Structural Features of Compounds with Tetrahedral Structures or Tetrahedral Anion Partial Structures Derived from Two Valence Electron Concentration Rules*

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The total and the partial valence electron concentrations (VEC), two variables which can be easily calculated from the composition of the compound and the valence electron numbers of the participating atoms, serve as useful parameters to predict probable structural features of compounds with a tetrahedral structure or a tetrahedral anion partial structure such as an anionic tetrahedron complex. The structural features to be predicted are the average number of nonbonding orbitals, the number of atoms in molecular structures, the average number of anion-anion bonds per anion or the average number of electrons which remain with the cation to be used either for cation-cation bonds or nonbonding orbitals.

Tetrahedral Structures

Tetrahedral structure compounds form a subset of the general valence compounds where each atom has, at most, four neighbors which are positioned at the corners of a surrounding tetrahedron. In normal tetrahedral structures, each atom in the structure has four tetrahedral neighbors. With defect tetrahedral structures, some atoms have less than four neighbor atoms.

Tetrahedral structures are found with ionic-covalent compounds which can be considered either as ionic or as covalent. For each hypothetical bonding state a valence electron concentration (VEC) rule can be formulated which allows certain structural features to be predicted. These two rules are: (1) the tetrahedral structure equation for the covalent bonding state and (2) the generalized 8 – N rule for the ionic bonding state.

Covalent Bonding State

Each atom forms four tetrahedral sp³ hybrid orbitals which overlap with the sp³ orbitals of the neighboring atoms. To form a sp³ hybrid, each atom needs four valence electrons. Each orbital not used for bonding must obtain a second electron and becomes a nonbonding orbital.

For a compound CₘAₙ⁻:

\[ m \times e_C + n \times e_A = (m + n) \times 4 + (m + n) \times N_{NBO} \]  

(Eq 1)

where \( N_{NBO} \) is the average number of nonbonding orbitals per atom.

Introducing the total VEC defined as:

\[ VEC = (m \times e_C + n \times e_A) / (m + n) \]  

(Eq 2)

one obtains:

\[ VEC = 4 + N_{NBO} \]  

(Eq 3)

which is the tetrahedral structure equation.

Calculation of VEC shows what kind of tetrahedral structure might be possible. Therefore, if VEC < 4, then no tetrahedral structure is possible. If VEC = 4, then normal tetrahedral structure (\( N_{NBO} = 0 \)) exists. If VEC > 4, then defect tetrahedral structure (\( N_{NBO} > 0 \)) exists.

If VEC > 6, the atoms have so few bonding orbitals that the defect tetrahedral structure consists of a noncyclic molecule with a finite number of atoms which can be calculated according to:

\[ N_{AM} = 2 / (VEC - 6) \]  

(Eq 4)

where \( N_{AM} \) is the number of atoms in the noncyclic molecule. Simple solutions of (Eq 4) are:

<table>
<thead>
<tr>
<th>N_{AM}</th>
<th>VEC</th>
<th>N_{AM}</th>
<th>VEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>6.2</td>
<td>5</td>
<td>6.4</td>
</tr>
<tr>
<td>9</td>
<td>6.22</td>
<td>4</td>
<td>6.5</td>
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<td>8</td>
<td>6.25</td>
<td>3</td>
<td>6.667</td>
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<td>7</td>
<td>6.286</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>6.333</td>
<td>1</td>
<td>8</td>
</tr>
</tbody>
</table>

Ionic Bonding State

The valence electrons of the cations are transferred to the anions for them to complete their octets. But if the cations need electrons for covalent bonds between themselves, not all their valence

Electrons are donated to the anions. Also the anions might need fewer electrons if they form covalent bonds between themselves.

For \( C_m A_n \):

\[
m \times (e_C - CC) = n \times (8 - e_A - AA) \quad \text{(Eq 5)}
\]

i.e., the valence electron donation by the cations equals the valence electron deficiency of the anions.

Introducing the partial valence electron concentration in respect to the anion, \( VEC_A \) defined as:

\[
VEC_A = \frac{m \times e_C + n \times e_A}{n} \quad \text{(Eq 6)}
\]

obtains:

\[
VEC_A = 8 + \left( \frac{m}{n} \right) \times CC - AA \quad \text{(Eq 7)}
\]

which is the generalized 8 – N rule. AA is the average number of anion-anion bonds per anion. CC is the average number per cation of cation-cation bonds and/or the average number of electrons which remain as nonbonding orbitals on the cations. Calculation of \( VEC_A \) shows what kind of valence compound exists. If \( VEC_A < 8 \), then it is a polyanionic valence compound with \( AA > 0 \); thus,

\[
AA = 8 - VEC_A \quad \text{(Eq 7a)}
\]

If \( VEC_A = 8 \), then it is a normal valence compound with \( CC = AA = 0 \). If \( VEC_A > 8 \), then it is a polycationic valence compound with \( CC > 0 \); thus

\[
CC = \left( \frac{n}{m} \right) \times (VEC_A - 8) \quad \text{(Eq 7b)}
\]

These rules are valid only if all bonds are two electron bonds and the compound is not metallic. To predict the most probable structural features of a compound, calculate the two parameters \( VEC \) and \( VEC_A \). Note that for main group elements the number of valence electrons corresponds to their group number in the Periodic Table. Using Eq 3 or 4 and Eq 7a or 7b provides information on the values of \( N_{NBO} \) (or \( N_{A/M} \)) and \( AA \) or \( CC \), respectively.

**Examples**

- **ZnP**\(_2\) and an isoelectronic compound with a normal tetrahedral structure having infinite anion-anion chains.
  
  \( VEC = 4 \rightarrow N_{NBO} = 0 \)
  
  \( VEC_A = 6 \rightarrow AA = 2 \)

- **GaSe** and an isoelectric compound with a defect tetrahedral structure having cation-cation dumbbells.
  
  \( VEC = 4.5 \rightarrow N_{NBO} = 0.5 \)
  
  \( VEC_A = 9 \rightarrow CC = 1 \)

- **I\(_2\)**, a molecular tetrahedral structure consisting of 6 atoms.
  
  \( VEC = 6.33, \text{ thus } N_{NBO} = 7/3 \text{ and } N_{A/M} = 6 \)
  
  \( VEC_A = 9.5, \text{ thus } CC = 3, \text{ if } AA = 0 \)

- **SiAs** and an isoelectric compound with a defect tetrahedral structure consisting of 4 atoms.
  
  \( VEC = 6.5, \text{ thus, } N_{NBO} = 5/2 \text{ and } N_{A/M} = 4 \)
  
  \( VEC_A = 13, \text{ thus, } CC = 5, \text{ if } AA = 0 \)

**Structures with a Tetrahedral Anion Partial Structure**

The tetrahedral structure equation in a modified form can also be used for structures where only the anion partial structure is tetrahedral. The equation now refers only to the atoms of the charged partial structure. It is assumed that the nontetrahedral cations transfer all their valence electrons to the other atoms. For \( C_m^{+} (A_n)^{2-} \text{ or } C_m^{+} (C_m^{+} A_n)^{2-} \), the modified tetrahedral structure equation and its derivative equation are given by:

\[
VEC' = 4 + N'_{NBO} \quad \text{(Eq 8)}
\]

If \( VEC' > 6 \):

\[
N'_{A/M} = 2 / (VEC' - 6) \quad \text{(Eq 9)}
\]

The primed values have the same meaning as above, but all apply to the charged anion partial structure.