}^9/2$	2	0	NaAsSe <sub>2</sub>	<i>o</i> P64	(61)	${}^9/2$	SR45A,27
${}^9/2$	2	0	AgAsS <sub>2</sub>	<i>m</i> S96	(15)	${}^9/2$	SR29,25
${}^9-2/2-667$	5/3	0	Tl <sup>1+</sup> Sb <sub>2</sub> S <sub>5</sub>	<i>m</i> P36	(14)	${}^9/2 + ({}^9-333/3)_2$	GNE82
${}^9-231/2-75$	13/8	0	Rb <sub>2</sub> As <sub>8</sub> S <sub>13</sub> ·H <sub>2</sub> O	<i>m</i> P96	(14)	${}^9/2 + ({}^9-333/3)_3$	SR52A,248
${}^9-231/2-75$	13/8	0	C <sub>2</sub> As <sub>8</sub> S <sub>13</sub>	<i>o</i> P184	(60)	${}^9/2 + ({}^9-333/3)_3$	SR52A,12
${}^9-333/3$	3/2	0	-As <sub>2</sub> O <sub>3</sub> I	<i>m</i> P20	(14)	${}^9-333/3$	SR44A,183
${}^9-333/3$	3/2	0	-As <sub>2</sub> O <sub>3</sub> II	<i>m</i> P20	(14)	${}^9-333/3$	SR41A,213
${}^9-333/3$	3/2	0	-As <sub>2</sub> S <sub>3</sub>	<i>m</i> P20	(14)	${}^9-333/3$	SR38A,30
[ ${}^9-333/4$ ]	3/2	0	-Sb <sub>2</sub> S <sub>3</sub>	<i>o</i> P20	(62)	${}^9-5/4 + [{}^9-2/4]$	SR42A,22
${}^9-333/3$	3/2	0	-As <sub>2</sub> O <sub>3</sub>	<i>c</i> F80	(227)	${}^9-333/3$	SR44A,342
${}^{21}0/6$	1	0	-GeS	<i>o</i> P8	(62)	${}^{21}0/6$	SR45A,76
${}^{21}0/6$	1	0	KSnAs	<i>h</i> P6	(186)	${}^{21}0/6$	KE88
${}^{52}10/2$	5/4	2/5	-P <sub>2</sub> S <sub>5</sub> α	<i>m</i> P18	(4)	${}^8-5/2 + {}^9-333/3 + {}^311/2 + {}^416/1^*$	SR30A,353
${}^{52}10/2$	5/4	2/5	-P <sub>2</sub> Se <sub>5</sub>	<i>o</i> P36	(33)	${}^8-5/2 + {}^9-333/3 + {}^311/2 + {}^416/1^*$	SR37A,121
${}^{52}10/2-5$	5/4	1/5	-P <sub>2</sub> S <sub>5</sub> β	<i>m</i> P18	(11)	${}^9-333/3 + {}^311/2$	SR41A,101
${}^{52}10/2-5$	5/4	1/5	-As <sub>4</sub> S <sub>5</sub>	<i>m</i> P18	(11)	${}^9-333/3 + {}^311/2$	SR39A,18
${}^9-5/0$	2	1/3	-PI <sub>2</sub>	<i>a</i> P6	(2)	${}^9-5/0$	SR20,254
${}^9-5/0$	2	1/3	NaSO <sub>3</sub>	<i>m</i> P16	(13)	${}^9-5/0$	SR20,331
${}^311/2$	1	1/3	-AsS realgar	<i>m</i> P32	(14)	${}^311/2$	SR16,269
${}^311/2$	1	1/3	-AsS II	<i>m</i> P32	(14)	${}^9-333/3 + ({}^311/2)_2 + {}^416/1^*$	SR42A,31
${}^311/2$	1	1/3	-SN	<i>m</i> P32	(14)	${}^311/2$	SR28,55
${}^311/2$	1	1/3	-AsS β	<i>m</i> S32	(15)	${}^311/2$	SR39A,19
${}^311/2$	1	1/3	-SeN	<i>m</i> S32	(15)	${}^311/2$	SR31A,82
${}^{72}12-67/1-5$	3/4	3/7	-As <sub>4</sub> S <sub>5</sub> β	<i>o</i> P28	(62)	${}^9-333/3 + ({}^416/1)_3^*$	SR39A,17
${}^{72}12-67/1-5$	3/4	3/7	-As <sub>4</sub> S <sub>5</sub> α	<i>o</i> P28	(62)	${}^9-333/3 + ({}^416/1)_3^*$	SR38A,29
${}^{72}12-67/1-5$	3/4	3/7	-P <sub>4</sub> S <sub>3</sub>	<i>o</i> P56	(62)	${}^9-333/3 + ({}^416/1)_3^*$	SR50A,55
${}^{72}12-67/1-5$	3/4	3/7	-P <sub>4</sub> Se <sub>3</sub>	<i>o</i> P112	(62)	${}^9-333/3 + ({}^416/1)_3^*$	SR23,402

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\* In the  ${}^416/1$  base tetrahedron the central atom has only one shared anion neighbour ( $n/m' = 1/2$ ) and this base tetrahedron is therefore not shown in Fig. 2. According to  $x = 1/2$  the central atom has two  $C'-C'$  bonds and one non-bonding orbital.

with a particular anionic tetrahedron complex might be formed.

An important characteristic of a classification based on these codes is the absence of a relation with the overall compositions of the compounds. For structures to have the same code one of the conditions is that the anionic tetrahedron complexes must

have the same  $n/m'$  and  $VEC_A$  values. For example, the structures of such apparently unrelated compounds as  $\text{In}_2\text{P}_3\text{S}_9$ ,  $\text{LiGaBr}_3$ ,  $\text{KSO}_3$  or  $\text{K}_3\text{SiTe}_3$  have the code  ${}^8-333/0$ . On the other hand, the compounds  $\text{Ca}_5\text{Ga}_2\text{As}_6$  and  $\text{Ca}_5\text{Sn}_2\text{As}_6$  can be considered for the consistent assignment to different codes. These compounds have the same overall formula, the

same space group, the same Wyckoff sequence, quite similar unit-cell dimensions and also infinite chains of two-corner-linked tetrahedra ( $C'AC' = 2$ ). From these considerations one might presume that the structures are isotypic; however, they are not. The first compound (code  $^{17}667/2$ ) is a polyanionic valence compound, while the second (code  $^{08}/2$ ) is a normal-valence compound without As—As bonds between neighbouring tetrahedra.

For the 290 structure types studied, one can distinguish 55 different classification codes. They are listed in Table 1 as a function of the  $n/m'$  ratios of the compounds. Among them, only three are surrounded by square brackets which indicate that there is no equipartition. The reader should note that the list is certainly not complete. Particularly for silicates, which are all normal-valence compounds with equipartition, more classification codes of the type  $^{08}/C'AC'$  with  $2 < C'AC' < 4$  exist.

The classification of the structure types, as proposed in Table 2, is performed in such a way that the codes of the compounds are grouped according to the most probable  $C'AC'$  values and not necessarily according to the observed ones. This allows a given structure type to be found more easily in the list even if there is no equipartition of the  $C'-A-C'$  links. Not included or only exceptionally included are structure types which are found mostly with oxygen- or halogen-containing compounds. For each type is given: the classification code, the  $n/m'$  ratio, the type formula name, the Pearson code (Pearson, 1967), the space-group number, the codes and numbers of the base tetrahedra involved and a literature reference. For polycationic compounds the  $x$  values are also listed.

We have considered as the  $C'$  atom the element positioned immediately to the left of the anion. There are isolated cases, such as  $Tl_4^+Hg_3(As_8Sb_2)S_{20}$ , where there are two kinds of equivalent central atoms. The  $n/m'$  value here is assumed to be 2 and the resulting code is  $^{29}/2$ .

There is on average a good agreement between the most probable base tetrahedra predicted from the composition and the observed base tetrahedra. If this is not the case one has to remember that the calculated parameters are average values. Whenever more complicated base tetrahedron combinations are found in a structure the average structural features will correspond to the calculated parameter values used in the code of the compound.

The proposed classification characterizes the base tetrahedron(a) used for the construction of the tetrahedron complex but not the details of linkages. The  $C'AC'$  parameter denotes only the average number of  $C'-A-C'$  links per tetrahedron; however, it is left open whether the tetrahedra are corner- or edge-linked. As an example, we may consider the  $^{08}/2$

compound  $AgPS_3$ , shown in the middle part of Fig. 4. The predicted most probable base tetrahedron can be edge-linked to result in the observed molecular double tetrahedron, but it could also be two-corner-linked to give an infinite tetrahedron chain or a ring. These differences in linkage cannot be predicted from simple calculations. They seem to depend on subtle differences in the environment. A good demonstration for this is offered by the  $^{08}/2$  compounds  $Na_2GeS_3$  and  $Na_2GeS_3 \cdot 7H_2O$ . They have the same classification code as  $AgPS_3$ .  $Na_2GeS_3$  has infinite chains of two-corner-linked  $GeS_4$  tetrahedra, but the hydrated compound  $Na_2GeS_3 \cdot 7H_2O$  has molecular edge-linked double tetrahedra. The water molecules occupy interstitial sites and do not contribute to the valence-electron pool but influence the kind of linkage of the  $GeS_4$  tetrahedra.

Any subclassification to characterize the different kinds of linkages of a given base tetrahedron(a) which may occur with the different structures belonging to one (main) category will be based entirely on experimentally determined structure features and is thus beyond the scope of this work. It can be added that Liebau (1985) has already proposed two parameters: linkedness and connectedness which may be used advantageously for a subclassification of structures with not too complicated tetrahedron linkages.

#### Limits to the use of the classification

The limits to the use of the classification are as follows:

(a) An anionic tetrahedron complex has to be formed and all the  $C'$  and  $A$  atoms must participate on the complex.

(b) The valence-electron contribution of the elements is clear in most cases, but there are exceptions: we always have  $Tl^{1+}$ ,  $Pb^{2+}$ , but sometimes  $Eu^{2+}$ . In the case of transition elements the valence is calculated from the observed structure of the tetrahedron complex.

(c) From a certain point on, the Zintl concept does not hold and the predicted structural features of the (metallic) compounds do not agree with observation. For example, for  $Ba_7Ga_4Sb_9$  (Cordier, Schaefer & Stelter, 1986) one calculates the code  $^{147}889/3 \cdot 5$ , but two relatively long Sb—Sb bonds are observed for nine anions instead of one (short covalent) bond.

(d) The occurrence of  $C'-C'$  bonds and/or electron lone pairs on the  $C'$  atoms can be predicted only for  $C'C' = 1, 2$  or  $3$  with 95% probability.

(e) Non-equipartition of the  $C'-A-C'$  links is unlikely but has been observed exceptionally in structures with codes  $^{08}/6$ ,  $^{08}/8$  and  $^{29}333/4$ .

In spite of certain limitations in the applicability of this classification scheme for structures with anionic



tetrahedron complexes, we believe that this approach is a useful one because:

(a) It permits, based on the generalized  $(8 - N)$  rule, a systematization of the structures.

(b) It allows the recognition of certain systematic trends such as the equipartition of the  $C'-A-C'$  links, the competition of  $C'-C'$  bonds with lone pairs, and so on.

(c) It will aid the synthesis of new compounds with particular structural features.

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## Electron Density Distribution around Hydrogen Atoms in Linear Molecules

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### Abstract

Electron densities around H atoms in linear HX molecules ( $X = \text{H, F, Cl, OLi, ONa, CN, CP, BeH, Li}$  and  $\text{Na}$ ) were calculated in two directions relating to the major and minor radii. A Hartree-Fock level of theory with the 6-311G(2d,p) or MC-311G(2d,p) basis sets was applied. Van der Waals radii of the H atoms in the isolated molecules were estimated at the position where the electron density is 0.005 a.u. ( $0.0337 \text{ e } \text{Å}^{-3}$ ). The anisotropy of both the electron density distributions and the van der Waals radii of the H atoms was clearly confirmed in all the molecules. The radii and the degree of anisotropy are linearly related to both the Mulliken atomic charges on the H atom and the electronegativity of the

substituent  $X$ . The minor radius of the H atom depends strongly on the substituent  $X$  and increases as the electronegativity of  $X$  decreases. The predicted radii provide us with useful hints for considering the size of the H atom in molecules in the crystal.

### 1. Introduction

The van der Waals radius of an atom in molecules in the major direction (sideways-on radius,  $r_s$ ), which is perpendicular to the chemical bond, is usually larger than that in the minor direction (head-on radius,  $r_h$ ) parallel to the chemical bond. This is called 'polar flattening' and has been pointed out quantitatively by Nyburg & Faerman (1985). They examined many