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Four-Connected Three-Dimensional Nets Generated from the 1,3-Stellated Cube: Topological Analysis and Distance-Least-Squares Refinement

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Abstract

The four-connected three-dimensional (3D) nets obtained by sharing the vertices, edges and faces of the 1,3-stellated cube (called the bru polyhedral unit) were enumerated by Alberti [*Am. Mineral.* (1979), **64**, 1188–1198]. This enumeration has been reexamined and the topological properties of the simpler nets have been determined. Among the 45 selected 3D nets, there are seven polyhedral subunits, eight three-connected two-dimensional (2D) nets and 16 types of one-dimensional (1D) subunit including chains, columns and tubes. Only four nets are represented by actual materials: brewsterite, heulandite, scapolite and stilbite. The only common subunit to these four nets is bru. Two nets, including scapolite, have tetragonal symmetry. Ten out of 45 3D nets were chosen for distance-least-squares refinement to obtain refined coordinates of T atoms and cell dimensions. This type of topological analysis provides useful information for the classification of framework structures. The concepts used here are yielding many additional 3D nets from other polyhedral units.

Introduction

Theoretical enumeration plays an important role in structural studies of zeolites and other framework materials. Many investigators have invented new four-connected 3D nets using different approaches [reviewed by Smith (1988); representative later publications include those of Akporiaye & Price (1989), Deem & Newsam (1989), Kirchner & McGuire (1992), O'Keeffe (1991), Smith (1989) and Wood & Price (1992)]. This has proven to be a useful tool for solving the unknown structures of microporous materials by matching cell dimensions and powder patterns with those calculated for hypothetical models. It also provides information about framework geometries that might be targets for the synthesis of technologically important materials.

The number of invented nets that are based on known subunits is increasing rapidly and Monte Carlo and simulated-annealing techniques can rapidly generate many thousands of nets. New subunits are being generated by the systematic application of geometrical algorithms to simple polyhedra, nets, chains, columns and tubes (Andries & Smith, 1992, 1993; Pluth & Smith, 1992, RP189). Furthermore, new nets and subunits (Smith & Pluth, 1992) are being discovered in the newly determined frameworks of both natural and synthetic microporous materials. Because different approaches have been explored in the various enumerations and because different methods are used in the descriptions of the nets, there has been no simple way, so far, to coordinate and compare the various sets of data. To make further progress in the systematic enumeration and classification of nets, it is important to develop a systematic universal classification of the building units in framework structures and to use the mathematical principles in describing framework topology and geometry. This is part of the program organized by Smith (1989).

The first step (Pluth & Smith, 1992, RP208) in characterizing a regular four-connected 3D net is the determination of the cell dimensions and space-group symmetry for a standard edge length ($\sim$3.1 Å is convenient for zeolites and other molecular sieves). The net is homogeneously transformed into the geometrical shape with the highest space-group symmetry. Approximate cell dimensions can be determined by simple measurement of a model built from plastic or metal tetrahedral 'stars' joined by plastic tubes. A better set of cell dimensions is generated by a distance-least-squares (DLS) optimization of the net geometry using a computer program (Baerlocher, Hepp & Meier, 1977). Cell dimensions from actual structures may be rather different from idealized ones because of geometrical distortion caused by atomic bonding and crinkling; furthermore, the space group may be reduced to a subgroup. Also useful for characterization are the circuit symbol for each T vertex and the subunits that constitute the framework: the types of 1D chains, columns and tubes, the 2D nets and the 3D polyhedra and cages. A database containing all this

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information is described by Pluth & Smith (1992, RP208). Each new net produced by enumeration or structure solution can be tested for novelty by searching the database, with care being taken to consider the possible geometrical distortion and lower symmetry of the new net. With the progress in the classification of building units and topological analysis of those four-connnected 3D nets already generated, it is possible to explore how subunits can be linked in new ways to produce further frameworks. An illustrative example is the systematic generation of four-connected 3D nets from the combination of three-connected 2D nets and a chain (Smith & Han, 1992). Another way to solve the unknown structure of a new microporous material is to calculate powder diffraction patterns of theoretical nets for direct comparison with observed patterns. Again, care is needed because changes in net geometry coupled with X-ray scattering from extra-framework species cause major changes in the positions and intensities of diffractions.

Alberti (1979) systematically invented 3D nets by linking together a low-symmetry polyhedral unit, the 1,3-stellated cube (bru unit). We have reexamined this enumeration and made DLS refinements for selected 3D nets. The results have been integrated into the database of the Consortium for Theoretical Frameworks (CTF).

Mathematical analysis

The bru polyhedral unit, which occurs in four known zeolite frameworks, consists of two 4-rings and four 5-rings. It is a 1,3-stellated cube with face symbol $4^2 5^4$ (Fig. 1). Meier (1968) called this secondary building unit 4-4-1. By sharing one, two, three and four vertices of the bru polyhedron, Alberti (1979) generated six different chains. 23 sheets were then generated through symmetry operations, such as t (translation), m (mirror), r (rotation) and i (inversion). These sheets were then connected by the interlayer linkages to generate 45 3D nets. The symmetry operations relating the two sheets include T (translation), M (reflection), R (twofold rotation) and G (glide reflection). In order to understand the topological properties of each net, a model was built from plastic stars and tubes. Cell dimensions and the highest space group were determined from each model. The cell dimensions were measured with a

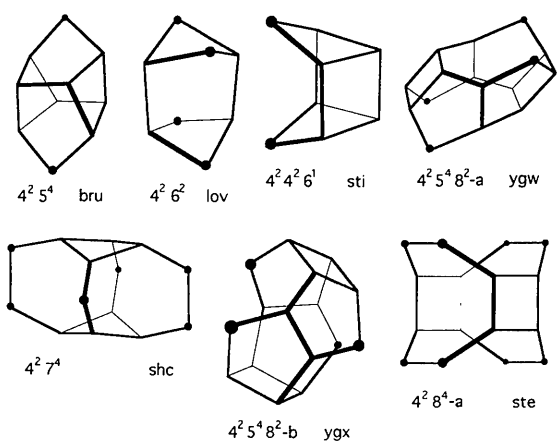

Fig. 1. Polyhedral units with labels and face symbols.

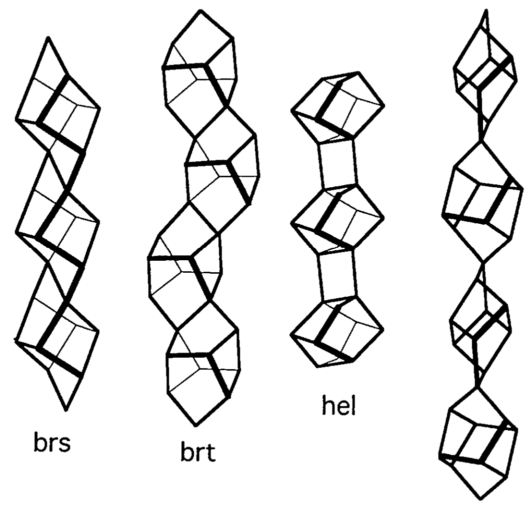

Fig. 2. Four major 1D subunits with labels.

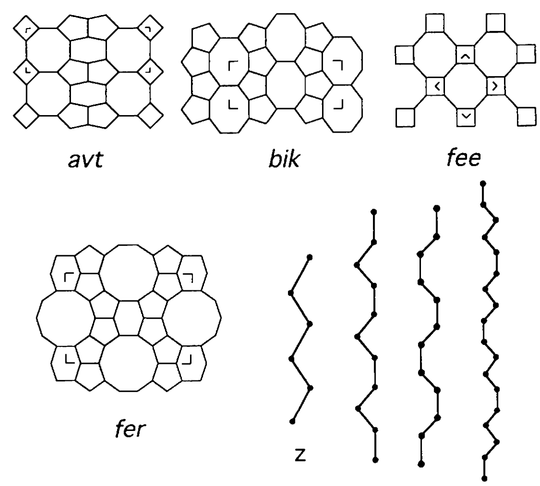

Fig. 3. Three-connected 2D nets and chains used in the alternative topological description of some of the 3D nets (Table 2, column 2).

Table 1. *Geometrical properties of regular 3D nets obtained by linkage of* bru *nets*

Alberti structure code	CTF number	Circuit symbol (Wells)	Z_c	Highest space group	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Structure type
$T(010)V_t$	659	$(4^25^27^2)_4(45^26^28)_2(45^26^28)_2(5^28^4)_1$	18	131:$P4_2/mmc$	7	7	17	90	90	90	–
$T[010]W_t$	660	$(4^25^37)_2(4^25^37)_2(45^47)_2(45^28^210)_2(5^48^2)_1$	18	13:$P2/b11$	8	17	7	115	90	90	–
$M(010)W_t$	602	$(4^25^36)_2(4^25^37)_2(45^47)_2(45^28^3)_2(5^48^2)_1$	36	12:$C12/m1$	17.5	18	7.5	90	116	90	Heulandite, HEU
$R[102]W_t$	661	$(4^25^36)_1(4^25^36)_1(4^25^37)_1(4^25^38)_1(45^47)_1$ $(45^47)_1(45^289^2)_1(45^29^3)_1(5^48^2)_1$	144	68:$Ccca$	17	26.5	16	90	90	90	–
$M(010)W_m$	603	$(4^35^27)_2(4^25^26^2)_4(45^28^3)_2(5^26^29^2)_1$	72	69:$Fmmm$	17.5	18	13.5	90	90	90	Stilbite, STI
$T(010)W_r$	662	$(4^25^36)_2(4^25^37)_2(45^47)_2(45^28^210)_2(5^48^2)_1$	36	54:$Pbab$	13	16.5	8	90	90	90	–
$M(010)W_r$	663	$(4^25^36)_2(4^25^37)_2(45^47)_2(45^28^3)_2(5^48^2)_1$	72	64:$Cmca$	16	17	13	90	90	90	–
$R[102]W_r$	664	Not determined, model destroyed	–	69:$Ccca$	33	57	16	90	90	90	–
$T[010]D_t$	665	$(4^25^27^2)_2(45^38^2)_1(45^28^3)_1$	8	10:$P2/m11$	7	8.5	6.5	110	90	90	–
$T[121]D_t$	666	$(45^37^2)_1(45^27^3)_2(45^27^3)_1$	16	12:$C12/m1$	9	13.5	6.5	90	120	90	–
$T[021]D_t$	667	$(45^38^2)_1(45^26^28)_2(45^268^2)_1$	16	12:$C12/m1$	8.5	13	6.5	90	100	90	–
$T[010]D_m$	668	$(4^25^27^2)_2(45^38^2)_1(45^28^3)_1$	16	51:$Pmmb$	7	16.5	6.5	90	90	90	–
$R[041]D_m$	669	$(45^38^2)_1(45^26^28)_1(45^26^28)_1(45^26^28)_1$	16	13:$P112/b$	8.5	17	6.5	90	90	120	–
$R[100]D_m$	670	$(4^25^27^2)_2(45^38^2)_1(45^28^3)_1$	32	67:$Cmma$	13.5	17.5	6.5	90	90	90	–
$T[010]Z_t$	671	$(4^25^26^2)_1(4^25^267)_1(45^368)_1(45^28^3)_1$	8	2:$P\bar{1}$	7.5	8	6.5	90	95	95	–
$M(010)Z_t$	591	$(4^25^26^2)_1(4^25^267)_1(45^368)_1(45^28^3)_1$	16	11:$P12_1/m1$	7.5	17.5	7	90	95	90	Brewsterite, BRE
$R[100]Z_t$	672	$(4^25^26^2)_1(4^25^267)_1(45^368)_1(45^28^3)_1$	16	13:$P112/b$	7	16.5	6.5	90	90	90	–
$R[001]Z_t$	673	$(4^25^26^2)_1(4^25^267)_1(45^368)_1(45^28^3)_1$	16	13:$P2/b11$	7	16.5	6.5	100	90	90	–
$R[101]Z_t$	674	$(4^25^26^2)_1(4^25^267)_1(45^368)_1(45^28^3)_1$	32	15:$B112/b$	10.5	16	9.5	90	90	95	–
$R[10\bar{1}]Z_t$	675	$(4^25^26^2)_1(4^25^267)_1(45^368)_1(45^28^3)_1$	32	15:$B2/b11$	10.5	16	9.5	95	90	90	–
$R[010]Z_t$	676	8:2 types each of $(4^25^26^2)_1(4^25^267)_1$ $(45^368)_1(45^28^3)_1$	16	2:$P\bar{1}$	7.5	16.5	7	95	95	90	–
$T[010]Z_m$	677	$(4^25^26^2)_1(4^25^267)_1(45^368)_1(45^28^3)_1$	16	11:$P12_1/m1$	8	14.5	6.5	90	100	90	–
$M(010)Z_m$	678	$(4^25^26^2)_1(4^25^267)_1(45^368)_1(45^28^3)_1$	32	59:$Pmmn$	14.5	16	6.5	90	90	90	–
$R[100]Z_m$	679	$(4^25^26^2)_1(4^25^267)_1(45^368)_1(45^28^3)_1$	32	57:$Pmab$	14.5	16	6.5	90	90	90	–
$R[100]Z_m$	680	$(4^25^26^2)_1(4^25^267)_1(45^368)_1(45^28^3)_1$	32	12:$C2/m11$	14.5	16	6.5	100	90	90	–
$R[201]Z_m$	681	16:4 types each of $(4^25^26^2)_1(4^25^267)_1(45^368)_1(45^28^3)_1$	128	15:$C12/c1$	19	19	16	90	93	90	–
$R[\bar{2}01]Z_m$	682	16:4 types each of $(4^25^26^2)_1(4^25^267)_1(45^368)_1(45^28^3)_1$	128	15:$C12/c1$	19	19	16	90	95	90	–
$T[010]Z_r$	683	$(45^47)_1(45^47)_1(45^48)_1(45^28^29)_1$	16	13:$P2/b11$	8	14	6.5	105	90	90	–
$M(010)Z_r$	684	$(45^47)_1(45^47)_1(45^48)_1(45^28^3)_1$	32	12:$C12/m1$	15	16	6.5	90	105	90	–
$R[201]Z_r$	685	$(45^47)_1(45^47)_1(45^47)_1(45^47)_1(45^48)_1$ $(45^48)_1(45^28^3)_1(45^28^29)_1$	128	68:$Ccca$	16.5	21.5	16	90	90	90	–
$T[010]E_t$	686	$(4^25^27^2)_1(4^25^27^2)_1(45^38^2)_1(45^28^3)_1$	16	51:$Pbmm$	9	12.5	6.5	90	90	90	–
$T[021]E_t$	687	$(45^37^2)_1(45^27^3)_1(45^27^3)_1(45^27^3)_1$	32	63:$Amma$	12.5	13.5	9.5	90	90	90	–
$R[100]E_t$	688	$(4^25^27^2)_1(4^25^27^2)_1(45^37^2)_1(45^38^2)_1(45^27^3)_1$ $(45^27^3)_1(45^27^28)_1(45^278^2)_1$	32	51:$Pmmb$	12.5	13.5	9.5	90	90	90	–
$T[010]E_m$	689	$(4^25^27^2)_1(4^25^27^2)_1(45^38^2)_1(45^26^29)_1$	32	65:$Cmmm$	12.5	19.5	7	90	90	90	–
$T[010]F_t$	690	$(4^25^36)_1(4^25^37)_1(45^47)_1(45^367)_1(45^368)_1$ $(45^368)_1(45^28^3)_1(45^28^29)_1$	16	2:$P\bar{1}$	8	13	7.5	115	90	90	–
$M(010)F_t$	691	$(4^25^36)_1(4^25^37)_1(45^47)_1(45^367)_1$ $(45^368)_1(45^368)_1(45^28^3)_1(45^28^3)_1$	32	11:$P12_1/m1$	13	16	7	90	110	90	–
$G[100]F_t$	692	$(4^25^36)_1(4^25^37)_1(45^47)_1(45^367)_1(45^368)_1$ $(45^368)_1(45^28^29)_1(45^28^29)_1$	32	14:$P12_1/a1$	13	16	7	90	110	90	–
$R[102]F_t$	693	16 types	128	15:$A112/a$	16	23	15.5	90	90	95	–
$R[10\bar{2}]F_t$	694	16 types	128	15:$A12/a1$	16	23	15.5	90	95	90	–
$T[010]F_r$	695	$(45^47)_2(45^47)_2(45^48)_1(45^48)_1(45^28^29)_1(45^28^29)_1$	32	57:$Pmab$	12.5	14.5	8	90	90	90	–
$M(010)F_r$	696	$(45^47)_2(45^47)_2(45^48)_1(45^48)_1(45^28^3)_1(45^28^3)_1$	64	63:$Ccmm$	12	16	15	90	90	90	–
$T[010]F_i$	697	$(4^25^36)_1(4^25^37)_1(45^47)_1(45^367)_1(45^368)_1(45^368)_1$ $(45^28^3)_1(45^28^29)_1$	32	14:$P2_1/b11$	12.5	14.5	8	92	90	90	–
$M(010)F_i$	698	$(4^25^36)_1(4^25^37)_1(45^47)_1(45^367)_1(45^368)_1(45^368)_1$ $(45^28^3)_1(45^28^3)_1$	64	62:$Pnma$	13	16	12.5	90	90	90	–
$R[100]F_i$	699	$(4^25^36)_1(4^25^37)_1(45^47)_1(45^367)_1(45^368)_1(45^368)_1$ $(45^28^3)_1(45^28^29)_1$	64	15:$A112/a$	13	16	12.5	90	90	92	–
$M(010)K_m$	100	$(45^48)_2(458^4)_1$	24	139:$I4/mmm$	12.5	12.5	7.5	90	90	90	Scapolite

ruler and are based on a 3.1 Å edge. A tolerance of up to 15% is suggested in searching for a match with cell dimensions of a zeolite of unknown structure. The geometrical properties of these 3D nets are listed in Table 1. Column 1 gives the structure code from Alberti (1979). Column 2 gives the catalog number of the Consortium for Theoretical Frameworks. Column 3 gives the circuit symbol for each crystallographic type of vertex (Wells definition: Smith, 1978). Column 4 lists the number of T atoms in a unit cell. For orthorhombic, monoclinic and triclinic symmetry, the axes are deliberately chosen to give $b > a > c$. The next seven columns give the highest space group and cell dimensions. Because all nets contain the odd-numbered 5-ring, regular alteration of atoms on the tetrahedral vertices is not possible.

Table 2. *Alternative topological description, subunits and pore space of theoretical nets obtained by linkage of* bru *units*

CTF number	Alternative topological description	Rings providing access to pores	1D subunits including chains, columns and tubes	2D three-connected nets	3D polyhedra and cages (*sensu lato*)	Pores, channels and access
659	(*c,h,s*)**avt*	4,5,8	abe, bhs, *c*, hen, *s*	*avt, brw*	bru, lov	3D-channel-sofa-8,8, rocker-8
660	–	4,5,8,10	hen	*brw*	bru, lov	2D-channel-verydistorted-10, nearelliptical-8
602	–	4,5,8,10	hel, hen, heu, *s′*	*brw*	bru, lov	2D-irregular-channel-chair-10, hammock-8
661	–	4,5,8,9	–	–	bru, lov	2D-channel-distorted-9,9
603	–	4,5,6,8,10	hen, heu, stl	*brw*	bru, sti	2D-irregular-channel-chair-10, elliptical- & rocker-8
662	–	4,5,8,10	hen	–	bru, lov	2D-channel-verydistorted-10, nearcircular-8
663	–	4,5,8,10	hen	*brw*	bru, lov	2D-channel-verydistorted-10, nearelliptical-8
664	–	4,5,8,9	hen	–	bru, lov	2D-channel-distorted-9,8
665	(*h′,z′*,4)**fee*; (*h,s′*)**bik*	4,5,8	abf, brs, *s′*, *z′*	*bik, brw, fee*	bru, lov, ygw	3D-channel-nearplanar-8, chair-8, nonplanar-8
666	(*c,h′,z′*)**fee*	4,5,7,8	alb, brs, *c*, *z′*	*bik, fee*	bru, lov, shc	3D-channel-distorted-8,7,7
667	–	4,5,6,8	brs	*bik, fee, hex*	bru, lov	2D-channel-nonplanar-8,8
668	(*h,s*)**bik*	4,5,8	abf, brs, *s*	*bik, brw, fee*	bru, lov, ygw	3D-channel-nonplanar-8,8,8
669	(*c′,h′,p′*)**fee*	4,5,6,8	brs, *c′*, *p′*	*bik, fee, hex*	bru, lov	2D-channel-distorted-8,8
670	(*h′,p′*,4)**fee*	4,5,8	bhs′, brs, *p′*	*bik, brw, fee*	bru, lov, ygx	3D-channel-nearelliptical-8,8, non-planar-8
671	–	4,5,6,8	brs	*brw, fee, nos*	bru, lov	2D-channel-nearelliptical-8, distorted-8
591	–	4,5,6,8	bre, brs	*brw*	bru, lov	2D-channel-chaiselongue-8, hammock-8
672	–	4,5,6,8	brs	*brw*	bru, lov	2D-channel-hammock-8, nearcircular-nonplanar-8
673	–	4,5,6,8	brs	*brw*	bru, lov	2D-channel-nearplanar-8, verydistorted-8
674	–	4,5,6,8	brs, hel	*hrw*	bru, lov	2D-channel-nearcircular-nonplanar-8,8
675	–	4,5,6,8	brs, hel	*brw*	bru, lov	2D-channel-nearhammock-8,8
676	–	4,5,6,8	brs, hel	–	bru, lov	2D-channel-nonplanar-8,8
677	–	4,5,6,8	brs, hel	–	bru, lov	2D-channel-nearcircular-8, nonplanar-8
678	–	4,5,6,8	brs, hel	*brw*	bru, lov	2D-channel-various-8,8
679	–	4,5,6,8	brs, hel	*brw*	bru, lov	2D-channel-nearhammock-8, distorted-8
680	–	4,5,6,8	brs, hel	*brw*	bru, lov	2D-channel-elliptical & distorted-8,8
681	–	4,5,6,8	brs, hel	*brw*	bru, lov	2D-channel-various-8,8
682	–	4,5,6,8	brs, hel	–	bru, lov	2D-channel-various-8,8
683	–	4,5,8,9	brs	–	bru, lov	2D-channel-distorted-8,9
684	–	4,5,8	brs	–	bru, lov	2D-channel-distorted-8,8
685	–	4,5,8,9	brs	–	bru, lov	2D-channel-distorted-8,9
686	(*h,s*)**biz*; (*z′*,4)**fee*	4,5,8	brt, *s*, *z′*	*biz, fee*	bru, lov, ygw	3D-channel-various-distorted-8,8,8
687	(*c,h′,z′*)**fee*	4,5,7,8	brt, *c*, *z′*	*biz, fee*	bru, lov, shc	3D-channel-distorted-8,7,7
688	(*c,h′,z′*,4)**fee*	4,5,7,8	brt, *c*, *z′*	*biz, fee*	bru, lov, shc	3D-channel-distorted-8,8,7
689	(*h,s*)**fer*; (*h′,p*,4)**fee*	4,5,6,8,10	abf, brt, *p*, *s*	*fee, fer*	bru, lov, ygw	3D-channel-nearcircular-10 with two bifurcations, chair-8, rocker-8
690	–	4,5,6,8,9	brt	–	bru, lov	2D-channel-distorted-8,8
691	–	4,5,6,8	brt	–	bru, lov	2D-channel-distorted-8,8
692	–	4,5,6,8,9	brt	–	bru, lov	2D-channel-distorted-8,9
693	–	4,5,6,8,9	brt	–	bru, lov	2D-channel-distorted-8,9
694	–	4,5,6,8,9	brt	–	bru, lov	2D-channel-distorted-8,9
695	–	4,5,8,9	brt	–	bru, lov	2D-channel-distorted-8,9
696	–	4,5,8	brt	–	bru, lov	2D-channel-elliptical-8,distorted-8
697	–	4,5,6,8,9	brt	–	bru, lov	2D-channel-distorted-8,9
698	–	4,5,6,8	brt	–	bru, lov	2D-channel-distorted-8,8
699	–	4,5,6,8,9	brt	–	bru, lov	2D-channel-distorted-8,9
100	(*c,s*)**fee*	4,5,8	alh, *c*, *s*	*hik, fee*	bru, lov, ste	3D-channel-hammock-8,8,8

Discussion

Topology

Topological properties of these 3D nets are given in Table 2. This shows the number of vertices around each ring between two pores, the types of subunits (including 1D, 2D and 3D building units) and the nature of the channel system. An alternative topological description is also given for those nets that can be constructed from other topological algorithms.

Polyhedral subunits. Besides the bru unit (1,3-stellated cube, 4^25^4), six other 3D polyhedra and cages (lov, sti, ygw, shc, ygx and ste) occur in the nets (Fig. 1). In addition to the four structures listed here, the bru unit also occurs in the structure of boggsite (Pluth & Smith, 1990). The lov unit, 4^26^2, is a 1,3-open cube that is obtained by removing the 1 and 3 edges. It is, of course, part of the bru unit. The sti unit, $4^24^26^1$, is a 1-open cube that also occurs in stilbite and $GaAsO_4^{2-}$. The ygw unit, $4^25^48^2$-*a*, is a 7,9,10′,12′-stellated hexagonal prism that occurs in yugawaralite. The shc unit, 4^27^4, is a 1,3-stellated 2,4-handle cube. The ygx unit, $4^25^48^2$-*b*, is a 7,10,9′,12′-stellated hexagonal prism. The ste unit, 4^28^4-*a*, is a 1,2,3,4-handle cube that also occurs in merlinoite and ECR-1.

1D and 2D subunits. There are eight three-connected 2D nets in this group of frameworks. Among them, *brw*, $(468)_2(68^2)_1$, occurs in 18 out of

Table 3. *Unit cells and coordinates of T atoms after DLS refinement for selected 3D nets*

	Coordinates				Unit cell						
CTF number	*T*1	*T*2	*T*3	*T*4	*a* (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	*R*†
	0.0	0.0	0.2988		7.5216	7.5216	17.974	90	90	90	0.008
659	0.0	0.2936	0.2152								
	0.25	0.1213	0.0								
	0.2784	0.0	0.0		7.2007	9.8141	6.9552	105.27	90	90	0.005
665	0.1609	0.1594	0.3284								
	0.1313	0.4730	0.9319								
	0.1601	0.1677	0.3224		10.027	14.129	6.919	90	114.10	90	0.01
666	0.0	0.1559	0.0								
	0.6950	0.0325	0.3883								
	0.2187	0.5	0.5		7.2283	18.869	6.9517	90	90	90	0.005
668	0.0814	0.0797	0.1640								
	0.0709	0.4120	0.8079								
	0.970	0.3020	0.0228	0.3045	8.3592	18.171	6.7324	90	90	123.07	0.007
669	0.0722	0.1655	0.1683	0.995							
	0.1052	0.4394	0.7071	0.5540							
	0.1318	0.0	0.0		13.291	19.255	6.8947	90	90	90	0.01
670	0.0730	0.0770	0.1657								
	0.0484	0.4032	0.7929								
	0.3703	0.2825	0.8795	0.9805	10.363	12.836	7.006	90	90	90	0.009
686	0.0713	0.25	0.0807	0.25							
	0.0	0.2683	0.0	0.2685							
	0.0694	0.25	0.25	0.0900	12.852	14.091	9.9605	90	90	90	0.01
687	0.0	0.1487	0.3422	0.5							
	0.3634	0.2977	0.4759	0.3858							
	0.5	0.3265	0.1747	0.0	12.240	14.297	9.4446	90	90	90	0.008
	0.1015	0.25	0.25	0.1101							
	0.0777	0.968	0.2066	0.1699							
688‡	*T*5	*T*6	*T*7	*T*8							
	0.0	0.1821	0.3211	0.5							
	0.1151	0.25	0.25	0.1010							
	0.8328	0.7188	0.4577	0.4210							
	0.0	0.0	0.1710	0.1671	13.249	20.595	7.2426	90	90	90	0.004
689	0.2775	0.1200	0.3103	0.0760							
	0.2839	0.2839	0.0	0.0							

† *R* = SQRT(SUM(W*(DO-D))**2/SUM(W*DO)**2).
‡ There are eight *T* atoms in the asymmetric unit.

the 45 nets. Others are: *hex*, *fee*, *bik*, *nos*, *fer*, *biz* and *avt*. There are 16 types of 1D subunits including chains, columns and tubes with brs, brt, hel and hen the most frequent (Fig. 2). The three chains brs, brt and hen were originally decribed as f_1, f_2 and *e*, respectively, by Alberti (1979).

Channel system. The linkages of the bru polyhedra generate either a 2D or a 3D channel system. Ten nets have 3D channel systems; the others have channels linked in 2D. The channels tend to be rather irregular and the windows are bounded by 7-, 8-, 9- and 10-rings, usually strongly nonplanar and noncircular. Access to the channel system in most nets is limited by 8-rings. The nonplanar and irregular shape reduces the effective free diameter of most windows to about that for a circular 7- or even 6-ring.

Alternative topological description. Eleven nets can be described by the combination of a three-connected 2D net with one or more 1D units. Nets *avt*, *bik*, *fee* and *fer* are shown in Fig. 3, as are chains *c*, *p*, *s* and *z*. In column 2 of Table 2, a prime (′) after a symbol for a chain indicates considerable distortion from the ideal shape. As an illustration of the combination of chains and a net, consider the first entry. For CTF net 659, some of the edges of net *avt* remain horizontal (*h*), whereas others are converted into either crankshaft (*c*) or saw (*s*) chains. For CTF net 665, some edges of the *fee* net are converted into distorted zigzag (*z*) chains. Another view of the 3D net shows conversion of some edges of the *bik* net into *s* chains. CTF 3D net 669 shows some edges of the *fee* net converted into distorted *c* or pentasil (*p*) chains In CTF 3D net 670, the conversion of some edges of the *fee* net into distorted *p* chains turns other edges into 4-rings. Descriptions for the other CTF nets follow the same symbolism.

The space group for net 659 has been changed from that in Alberti (1979) and a new unit cell has been chosen for net 100. Net 676 has a 2D layer of pseudo-square shape, approximately 7 by 7 Å. From this layer, a new polytype with pseudotetragonal symmetry could be generated by pseudo-screw-axis 4_1 or 4_3.

DLS refinement

Ten nets were selected from the total of 45 because of their higher symmetry and elegant structure. The initial coordinates were measured from the models. Using the *DLS* program (Baerlocher, Hepp & Meier, 1977), unit-cell parameters and atomic coordinates were refined. The T–O, O–O and T–T distances were set to 1.628, 2.6585 and 3.1053 Å, respectively. Table 3 lists the refinement results including T-atom coordinates, unit cells and R factors. The highest space group for each net is used in the refinement and R varies from 0.01 to 0.004. Unit-cell changes are usually within 15% owing to geometrical distortion. These refined results can be used for powder-pattern calculation and comparison with unknown phases.

Concluding remarks

Four nets in this family occur in known mineral structures. Although the other nets are possible candidates for zeolite phases with as yet unsolved structures, no likely matches turned up in a comparison of theoretical and observed cell dimensions and space groups. Examination of twinned crystals of the four zeolite families should give clues to the possibility of finding new minerals with bru-based nets. Presumably, the connectivity across the twin contact might match one of these in the theoretical nets. Because all the theoretical nets contain odd-number rings, alternation of elements in the T sites, as in aluminophosphates, is not possible.

This study extends the enumeration of nets based on the bru polyhedral subunit and provides a topological description of each net. Further studies on selected polyhedral units will yield many more theoretical 3D nets of both mathematical and practical value.

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On Integrating the Techniques of Direct Methods with Anomalous Dispersion. III. Estimation of Two-Wavelength Two-Phase Structure Invariants

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Abstract

For diffraction data at two wavelengths from a crystal with anomalous scatterers, there are six types of two-phase structure invariants for Friedel pairs. Two of the six are single-wavelength invariants; the other four are mixed-wavelength invariants. It is shown that the latter can be estimated by a straightforward extension of results from the probabilistic direct-methods theory for the single-wavelength anomalous scattering case described in paper I [Hauptman (1982). *Acta Cryst.* A**38**, 632–641]. Statistical tests of the mixed-wavelength estimates are reported for small-molecule and macromolecular examples.

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