

Archimedean polyhedra as the basis of tetrahedrally-coordinated frameworks

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Summary. The linkage of Archimedean polyhedra has been studied to provide trial models for tetrahedrally-coordinated structures such as zeolites. The cuboctahedron, rhombicuboctahedron, snub cube, icosidodecahedron, rhombicosidodecahedron, and snub dodecahedron cannot be used because four edges meet at a corner. The truncated tetrahedron, truncated cube, and truncated dodecahedron have triangular faces, and are unlikely to occur in silicate frameworks because of the instability of 3-rings. The truncated icosahedron and truncated icosidodecahedron have fivefold symmetry and cannot form four-connected frameworks with lattice symmetry. The truncated octahedron and truncated cuboctahedron may be linked either directly, in combination, or with square, hexagonal, or octagonal prisms. There are nine structures of which four are represented by sodalite, Linde A, faujasite, and ZK-5. The other five have the following properties: truncated octahedra linked H(H-S), $Fd\bar{3}m$, a 17.5 Å; truncated octahedra linked H(H-S) and (H-H), $P6_3/mmc$, a 12.4, c 20.5 Å; truncated octahedra linked H'(H-S) and (H-H), $P6_3/mmc$, a 17.5, c 28.5 Å; truncated cuboctahedra linked O'(S-S), $Im\bar{3}m$, a 15.1 Å; truncated octahedra linked to truncated cuboctahedra H'(S-S), $Fm\bar{3}m$, a 31.1 Å. The first symbol specifies the linking unit (H hexagon, H' hexagonal prism, O' octagonal prism) while the symbols in brackets specify the type of faces opposing across the contact (S square).

SODALITE, Linde A, and faujasite are based on frameworks in which the tetrahedral centres lie at the corners of truncated octahedra linked together in different ways, as has already been recognized (Reed and Breck, 1956; Barrer, Bultitude, and Sutherland, 1957; Bergerhoff, Baur, and Nowacki, 1958; Broussard and Shoemaker, 1960). All the ways of linking together truncated octahedra have been enumerated by Smith (1963) as part of a structural classification of zeolites. Linde A also can be visualized as formed from the truncated cuboctahedron, another of the Archimedean polyhedra. Thus, it seemed desirable to investigate systematically all tetrahedrally-coordinated frameworks related to Archimedean polyhedra to provide trial structures for uncharacterized zeolites, and to assist with structural classification. A similar approach using other structural units has been used by Dent Glasser and Smith

(1958), Barrer and Kerr (1959), Gottardi and Meier (1962), and Smith and Rinaldi (1962), who were able to predict the structures of gmelinite, levynite, dachiardite, and gismondine, respectively. For an extensive discussion of networks the reader is referred to the series of papers by A. F. Wells *et al.*, of which the latest is by Wells and Sharpe (1963).

While this paper was being prepared, Meier and Kokotailo (1963) published an abstract on the structure of synthetic zeolite ZK-5, whose synthesis was described by Kerr (1963). The structure of this zeolite is that of truncated cuboctahedra linked in the pattern H'(O-S) as described later in this paper.

Archimedean polyhedra are composed of regular faces, not all of the same kind, with the faces arranged in the same order around each vertex. The group comprises the truncated tetrahedron, cuboctahedron, truncated cube, truncated octahedron, small rhombicuboctahedron, truncated cuboctahedron, snub cube, icosidodecahedron, truncated dodecahedron, truncated icosahedron, small rhombicosidodecahedron, truncated icosidodecahedron, and snub dodecahedron, in addition to the infinite series of prisms and antiprisms (see Coxeter, 1947; Cundy and Rollett, 1951).

In an aluminosilicate framework, the tetrahedral centres (T) are coordinated four times to other centres via the oxygen atoms. Consequently, when linked polyhedra are used to represent an aluminosilicate framework, with the tetrahedral centres lying at the corners of the polyhedra, there must be four edges meeting at each polyhedral vertex. The length of the polyhedral edge depends on the T -O distance and on the O- T -O bond angle. Smith and Bailey (1963) have shown that in frameworks the T -O distance varies linearly with Al content from 1.61 Å for Si-O to 1.75 Å for Al-O. The O- T -O bond angle varies considerably, but is often near 140° (Liebau, 1961). A T - T distance of 3.12 Å has been used for the present calculations, and a variation of about 5 % each way should account for the effects of different values of Al substitution and for changes of bond angle.

Six of the polyhedra (cuboctahedron, rhombicuboctahedron, snub cube, icosidodecahedron, rhombicosidodecahedron, and snub dodecahedron) are not suitable for 4-connected frameworks because they already have four edges meeting at each vertex, and because additional edges would appear when polyhedra were joined together. Three more (truncated icosahedron, truncated dodecahedron, and truncated icosidodecahedron) have pentagonal faces and cannot be joined together to give 4-connected frameworks with lattice symmetry. Three-membered

rings are very uncommon in silicates (benitoite is an example with such rings) and it was decided not to list modifications requiring these rings because of the probable instability of such forms. This eliminates the truncated tetrahedron, truncated cube, and the antiprisms from consideration. (As an example of a framework containing 3-rings, consider truncated cubes in contact on the cube faces. The voids between the cubes consist of regular octahedra.)

Remaining for consideration are the truncated octahedron, truncated cuboctahedron, and the prisms. The possible forms may be enumerated by considering systematically all ways of placing faces in contact, combined with all combinations of opposing faces from the joined polyhedra. They may be simply described by listing the type of contact (S square face, S' cube, H hexagonal face, H' hexagonal prism, O octagonal face, O' octagonal prism) and the types of polyhedral faces opposing across the contact, the latter being in parenthesis.

It is not possible to form 4-connected frameworks just from linked prisms. The truncated octahedron, which contains square and hexagonal faces, may be joined either by S, S', H, or H', while the truncated cuboctahedron, which has octagonal faces as well, may be joined by O or O' in addition to S, S', H, or H'. Certain combinations of linkage do not produce frameworks because the angular relations are unsuitable. Thus, the H(S-S) and H'(S-S) structures for the truncated octahedra do not close, leaving small re-entrant angles between the polyhedra. Similar incomplete structures result for the O(H-S), O'(H-S), H(S-S), and H'(S-S) combinations of the truncated cuboctahedra. It is possible that such incomplete structures may be turned into structures with lattice symmetry if the polyhedra are distorted from the ideal shape. Because such polyhedra are no longer Archimedean, such a development is outside the scope of this paper. Table I shows the pertinent data for the structures with lattice symmetry. Some of the structures are shown in figs. 1 and 2.

The Linde A zeolite may be described in four different ways, while the O'(S-S) and H(O-S) combinations of the truncated cuboctahedra are also identical. The H(H-S) and H'(H-S) combinations of the truncated octahedron have these units at the sites of the atoms in diamond (or blende), while the H'(H-S) + (H-H) variety has the units at the atomic sites of wurtzite. An infinite number of polytypes can be made by joining together sheets of truncated cuboctahedra taken from the (111) layers of the blende analogue and of the (0001) layers of the wurtzite type. In addition, another infinite series can be made by replacing

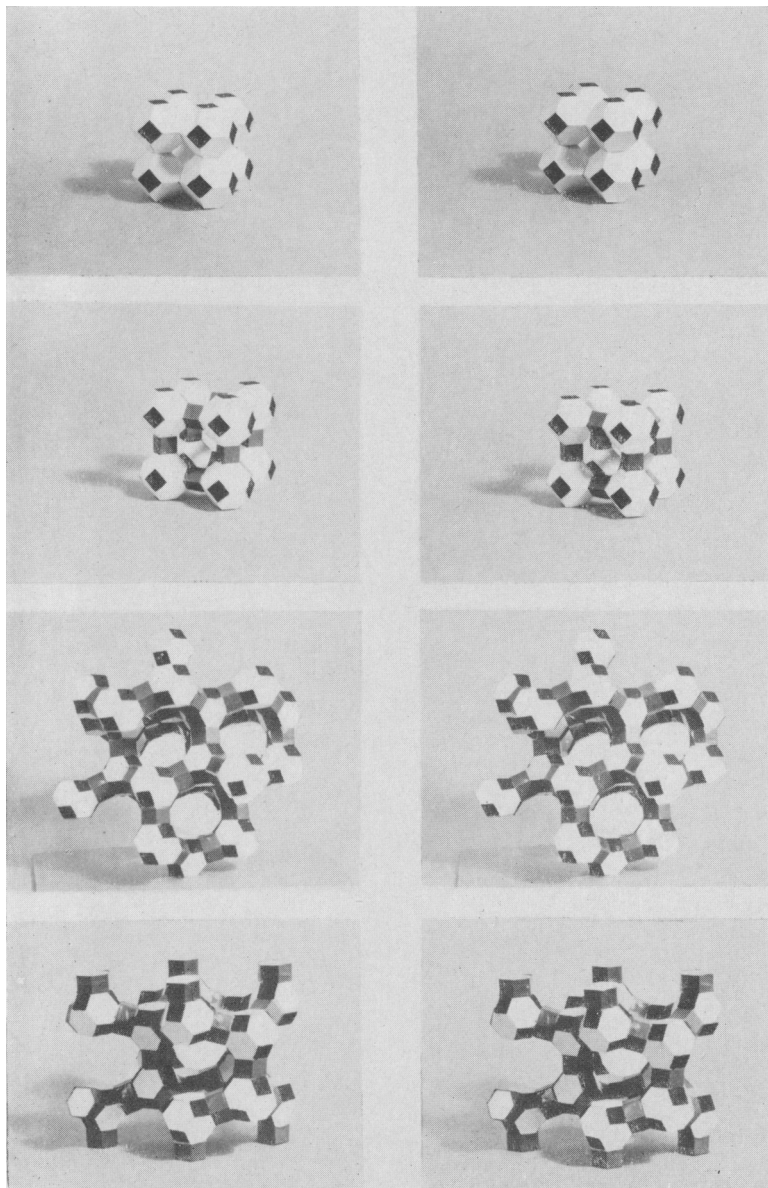


FIG. 1. Stereoscopic pairs of structures formed by linkage of truncated octahedra. The dark squares and white hexagons belong to the truncated octahedra while the grey squares show the sides of the linking prisms. Top to bottom: *a*, sodalite, $S(H-H)$; *b*, Linde A, $S'(H-H)$; *c*, faujasite, $H'(H-S)$; *d*, wurtzite analogue of faujasite, $H'(H-S)$ and $(H-H)$.

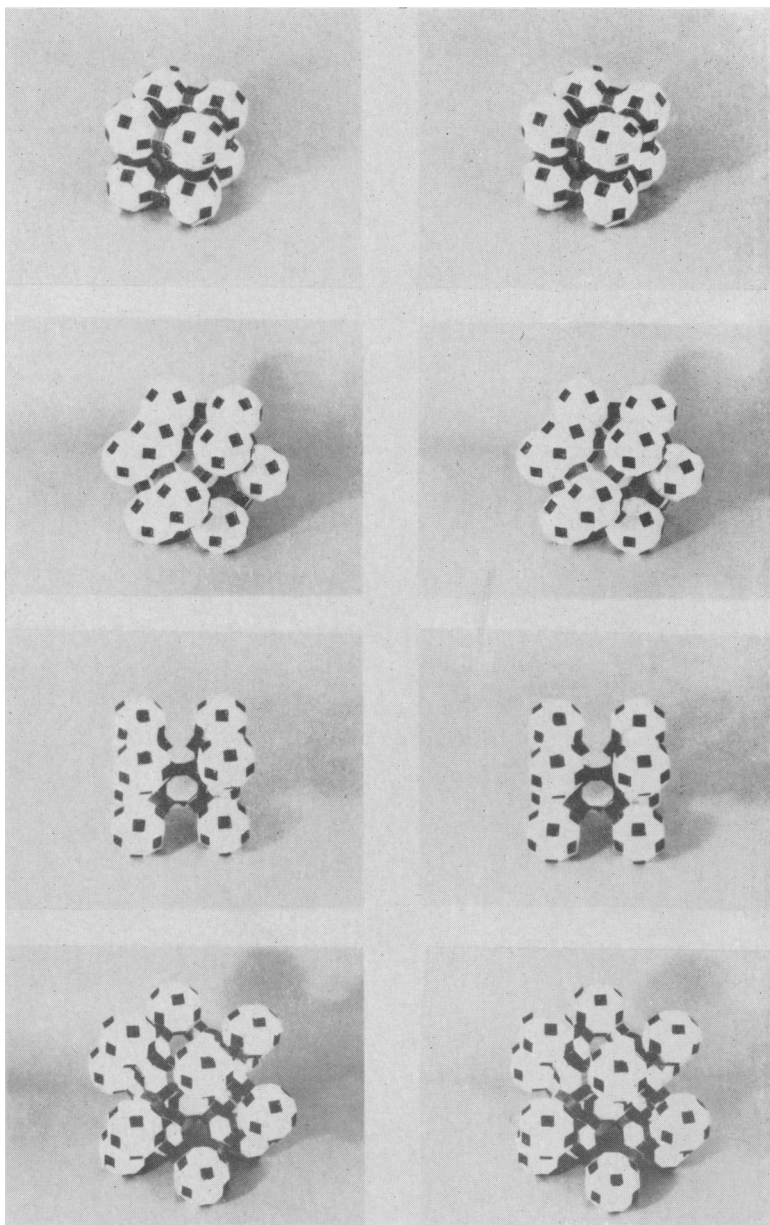


FIG. 2. Stereoscopic pairs of structures formed by linkage of truncated cuboctahedra. The dark squares, white hexagons, and white octagons belong to the truncated cuboctahedra, while the grey squares show the linking prisms. Top to bottom: *a*, O'(S-S); *b*, Linde A, S'(H-H); *c*, ZK-5, H'(O-S); *d*, H'(S-S).

layers of hexagonal prisms by hexagonal faces. The H'(S-S) type of linked truncated octahedra and truncated cuboctahedra is analogous to the fluorite structure with the truncated octahedra in the positions of the fluorine atoms and the truncated cuboctahedra in the positions of the calcium atoms.

TABLE I. Properties of frameworks formed from Archimedean polyhedra

Components	Space group	<i>a</i>	<i>c</i>	Number of tetrahedra	Example
<i>Structures formed from truncated octahedra</i>					
S(H-H)	<i>Pm3m</i>	8.8 Å	—	12	Sodalite
S'(H-H)	<i>Pm3m</i>	11.9	—	24	Linde A
H(H-S)	<i>Fd3m</i>	17.5	—	96	—
H'(H-S)	<i>Fd3m</i>	24.7	—	192	Faujasite
H(H-S) and (H-H)	<i>P6₃/mmc</i>	12.4	20.5 Å	64	—
H'(H-S) and (H-H)	<i>P6₃/mmc</i>	17.5	28.5	128	—
<i>Structures formed from truncated cuboctahedra</i>					
O(S-S) ≡ S'(H-H) ≡ Linde A					
O'(S-S)	<i>Im3m</i>	15.1	—	48	—
H(O-S) ≡ O'(S-S)					
H'(O-S)	<i>Im3m</i>	18.7	—	96	ZK-5
<i>Structures formed from both truncated octahedra and truncated cuboctahedra</i>					
H(S-S) ≡ Linde A					
H'(S-S)	<i>Fm3m</i>	31.1	—	384	—

Of the nine simple forms listed in table I, only four have so far been found to occur in chemical substances: sodalite, Linde A, faujasite, and ZK-5. It is possible that others of the series will be found in synthetic materials grown under conditions of high supersaturation similar to those for Linde A, for the X and Y varieties of faujasite, and for ZK-5. Evidence is accumulating that there are subtle relations between the exchangeable cations, the water of hydration, and the type of aluminosilicate framework resulting from synthesis. By suitable manipulation of composition and temperature it may be possible to control the type of framework and hence to produce at will any of these theoretical structures.

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