



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:

Hexagonal **DOH** 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 the hexagonal two-dimensional Periodic Building Unit (PerBU) shown in Figure 2(a). 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 PerBU 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. [Compare this PerBU with the PerBUs in **DDR**, **MEP** and **MTN**]

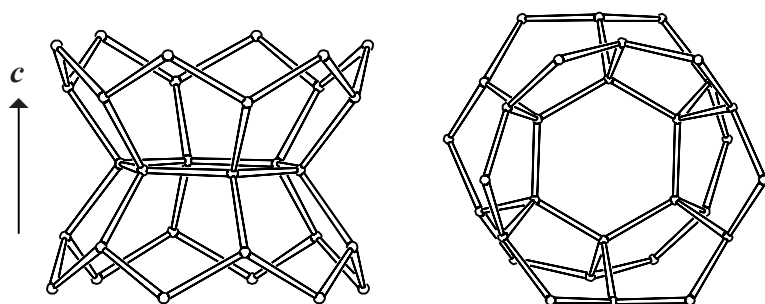


Figure 1. T30-unit in the clathrasil family viewed perpendicular to c and approximately along the (hexagonal) $[110]$ direction (left) and along the cup-axis c (right). Two "zigzag" 12-rings are connected through a common 6-ring to form two half cages or a 12-ring double cup.

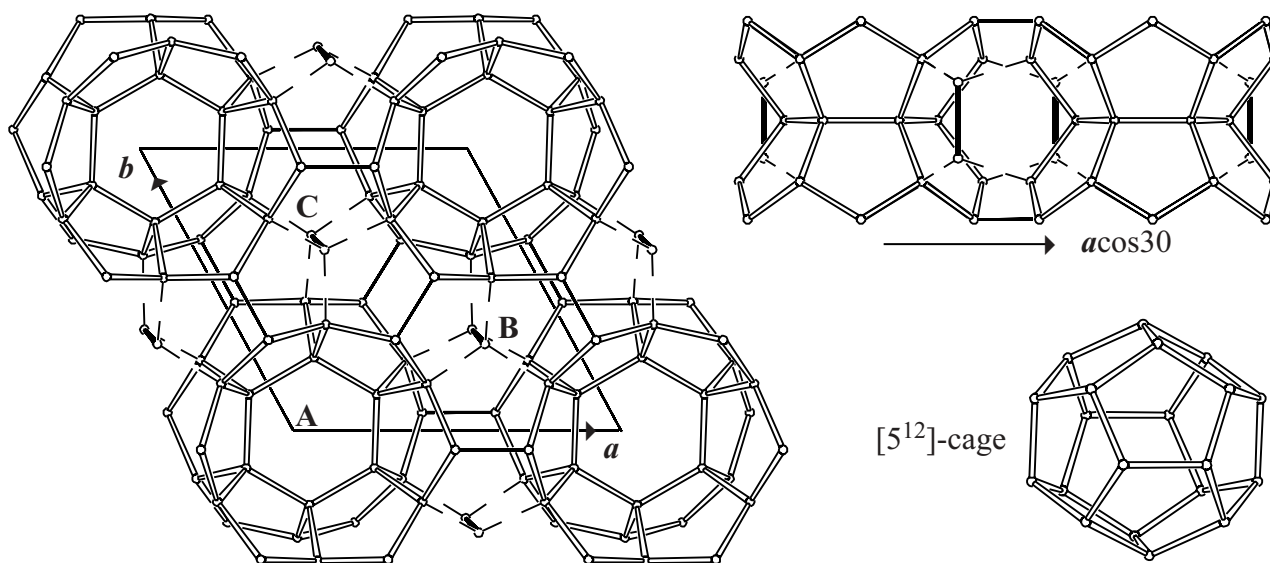


Figure 2. Hexagonal PerBU viewed along the cup-axis c (left), and along b (top right). Connections to the space filling dimers (in heavy bold) are dashed. The in-set shows the $[5^{12}]$ -cage. The repeat unit of the PerBU consists of 34 T atoms: the T30-unit and two dimers.



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 of the **AC** stacking is equal to the **AB** (or **BC**, or **CA**) connection mode and is therefore not shown separately in Figure 3.

(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(b).

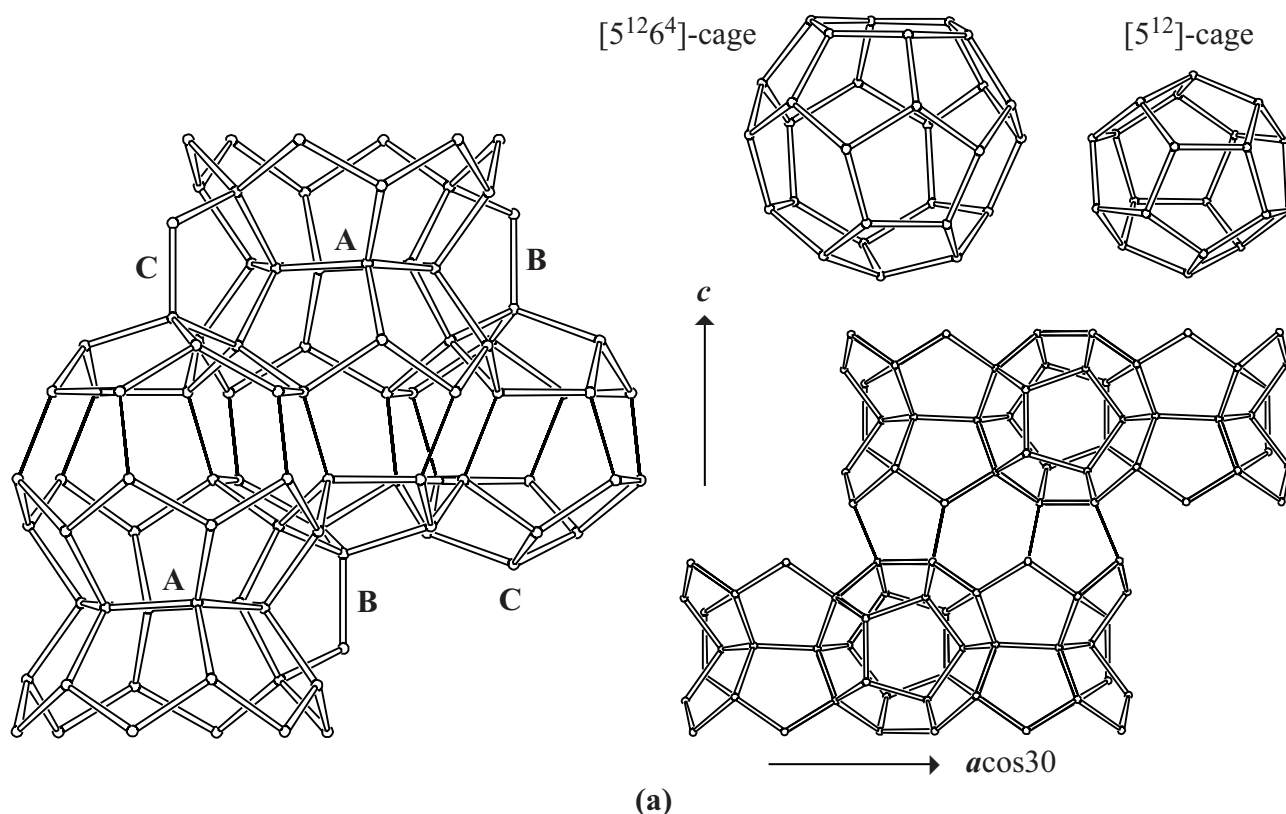


Figure 3. (a): Connection mode (1) (**AB**, **BC** or **CA** connection mode) viewed approximately along $[110]$ (left). In the perspective drawing only one set of **A**, **B** and **C** positions in each (shifted) PerBU is given in order to illustrate the new inter-layer cages formed. The projection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

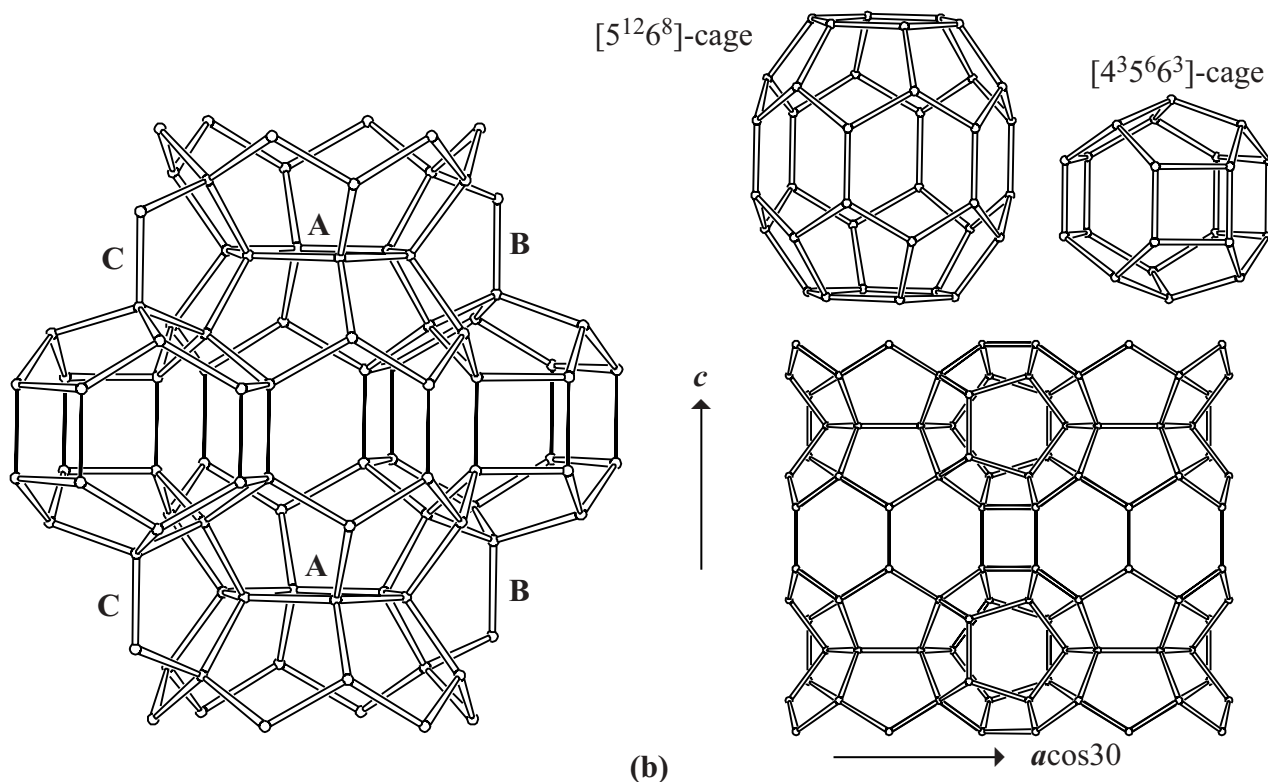


Figure 3 [Cont'd]. (b): Connection mode (3) (*AA*, *BB* or *CC* connection mode) viewed approximately along [110] (left). In the perspective drawing only one set of *A*, *B* and *C* positions in each (shifted) PerBU is given in order to illustrate the new inter-layer cages formed. The projection along *b* (bottom right) shows the connection mode between complete PerBUs. The inter-layer cages are shown at the top right. In **DOH** only connection mode (3) is observed. [In **MTN** only mode (1) is observed]

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

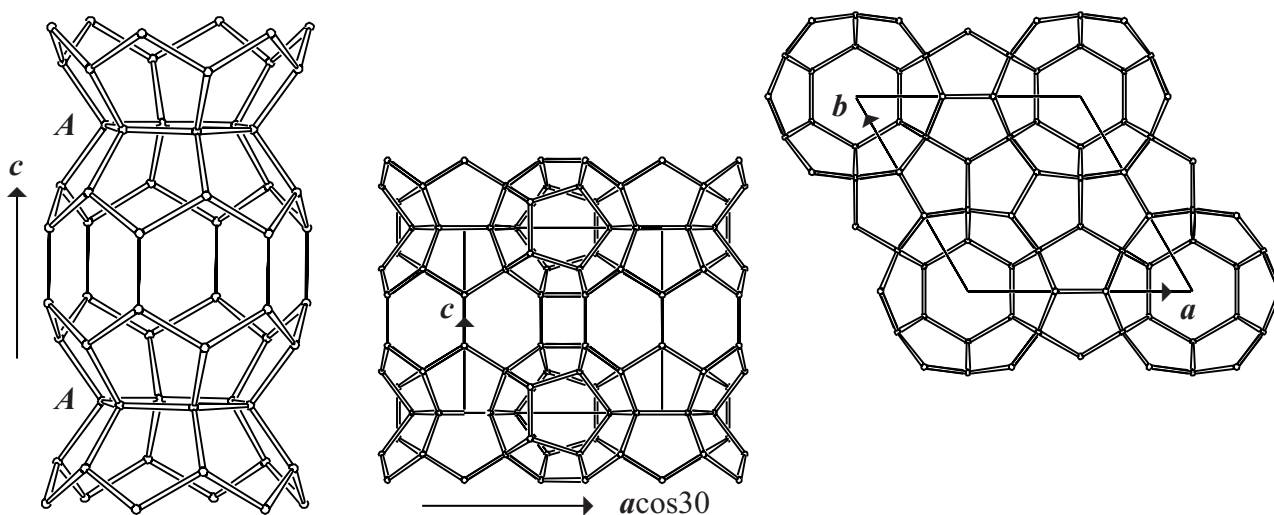


Figure 4. Unit cell content in **DOH** viewed along [110] (left), along *b* (middle), and along *c* (right). In the perspective drawing (left) each PerBU is represented by one T30-unit. The stacking sequence is given in italics. The italic letters give the position of the T30-unit relative to the *A* position in the first PerBU.

4. Channels and/or cages:

The [5¹²]-cage in the PerBU is shown in Figure 1. The two types of inter-layer cages in **DOH** are depicted in Figure 3(b). The **pore descriptor** is added. Apertures are formed by 6-rings only. ▲

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**). ▲