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Enumeration of 4-connected 3-dimensional nets and classification of framework silicates, II. Perpendicular and near-perpendicular linkages from 4.8^2, 3.12^2 and 4.6.12 nets

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Abstract

Systematic enumeration is given of 4-connected 3D nets obtained by adding perpendicular or near-perpendicular linkages to 4.8^2, 3.12^2 and 4.6.12 nets. Out of the 79 simpler nets, 8 are represented by paracelsian, merlinoite, gismondine, harmotome/phillipsite, feldspar, banalsite, gmelinite, and chabazite.

Introduction

The concepts and nomenclature used here were described in Part I (Smith, 1977), and are based on the pioneering ideas of A. F. Wells now gathered together in Wells (1977). The second part describes 4-connected 3D frameworks obtained by adding a perpendicular or near-perpendicular branch to each node of the 4.8^2, 3.12^2, and 4.6.12 types of 3-connected 2D nets which have congruent nodes but more than one kind of ring (Wells, 1977, Fig. 14.1).

Enumeration of frameworks from 4.8^2 net

The results of Smith and Rinaldi (1962) and Smith (1968) are codified and extended here. Each 4-ring can have the following possible sequences of up (U) and down (D) linkages: *UUUU, UUUD, UDUD*, or *UUDD*, plus the four inverted sequences obtained by interchanging U and D. A vertical double-crankshaft chain can be obtained by linking alternate *UUDD* and *DDUU* horizontal rings. Double-crankshaft chains can be cross-linked into an infinity of 3D frameworks in which the sequence of U and D around the 8-rings is changed. A convenient nomenclature for the sequence round the 8-rings is: C means change of direction between vertical linkages from two nodes connected by a horizontal branch between two 8-rings, S means no change; c and s are corresponding symbols for two nodes connected by a horizontal branch between an 8-ring and a 4-ring. Smith and Rinaldi (1962) enumerated the 18 frameworks (Fig. 1) with only one type of 8-ring or only two types of adjacent 8-rings. Only 6 have congruent nodes (Table 1) whereas the others have two, three, or four types of nodes. (Actually there are only two types of Schläfli symbols because some topologically-distinct nodes have the same symbol: see appendix.) Framework no. 6 (paracelsian) was already described in Part 1 because of its simple hexagonal 2D net. Frameworks 17, 23, and 24 are the basis of known mineral structures (merlinoite, gismondine, phillipsite; Table 1). The remaining two frameworks with congruent nodes (nos. 9a and 11) have not yet been recognized in known crystal structures. Framework 17 is particularly interesting because it contains a dodecagonal prism: note that it contains two different sequences around the 8-rings. Framework 23 is remarkable because it has double-crankshaft chains in two directions with consequent tetragonal symmetry. Seven nets have only one type of sequence around the 8-rings while others have two types.

Because the double-crankshaft chain has a mirror operation between each pair of adjacent 4-rings, all the 3D nets have a mirror plane perpendicular to the 8.5A axis in the highest space group (Table 1). Figure 2 shows an alternative way of linking the 4-rings to give a twisted *UUDD* chain, which has a different way of linkage into the 8-rings. For the untwisted chain, the 4-rings superimpose in projection as also do the branches to adjacent 4-rings. For the twisted chain, the 4-rings are rotated alternately clockwise and anticlockwise, thereby removing the superimposition, and the connecting branches are no longer perpendicular to the 2D net. Furthermore the pairs of horizontal branches which were originally superimposed now radiate outwards at 90°. Smith (1968) used the terms *flexible* and *inflexible* to describe the two types of 3D nets produced, respectively, from untwisted and twisted *UUDD* chains. Table 2 lists and Figure 3 depicts the thirteen 3D nets obtained

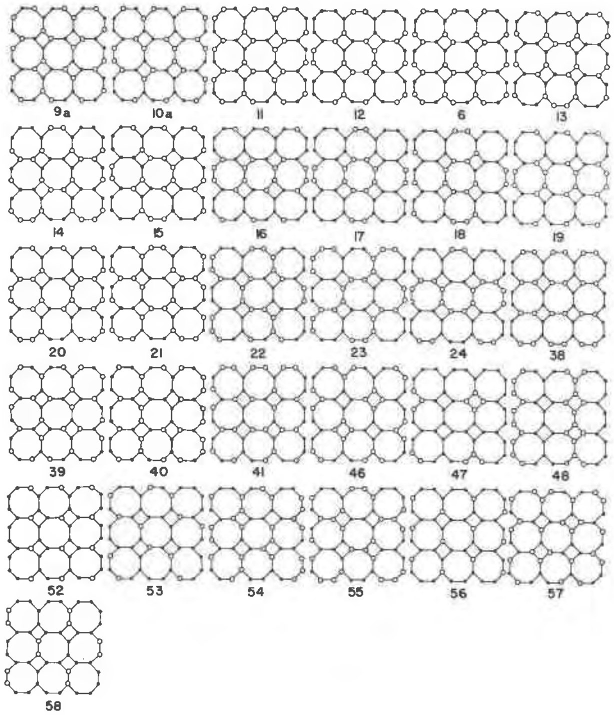

Fig. 1. Assignments of upward (dot) and downward (circle) branches to 4.8^2 2D net in "untwisted" frameworks listed in Tables 1 and 3.

from twisted *UUDD* chains and a 4.8^2 2D net with only one type of 8-ring or two types of adjacent 8-rings. Four have nodes with only one Schläfli symbol, one has nodes with two types of Schläfli symbol, and the remainder have three or more Schläfli symbols.

Table 3 and Figures 1 and 3 give corresponding information for 3D nets containing either untwisted or twisted chains based on *UDUD* or *UUUD* rings, and either untwisted or twisted cubes based on *UUUU* rings. The combination of *SsSsSsSsSs* sequence with *UUUU* rings gives a double sheet instead of a 3D net. Out of the 25 hypothetical frameworks, only one has been found to occur in a chemical substance, namely the mineral banalsite. Net 46 was incorrectly proposed as the structure of the zeolite Na–P1 (Barrer *et al.*, 1959), and the correct structure actually is based on net 23 (Baerlocher and Meier, 1972).

From the viewpoint of molecular sieving, all the frameworks based on the 4.8^2 net have small cages, channels or windows. The largest window is based on an 8-ring, and the zeolites merlinoite, gismondine, harmotome, and phillipsite all contain small cages with the water molecules strongly bonded to exchangeable cations and framework oxygens. Twisting of the chains or cubes tends to reduce the space between the framework oxygens, as exemplified by feldspar and banalsite which are anhydrous; indeed G. O. Brunner (see Smith, 1974, vol. 1, p. 39) described the feldspar structure as being based on oxygens in near-close-packing.

Enumeration of frameworks from 3.12^2 net

Although there are no known substances with 3-rings in a framework, it is interesting mathematically to enumerate the frameworks based on a 3.12^2 net.

There are only two ways of arranging up and down linkages around a 3-ring: *sss* and *scc*. An *sss* ring combines with another ring to give a capped trigonal prism with six outgoing branches, while *scc* rings can be linked into an infinite chain. Table 4 and Figure 4 show the simpler 4-connected 3D nets obtained by linking the *sss* prisms or the *scc* chains.

The easiest way to envisage the linkage of the trigonal prisms is to replace each node in the 3D nets obtained from the 6^3 2D net (Part I) by a 3-ring, so that each pair of nodes joined by a vertical branch becomes a trigonal prism. Thus the tridymite net (Part I, Table 1, no. 2) becomes net 64. The cristobalite net (Part I, Table 1, no. 1), however, presents a complication because of the 180° rotation of successive 2D nets. Figure 5(a) shows how this rotation can be accommodated topologically to permit linkage of twisted trigonal prisms. Ring B′ lies under ring A, and is connected horizontally to ring B which is over ring C′. The circuit is completed by linkage through rings C and A′. Figure 5(b) is an idealized version in which the pairs of rings are exactly superimposed by changing the rotation angle from Figure 5(a). The nodes now lie on a kagomé 2D net (Schläfli symbol 3.6.3.6), and an original 12-ring is now represented by a truncated equilateral triangle such as circuit *abcdefghijkl*. Unlike the cristobalite net, the new net (Table 4, no. 65) has hexagonal symmetry, and the nodes have the Schläfli symbol $3.4^2.9^3$. Wells (1977, Fig. 9.3) showed how the quartz and NbO structures are obtained by replacing triangles in a kagomé net by triangular helices, and net 65 is a more complex topological arrangement in which the triangles of the kagomé net are replaced by a staggered linkage of trigonal prisms.

Returning to the simple replacement of each node of the 6^3 net by a trigonal prism, Table 4 lists nets 66 to 71, which are analogous to nets 3 to 8 in Pt. I. Omitted are the complex nets which would be analogous to the $SSCCCC_2$ and $SSSSCC_2$ nets in Figure 2

Table 1. Simpler structures with 4.8² net and untwisted *UUDD* crankshaft

Arbitrary number	Sequence(s) around 8-rings	Z_t	Schläfli symbol(s)	Highest space group	Z_c	a	b	c	γ
9a	CcCcCcCc; CsCsCsCs	16	$4^2 6^3 8$	I4/mcm	32	14	-	8.5	-
10a	CcCcCcSs; CcSsCsCs	32	$(4^3 6^2 8)_1 (4^2 6^3 8)_3$	$P112_1/m$	32	14	14	~8.5	~90
11	CcCcCsCs	16	$4^2 6^3 8$	Pbcm	16	7	14	8.5	-
12	CcCcScSc; SsSsCsCs	32	$(4^3 6^2 8)_1 (4^2 6^3 8)_1$	Cmcm	64	20	20	~8.5	-
13	CcCsCsSs; CcCcScCs	32	$(4^3 6^2 8)_1 (4^2 6^3 8)_3$	$P112_1/m$	32	14	14	~8.5	~90
6	CcCsCcCs	8	$4^2 6^3 8$	Cmcm	16	9	10	8.5	-
14	CcScCcSc; CsSsCsSs	16	$(4^3 6^2 8)_1 (4^2 6^3 8)_1$	Cmcm	32	14	14	~8.5	-
15	CcCcSsSs; CcScSsCs	32	$(4^3 6^2 8)_1 (4^2 6^3 8)_1$	$P112_1/m$	32	14	14	~8.5	~90
16	CcSsCcSs	8	$(4^3 6^2 8)_1 (4^2 6^2 8^2)_1$	B112/m	16	7	14	~8.5	~95
17	ScScScSc; SsSsSsSs	16	$4^3 6^2 8$	I4/mmm	32	14	-	~8.5	-
18	CcScScSs; SsSsSsCc	32	$(4^3 6^2 8)_3 (4^2 6^3 8)_1$	$P112_1/m$	32	14	14	~8.5	~90
19	CcScCsSs	16	$(4^3 6^2 8)_1 (4^2 6^3 8)_1$	Pnmm	16	7	14	~8.5	-
20	CcCsScSs; CcSsScCs	32	$(4^3 6^2 8)_3 (4^2 6^3 8)_1$	$P112_1/m$	32	14	14	~8.5	~92
21	CcSsCsSc	16	$(4^3 6^2 8)_1 (4^2 6^3 8)_1$	Abam	32	14	14	~8.5	-
22	SsSsCsSc; SsScScCc	32	$(4^3 6^2 8)_3 (4^2 6^3 8)_1$	$P112_1/m$	32	14	14	~8.5	~90
23	SsScSsSc	8	$4^3 6^2 8$	$I4_1/amd$	16	~8.5	-	10	-
24	SsSsScSc	16	$4^3 6^2 8$	Amam	32	14	14	8.5	-

Observed structures

Type	Name		Actual space group	a	b	c	β
6	paracelsian, hurlbutite, danburite see paper I						
17	$BaAlSi_2O_6(Cl,OH)$	Solov'eva et al. (1972)	I4/mmm	14.194	-	9.234	
17	merlinoite	Galli et al. (1977)	Immm	14.118	14.250	9.962	
23	gismondine	Fischer (1963)	$P12_1/c1$	10.02	10.62	9.84	92.42
23	zeolite P1	Baerlocher and Meier (1972)	<I4	10.043	-	10.043	-
23	garronite	Gottardi and Alberti (1974)	tetragonal?	~10	-	~10	-
24	harmotome	Rinaldi et al. (1974)	$P12_1/m1$	9.879	14.139	8.693	124.81
24	phillipsite	do.	$P12_1/m1$	9.865	14.300	8.668	124.20
6	$Na_2ZnSi_3O_8$	Hesse et al. (1977)	$P2_1$	6.660	8.629	6.411	103.70

of Pt. I, and the nets analogous to those for beryllonite and its theoretical hexagonal polymorph in Figure 3. Net 72 is the analog of the newly discovered net 8a, which is a third simple way of assigning *SSSSCC* rings to the 6^3 net (Fig. 6). This 8a net can be envisaged as the alternation of chains of type *ṠṠ* and *ṠCCṠ* parallel to the *b*-axis of the cell in Table 4; polytypism is possible by changing the relative positions of the *ṠCCṠ* chains, and also by intermixing with the *ṠSCCSṠ* chains in the $SSSSCC_2$ type of net.

Of the infinite number of nets with more than one sequence around the 12-rings, net 73 is particularly interesting because it is composed of dodecagonal prisms (*SsSsSsSsSsSs*) separated by *CsCsCsCsCsCs* rings. Net 8b (Fig. 6, Table 4) is analogous in the series based on the 6^3 net. Use only of the *SsSsSsSsSsSs* sequence gives a double sheet instead of a 4-connected 3D net.

Only nets 64 and 65 have congruent nodes. All the nets based on *scc* rings have incongruent nodes because of the parity problem in the placement of symbols on adjoining 3- and 12-rings. Only the seven nets with relatively low Z_t are listed in Table 4. The first five nets (nos. 74–78) have only one type of sequence in the 12-rings, whereas the next two nets were selected for inclusion because of their high symmetry, even though they have two types of sequence in the 8-rings. Several sets have remarkable channel systems.

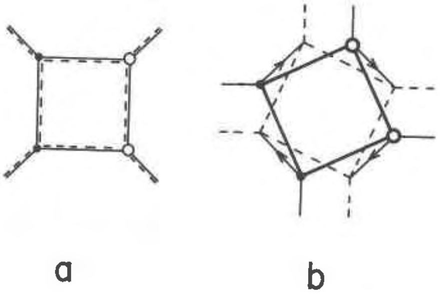

Fig. 2. Comparison of linkages of (a) untwisted and (b) twisted chains of *UUDD* type viewed along the chains. The continuous and dashed lines show different heights. In (a) all linkages superimpose in pairs, and the dots and circles would interchange for the ring shown in dashed lines. Furthermore the vertical linkages are invisible, whereas in (b) the near-vertical linkages are visible with arrows showing the displacement along the chain.

Net 65 has channels intersecting in 3D *via* 8-rings. All the others have at least a set of one-dimensional channels limited by a 12-ring. In net 76, the largest window between the channels is a 6-ring. An 8-ring is the limit in nets 64, 74, 75, and 77–80. Both 8- and 12-rings occur in nets 65, 68, 70, and 73. Chair-shaped 12-rings occur in net 67, while net 69 has both chair- and boat-shaped 12-rings. In nets 71 and 72, only one trigonal prism out of six is at a different level, with the result that it is almost meaningless to define a window between the channels. Formally, net 71 can be said to have chair-shaped 16-rings and net 72 zigzag 20-rings.

Enumeration of frameworks from 4.6.12 net

For the 4.6.12 net, Fig. 7 and Table 5 list those 4-connected 3D nets with the greater degree of congruency. Only three 3D nets plus an infinite polytypic series have congruent nodes.

The two simplest members of the polytypic series are represented by the natural zeolites gmelinite (no. 82) and chabazite (no. 83), as already recognized by Kokotailo and Lawton (1964). Both nets consist of hexagonal prisms linked by 4-rings. In gmelinite, the 4-rings form double-crankshaft chains (*UUDD*) as in feldspar, but in chabazite the alternation of the linking 4-rings excludes the development of chains. Whereas gmelinite has infinite channels bounded by 12-rings and connected sideways by 8-rings, chabazite has near-ellipsoidal cages bounded by two 6-rings, twelve 4-rings, and six 8-rings. The 8-rings in chabazite provide a 3-dimensional channel system. Stacking faults in gmelinite (Fischer, 1966) can be considered as an intergrowth of chabazite stacking, and reduce the maximum size of the channel system from a 12-ring to an 8-ring. Algebraically the stacking of gmelinite and chabazite can be represented by

Table 2. Simpler structures with 4.8^2 net and twisted *UUDD* crankshaft

Arbitrary number	Sequence(s) around 8-rings	Z_t	Schläfli symbols	Highest space group	Z_c	a	b	c	β
25	SsSsSsSs; ScScScSc	16	$4^2 6^3 8$	Amma	32	13	13	~8.5	-
26	SsCsSsCs; CcScCcSc	8	$4^2 6^3 8$	C12/m1	16	~8.5	13	7	116°
27	CcCcCcSs; CcSsCsCs	32	complex	P$\bar{1}$	32	13	13	~8.5	~90°
28	CsCsCcCc; CsScCcSs	32	complex	P12/a1	32	13	13	~8.5	~90°
29	CcCcCcCc; CsCsCsCs	16	$4^2 6^3 8$	Abaa	32	13	13	~8.5	-
30	CsSsSsCs; ScCcCcSc	32	complex	P$\bar{1}$	32	13	13	~8.5	~90°
31	SsSsCcCc; SsCsCcSc	32	complex	P12_1/a1	32	13	~8.5	13	~90°
32	SsCsCcCs; ScCsCcCc; SsScScCc; SsScSsCs	32	complex	P$\bar{1}$	32	13	13	~8.5	~90°
33	SsScSsSc; CcCsCcCs	16	complex	P$\bar{1}$	16	9	9	~8.5	~90°
34	CcCsScSs; CcSsScCs	32	complex	P$\bar{1}$	32	13	13	~8.5	~90°
35	CcSsCcSs	32	$4^2 6^3 8$	P4_2/n	32	13	-	~8.5	-
36	SsSsSsCc; CcScScSs	32	complex	P$\bar{1}$	32	13	13	~8.5	~90°
37	CcScCsSs; SsSsScSc	32	$(4^2 6^3 8)_3 (4^2 6^2 8^2)_1$	P12_1/m1	32	13	13	~8.5	~90°
	Observed structures								
Type	Name		Reference						
26	feldspar		Smith (1974)	several types resulting from cation ordering and framework distortion.					

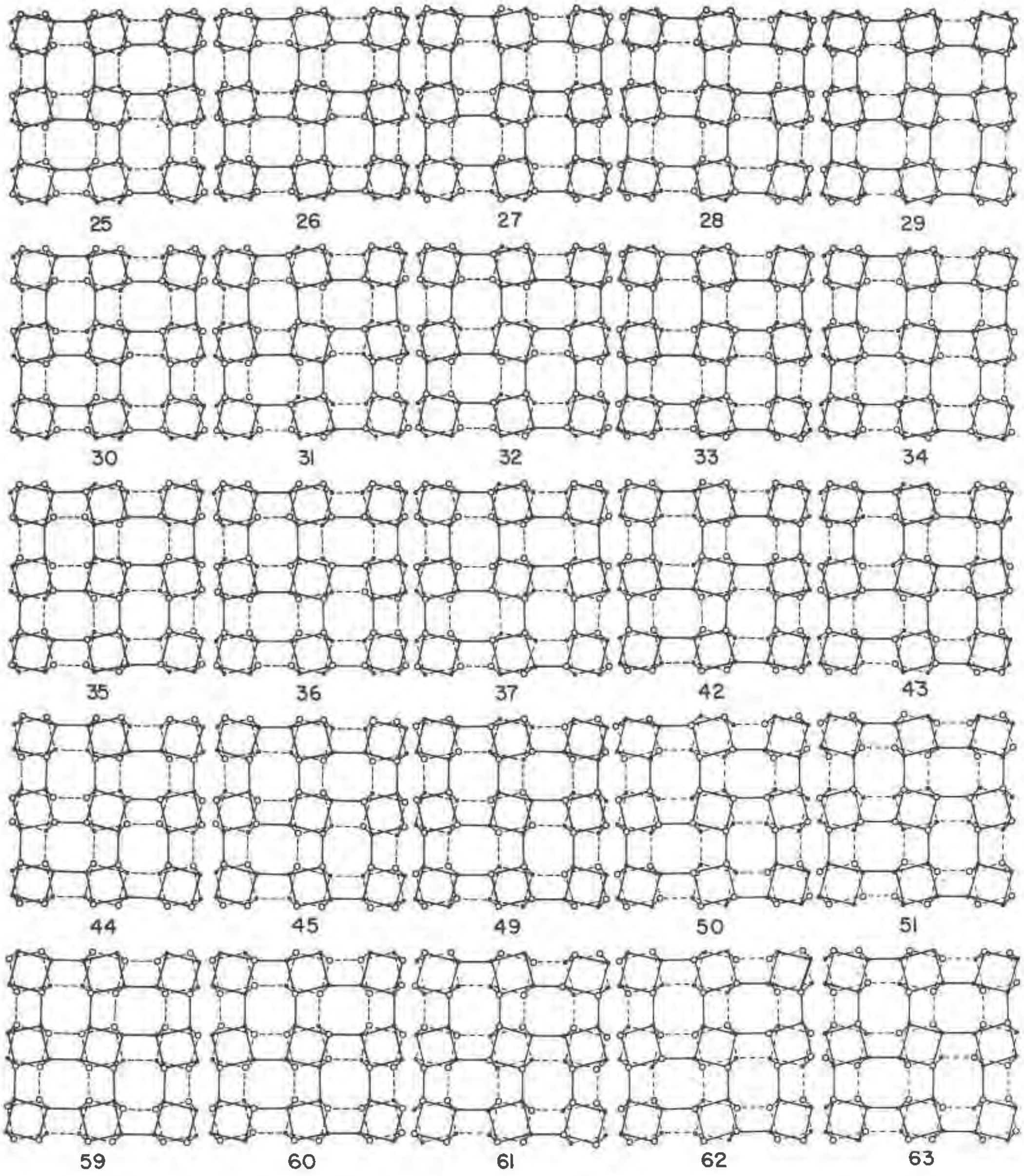

Fig. 3. Assignments of upward (dot) and downward (circle) branches to 4.8^2 2D net in "twisted" frameworks listed in Tables 2 and 3

$\dot{A}\dot{B}$ and $\dot{A}B\dot{C}$, respectively, and an infinite series of regular polytypes, such as $\dot{A}BA\dot{C}$, is possible.

Currently unknown among observed structures is net 81, which has the same cell geometry as gmelinite but a different space group. It also has a 1-dimensional channel system bounded by 12-rings, but access between adjacent channels is only by 6-rings instead of 8-rings in gmelinite. Instead of the *UUDD* chain in gmelinite, a *UDUD* chain occurs in net 81. There is no analog to chabazite, because the 4-rings can be linked to the 6-rings in only one way if the *CcCc* and *CcCcCc* sequences are to be preserved. Because the X-ray powder patterns for materials with gmelinite and net-81 structures would be quite similar, care should be taken with identification of powder patterns which index on a hexagonal cell with $a \sim 14$ and $c \sim 10$A. If possible, single-crystal data on the space group should be obtained, but systematic absences in a powder pattern might be sufficient.

Nets 84 and 85 have orthorhombic cells with the

Table 3. Simpler structures with 4.8^2 net and *UDUD*, *UUUD*, or *UUUU* linkages

Arbitrary number	Sequence(s) around 8-rings	Z_t	Schläfli symbols	Highest space group	Z_c	a	b	c
(a) untwisted UDUD								
38	ScScScSc	8	$4^26^28^2$	$P4_2/mmc$	8	7	-	~7.5
39	CcCcCcCc	8	4.6^5	I4/mcm	16	10	-	~7.5
40	ScCcScCc	8	$(4^26^28^2)_14.6^5)_1$	Cmmm	16	~7.5	14	7
41	ScScCcCc	32	$(4^26^28^2)_1(4.6^5)_1$	$P4_2/mmc$	32	14	14	~7.5
(b) twisted UDUD								
42	ScScScSc	8	$4.6^4.8$	$I\bar{4}2m$	16	9	-	~7.5
43	CcCcCcCc	16	$4.6^4.8$	Icma	32	9	15	9
44	ScCcScCc	16	$4.6^4.8$	Abma	32	13	13	~7.5
45	ScScCcCc	32	$4.6^4.8$	Pcc2	32	13	13	~7.5
(c) untwisted UUUU								
-	SsSsSsSs	double sheet						
46	CsCsCsCs	8	$4^3.8^3$	Im3m	16	10	-	-
47	CsCsSsSs	16	$(4^46^2)_1(4^38^3)_1$	Ammm	32	10	20	~9.5
48	CsSsCsSs	8	$(4^46^2)_1(4^38^210)_1$	Cmmm	16	~9.5	14	7
(d) twisted UUUU								
-	SsSsSsSs	double sheet						
49	CsCsCsCs	8	4^38^210	I422	16	8	-	~10.5
50	CsCsSsSs	32	complex	P422	32	12	-	~10.5
51	CsSsCsSs	16	$(4^36^28)_1(4^38^3)_1$	$P\bar{4}m2$	16	8	-	12
(e) untwisted UUUD								
52	CcScCsSs	8	complex	Pm2m	8	7	7	~8.5
53	CcCcSsSs	16	complex	$Pb2_1m$	16	10	10	~8.5
54	CcScSsCs	16	complex	P11m	16	10	10	~8.5*
55	SsCsScCc	16	complex	Cm2m	32	14	14	~8.5
56	ScCsScCs	16	complex	Pbmm	16	7	14	~8.5
57	CcCcCsCs	16	$(4^38^3)_1(4^26^38)_1$	Cmcm	32	14	14	~8.5
58	ScScSsSs	16	$(4^46^2)_1(4^36^28)_1$	Cmmm	32	14	14	~8.5
(f) twisted UUUD								
59	CcScCsSs; ScScSsSs	16	complex	B11m	32	~12.5	~12.5	8*
60	CcCcSsSs	16	complex	P1a1	16	9	9	8†
61	CcScSsCs	16	complex	$P112_1$	16	9	9	8*
62	CcCcCsCs; ScCcSsCs	16	complex	C121	32	~12.5	~12.5	8†
63	ScCsScCs	32	complex	Pba2	32	~12.5	~12.5	8
Observed structure								
43	banalsite	Haga (1973)		Icma		9.983	16.755	8.496

* γ~90° † β~90°

same dimensions but different space groups. Both have channels bounded by a 12-ring, but net 85 has channel walls bounded by 4- and 6-rings whereas net 84 has near-ellipsoidal 10-rings as windows between the main channels. In net 84, the 4-rings occur as cubes, and it might be worth looking for this net in products of syntheses from bulk compositions close to those which produce Linde Type A zeolite. In net 85, three-quarters of the 4-rings link together as *UUDD* chains while the other one-quarter cross-link

Table 4. Simpler frameworks with 3.12^2 net and (near)-perpendicular linkages

Number	Sequence in 12-ring	Sequence in 3-ring	Schläfli symbol	Z_t	Z_c	Space Group	a	b	c
			congruent nets						
-	SsSsSsSsSsSs	sss	double sheet						
64	CsCsCsCsCsCs	sss	$3.4^2.8^3$	12	12	$P6_3/mmc$	11	-	10
65*	CsCsCsCsCsCs	sss	$3.4^2.9^3$	6	6	R32	7	(α~75°)	
			some non-congruent nets						
66	SsCsCsSsCsCs	sss	$(3.4^3.6^2)_1(3.4^2.8.10^2)_2$	12	24	Immm	11	20	10
67	SsSsCsSsSsCs	sss	$(3.4^3.6^2)_2(3.4^2.12^3)_1$	12	24	Imcm	11	20	10
68	SsCsSsCsCsCs	sss	$(3.4^3.6^2)_1(3.4^2.8^2.12)_2$	24	48	Abam	20	22	10
69	SsSsSsCsSsCs	sss	$(3.4^3.6^2)_2(3.4^2.12^3)_1$	24	48	Amam	20	22	10
70	$SsSsCsCsCsCs_1$	sss	complex	24	48	Amam	11	40	10
71	$SsSsSsSsCsCs_1$	sss	complex	36	36	$P\bar{6}2m$	20	-	10
72	$SsSsSsSsCsCs_3$	sss	$(3.4^3.6^2)_2(3.4^2.8^2.10)_1$	72	72	Pbmm	20	34	10
73	SsSsSsSsSsSs SsCsCsSsCsCs	sss	complex	48	48	P6/mmm	22	-	10
74	ScSsScScSsSc	scc	$(3.4^2.6.7.8)_2(3.4.8^4)_1$	12	24	Cmmm	11	20	10
75	SsScCcSsScCc	scc	$(3.4^2.6^2.8)_2(3.6^3.8^2)_1$	12	24	Imam	11	20	10
76	CcCcCsCcCcCs	scc	$(3.4.6^3.7)_1(3.6^5)_2$	12	24	Cmcm	11	20	10
77	ScCsCcScCsCc	scc	$(3.4.5.6^2.7)_2(3.4.6^2.8^2)_1$	12	24	Immm	11	20	10
78	SsSsScScScSc	scc	$(3.4^2.5.6.7)_2(3.4.8^4)_1$	24	24	Pbmm	11	20	10
79	SsSsSsSsSsSs ScScScScScSc	scc	$(3.4^2.5.6.7)_2(3.4.8^4)_1$	36	36	P6/mmm	20	-	10
80	CcCcCcCcCcCc CsScCsScCsSc	scc	complex	36	36	P6/m	20	-	10
		Addendum:	new nets from 6^3 net.						
8a	$SSSSCC_3$		complex	24	24	Pbmm	10	16	8.5
8b	SSSSSS;SCCSCC		$(4^2.6^4)_3(6^3.8^3)_1$	16	16	P6/mmm	11	-	8.5

*for 12-ring distorted into triangular shape.

the chains. Net 86 can be constructed entirely by cross-linking cubes as for net 84, and the 6-rings are congruent. However, the 12-rings are of two types, one type pairing with another 12-ring to form a dodecahedral prism, while the other type is crown-shaped and linked by three 4-rings to another crown-shaped ring above and by three more 4-rings to one below. Net 86 has a remarkable channel system bounded by near-circular 12-rings perpendicular to the hexagonal axis and very elliptical 12-rings in three horizontal directions. Net 87, which has the same cell dimensions *and space group* as net 86, has a channel system bounded by a 12-ring in the hexagonal direction and 8-rings in the horizontal directions. It can be constructed from *UUDD* chains cross-linked through cubes. Alternatively it can be constructed from dodecahedral prisms cross-linked *via* cubes, as can net 86. Two further ways of cross-linking dodecahedral prisms and cubes are represented by nets 88 and 89, both of which contain *UUDD* chains.

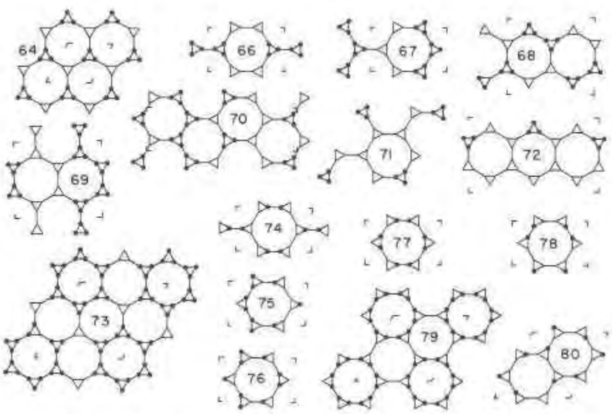

Fig. 4. Assignments of upward (dot) and downward (no dot) branches to 3.12^2 net in frameworks listed in Table 4.

Conclusion

Systematic enumeration of nets based on (near)-

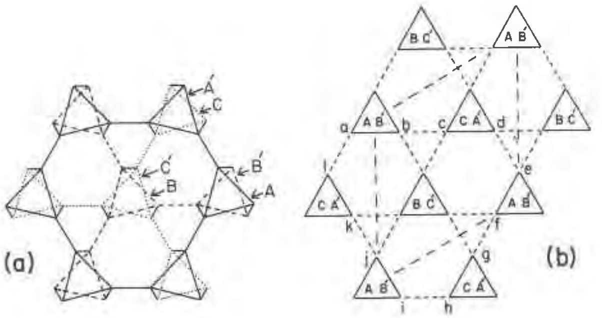

Fig. 5. Net 65 (Table 4). See text for explanation.

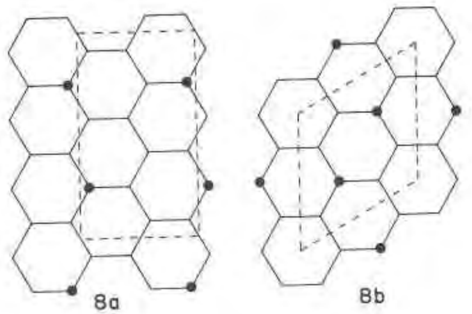

Fig. 6. Assignments of upward (dot) and downward (no dot) branches to nets 8a and 8b based on the 6^3 net.

perpendicular linkages from the 4.8^2 2D net reveals many possible 3D nets of which some of the simpler ones are represented by natural materials. Unfortunately feldspar has two types of nodes (see appendix), and several nets with congruent nodes are not represented so far by natural or synthetic materials. Hence it is not possible to adopt the psychologically appealing suggestion that only simple congruent nets would be represented by real chemical substances. The discovery that many nets have the same geometry of the unit cell, and that two of the nets even have the same space group (nets 86 and 87), provides a warning that theoretical frameworks should not be casually assigned to unknown structures merely on the basis of matching of cell dimensions or perhaps even of matching of symmetry. Finally it is necessary to reiterate that geometrical distortion of a net can lead to quite different cell dimensions and symmetry from

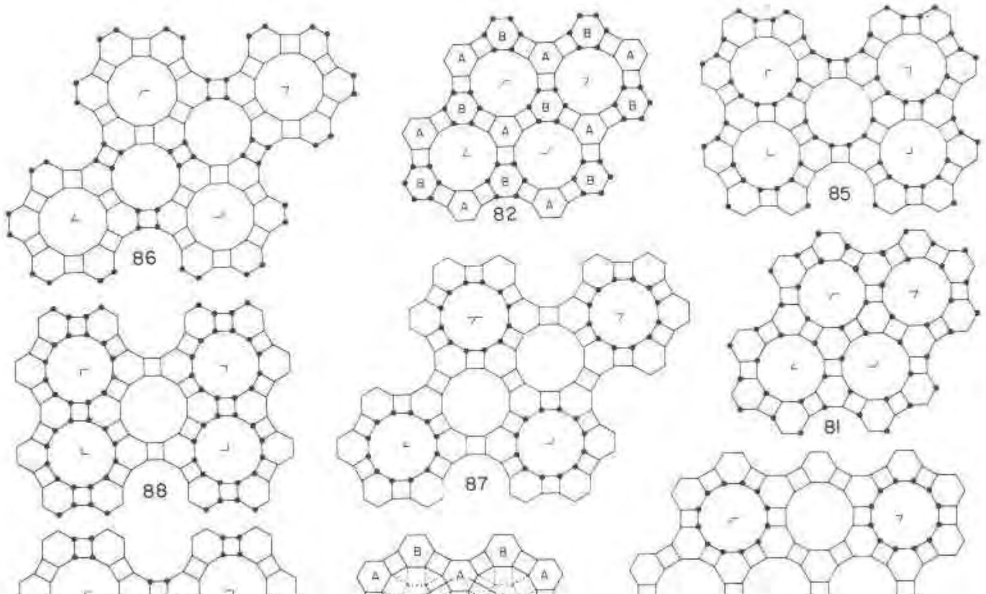

Fig. 7. Assignments of upward (dot) and downward (no dot) branches to 4.6.12 net in frameworks listed in Table 5. The symbols A, B, and C refer to different levels of the hexagonal prisms in nets 82 and 83.

Table 5. Simpler frameworks with 4.6.12 net and (near)-perpendicular linkages

Number	Sequence in 12-ring	Sequence in 6-ring	Sequence in 4-ring		Z_t	Z_c	Space Group	a	b	c
				congruent nets						
81	CcCcCcCcCcCc	CcCcCc	CcCc	4.6^5	24	24	P6/mcc	14	-	10
82	ScScScScScSc	SsSsSs	CsCs	$4^3.6^2.8$	24	24	$P6_3/mmc$	14	-	10
83	do.	do.	do.	$4^3.6^2.8$	12	12	$R\bar{3}m$	9	(α ~94°)	
-	SsSsSsSsSsSs	SsSsSs	SsSs	double sheet						
				some non-congruent nets						
84	CsCsSsCsCsSs	CsCsSs	SsSs	$(4^4.6^2)_1(4^3.6.8^2)_2$	24	48	Cmmm	14	24	10
85	CsSsSsCsSsSs	ScCcSc	ScSc	$(4^3.6^3)_2(4^2.6^3.8)_1$	24	48	Ccmm	14	24	10
86	SsSsSsSsSsSs CsCsCsCsCsCs	CsCsSs	SsSs	$(4^2.6^2)_1(4^3.6.8^2)_2$	72	72	P6/mmm	24	-	10
87	SsSsSsSsSsSs	ScSsSc	ScSc SsSs	complex	72	72	P6/mmm	24	-	10
88	SsSsSsSsSsSs	SsScSc	ScSc SsSs		24	48	Immm	14	24	10
89	SsSsSsSsSsSs	ScSsSc SsSsSs	ScSc SsSs		96	96	P6/mmm	28	-	10

Observed structures

Type	Name	Reference	Actual space group	a	b	c
82	gmelinite	Fischer (1966); Smith (1976)	$P6_3/mmc$	13.75	-	10.05
83	chabazite	Smith (1976)	$R\bar{3}m$?	9.4	(α ~94°)	

those listed in the tables, as is particularly displayed by the change of cell dimensions in varieties of chabazite (see papers listed in Smith, 1976).

Appendix

The Schläfli symbol can be defined in more than one way. A. F. Wells uses the six shortest circuits around each tetrahedral node. This leads to the same symbol for topologically-different nodes in some nets. Originally I used the shortest circuits which did not have a cross branch. Thus in Figure 8, I used the 7-element circuit *abcghij* rather than the 6-element circuit *abcfed* because the branch *eb* crossed the shorter circuit. There are two topologically different nodes in net 26 (feldspar), whose symbols are $4^2.6^3.8$ and $4^2.6^2.8.10$ in my definition, but are $4^2.6^3.8$ for both nodes in the Wells definition. Unfortunately some topologically-different nodes in complex nets have the same symbol even for my definition, and for simplicity I abandoned my definition in favor of the Wells definition. Only a much more complex symbol, perhaps involving a matrix of nodal separations, can yield a precise characterization of nets. Note that six nets in this paper have the symbol $4^2 6^3 8$ (Wells definition).

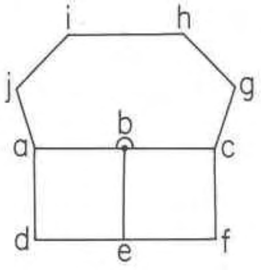

Fig. 8. Illustration of definition of Schläfli symbol. See text.

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