

1. Periodic Building Unit – 2. Connection mode – 3. Projections of the unit cell content  
4. Channels and/or cages – 5. Supplementary information

## 1. Periodic Building Unit (PerBU):

Trigonal **DDR** belongs to the clathrasil family and can be built using the 12-ring double cups, shown in Figure 1. The 12-ring double cups consist of 30 T atoms. T30-units are connected into a hexagonal layer. The "empty" spaces between the T30-units are filled with T2-dimers. The connection of T30-units through the dimers generates  $[5^{12}]$ -cages in the layer. The layer reveals two types of nest-like recesses: site **A** with the 6-ring and site **B** (and site **C**) where  $[5^{12}]$ -cages share faces. This layer is equal to the PerBU in **DOH** and **MTN**. The two-dimensional PerBU in **DDR** is obtained when 6-rings from an additional 6-ring layer (bold in Figure 2) are stacked on top of the **C** sites. This stacking generates (small)  $[4^35^66^1]$ -cages. [Compare this PerBU with the PerBU in **MEP**]

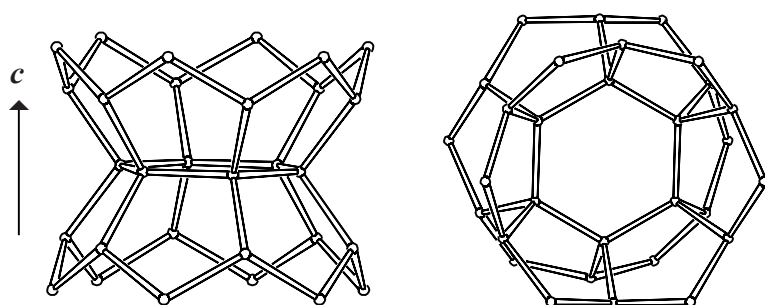


Figure 1. T30-unit in the clathrasil family viewed perpendicular to  $c$  and approximately along the (hexagonal)  $[110]$  direction (left) and along the cup-axis  $c$  (right). Two "zigzag" 12-rings are connected through a common 6-ring to form two half cages or a 12-ring double cup.

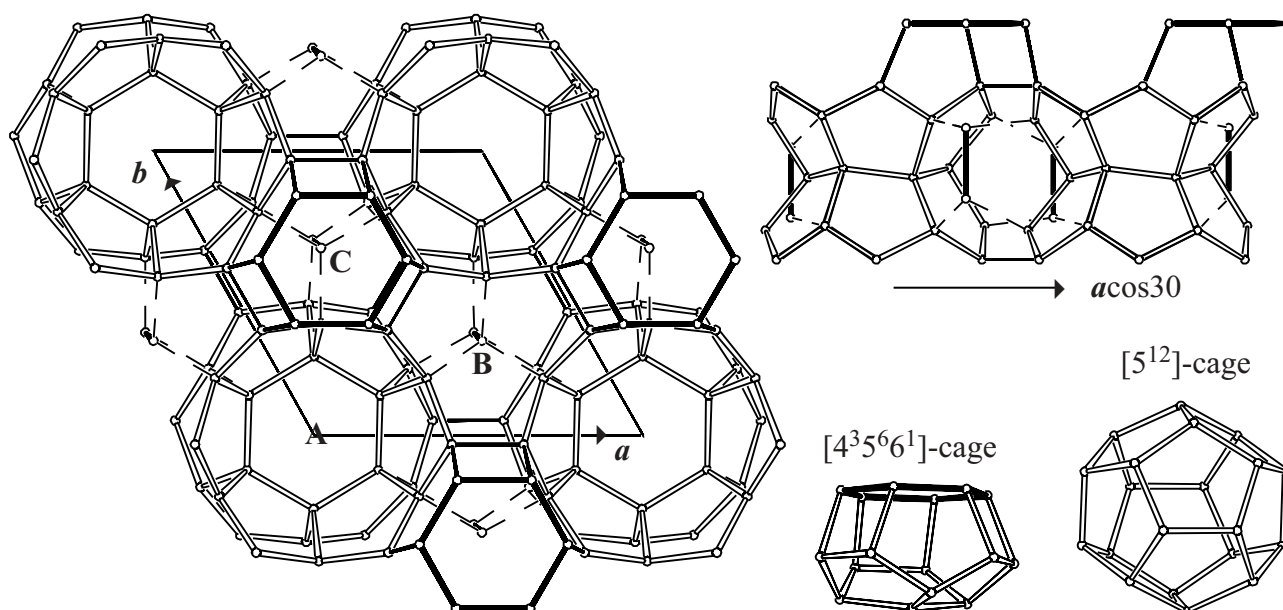


Figure 2. Hexagonal PerBU in **DDR** viewed along the cup-axis  $c$  (left) and along  $b$  (top right). Connections to the space filling dimers (in heavy bold) are dashed. The additional 6-ring layer is also in bold. The in-set shows the  $[5^{12}]$ - and  $[4^35^66^1]$ -cages. The repeat unit of the PerBU consists of 40 T atoms: the T30-unit, a 6-ring and two dimers.



## 2. Connection mode:

Neighboring PerBUs can be connected through O-bridges along  $+c$  in three different ways:

(1) the second PerBU is shifted by  $+(2/3a + 1/3b)$  before connecting it to the first PerBU. The T30-units in the second PerBU are centered at  $(2/3, 1/3)$ . This position is usually denoted as the **B** position as illustrated in Figure 2. The same connection mode can be repeated: a third PerBU is shifted with respect to the second layer by (again)  $+(2/3a + 1/3b)$ . The T30-units are now centered at  $(4/3, 2/3)$  [or, equivalently, at  $(1/3, 2/3)$ ]. 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  $(2a + b)$  [or zero, i.e. the **A** position]. The resulting stacking sequences, exhibiting the same connection mode, are denoted as **AB**, **BC** and **CA**, respectively, in analogy to stacking of dense packed spheres. The connection mode is illustrated in Figure 3(a).

(2) the second and third PerBUs are shifted by  $-(2/3a + 1/3b)$  before connecting them along  $+c$  to the previous PerBU. The resulting stacking sequences **AC**, **CB** and **BA**, with the same connection mode are obtained. The connection mode is illustrated in Figure 3(b).

(3) the second PerBU has a zero lateral shift along  $a$  and  $b$ . This connection mode leads to an **AA**, **BB** or **CC** stacking sequence depending on whether the added PerBU is connected to a PerBU with T30-units in the **A**, **B** or **C** position, respectively. The connection mode is illustrated in Figure 3(c).

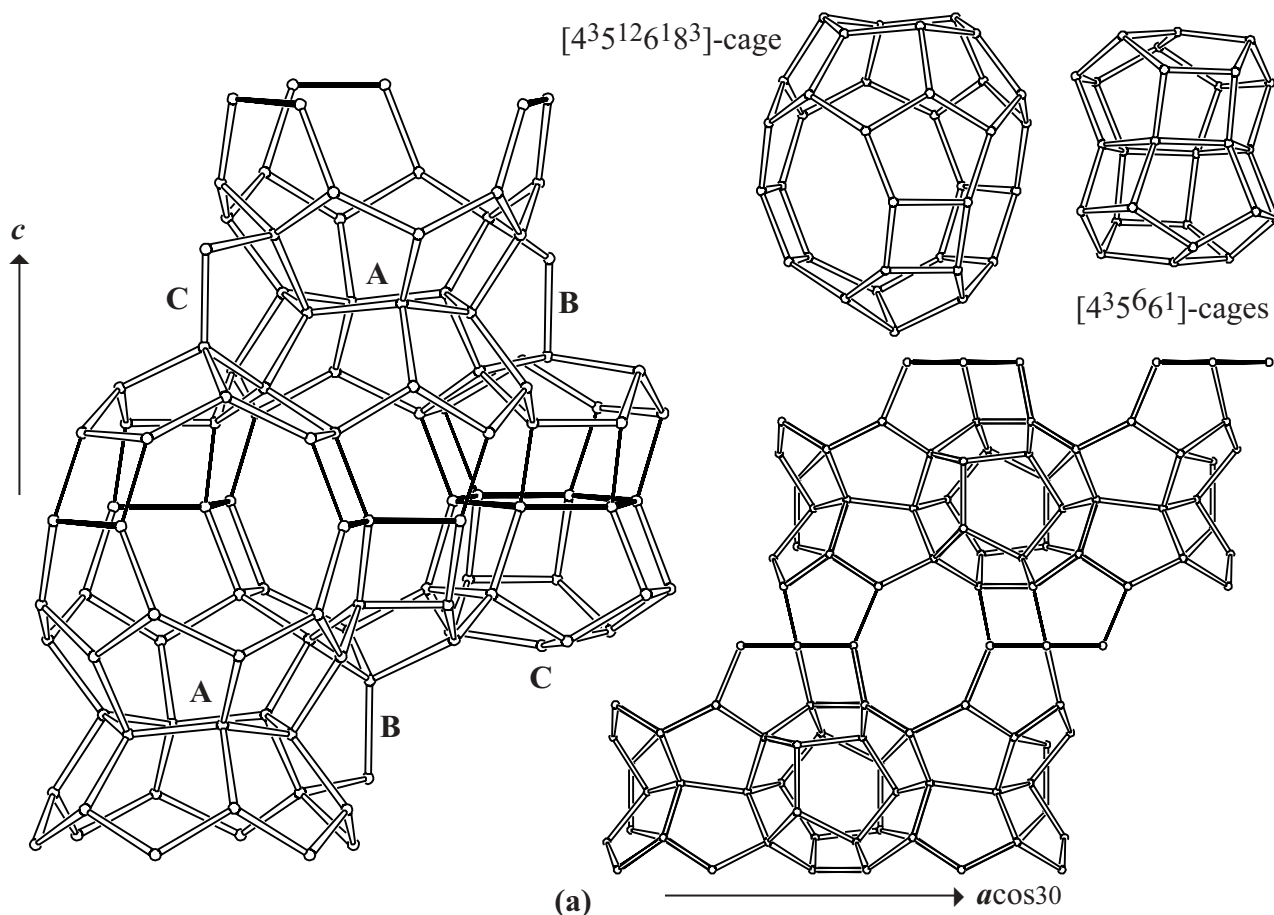


Figure 3. (a): Connection mode (1) (**AB**, **BC** or **CA** connection mode) viewed approximately along  $[110]$  (left). In the perspective drawing only one set of **A**, **B** and **C** positions in each (shifted) PerBU is given in order to illustrate the new inter-layer cages formed. The projection along  $b$  (bottom right) shows the connection mode between complete PerBUs. (Parts of) the additional 6-rings are in bold. The inter-layer cages are shown at the top right. [Figure 3 is continued on next page]

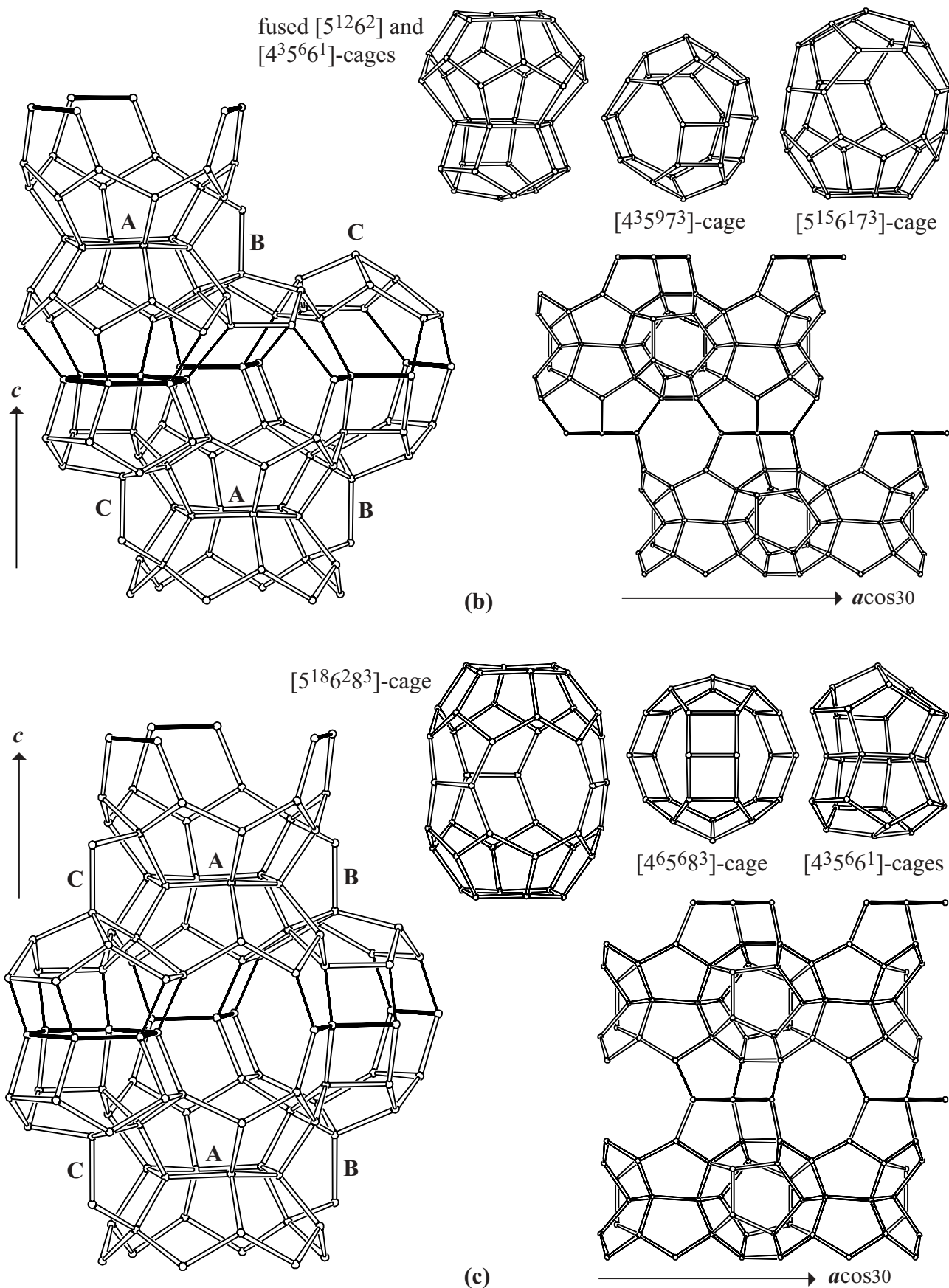
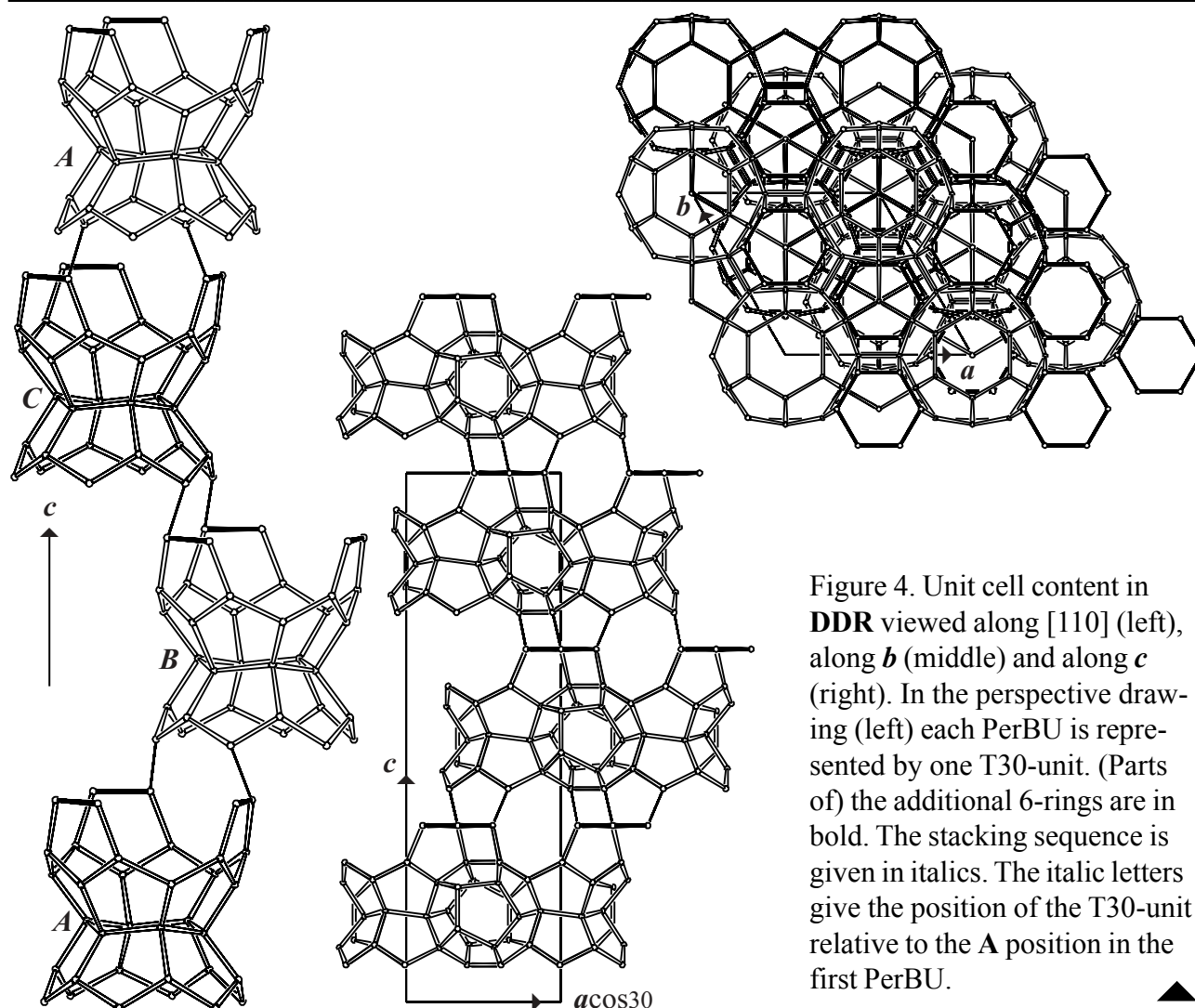


Figure 3 [Cont'd]. (b): Mode (2) (*AC*, *CB* or *BA* connection mode) and (c): mode (3) (*AA*, *BB* or *CC* connection mode) viewed approximately along  $[110]$  (left). In these drawings only one set of **A**, **B** and **C** positions in each (shifted) PerBU is given in order to illustrate the new inter-layer cages formed. The projection along *b* (bottom right) shows the connection mode between complete PerBUs. (Parts of) the additional 6-rings are in bold. The inter-layer cages are shown at the top right.

In **DDR** only connection mode (1) is observed. ▲

### 3. Projections of the unit cell content: See Figure 4.



### 4. Channels and/or cages:

The  $[5^{12}]$ -cage and  $[4^35^66^1]$ -cage in the PerBU are shown in Figure 1. The two new types of inter-layer cages in **DDR** are depicted in Figure 3(a). The **pore descriptor** is added. **DDR** can be considered as link between zeolites and clathrasils because it possesses zeolitic properties through a two-dimensional pore system along  $\langle 100 \rangle$  with 8-ring windows. ▲

### 5. Supplementary information:

#### *Other framework types containing a layer of (modified) T30-units*

Three other framework types can be constructed using the (modified) PerBU described in Section 1. They belong to the clathrasil family.

In the **INTRO** pages links are given to detailed descriptions of these framework types (choose: **Clathrasils**). There is also a link provided to a summary of the Periodic Building Units used in the building schemes of these framework types (choose: **Appendix; Figure 10**). ▲