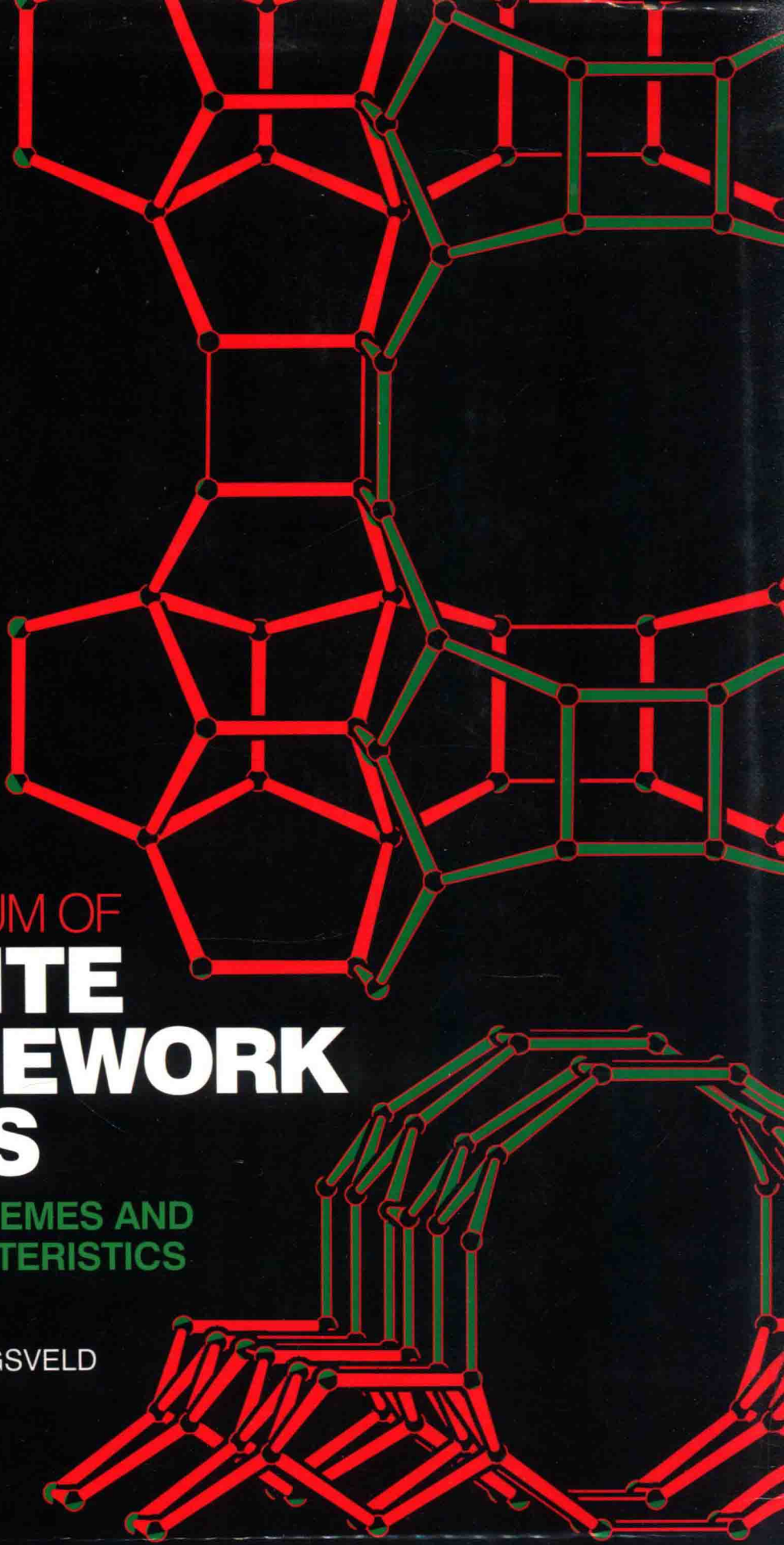

COMPENDIUM OF ZEOLITE FRAMEWORK TYPES

BUILDING SCHEMES AND TYPE CHARACTERISTICS

HENK VAN KONINGSVELD

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PREFACE

The *Atlas of Zeolite Framework Types*[1] contains 168 topological distinct tetrahedral TO4 frameworks where T may be Si, Al, P, Ga, B, Be etc. The compiled framework types, characterized by Framework Type Codes consisting of three capital letters, do not depend on the composition, distribution of the various T atoms, cell dimensions or symmetry. Their frameworks exhibit such a diversity of four-connected three-dimensional nets that finite and infinite component units were introduced to describe their topologies.

Finite units were introduced by Meier[2,3] and Smith[4]. The secondary building units (SBUs) of Meier, e.g., 4-, 5- or 6-rings, are invariably non-chiral. This means that only one kind of SBU rather than enantiomeric pairs is needed to assemble the three-dimensional framework. The assemblage of the structure does not necessarily involve crystallographic symmetry operations.

The finite structural subunits (SSUs) developed by Smith are often of greater complexity (e.g., polyhedral cages). The SSUs represent a structural feature. They are not, however, SBUs in the sense just mentioned because very often the framework cannot be constructed from SSUs alone. Frequently, SSUs need to share corners, edges or faces to complete the framework.

The SBUs, as such, are not meant to describe precursors from which the zeolite grows. On the other hand, inspection of the systematic in existing framework types may give clues to choose targets for synthesis because equal segments in different frameworks, like (some of) the polyhedral cages, may play a role during crystal growth.

Several authors extensively discussed infinite units, e.g., chains and layers[5–8]. The 5-ring zeolites were described in terms of component chains[9] as well as in terms of layers[10].

In this "Compendium", each framework type is described using Periodic Building Units (PerBUs) defined in the next Section. Most framework types are covered using two pages for each framework type. The first page gives a pictorial description of how the framework can be built using PerBUs. The second page shows the larger cages, cavities and/or channels in the framework. All drawings are prepared using the ORTEP program of Carroll K. Johnson[11] using atomic coordinates of ideal TO2 frameworks in the highest possible symmetry. The atomic coordinates are obtained from http://www.iza-structure.org/databases/ and from references cited there. Only T atoms are drawn. Open circles are tetrahedral coordinated T atoms; bridging oxygen atoms, about midway between T atoms, are left out for clarity.

Three appendices are added. The first appendix gives a survey of cages as type characteristics. The second appendix summarizes the pore descriptors of those channels and cavities that appear in more than one framework type. Finally, the third appendix depicts the channel intersections and other cavities tabulated in Appendix 2.

The "Compendium" contains information that is complementary to the data listed in the Atlas[1] from which the topological symmetry, unit cell data and pore dimensions in a "real" structure

with a particular framework type can be obtained. The entries on each page are described in more detail in the Introduction.

It does not seem possible to assemble such a compilation free of errors. The author will therefore be grateful for any additions and/or corrections for future updates.

Thanks are due to Christian Baerlocher and Lynne McCusker for many helpful discussions.

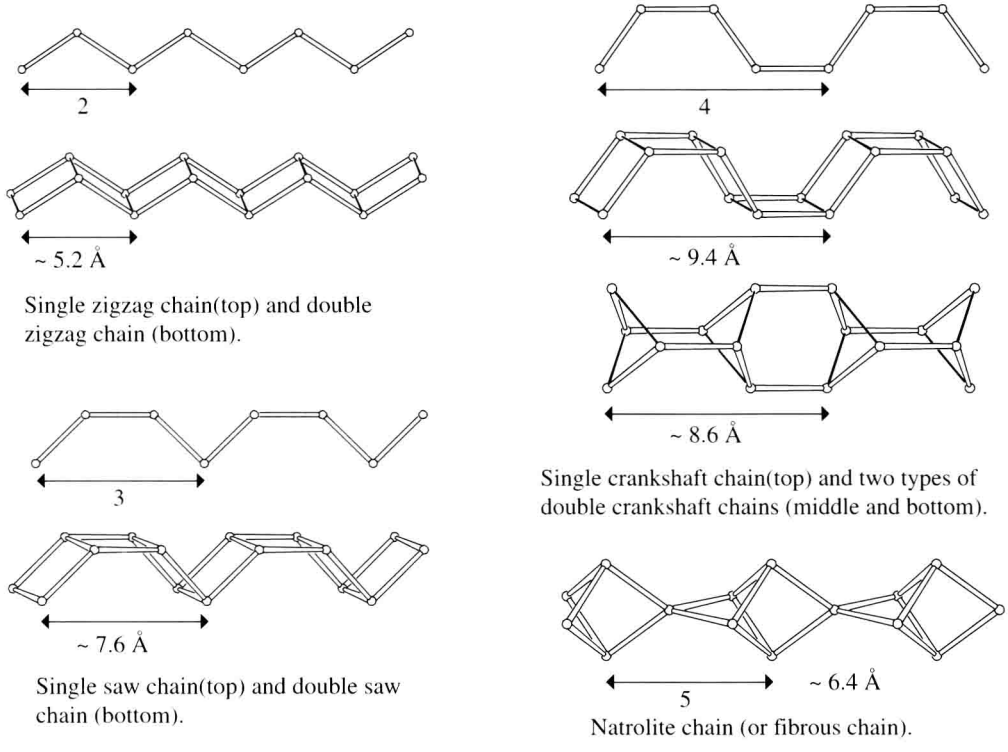
February 2007 Henk van Koningsveld

INTRODUCTION: ENTRIES USED IN EACH FRAMEWORK TYPE DOCUMENT

1. The Periodic Building Unit (PerBU)

Crystal structures, which are periodically ordered in three dimensions, are ordered structures (regular crystalline solids). In this sense, chemical disorder (e.g., different cations on a particular site) and dynamic disorder (e.g., rotational disorder of template molecules) are excluded. Structural disorder within cavities of zeolite frameworks is also excluded. In this "Compendium", the frameworks are built from periodic 0-, 1-, or 2-dimensional structurally invariant Periodic Building Units (PerBUs). The PerBUs are built from smaller units composed of a limited number of T atoms by applying simple operation(s) to the smaller unit, e.g., translation, rotation. The zeolite framework types are analyzed in terms of these component PerBUs. The infinite PerBUs, like (multiple) chains, tubes and layers, and finite PerBUs, like (double) 4-rings, (double) 6-rings and cages, are far from unique. However, they are common to several zeolite framework types and allow an easy description of the frameworks. Infinite PerBUs and finite PerBUs can be used to build the zeolite frameworks. 6-Ring layers are frequently curled up to form tubes of 6-rings.

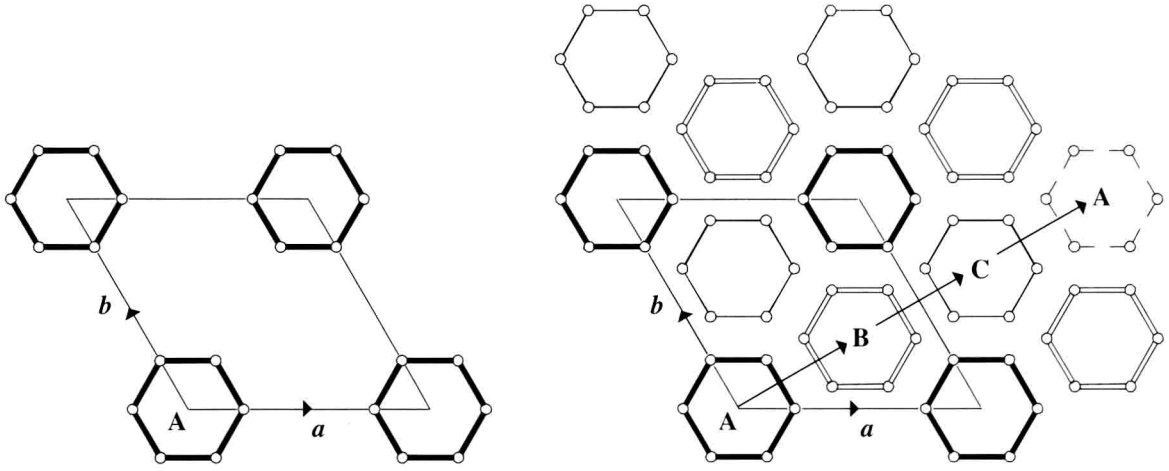
Many PerBUs can readily be constructed from (infinite) chains shown in Scheme 1. Three of these chains, with identity periods of ~m*2.5 Å, are referred to as zigzag chain, saw chain and crankshaft chain with $m = 2$, 3 and 4, respectively. The number of T atoms in the independent repeat unit along the



Scheme 1. Some examples of frequently occurring chains in zeolite frameworks. The number of T atoms in the repeat unit (of the single chain) and the length of the identity period are indicated.

chain axis equals m. The fibrous zeolites can be built using the natrolite chain. The unit cell dimension in a certain direction very often reflects the presence of zigzag, saw or crankshaft chains in that direction.

A large number of framework types can be constructed using a hexagonal PerBU consisting of an array of non-connected 6-rings shown in Scheme 2. They all belong to the so-called ABC-6-family. In these framework types the unit cell dimension along the hexagonal axis is about $n \times 2.55$ Å, where n is the number of PerBUs connected along the hexagonal axis.



Scheme 2. The two-dimensional Periodic Building Unit (PerBU) in the ABC-6-family consists of a hexagonal array of non-connected planar 6-rings (in bold), which are related by pure translations along ***a*** and ***b***. The 6-rings are centered at (0,0) in the ***ab*** layer. This position is usually called the **A** position. Neighboring PerBUs can be connected along the hexagonal ***c*** axis through tilted 4-rings in three different ways:

(1) The next layer is shifted by $+(\frac{2}{3}\boldsymbol{a}+\frac{1}{3}\boldsymbol{b})$ before connecting it to the first layer. The 6-rings in the second layer are centered at $(\frac{2}{3}, \frac{1}{3})$. This position is usually denoted as the **B** position (Scheme 2, right). The same connection mode can be repeated: a third PerBU is shifted with respect to the second layer by (again) $+(\frac{2}{3}\boldsymbol{a}+\frac{1}{3}\boldsymbol{b})$. The 6-rings are now centered at $(\frac{4}{3}, \frac{2}{3})$ (or, equivalently, at $(\frac{1}{3}, \frac{2}{3})$). This position is called the **C** position. Adding a fourth layer with the same connection mode gives a shift with respect to the first layer of $(2\boldsymbol{a}+\boldsymbol{b})$ [or zero] and an **A** position of the 6-rings is again obtained.

(2) the added layers are shifted by $-(\frac{2}{3}\boldsymbol{a}+\frac{1}{3}\boldsymbol{b})$ before connecting them along $+\boldsymbol{c}$ to the previous layer.

(3) the added layer has a zero lateral shift along ***a*** and ***b***.

The Scheme shows the PerBU in the ABC-6-family (left) and illustrates the definition of the 6-ring positions in neighboring PerBUs with respect to each other (right). The distance between two neighboring PerBUs is about 2.55 Å.

2. Connection mode

The relative orientation of neighboring PerBUs, or the connectivity of the PerBUs, can be described in terms of connection modes, which describe the symmetry elements (including lateral translation components given in fractions of the basis vectors of the invariant PerBU) that relate the PerBUs to each other. The connection mode (e.g., a rotation of 180° about an axis parallel to $\boldsymbol{a}$ followed by a shift of $\frac{1}{2}\boldsymbol{a}$) has been replaced with the shorter "a screw rotation of 180° about $\boldsymbol{a}$". When neighboring PerBUs are "related by a shift of (e.g., $\frac{1}{2}(\boldsymbol{a}+\boldsymbol{b})$)", all equivalent positions (obtained after pure translations along $\boldsymbol{a}$ and $\boldsymbol{b}$) are implied.

3. Channels and/or cages

The cages, cavities and channels (the type characteristics) are described using the pore descriptor. According to the IUPAC Recommendations 2001[12] the pore system is described with the general pore descriptor

$$\{\boldsymbol{D}\ [n^m]_i\ [uvw]\ (\boldsymbol{W}_{(\mathrm{eff})})\}$$

where

$\boldsymbol{D}$ is the dimensionality of the pore system. For cages $\boldsymbol{D}=0$. For cavities (i.e., cages with at least one window large enough ($n>6$) to allow diffusion of guest species) $\boldsymbol{D}=1$, 2 or 3. For channels, $\boldsymbol{D}=1$. For intersections of channels or systems of interconnected channels, $\boldsymbol{D}=2$ or 3;

$[n^m]_i$ is the shape of the pore, where m is the number of n-rings (or windows) defining the faces of the polyhedral pore and Σm_i is the total number of faces; a polyhedron is called a cage when the largest ring size has $n=6$.

$[uvw]$ is the direction of the channel. The term $[uvw]$ can be replaced by $\langle uvw \rangle$ to indicate that all crystallographic equivalent directions are involved.

$(\boldsymbol{W}_{(\mathrm{eff})})$ is the effective channel width. In topological description this is the smallest n-ring that determines the accessibility of the pore system to guest species along the dimension of infinite extension.

If more than one pore system is present, the descriptions are separated by a slash (/).

A survey of cages ($\boldsymbol{D}=0$) as type characteristics is added in Appendix 1. The polyhedrons are arranged in increasing number of T atoms (n) defining the smallest faces of the polyhedron and in increasing number of faces (Σm_i). Appendix 2 and Appendix 3 summarizes those channels ($\boldsymbol{D}=1$) and cavities ($\boldsymbol{D}\geq 1$) that appear in more than one framework type. An extensive compilation of polyhedral units in zeolites is published by Smith[13]. A list of those polyhedral units (or Composite Building Units) that are found in at least two different framework types is also published in the new edition of the Atlas[14].

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BUILDING SCHEMES AND TYPE CHARACTERISTICS

(arranged by the framework type code in alphabetical order)

ABW Building Scheme

1. Periodic Building Unit

ABW can be built using the zigzag chain (bold in Figure 1) running parallel to ***b***. The two-dimensional PerBU is obtained when zigzag chains are connected along ***c*** into a layer of (fused) 6-ring chairs as shown in Figure 1.

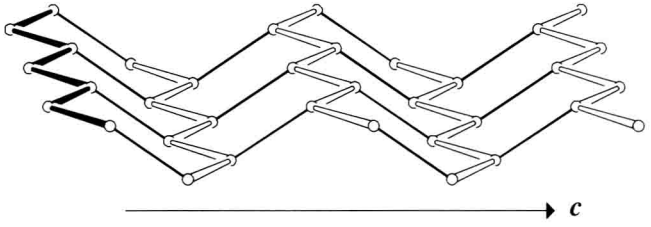

Fig. 1. PerBU, constructed from zigzag chains, viewed along ***b***.

2. Connection mode

Neighboring PerBUs, related along ***a*** by a shift of $\frac{1}{2}(\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c})$, are connected along ***a*** through 4-rings as depicted in Figure 2.

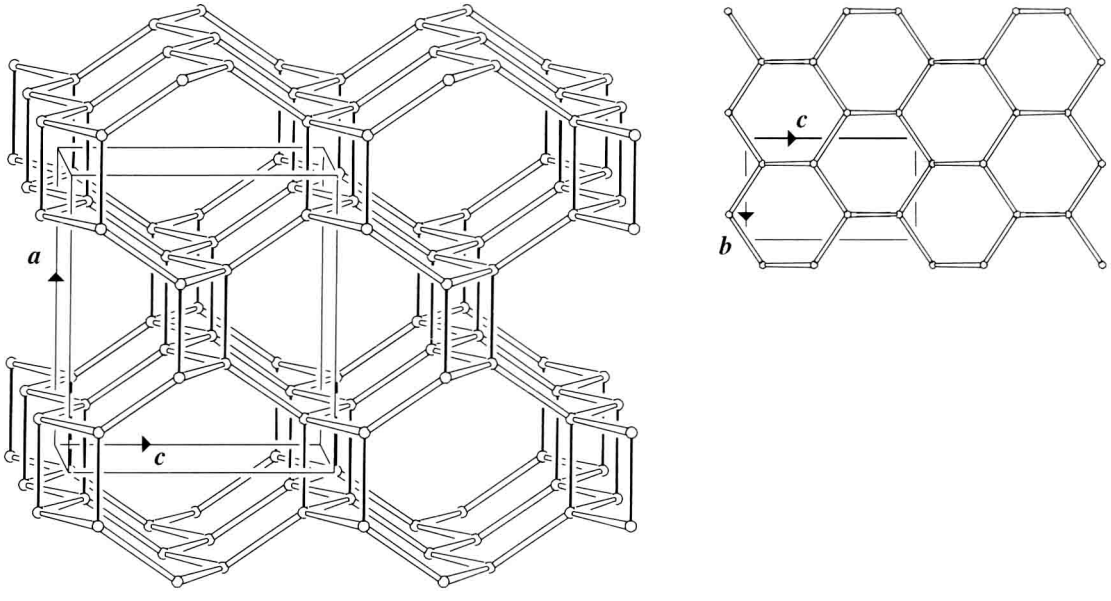

Fig. 2. Connection mode and unit cell content viewed along ***b*** (left) and projection of the unit cell content along ***a*** (right).

3. Channels and/or cages

Non-interconnecting 8-ring channels (Figure 3) are parallel to ***b***. The channel is topologically equivalent to the channel in **JBW**.

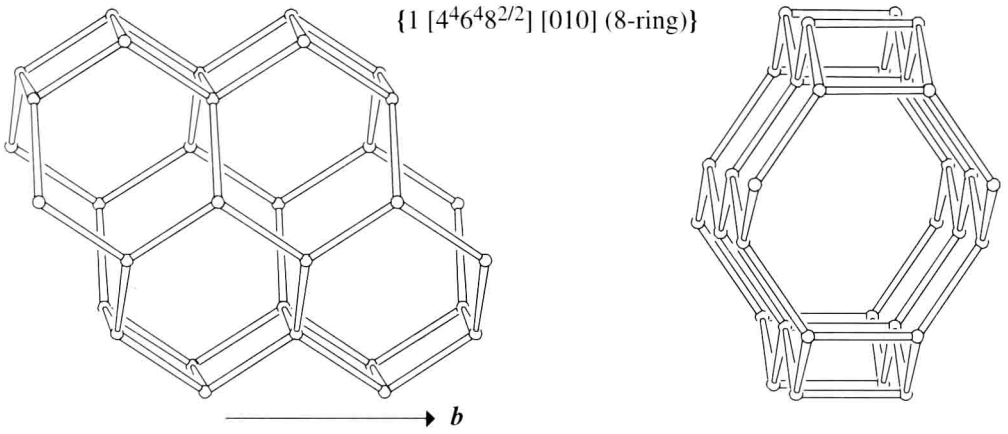

Fig. 3. Channel (with side-pockets) viewed perpendicular to the channel axis (left) and along the channel axis (right).

ACO Building Scheme

1. Periodic Building Unit

Cubic **ACO** can be built using the double 4-ring (D4R) as zero-dimensional PerBU (bold in Figure 1).

2. Connection mode

Neighboring D4Rs are related by shifts of $\frac{1}{2}(\boldsymbol{a}+\boldsymbol{b}+\boldsymbol{c})$. All eight T-sites in a D4R are singly connected to other D4Rs. 8-Ring windows are formed.

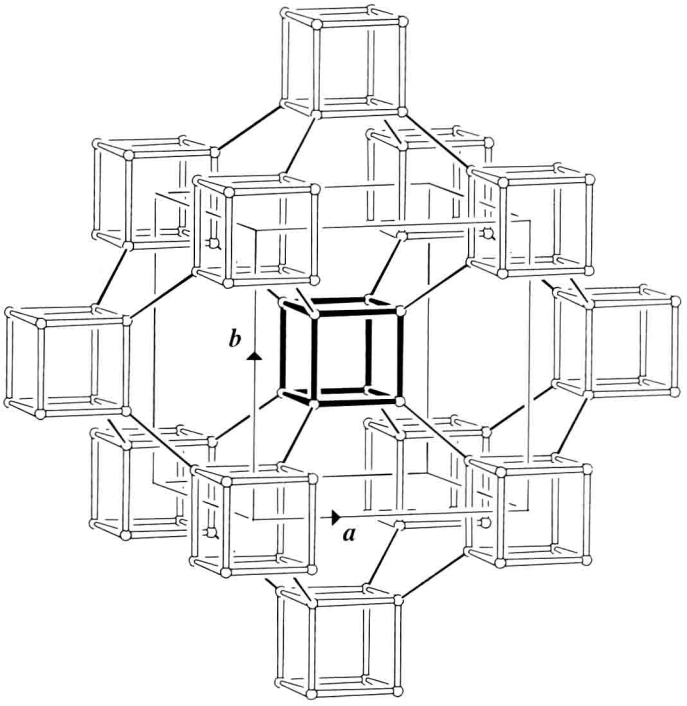

Fig. 1. Connection mode and unit cell content viewed along a cube axis.