Cooper, Hutchinson, Morgan & Mathey (1979). Furthermore, if the value of $K(MM)$ is set to zero we see a drop of only ~30% in the energy of the $M \equiv M$ stretch, indicating that most of the contribution to the force field at the metal atoms is from elsewhere in the structure. Clearly, the previous workers' neglect of the other contributions to the force field lead to a substantial overestimate of $K(MM)$ as well as an improper ranking of $K(MM)$ values for related compounds. Moreover, the use of a more generalized force field with fewer parameters has given us a vibrational model that is well determined by the available IR and Raman spectra without neglect of any interactions.

We thank W. R. Busing for useful discussions and the Academic Computer Services at Arizona State University for a generous allocation of computer time.

References

BONDI, A. (1964). *J. Phys. Chem.* **68**, 441-451.

BRATTON, W. K., COTTON, F. A., DEBEAU, M. & WALTON, R. A. (1971). *J. Coord. Chem.* **1**, 121-131.

BRENCIC, J. V. & COTTON, F. A. (1969). *Inorg. Chem.* **8**, 7-10.

BUSING, W. R. (1980). *WMIN.* Report ORNL-5747. Oak Ridge National Laboratory, Tennessee.

CLARK, J. H. & FRANKS, M. L. (1975). *J. Am. Chem. Soc.* **97**, 2691-2697.

CLARK, J. H. & FRANKS, M. L. (1976). *J. Am. Chem. Soc.* **98**, 2763-2767.

COSTA, G., PAULUZZI, E. & PUXEDDU, A. (1957). *Gazz. Chim. Ital.* **81**, 885-895.

COTTON, F. A. & BRIGNOLE, A. B. (1972). *Inorganic Synthesis*, Vol. XIII, edited by F. A. COTTON, pp. 87-89. New York: McGraw-Hill.

COTTON, F. A., FRENZ, B. A., STULTS, B. R. & WEBB, T. R. (1976). *J. Am. Chem. Soc.* **98**, 2768-2773.

COTTON, F. A., MESTER, A. C. E. & WEBB, T. R. (1974). *Acta Cryst.* B**30**, 2768-2770.

COTTON, F. A. & WILKINSON, G. (1980). *Advanced Inorganic Chemistry*, 4th ed., p. 1099. New York: Interscience.

GILBERT, T. L. (1968). *J. Chem. Phys.* **49**, 2640-2641.

JOHNSON, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee.

JOHNSON, M. K., CANNON, R. D. & POWELL, D. B. (1981). *Spectrochim. Acta Part A*, **37**, 995-1006.

JOHNSON, M. K., CANNON, R. D. & POWELL, D. B. (1982). *Spectrochim. Acta Part A*, **38**, 307-315.

KETTERINGHAM, A. P., OLDHAM, C. & PEACOCK, C. P. (1976). *J. Chem. Soc. Dalton Trans.* pp. 1640-1642.

KOSMIN, P. A., SURAZHSKAYA, M. D., LARINA, T. B., KOTELNIKOVA, A. S. & MISAILOVA, T. V. (1980). *Koord. Khim.* **6**, 1256-1258.

NAKAMOTO, K. (1963). *Infrared Spectra of Inorganic and Coordination Compounds*, p. 282. New York: John Wiley.

PAULING, L. (1960). *The Nature of the Chemical Bond*, 3rd ed., p. 261. Ithaca: Cornell Univ. Press.

SAN FILIPPO, J. & SNIADOCH, H. (1973). *Inorg. Chem.* **12**, 2326-2333.

SCHACHTSCHNEIDER, J. H. (1965). *Normal Mode Programs.* Technical Reports 57-65 and 231-264. Shell Development Co., Emeryville, California.

SHRIVER, D. F. & COOPER, C. B. (1980). *Advances in Infrared and Raman Spectroscopy*, Vol. 6, edited by R. J. H. CLARK & R. E. HESTER, pp. 127-157. Philadelphia: Heyden.

SHRIVER, D. F., COOPER, C. B., HUTCHINSON, B., MORGAN, J. & MATHEY, Y. (1979). *Inorg. Chem.* **18**, 2048-2049.

SHRIVER, D. F., MATHEY, Y. & GREIG, D. R. (1982). *Inorg. Chem.* **21**, 3409-3413.

SLATER, J. C. (1964). *J. Chem. Phys.* **41**, 3199-3204.

Acta Cryst. (1986). B**42**, 538-544

Relation Between Tetrahedron Connections and Composition for Structures with Tetrahedral Anion Complexes*

BY ERWIN PARTHÉ AND NORA ENGEL†

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 24 quai Ernest Ansermet, CH-1211 Genève 4, Switzerland

(*Received* 20 *March* 1986; *accepted* 11 *June* 1986)

Abstract

For the classification of structures with tetrahedral anion complexes such as silicates or phosphates different parameters have been proposed, such as Zoltaï's tetrahedral sharing coefficient or Liebau's connectedness and linkedness. Another parameter, labelled *TT*, is discussed here, which denotes the average per tetrahedron of the sum (over all four corners of a tetrahedron) of the number of tetrahedra which are connected with one corner of the tetrahedron considered. If there are only isolated or corner-connected tetrahedra in the structure the *TT* parameter corresponds simply to the average number of tetrahedron-tetrahedron connections per tetrahedron. The *TT* parameter can be related to Zoltaï's sharing coefficient and Liebau's connectedness and linkedness. The particular advantage of the introduction of the *TT* parameter is that it can be obtained

* The main part of this paper is a modified version of one chapter of the PhD thesis submitted by N. Engel to Geneva University.

† Present address: Département de Minéralogie du Muséum d'Histoire Naturelle, 1 route de Malagnou, CH-1211 Genève 6, Switzerland.

0108-7681/86/060538-07$01.50

in a very simple way from the composition of the compound. The formula relating *TT* and composition is independent of the particular kind of atoms which form the tetrahedra and is thus valid for all kinds of structures with tetrahedral anion complexes such as phosphates, silicates, fluoroberyllates and others. The formula is equally valid for corner- or edge-linked tetrahedral anion complexes. The usefulness of this formula is demonstrated on different examples. The formula permits the prediction of possible tetrahedron connections and serves also as a check on the correctness of a structure determination.

Introduction

Since the time of Machatschki and Bragg, the different kinds of tetrahedron connections have formed the basis for a structural classification of silicates in neso-, soro-, cyclo-, ino-, phyllo- and tectosilicates. Zoltaï (1960) gave the first mathematical formulation of the tetrahedron connection in silicates and other structures built up of tetrahedral anion complexes by introducing the tetrahedral sharing coefficient, c_Z, which is defined as the average number of tetrahedra participating in sharing of a tetrahedral corner. It varies between 1 (for nesosilicates with isolated tetrahedra) and 2 (for tectosilicates). The tetrahedral sharing coefficient for tetrahedral structures has been related (Parthé, 1964) to the valence-electron numbers of the participating atoms and the valence-electron concentration of the compound. The corresponding equation is discussed in the *Appendix*.

In 1969 Coda presented a modified sharing coefficient (c_C) for the classification of silicates, which can be obtained from Zoltaï's coefficient by means of

$$c_C = 4(c_Z - 1). \qquad (1)$$

c_C is defined by Coda as the average number of O atoms per tetrahedron which are shared with other tetrahedra. He considered only silicates with isolated tetrahedra or with tetrahedra connected by corners only to a maximum of four other tetrahedra. Coda's coefficient varies between 0 (for nesosilicates) and 4 (for tectosilicates).

The tetrahedra in the structures with tetrahedral anion complexes can be classified according to Liebau (1985) by means of two parameters: linkedness and connectedness. *Linkedness* indicates the number of anions shared between two adjacent tetrahedra. *Connectedness* of a tetrahedron is defined as the number of tetrahedra which share anions with a given tetrahedron.

Definition of the *TT* parameter

We shall introduce here a parameter, which we have labelled *TT* in analogy to the *AA* or *CC* parameters which characterize the anion–anion or cation–cation connections in polyanionic or polycationic valence compounds (Parthé, 1973). It corresponds numerically to Coda's coefficient, but differs in its definition in that it allows the possibility of edge-connected tetrahedra and also extension to other compounds with tetrahedral anion complexes, other than silicates or phosphates. The *TT* parameter is defined as the average per tetrahedron of the sum (over all four corners of a given tetrahedron) of the number of tetrahedra connected with one corner of the given tetrahedron. For structures with only isolated tetrahedra ($TT = 0$) or with tetrahedra which are not edge-connected but only corner-connected, the *TT* value corresponds to the average value of Liebau's connectedness. *TT* is then equivalent to the average number of tetrahedron–tetrahedron connections per tetrahedron. The *TT* parameter which has been used in a previous publication (Parthé, 1980) was defined in this simple form because only structures with isolated or corner-connected tetrahedra had been considered at this time. However, more and more structures have become known, most of them determined recently, which are characterized by edge-connected tetrahedra. It is thus advantageous to have a classification parameter which allows for corner- and edge-connected tetrahedra and which in addition can be quickly calculated from the chemical composition of the compound.

Mineralogists and others, working intensively with structures characterized by tetrahedral anion complexes, associate a particular kind of tetrahedron connection pattern with each composition. This is not so evident for those not directly involved in this field. To recognize the kind of possible tetrahedron connection – for example, in $Na_3Mg_2P_5O_{16}$ – requires a certain effort. It is the purpose of this note to show that, under certain conditions, *TT* values can be calculated quickly by means of a simple formula. By defining *TT* in the above way, it will be possible, as shown below, to obtain a relation between *TT* and the composition of the compound which is independent of the linkedness of the tetrahedra.

The tetrahedral sharing coefficient, its modified version, the connectedness and the linkedness, which have been used so far to classify structures with tetrahedral anion complexes, were formulated on the basis of strictly geometrical considerations, their relation with the numbers of valence electrons of the atoms present having been ignored. It will be shown here that a relation between *TT* and the composition of the compound can be derived assuming that (*a*) all anions in the tetrahedral anion complex complete their octets and (*b*) the compound is a normal valence compound.

TT and its relation to the composition of the compound

Let us assume a structure with composition $C_mC'_{m'}A_n$ with a tetrahedral anion complex $C'_{m'}A_n$.

Each tetrahedron consists of a central atom C', tetrahedrally coordinated by four anions A of which some may be shared with another tetrahedron. The C atoms which serve as cations do not participate in the formation of the tetrahedra; however, the valence electrons which they provide - there are me_C electrons - exactly complete the octets of all atoms in the tetrahedral anion complex. As seen in Fig. 1, an isolated tetrahedral anion complex needs 32 valence electrons in order that its five atoms have complete octet shells (which consist formally of lone electron pairs and/or shared two-electron bonds between C' and A). If a tetrahedron is corner-connected with another tetrahedron only 28 valence electrons per tetrahedron are necessary, *i.e.* four electrons less. If a tetrahedron is corner-connected with two other tetrahedra or edge-connected with one other tetrahedron only 24 electrons per tetrahedron are necessary, *i.e.* eight electrons less.

In general, when TT indicates the average per tetrahedron of the sum (over the four corners of a given tetrahedron) of the number of the tetrahedra connected with one corner, the average number of valence electrons needed for one tetrahedron, in order that all atoms complete their octet, is $32-4TT$. Thus

$$\underset{\text{total No. of valence electrons}}{me_C + m'e_{C'} + ne_A} = \underset{\text{No. of tetrahedra}}{m'} \cdot \underset{\text{average No. of electrons for one tetrahedron}}{(32-4TT)}$$

$$\text{for } 0 \leq TT \leq 4 \quad (2)$$

where e_C, $e_{C'}$ and e_A are the valence electrons of the elements which serve as cations (C or C') and as anions (A), and m, m' and n are composition parameters.

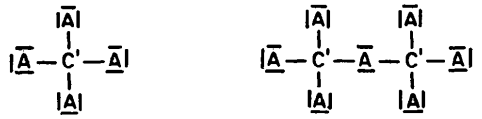
The compounds considered are normal valence compounds for which the compensation of the charges can be expressed by

$$me_C + m'e_{C'} = n(8-e_A). \quad (3)$$

Inserting (3) in (2) one obtains

$$TT = 2(4-n/m') \qquad \text{for } 0 \leq TT \leq 4. \quad (4)$$

The value of TT does not depend on e_C, $e_{C'}$ or e_A but only on n and m'. Equation (4) is thus valid not only for silicates and phosphates, but for all structures with tetrahedral anion complexes. Further, it applies not only to structures with corner-linked tetrahedra, but also to those with edge-linked tetrahedra if one takes care that the tetrahedron-tetrahedron connections are counted according to each corner of the tetrahedron. In the case of a tetrahedron which is edge-linked to a second, two corners of the considered tetrahedron each have one tetrahedron connection, *i.e.*, the sum, as defined above, has the value of 2. For an edge-linked double tetrahedron, as observed, for example, with Al_2Cl_6, the value of TT is 2.



32 electrons/tetrahedron 28 electrons/tetrahedron

Fig. 1. Electron count for the case of completed octets of all atoms in an isolated tetrahedron and a corner-shared double tetrahedron.

The conditions for the application of this simple formula are as follows:

(*a*) A tetrahedron corner may be either unshared or shared with only one other tetrahedron ($0 \leq TT \leq 4$; for a relaxation of this condition see *Appendix*).

(*b*) The compound must be a normal valence compound (which is nearly always the case).

(*c*) There should be no ambiguity as to which atoms serve as central atoms (C') and which are outside of the tetrahedra (C). There should be either no other anions beside those forming the tetrahedron (A) or these extra anions have been properly subtracted from the formula to obtain the correct n/m' ratio. This condition is the most restrictive which limits the unreserved use of equation (4).

The interpretation of TT values depends on the linkedness of the tetrahedra.

(*a*) *Tetrahedra are isolated or corner-linked*

The simplest interpretation of TT is as follows:

If	$n/m' = 4$	$TT = 0$	isolated tetrahedra
	$n/m' = \frac{7}{2}$	$TT = 1$	double tetrahedra
	$\frac{7}{2} \geq n/m' > 3$	$1 \leq TT < 2$	limited chains of tetrahedra
	$n/m' = 3$	$TT = 2$	infinite chains or rings of tetrahedra
	$n/m' = \frac{5}{2}$	$TT = 3$	each tetrahedron connected with three other tetrahedra
	$n/m' = 2$	$TT = 4$	each tetrahedron with four connections.

For chains with a limited number of tetrahedra their length CL (=number of corner-linked tetrahedra in a chain) can be calculated according to

$$CL = 2/(2-TT) = 1/[(n/m')-3]$$
$$\text{for } 0 \leq TT < 2 \text{ and linkedness 0 or 1.} \quad (5a)$$

The simplest solutions of n/m', TT and CL are listed in the upper part of Table 1. The chain length expressed by CL applies to the most common case of an unbranched chain of tetrahedra. If the chain is branched, CL indicates the total number of tetrahedra in the chain. In compounds where different kinds of chains occur the parameter CL indicates the average chain length. One example is kilchoanite, $Ca_3Si_2O_7$ (Taylor, 1971), for which one calculates that $CL = 2$ but which is characterized by an isolated tetrahedron ($CL = 1$) and a finite chain of three corner-connected tetrahedra ($CL = 3$).

Table 1. *Simple solutions of n/m', TT and CL or CL^* for structures with finite tetrahedron chains*

Adjacent tetrahedra linked by a common corner only

n/m'	4	$\frac{7}{2}$	$\frac{10}{3}$	$\frac{13}{4}$	$\frac{16}{5}$	$\frac{19}{6}$	...	$3(CL+1)/CL$	...	3
TT	0	1	$\frac{4}{3}$	$\frac{6}{4}$	$\frac{8}{5}$	$\frac{10}{6}$	...	$2(CL-1)/CL$	...	2
CL	1	2	3	4	5	6	...	CL	...	∞

Adjacent tetrahedra linked by a common edge only

n/m'	4	3	$\frac{8}{3}$	$\frac{5}{2}$	$\frac{12}{5}$	...	$2(CL^*+1)/CL^*$	...	2
TT	0	2	$\frac{8}{3}$	3	$\frac{16}{5}$	...	$4(CL^*-1)/CL^*$	...	4
CL^*	1	2	3	4	5	...	CL^*	...	∞

(*b*) *Tetrahedra are edge-linked*

The most simple case, a molecule of two edge-linked tetrahedra, can be considered as a special case of a tetrahedron ring consisting of two tetrahedra only. The corresponding TT value is 2 and $n/m'=3$. If each tetrahedron is edge-linked with two tetrahedra one has a straight infinite chain where $TT=4$ and $n/m'=2$. In between these two extremes one might find finite chains of edge-linked tetrahedra. If CL^* indicates the number of tetrahedra in the chain of edge-linked tetrahedra one can calculate that

$$CL^* = 4/(4-TT) = 2/[(n/m')-2]$$

$$\text{for } 0 \le TT \le 4 \text{ and linkedness } 2. \quad (5b)$$

The solutions of n/m', TT and CL^* according to (5*b*) are listed in the lower part of Table 1.

(*c*) *Tetrahedra are corner-linked and edge-linked*

It does not seem possible to predict when the tetrahedra are corner-linked and when they will be edge-linked. Equation (4) is always valid, also for mixed cases. Examples are $Ca_3Al_2As_4$ (Cordier, Czech, Jakowski & Schäfer, 1981) or $CaGa_2Se_4$ (Klee & Schäfer, 1981) where $AlAs_4$ or $GaSe_4$ tetrahedra are connected by two common corners and one common edge to form a two-dimensional net. Hence $TT=4$ in agreement with $n/m'=2$.

Notation of the tetrahedron connections

Predictions of possible tetrahedron connections, obtained from the composition by means of (4), (5*a*) or (5*b*) can be written down by using a crystal-chemical formula (Parthé, 1980). For simplicity we restrict our considerations here to structures with isolated or corner-linked tetrahedra. The number of tetrahedron connections that a given tetrahedron has is indicated as an exponent following the chemical formula of the tetrahedron. The exponent is surrounded by square brackets, the number being preceeded by a +-sign to characterize it as a 'self-coordination' number. The average value of the numbers given in the exponents should correspond to the calculated TT value of the compound. For a finite tetrahedral anion complex ($TT<2$, or in the case of a ring $TT=2$) it is not necessary to denote the exponent. Instead the formula of the finite tetrahedral anion complex is placed inside square brackets with the number of atoms inside the brackets corresponding exactly to the number of atoms in the finite complex. (Note that in our convention round brackets enclose the simplest possible formula for an infinite tetrahedral anion complex.) The finite complex can be further characterized by one of the pictorial prefix symbols (see Parthé, 1980) which describe, for example, the length of a tetrahedron chain or the number of tetrahedra in a ring. It might be added here that for a calculated TT value of 2 and corner-linked tetrahedra it is not possible to predict if either an infinite chain or a ring is formed. For infinite tetrahedral anion complexes the dimensionality of the complex can be indicated in the conventional way by prefixes $(^1_\infty, ^2_\infty, ^3_\infty)$.

Examples of TT values calculated from the composition and crystal-chemical formulae corresponding to the observed crystal structures are listed in Table 2. The left-hand side of the table lists examples of structures with corner-linked tetrahedra and the right-hand side those with edge-linked tetrahedra.

Correlation between the TT parameter and the other classification parameters for structures with tetrahedral anion complexes

The TT parameter is numerically equal to Coda's modified tetrahedral sharing coefficient. However, the definition of TT is different from that for c_C (see above). The TT parameter is valid for structures with tetrahedral anion complexes for any values of the linkedness and connectedness.

The relation with Zoltaï's tetrahedral sharing coefficient is given by

$$TT = 4(c_Z - 1). \quad (6)$$

The parameter TT can be related with Liebau's connectedness and linkedness for which we repeat here their definitions:

s = connectedness is the number of $C'A_4$ tetrahedra that share anions with the $C'A_4$ tetrahedron considered.

L = linkedness is the number of anions shared between two adjacent $C'A_4$ tetrahedra.

The relation between TT, s and L is as follows

$$TT = (1/Zm') \sum_i^{Zm'} (s_i \langle L \rangle_i). \quad (7)$$

The summation is made over the Zm' tetrahedra found in one unit cell assuming that there are Z formula units $C_mC'_{m'}A_n$ per unit cell.

$\langle L \rangle_i$ is the average value of the linkedness of the $C'A_4$ tetrahedron i. The calculation of the average is only necessary in the case where the s tetrahedra which share anions with the tetrahedron do not each

Table 2. *Examples of structures with tetrahedral anion complexes arranged according to decreasing n/m' ratios and increasing TT values up to $TT = 4$. The crystal-chemical formulae correspond to the experimentally observed compounds*

	TT	*CL*	Isolated tetrahedra / Corner-linked tetrahedra	*CL**	Edge-linked tetrahedra
$C'A_4$	0		$Ca_3Al_2[SiO_4]_3$, $Ca_3[PO_4]_2$, $Cs_2[BeF_4]$, $Ba_4[SiAs_4]$		
C'_2A_7	1	2	$Sc_2^{\ddagger}[Si_2O_7]$, $Mg_2^{\ddagger}[P_2O_7]$, $K_2^{\ddagger}[S_2O_7]$, $Na_2Li^{\ddagger}[Be_2F_7]$		
C'_3A_{10}	1·33	3	$Ca_3H_2^{\ddagger}[Si_3O_{10}]$, $Na_5^{\ddagger}[P_3O_{10}]$		
C'_4A_{13}	1·5	4	$Na_4Sc_2^{\ddagger}[Si_4O_{13}]$, $Ba_3^{\ddagger}[P_4O_{13}]$		
C'_5A_{16}	1·6	5	$Na_4Sn_2^{\ddagger}[Si_5O_{16}].H_2O$, $Na_3Mg_2^{\ddagger}[P_5O_{16}]$		
C'_6A_{19}	1·67	6	$Ca_4^{\ddagger}[P_6O_{19}]$ (tromelite)		
$C'A_3$	2	—	$Na_{2\infty}^{1}(GeS_3)^{[+2]}$, $Cs_{\infty}^{1}(BeF_3)^{[+2]}$, $Ca_{3\infty}^{1}(AlAs_3)^{[+2]}$, $Na_3②[P_3O_9]$, $K_2Sr②[P_4O_{12}]$	2	$②[Ga_2Cl_6]$, $Ba_6②[Al_2Sb_6]$
C'_5A_{14}	2·4	—	$Er(PO_3)_3^{[+2]}(PO_{2\cdot5})_2^{[+3]}$		
C'_4A_{11}	2·5	—	$Ca_2Mg_5(OH)_{2\infty}^{1}((SiO_3)^{[+2]}(SiO_{2\cdot5})^{[+3]})_4$, $Ca((PO_3)^{[+2]}(PO_{2\cdot5})^{[+3]})_2$		
C'_8A_{21}	2·75	—	$Ba_5((SiO_3)^{[+2]}(SiO_{2\cdot5})_3^{[+3]})_2$		
C'_2A_5	3	—	$Al_2(OH)_{4\infty}^{2}(SiO_{2\cdot5})_2^{[+3]}$, $Rb_{\infty}^{2}(BeF_{2\cdot5})_2^{[+3]}$		
$C'_{10}A_{23}$	3·4	—	$Rb_6((SiO_{2\cdot5})_3^{[+3]}(SiO_2)_2^{[+4]})_2$		
C'_4A_9	3·5	—	$K_2((SiO_{2\cdot5})^{[+3]}(SiO_2)^{[+4]})_2$		
$C'A_2$	4	—	${}_{\infty}^{3}(BeF_2)^{[+4]}$, ${}_{\infty}^{3}(SiO_2)^{[+4]}$	∞	${}_{\infty}^{1}(SiS_2)^{[+4]}$, $K_{2\infty}^{1}(SiP_2)^{[+4]}$

share the same number of anions with it, *i.e.* there are edge-linked and corner-linked tetrahedra. $\langle L\rangle_i$ is defined as

$$\langle L\rangle_i = (1/s_i)\sum_{j}^{s_i} L_j. \qquad (7a)$$

Note that if $s_i = 0$, it follows that $L_i = 0$ and $\langle L\rangle_i = 0$. An example where the s adjacent tetrahedra do not each share the same number of anions with the tetrahedron of interest is found in $Ca_3Al_2As_4$ [$s = 3$, $\langle L\rangle = (2+1+1)/3 = 4/3$ and since all tetrahedra are identical $TT = 4$].

It is much more common that all tetrahedra adjacent to a given tetrahedron share the same number of anions with the given tetrahedron. In this case $\langle L\rangle_i = L_i$ and equation (7) simplifies to (7′):

$$TT = (1/Zm')\sum_{i}^{Zm'}(s_iL_i). \qquad (7')$$

This equation still allows the average linkedness of different tetrahedra in the structure to be different. An example of this case is kilchoanite, $Ca_3Si_2O_7$ (see above). For the isolated tetrahedron $s = 0$ and $L = 0$, but for the chain of the three corner-linked tetrahedra $L = 1$ for each tetrahedron and $s = 1$, 2 and 1, respectively. If one writes the chemical formula as $Ca_6[SiO_4]^{\ddagger}[Si_3O_{10}]$, then with $m' = 4$ one calculates $TT = 1$.

For the great majority of the compounds with tetrahedral anion complexes all tetrahedra have the same average linkedness. This brings us to the simplest form of equation (7)

$$TT = L\langle s\rangle \qquad (7'')$$

where $\langle s\rangle$ is the average value of the connectedness of all tetrahedra in one unit cell.

In the majority of the silicates the tetrahedra are either all isolated or all corner-linked and then $TT = 0$ or $TT = \langle s\rangle$, respectively, *i.e.* in this case one may equate TT with the average value of the connectedness or rephrase TT as the average number of tetrahedron–tetrahedron connections per tetrahedron without further specification.

The maximum value of *TT* for a given central atom and anion

By combining (3) and (4) in order to eliminate n one obtains

$$TT = 8 - [2/(8-e_A)][(me_C/m') + e_{C'}] \quad \text{for } 0 \le TT \le 4 \qquad (8)$$

which can be transformed to

$$me_C/m' = \tfrac{1}{2}(8-TT)(8-e_A) - e_{C'} \quad \text{for } 0 \le TT \le 4. \qquad (9)$$

We note that me_C/m' corresponds to the charge of the tetrahedral anion complex per tetrahedron. Fig. 2 presents two diagrams with me_C/m' as ordinate and TT or n/m' as abscissa, one for $e_A = 6$ and the second for $e_A = 7$.

The maximum value of TT for a given central atom (C') and anion (A), denoted TT_{max}, corresponds, according to (4), to $(n/m')_{min}$ or, according to (8), to $(me_C/m')_{min}$. The limiting case is obtained from (8) if $m = 0$ which results in

$$TT_{max} = 8 - 2e_{C'}/(8-e_A) \quad \text{for } 0 \le TT \le 4. \qquad (10)$$

The TT_{max} value applies to a neutral compound of composition $C'_{8-e_A}A_{e_{C'}}$ or $C'A_{4-\frac{1}{2}TT_{max}}$.

The neutral compound with TT_{max} corresponds to a degenerate case of the structures with tetrahedral anion complexes where the available valence electrons of the C' and A atoms are fully sufficient to complete the octets of all atoms of the tetrahedral complex. Thus there are no more cations C necessary. In Fig. 2 the plots of the compounds with TT_{max} are found on the base lines. The crystal-chemical formulae of these compounds are listed in Table 3. This table can be used to grasp quickly the degree to which a tetrahedron connection can be increased with a given central atom and given anions. For example, it is impossible to have sulfate structures where each tetrahedron has more than two corners that are each shared with another tetrahedron. On the other hand one can conclude that aluminates in which one tetrahedron corner is connected with two other tetrahedra may exist, as is demonstrated for $CaAl_4O_7$ in the *Appendix*.

It should be mentioned that neutral compounds in which there are several kinds of C' or A atoms also exist. For these compounds the parameters $e_{C'}$ and e_A in equation (10) have to be replaced by mean values.

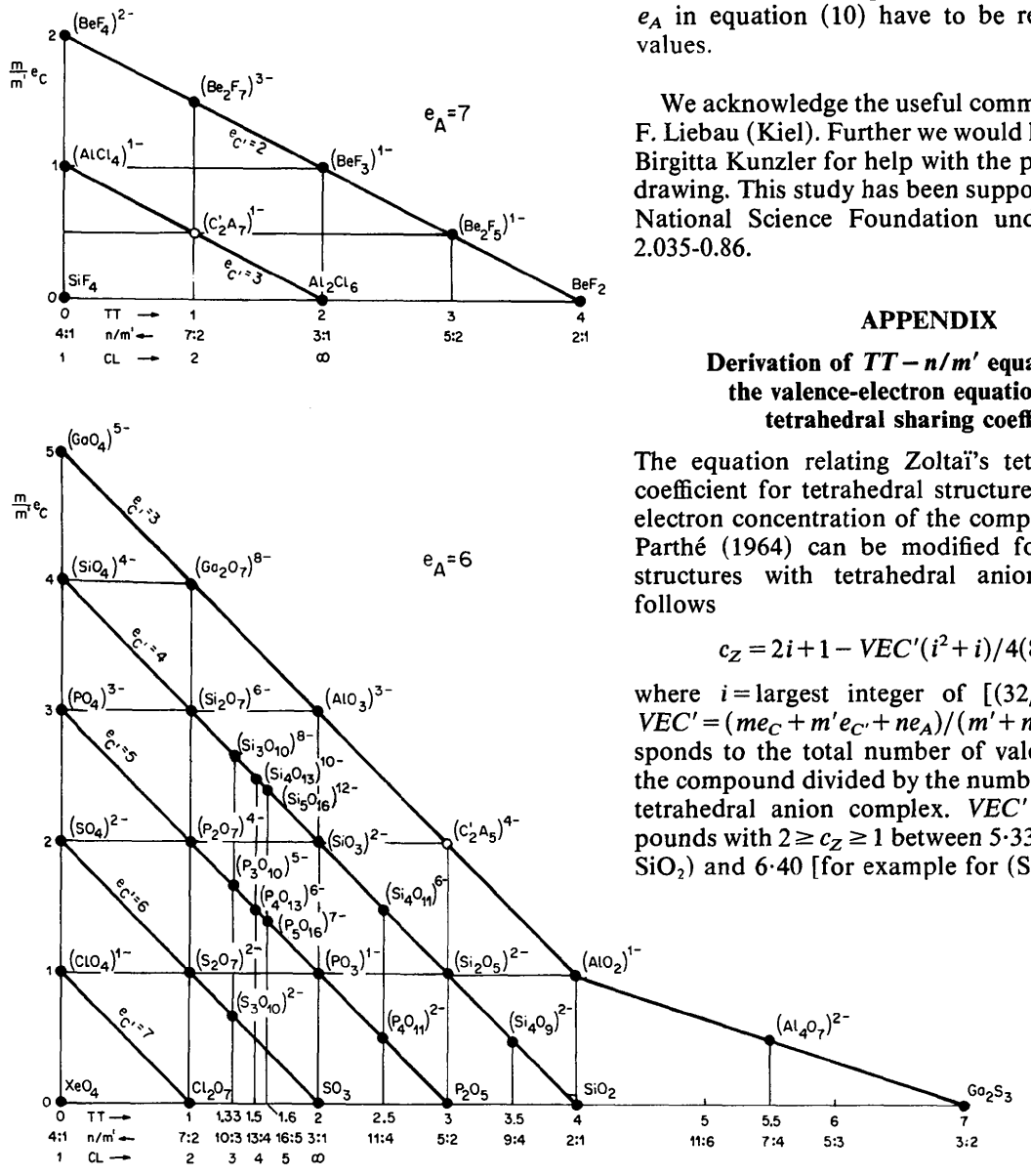


Fig. 2. Charge of the tetrahedral anion complex per tetrahedron as a function of TT. Equation (9) was used for the construction of the lines at $0 \leq TT \leq 4$. The line plotted for $TT > 4$ was obtained from (3) and (14*b*). Full circles correspond to tetrahedral anion complexes which have been found experimentally; open circles to anion complexes which have not yet been found. For reasons of limited space the tetrahedral anion complexes of the hexaphosphate tromelite $Ca_4\{[P_6P_{19}]$ (Corbridge, 1978) and of other more complicated silicates and phosphates listed in Table 2 have not been plotted here.

We acknowledge the useful comments of Professor F. Liebau (Kiel). Further we would like to thank Mrs. Birgitta Kunzler for help with the preparation of the drawing. This study has been supported by the Swiss National Science Foundation under contract No. 2.035-0.86.

APPENDIX

Derivation of $TT - n/m'$ equations from the valence-electron equation for the tetrahedral sharing coefficient

The equation relating Zoltaï's tetrahedral sharing coefficient for tetrahedral structures to the valence-electron concentration of the compound as given by Parthé (1964) can be modified for application to structures with tetrahedral anion complexes as follows

$$c_Z = 2i + 1 - VEC'(i^2 + i)/4(8 - VEC') \quad (11)$$

where i = largest integer of $[(32/VEC') - 4]$ and $VEC' = (me_C + m'e_{C'} + ne_A)/(m' + n)$ which corresponds to the total number of valence electrons of the compound divided by the number of atoms in the tetrahedral anion complex. VEC' varies for compounds with $2 \geq c_Z \geq 1$ between 5·33 (for example for SiO_2) and 6·40 [for example for $(SiO_4)^{4-}$].

Table 3. *Composition and crystal-chemical formulae for the neutral compounds with degenerated tetrahedral anion complexes*

$e_{C'}$	e_A	TT_{max}	Crystal-chemical formulae
2	7	4	$^3_\infty(BeF_2)^{[+4]}$
3	7	2	②$[(AlCl_3)_2^{[+2]}]$*
4	7	0	$[SiF_4]$
4	6	4	$^3_\infty(SiO_2)^{[+4]}$
5	6	3	⑨$[(PO_{2\cdot5})_4^{[+3]}]$, $^2_\infty(PO_{2\cdot5})_2^{[+3]}$, $^3_\infty(PO_{2\cdot5})_2^{[+3]}$
6	6	2	$^1_\infty(SO_3)^{[+2]}$, ③$[(SO_3)_3^{[+2]}]$
7	6	1	$^0_\infty[Cl_2O_7]$
8	6	0	$[XeO_4]$

* Al_2Cl_6 is 'bicyclic', that means the two tetrahedra have a common edge ($s=1$, $L=2$, $CL^*=1$).

Table 4. *Formulae of the tetrahedral anion complexes for different values of TT independent of the kind of tetrahedron linkage*

Each tetrahedron corner unshared or shared with one other tetrahedron	$TT=0$ $C'A_4$	1 $C'A_{7/2}$	2 $C'A_3$	3 $C'A_{5/2}$	4 $C'A_2$
Each tetrahedron corner shared with one or two tetrahedra	$TT=4$ $C'A_2$	5 $C'A_{11/6}$	6 $C'A_{5/3}$	7 $C'A_{3/2}$	8 $C'A_{4/3}$
Each tetrahedron corner shared with two or three tetrahedra	$TT=8$ $C'A_{4/3}$	9 $C'A_{5/4}$	10 $C'A_{7/6}$	11 $C'A_{13/12}$	12 $C'A$

Equation (11) is valid for compounds having tetrahedral sharing coefficients between 1 and 4, that means it is applicable also to compounds where more than two tetrahedra are connected with the corner of a given tetrahedron, as, for example, in $CaAl_4O_7$ or Ga_2S_3 and $Ca_3Al_2Ge_3$ or ZnS.

The most important step for the simplification of equation (11) is the replacement of VEC' by use of (3). Noting that

$$VEC'/(8-VEC') = n/m' \qquad (12)$$

it is now possible to rewrite (11) as follows

$$c_Z = 3-\tfrac{1}{2}(n/m') \quad \text{for } 1\le c_Z\le 2,$$
$$6{\cdot}40 \ge VEC' \ge 5{\cdot}33 \qquad (13a)$$
$$c_Z = 5-\tfrac{3}{2}(n/m') \quad \text{for } 2\le c_Z\le 3,$$
$$5{\cdot}33 \ge VEC' \ge 4{\cdot}57 \qquad (13b)$$
$$c_Z = 7-3(n/m') \quad \text{for } 3\le c_Z\le 4,$$
$$4{\cdot}57 \ge VEC' \ge 4{\cdot}00. \qquad (13c)$$

Making use of (6), equations (13) transform into

$$TT = 1[8-2(n/m')] \quad \text{for } 0\le TT\le 4,$$
$$4 \ge n/m' \ge 2 \qquad (14a)$$
$$TT = 2[8-3(n/m')] \quad \text{for } 4\le TT\le 8,$$
$$2 \ge n/m' \ge \tfrac{4}{3} \qquad (14b)$$
$$TT = 3[8-4(n/m')] \quad \text{for } 8\le TT\le 12,$$
$$\tfrac{4}{3} \ge n/m' \ge 1. \qquad (14c)$$

Equation (14*a*), which is identical to (4), applies to the case where each tetrahedron corner is either unshared or connected with one other tetrahedron. Equation (14*b*) applies to the case where each tetrahedron corner is connected with one or two tetrahedra, and equation (14*c*) where each corner is connected with two or three tetrahedra. Equations (14) serve to calculate the simplest formulas of the tetrahedral anion complexes with TT varying from 0 to 12 as given in Table 4.

As an example for the application of (14*b*) and Table 4 we consider $Ca_3Al_2Ge_3$ (Cordier & Schäfer, 1982). The ratio $n/m'=\frac{3}{2}$ leads to $TT=7$ which agrees well with the observed structural features. The $AlGe_4$ tetrahedra are corner-connected to a framework in such a way, that three corners of each tetrahedron are connected with two other tetrahedra and one corner with one other tetrahedron.

As another example we can discuss $CaAl_4^{[4f]}O_7$ with $n/m'=\frac{7}{4}$ which results in $TT=5\frac{1}{2}$ (see also Fig. 2). As the simplest solution one can assume that the tetrahedral anion complex might be built up of equal amounts of $(C'A_{11/6})^{[+5]}$ and $(C'A_{5/3})^{[+6]}$ tetrahedra. A possible crystal-chemical formula is thus $Ca^3_\infty((AlO_{11/6})_2^{[+5]}(AlO_{5/3})_2^{[+6]})$ which corresponds to the experimentally observed structural features of $CaAl_4O_7$ (Goodwin & Lindop, 1970; Ponomarev, Kheiker & Belov, 1971). The structure had actually not been described in such a way. That the proposed crystal-chemical formula is correct was verified by us after calculating a complete list of interatomic distances.

References

CODA, A. (1969). *Rend. Soc. Ital. Mineral. Petrol.* **25**, 197-226.

CORBRIDGE, D. E. C. (1978). *Phosphorus, an Outline of its Chemistry, Biochemistry and Technology.* Amsterdam: Elsevier.

CORDIER, G., CZECH, E., JAKOWSKI, M. & SCHÄFER, H. (1981). *Rev. Chim. Miner.* **18**, 9-18.

CORDIER, G. & SCHÄFER, H. (1982). *Z. Anorg. Allg. Chem.* **490**, 136-140.

GOODWIN, D. W. & LINDOP, A. J. (1970). *Acta Cryst.* B**26**, 1230-1235.

KLEE, W. & SCHÄFER, H. (1981). *Z. Anorg. Allg. Chem.* **479**, 125-133.

LIEBAU, F. (1985). *Structural Chemistry of Silicates.* Berlin: Springer.

PARTHÉ, E. (1964). *Crystal Chemistry of Tetrahedral Structures*, p. 95. New York: Gordon & Breach.

PARTHÉ, E. (1973). *Acta Cryst.* B**29**, 2808-2815.

PARTHÉ, E. (1980). *Acta Cryst.* B**36**, 1-7.

PONOMAREV, V. I., KHEIKER, D. M. & BELOV, N. V. (1971). *Sov. Phys. Crystallogr.* **15**, 995-998.

TAYLOR, H. F. W. (1971). *Mineral. Mag.* **38**, 26-31.

ZOLTAÏ, T. (1960). *Am. Mineral.* **45**, 960-973.