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ENUMERATION OF 4-CONNECTED 3-DIMENSIONAL NETS AND THE CLASSIFICATION OF FRAMEWORK SILICATES: BODY-CENTRED CUBIC NETS BASED ON THE RHOMBICUBOCTAHEDRON

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Abstract

Nets may be constructed by placing rhombicuboctahedra at the lattice points of a body-centred cubic lattice and connecting the opposing octagonal faces of each pair of next-nearest-neighbor rhombicuboctahedra by a segment of crankshaft chain. Two families of nets occur, depending on the relative disposition of the chains to the edges of the octagonal rings to which they are linked. As the number of chain links between rhombicuboctahedra must be odd, there are two possible infinite series of structures with *n*, the number of crankshaft links, equal to $2N + 1$ ($N = 0,1,2...$). Structural representatives of this family include the two synthetic zeolites rho and ZK-5, and the natural zeolite paulingite. Additional families of nets may be derived by systematic application of inverse sigma-transformations.

Keywords: nets, framework structures, zeolites.

Sommaire

On peut construire des réseaux en plaçant des rhombicuboctaèdres aux noeux d'une maille cubique centrée et en liant les faces octagonales opposées de chaque paire de rhombicuboctaèdres avoisinants par un segment d'une chaîne en vilebrequin. Il en résulte deux familles de réseaux, selon la disposition relative des chaînes par rapport aux bordures des anneaux octagonaux auxquels elles sont liées. Vu le nombre impair de chaînes faisant le lien entre rhombicuboctaèdres, il y a deux séries infinies de structures possibles ayant *n*, le nombre de liens de chaînes en vilebrequin, égal à $2N + 1$ ($N = 0, 1, 2...$). Les structures qui représentent cette famille comprennent deux zéolites synthétiques (rho et ZK-5) et la zéolite naturelle paulingite. On peut dériver des familles additionnelles de réseaux par l'application systématique de transformations sigma inverses.

(Traduit par la Rédaction)

Mots-clés: réseaux, structures à charpente, zéolites.

Introduction

Previous papers in this series (Smith 1977, 1978, 1979, 1983, Smith & Bennett 1981, 1984, Smith & Dytrych 1984, 1986, Bennett & Smith 1985, Hawthorne & Smith 1986) have enumerated 4-connected 3-dimensional nets by considering out-of-plane linkages between parallel 3-connected 2-dimensional nets. Further nets are given in Bennett *et al.* (1986). The present paper, the twelfth in this series of theoretical papers, takes a rather different approach. We consider the relationships between body-centred cubic nets involving the great rhombicuboctahedron, two of which were already presented by Smith & Bennett (1981). Here we examine these nets from a different viewpoint, and show that there is an infinite series of high-symmetry nets forming an ordered series that includes the nets for the synthetic zeolite rho and the natural zeolite paulingite. A second infinite series includes the net for the synthetic zeolite ZK-5. These hypothetical arrangements are important with regard to the possible structural characterization of unknown zeolite structures from powder-diffraction data.

TABLE 1. PROPERTIES OF RHOMBICUBOCTAHEDRON AND TRUNCATED OCTAHEDRON NETS

N	Figure number	Arbitrary number	Z_t	Circuit Symbol	Z_c	Space group	a(Å)
				[100] Rhombicuboctahedron Series			
0	3a	206	24	$(4^3.6^3)$	48	Im3m	14.7
1	3b	403	72	$(4^3.6^3)_1(4^2.6^3.8)_2$	144	Im3m	18.9
2	3c	404	120	$(4^3.6^3)_2(4^3.6^2.8)_3$	240	Im3m	25.1
3	3d	405	192	$(4^2.6^3.8)_1(4^3.6^2.8)_1(4^3.6.8^2)_1(4^2.6^3.8)_1$	384	Im3m	29.4
4	3e	406	336	$(4^3.6^3)_3(4^3.6^2.8)_{11}$	672	Im3m	35.4
				[110] Rhombicuboctahedron Series			
1	4b	205	48	$(4^3.6^2.8)$	96	Im3m	18.9
2	4c	407	144	$(4^3.6^3)_2(4^2.6^3.8)_1$	288	Im3m	25.1
3	4d	408	192	$(4^3.6^3)_1(4^3.6^2.8)_2(4^2.6^3.8)_1$	384	Im3m	29.4
4	4e	409	336	$(4^3.6^3)_3(4^3.6^2.8)_{11}$	672	Im3m	35.4
				Truncated Octahedron Series			
0	5a	108	6	$(4^2.6^4)$	12	Im3m	8.5
1	5b	410	30	$(4.6^5)_4(6^6)_1$	60	Im3m	13.8
2	5c	411	60	$(4^3.6^2.8)_4(6^2.8^4)_1$	120	Im3m	18.8
3	-	-	-	-	-	-	-
4	5d	412	216	$(4^3.6^3)_4(4^3.6^2.8)_1(4^3.8^3)_1(4^2.6^3.8)_1$ $(4^2.6.8^3)_1(4.6.8^4)_1$	432	Im3m	29.0

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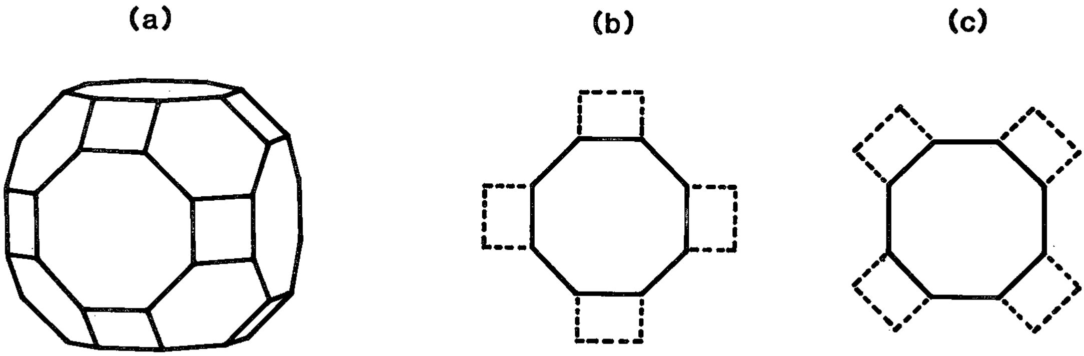

FIG. 1. (a) Clinographic view of a rhombicuboctahedron; (b), (c) attitude of the crankshaft chains with regard to the octagonal face of the rhombicuboctahedron for the [100] and [110] series, respectively.

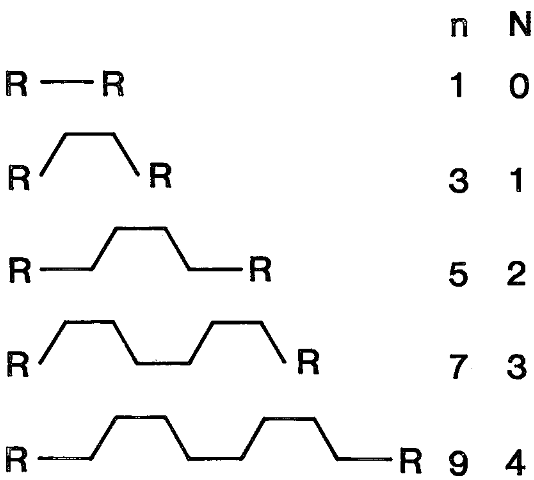

FIG. 2. Diagrammatic representation of the linkage between translationally equivalent rhombicuboctahedra (denoted by *R*).

ENUMERATION

The rhombicuboctahedron nets

The rhombicuboctahedron (Fig. 1a) is a prominent feature in the frameworks of at least four cubic zeolites, namely the synthetic zeolites rho, ZK–5 and N, and the mineral paulingite. Three of these structures (rho, ZK–5 and paulingite) have the same space group, *Im*3*m,* and have rhombicuboctahedra centred on the lattice points of the body-centred unit cell. The rhombicuboctahedra are oriented with their octagonal faces orthogonal to the axes of the unit cell. Rhombicuboctahedra equivalent by virtue of the primitive cubic lattice translation are linked through their opposing octagonal faces by fragments of double crankshaft chains. These crankshaft chains may have two different types of configuration with regard to the octagonal faces to which they are linked. In paulingite, the crankshaft chains are linked to those octagonal edges orthogonal to [100] (Fig. 1b). In ZK–5, the crankshaft chains are linked to those octagonal edges orthogonal to [110] (Fig. 1c).

Denoting the rhombicuboctahedron by the letter *R,* the linkage along one unit cell axis may be diagrammatically represented in a very simple fashion (Fig. 2). Because of the geometry of the double crankshaft chain, there must always be an odd number of links between rhombicuboctahedra, and thus we can define two possible series of structures with *n,* the number of crankshaft links, equal to $2N + 1$ ($N = 0,1,2...$).

The nets for N from 0 to 4 are projected in Figures 3 and 4. For $N = 0$, the nets are the same in the [100] and in the [110] series, as the opposing octagonal faces of next-nearest-neighbor rhombicuboctahedra are directly linked through square circuits of edges ($n = 1$). As it is through the crank part of the chain that the two different types of linkage arise, the absence of this part of the crankshaft linkage for $n = 1$ means that the nets of the two series are not distinct in this case. The details of the various nets, including circuit symbols, are given in Table 1.

For $N = 0$, both series have the same net, and this is the framework of the synthetic zeolite rho. For $N = 1$, the net of the [110] series corresponds to the framework of the synthetic zeolite ZK–5, and for $N = 4$, the net of the [100] series corresponds to the framework of the natural zeolite paulingite. Stereoviews of paulingite, rho and ZK–5 are given in Meier & Olson (1978). The vacant members of both series are potential zeolite frameworks.

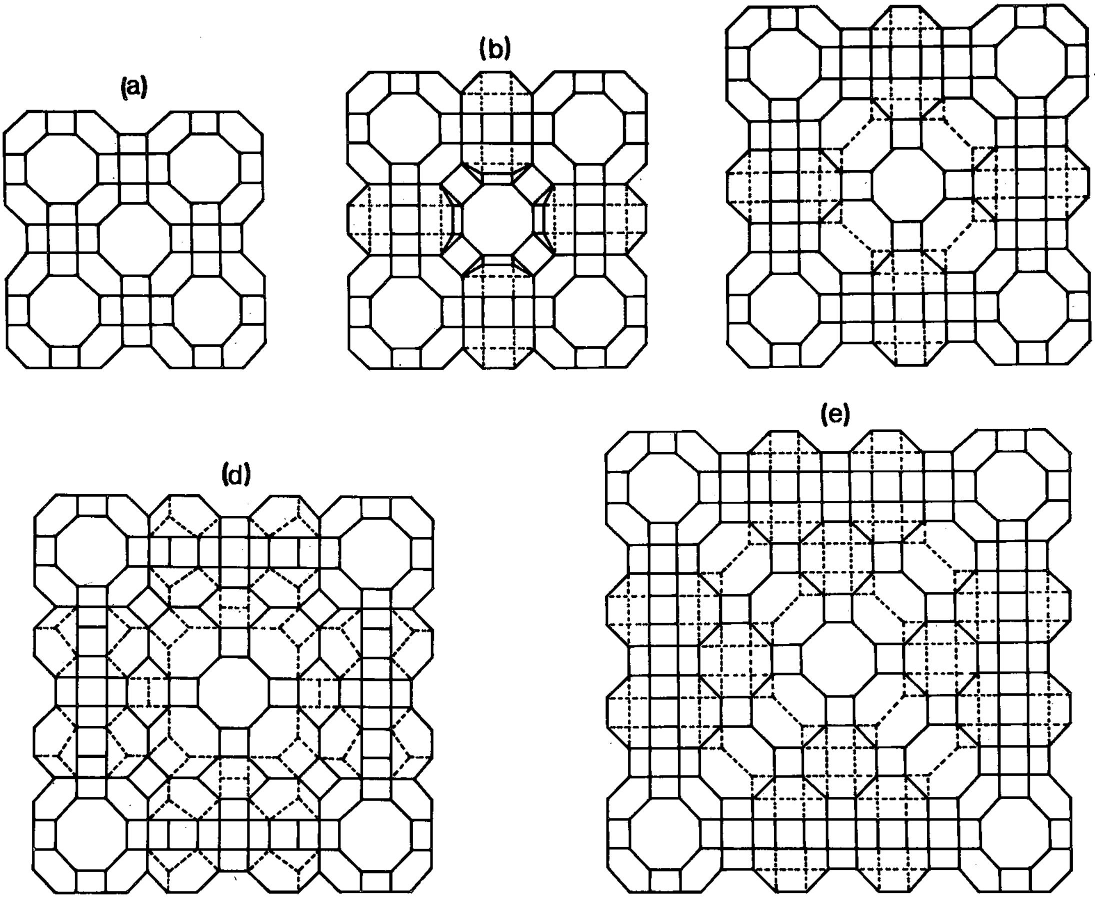

FIG. 3. Nets of the [100] rhombicuboctahedron series for (a) $N = 0$ (zeolite rho); (b) $N = 1$; (c) $N = 2$; (d) $N = 3$; (e) $N = 4$ (paulingite). Connections denoted by broken lines are further away than those denoted by full lines.

The truncated octahedron nets

Shoemaker *et al.* (1973) showed how the rhombicuboctahedron may be related to the truncated octahedron by an operation that they termed a σ-transformation. Consider the truncated octahedron to be defined by the forms {111} and {100}. There are mirror planes parallel to {100}, and all of the vertices of the truncated octahedron lie on these mirror planes. The σ-transformation involves taking each vertex on a specific mirror-plane, splitting it into two vertices and moving these vertices off the mirror plane such that the mirror symmetry is retained and the edge joining the new vertices passes through the position of the original vertex. If this σ-transformation is done on all three {100} mirror planes of a truncated octahedron (σ^3-transformation), the resulting polyhedron is a rhombicuboctahedron. Similarly, the truncated octahedron may be derived from the rhombicuboctahedron by the inverse σ-transformations (σ^{-3}-transformation).

We may use the inverse σ-transformation to derive a series of nets (Fig. 5, Table 1) analogous to the [100] (rho-paulingite) series, but based on the truncated octahedron rather than the rhombicuboctahedron. For $N = 0$, the net is the framework of the sodalite structure; for $N = 3$, some of vertices are 3-connected and, hence, this example is not considered here. The remaining nets are potential zeolite-type structures. As indicated by Smith & Bennett (1981), σ^{-1}- and σ^{-2}-transformations can also be used to produce various derivative tetragonal nets of space-group symmetry $I4/mmm$ and cell dimensions that are various combinations of the corresponding values given in Table 1; however, we have restricted our attention to the cubic nets.

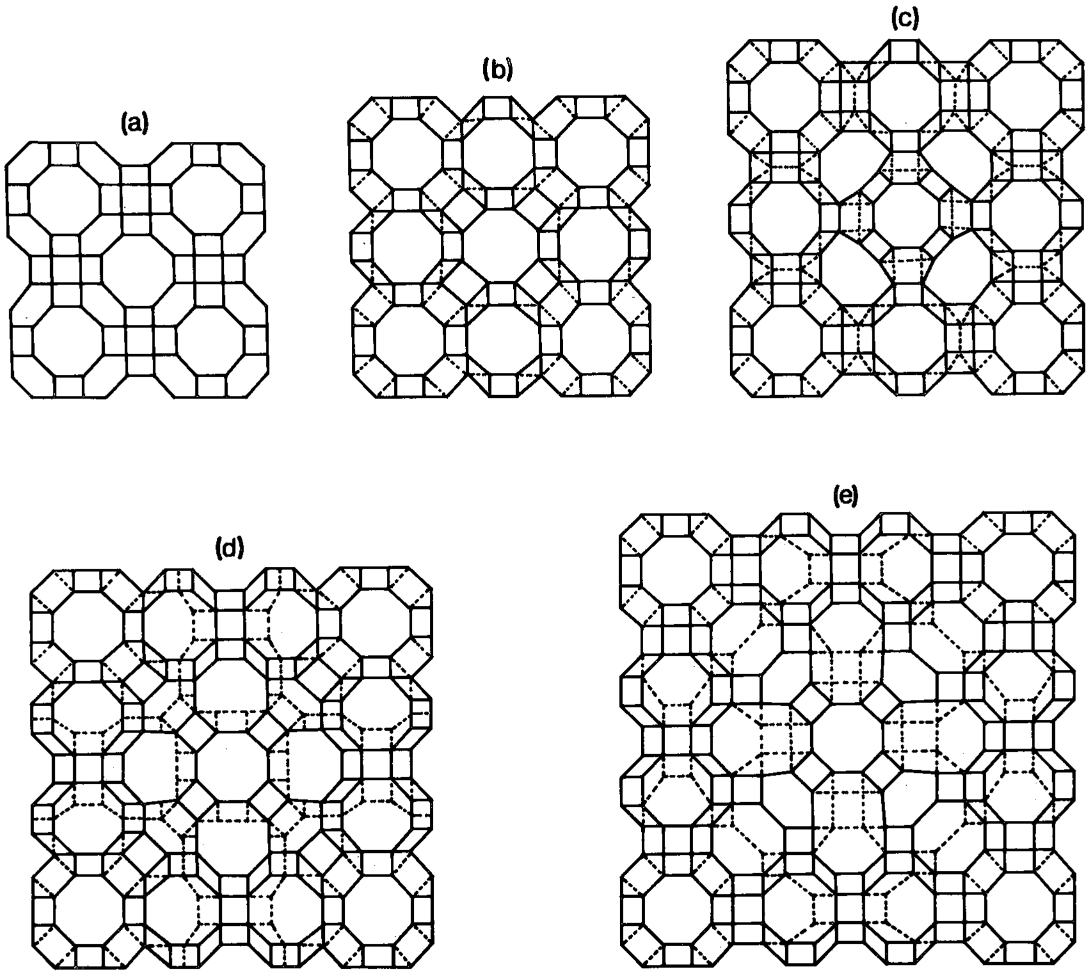

FIG. 4. Nets of the [110] rhombicuboctahedron series for (a) $N = 0$ (zeolite rho); (b) $N = 1$ (zeolite ZK-5); (c) $N = 2$; (d) $N = 3$; (e) $N = 4$.

The inverse σ-transformation may not be used with the [110] rhombicuboctahedron series. This transformation can only be done on a plane of mirror symmetry; this condition is necessary but not sufficient. As we are considering 4-connected nets, the vertices must remain 4-connected after this transformation. Thus the vertices that are mapped onto the mirror plane by the σ^{-1}-transformation can only be the intersection of edges that are parallel or perpendicular to the mirror plane; if a σ^{-1}-transformation is done on vertices that have incident edges inclined to the mirror plane, the resultant vertices are no longer 4-connected. Consequently, there are no truncated octahedron nets related to the [110] rhombicuboctahedron-series nets.

CONCLUSION

The space groups and cell dimensions of all these nets should be useful in the evaluation of possible structural models for fine-grained cubic zeolite-type phases. However, it is necessary to bear in mind that these parameters were derived for ideal nets. The presence of additional non-framework cations and both bonded and 'zeolitic' water may perturb the cell dimensions somewhat from their ideal values, and also may reduce the space-group symmetry to some subgroup of the ideal *Im*3*m* symmetry. All the nets contain considerable pore volume, to which access is limited by 8- and 6-rings. Several cages occur in each net, including the 4^26^4 and 6^26^6 cages, that

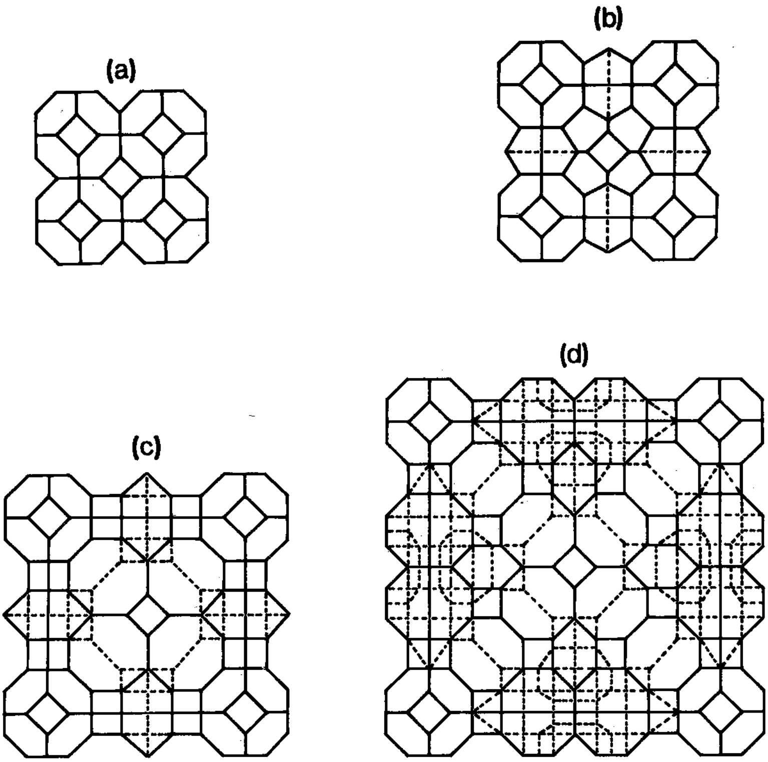

FIG. 5. Nets of the truncated octahedron series for (a) $N = 0$ (sodalite); (b) $N = 1$; (c) $N = 2$; (d) $N = 4$.

appear to be promising candidates for invention of new nets. Although the net of zeolite *N* (Fälth & Andersson 1982) contains the great rhombicuboctahedron, the face-centred symmetry rules out a direct relationship to the present series of nets.

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