

intend to describe other methods of investigation of local and global geometrical/topological properties of M^3 and also to illustrate each of the suggested methods by examples of the crystal-chemical analysis of various classes of substances and some model systems.

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Uninodal 4-Connected 3D Nets. III. Nets with Three or Four 4-Rings at a Vertex

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Abstract

A description is given of 4-connected nets with one kind of vertex in which at least three of the shortest rings containing each pair of edges are 4-rings. 21 such nets are identified and characterized topologically. Some correspond to well known zeolite structures, but most are believed to be new.

Introduction

This paper continues a description and characterization of 4-connected nets with one kind of vertex (uninodal). Previous papers described nets without 4-rings or 3-rings (O'Keeffe & Brese, 1992) and with 3-rings (O'Keeffe, 1992). Only nets (realizable nets) that have a conformation with four equal edges corresponding to shortest distances between vertices are considered. The reader is referred to O'Keeffe & Brese (1992) for an account of how the nets were discovered, other criteria for inclusion,

Table 1. Correspondence of the numbering of nets in this paper (first column) with earlier names and numbers

The three-letter code is that of Meier & Olson (1992).				
44	#16	W*8	–	O'Keeffe (1991)
45	#13	D8	–	O'Keeffe (1991)
46	203	Faujasite	FAU	Smith & Bennett (1981)
47	202	Zeolite type A	LTA	Smith & Bennett (1981)
48	206	Zeolite rho	RHO	Smith & Bennett (1981)
49	83	Chabazite	CHA	Smith (1978)
50	205	Zeolite ZK5	KFI	Smith & Bennett (1981)
51	82	Gmelinite	GME	Smith (1978)
52	23	Gismondine	GIS	Smith (1978)
53	17	Merlinoite	MER	Smith (1978)
55	46	–	–	Smith (1978)
63	49	–	–	Smith (1978)

and for definitions of terms such as 'coordination sequence' and 'Schläfli symbol' that are used here. That paper also indicates why the data presented here are of interest and are expected to be reasonably complete. It might be noted that other recent enumerations of 4-connected nets (*e.g.* Han & Smith, 1994; Boisen, Gibbs

Table 2. Crystallographic data for nets with unit edges

Vertices are in general positions unless specified and the origin is chosen at a center in centrosymmetric structures. r is the number of vertices per unit volume and d_2 is the next-shortest distance.

Net	Space group	$a(b, c)$	x, y, z	r	d_2
44	$Im\bar{3}m$	$4 + 8^{1/2}$	$1/2a, (6 + 8^{1/2})/a, (6 + 32^{1/2})/a$	0.302	1.414
45	$I4_1/amd$	4, 4	$3/8, 7/8, 0$	0.500	1.414
46	$Fd\bar{3}m$	$20/(18^{1/2} - 3^{1/2})$	$(6^{1/2} - 1)/40, 1/8, 3/8 - 2x$	0.380	1.414
47	$Pm\bar{3}m$	$1 + 8^{1/2}$	$24(k), y = 2/(4 + 2^{1/2}), z = y/2$	0.428	1.414
48	$Im\bar{3}m$	$2 + 8^{1/2}$	$48(i), x = (2^{1/2} - 1)/4$	0.426	1.414
49	$R\bar{3}m$	4.429, 4.695	0.106, 0.441, 0.060	0.451	1.414
50	$Im\bar{3}m$	$2/3^{1/2} + 8^{1/2} + 2$	$1/2a, 1/4 - x/3^{1/2}, 2y - x$	0.448	1.414
51	$P6_3/mmc$	4.418, 3.149	0.333, 0.440, 0.091	0.451	1.414
52	$I4_1/amd$	$10/3, 80^{1/2}/3$	$16(g), x = 3/20$	0.483	1.414
53	$I4/mmm$	4.482, 3.312	0.112, 0.269, 0.151	0.481	1.414
54	$R\bar{3}m$	6.0, 2.475	0.238, 0.310, 0.136	0.446	1.211
55	$Im\bar{3}m$	$2 + 2/3^{1/2}$	$16(f), x = 3^{1/2}/(4 + 48^{1/2})$	0.510	1.414
56	$P6_222$	$3, 27^{1/2}/2$	$1/2, 1/3, 0$	0.596	1.225
57	$Cccm$	3.060, 2.545, 3.658	0.136, 0.110, 0.137	0.562	1.173
58	PA_2/mcm	2.781, 3.729	0.090, 0.347, 0.134	0.555	1.223
59	$I4_122$	1.950, 7.309	0.048, 0.25, 0.057	0.576	1.170
60	$P4_222$	1.982, 3.579	0.034, 0.25, 0.139	0.569	1.125
61	$P6_222$	$2, 3/(4 - 12^{1/2})$	$1/2, 1/4, 1/3^{1/2} - 1/2$	0.619	1.225
62	PA_2/nmm	2.795, 3.640	0.099, 0.154, 0.134	0.563	1.193
63	$I422$	2.984, 2.874	0.083, 0.222, 0.151	0.625	1.0
64	$P6_222$	$2, 3/(4 - 12^{1/2})$	$1/4, 0, (2 - 3^{1/2})/3$	0.619	1.225

& Bukowinski, 1994) have not identified any uninodal nets that are not in my catalog [although structures 11, 13 and 16 of the latter are based my #84 (O'Keeffe, 1995)].

In the earlier papers (O'Keeffe & Brese, 1992; O'Keeffe, 1992), an effort was made to match the nets with features of known crystal structures. Two omissions in the second paper are noted here: (a) in cubic metaboric acid, HBO_2 (Zachariasen, 1963), the B atoms correspond to the vertices of net #37 (with —O— links corresponding to edges); (b) net #38 is found as the Ni arrangement in heazlewoodite, Ni_3S_2 (Parise, 1980).

Uninodal nets with more than four 4-rings meeting at a vertex cannot be constructed, but it should be mentioned that 4^6 vertices do exist in nets with more than one kind of vertex. Thus, the net of the four nearest neighbors of each atom in sulvanite, Cu_3VS_4 (Trojer, 1966), has vertices 4^28^4 (Cu), 4^6 (V) and 4^36^3 (S). Here, nets with either four or three 4-rings meeting at a vertex are considered. There remain 38 uninodal nets with two 4-rings at each vertex and 26 uninodal nets with just one 4-ring at each vertex.

Descriptions of nets

Some of the nets have been described before, and indeed some are familiar as the nets of the framework of natural or synthetic zeolites. Table 1 identifies such nets and provides a concordance with previous catalogs. Table 2 gives crystallographic data for the nets in their maximum-symmetry conformations and with unit edges. Where these constraints do not uniquely determine the coordinates of the vertices, the conformation reported is one of maximum volume. Table 3 lists the sequence of topological neighbors (the coordination sequence) for the first ten shells and Table 4 gives the 'short' and 'long'

Table 3. Numbers of k th neighbors, n_k , for nets ($n_1 = 4$ in every case)

The net numbering is the same as in Table 2. ρ_{10} is the cumulative sum of $n_i/1000$ (O'Keeffe & Brese, 1992).

Net	n_2	n_3	n_4	n_5	n_6	n_7	n_8	n_9	n_{10}	ρ_{10}
44	8	13	20	29	41	56	73	93	116	0.453
45	8	13	21	34	52	71	90	115	147	0.555
46	9	16	25	37	53	73	96	120	145	0.578
47	9	17	28	42	60	81	105	132	162	0.640
48	9	17	28	42	60	81	105	132	162	0.640
49	9	17	29	45	64	85	110	140	173	0.676
50	9	17	29	45	64	86	112	141	173	0.680
51	9	17	29	45	65	89	116	144	175	0.693
52	9	18	32	48	67	92	120	150	185	0.725
53	9	18	32	49	69	93	121	153	189	0.737
54	9	18	31	49	73	99	129	165	203	0.780
55	9	19	35	52	72	100	131	163	201	0.786
56	9	18	31	49	75	101	129	165	205	0.786
57	9	18	34	56	82	112	147	187	231	0.880
58	9	18	33	54	81	113	149	189	233	0.883
59	9	18	36	60	86	117	153	194	240	0.917
60	9	18	36	61	89	122	160	203	252	0.954
61	9	18	34	56	84	118	159	210	265	0.957
62	9	18	35	59	89	127	169	213	265	0.988
63	9	19	39	64	97	136	171	217	271	1.027
64	9	18	36	59	89	131	180	238	304	1.068

Schläfli symbols and ring statistics. Note that the nets have only been checked for the existence of rings up to 18-rings, and that, as an N -ring is shared by N vertices, the number of rings per vertex may be obtained by dividing the numbers in the table by N . All uninodal nets that I have discovered with two or more 4-rings meeting at a vertex contain only even rings. This is not necessarily the case for nets with more than one kind of vertex; for example, the net of the coesite structure, which has two 4-rings at each of the two kinds of vertex, contains 9-rings.

Nets with four 4-rings at a vertex. Only two uninodal nets (numbers 44 and 45) with four 4-rings meeting at a

Table 4. Long and short Schläfli symbols and ring counts (N_i) in netsThe net numbering is the same as in Table 2. Z_i is the number of vertices in the topological repeat unit.

Net	Z_i	Short	Long	N_4	N_6	N_8	N_{10}	N_{12}	N_{14}	N_{16}	N_{18}	N_{24}
44	48	$4^4.6^2$	4.4.4.8.4.12	4	3	1	5	1	0	0	0	3
45	16	$4^4.6^2$	4.4.4.12.4.12	4	3	0	0	3	0	0	0	—
46	48	$4^3.6^3$	4.4.4.6.6.12	3	2	4	0	9	0	0	0	—
47	24	$4^3.6^2.8$	4.6.4.6.4.8	3	5	1	0	8	0	0	42	—
48	24	$4^3.6^3$	4.4.4.6.8.8	3	1	2	10	0	0	0	42	—
49	12	$4^3.6^2.8$	4.4.4.8.6.8	3	1	6	0	1	0	0	0	—
50	48	$4^3.6^2.8$	4.4.4.8.6.8	3	1	6	0	0	14	0	21	—
51	24	$4^3.6^2.8$	4.4.4.8.6.8	3	1	6	0	7	0	0	0	—
52	8	$4^3.6^2.8$	4.4.4.8 ₂ .8.8	3	0	4	0	0	0	0	0	—
53	16	$4^3.6^2.8$	4.4.4.8 ₂ .8.8	3	0	4	10	0	14	0	0	—
54	12	$4^3.6^2.8$	4.4.4.8 ₆ .8 ₃ .8 ₃	3	0	18	0	2	21	4	0	—
55	8	$4^3.6^2.8$	4.8 ₂ .4.8 ₂ .4.8 ₂	3	3	6	15	0	0	0	0	—
56	12	$4^3.6^2.8$	4.4.4.8 ₆ .8 ₃ .8 ₃	3	0	18	0	0	168	0	0	—
57	8	$4^3.6^2.8$	4.4.4.8.8.10 ₂	3	0	2	10	54	0	0	0	—
58	16	$4^3.6^2.8$	4.4.4.8 ₂ .8.12 ₈	3	0	3	5	24	140	0	0	—
59	8	$4^3.6^2.8$	4.4.4.10 ₂₀ .10 ₆ .10 ₁₂	3	0	0	50	0	0	0	0	—
60	8	$4^3.6^2.8$	4.4.4.10 ₁₈ .10 ₆ .10 ₁₂	3	0	0	50	72	0	0	0	—
61	12	$4^3.6^2.8$	4.4.4.8.8.10 ₂	3	0	2	10	48	0	0	0	—
62	8	$4^3.6^2.8$	4.4.4.8.10 ₄ .10 ₁₂	3	0	1	40	48	0	0	0	—
63	8	$4^3.8^2.10$	4.8.4.8.4.10 ₁₂	3	3	2	50	40	0	0	0	—
64	12	$4^3.6^2.8$	4.4.4.10 ₂₄ .10 ₄ .10 ₁₀	3	0	0	50	0	0	0	0	—

vertex have been found. These have been described and illustrated before (O'Keeffe, 1991). Net 44 is the least dense uninodal net without 3-rings. If the edge length were 3.05 Å (appropriate for Si—Si distances in a silicate framework), the framework density would be

10.6 vertices per 1000 Å³; this appears to be close to the minimum for a framework silicate (Hyde, 1994). This net is also one of only two [the other is net 26 (O'Keeffe, 1992)] containing 24-rings. Accordingly, it is conjectured that 24-rings are the largest possible in realizable uninodal nets.

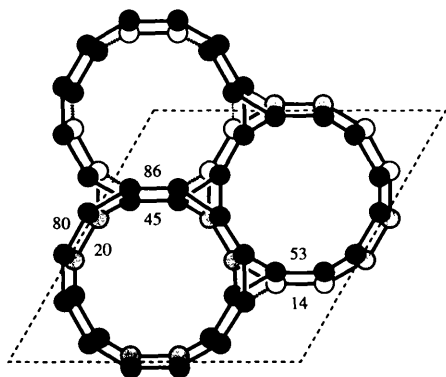


Fig. 1. Net 54 projected on (001). Numbers represent elevations in multiples of $c/100$. Almost vertical edges (e.g. from vertices at elevation 45–86) are not shown.

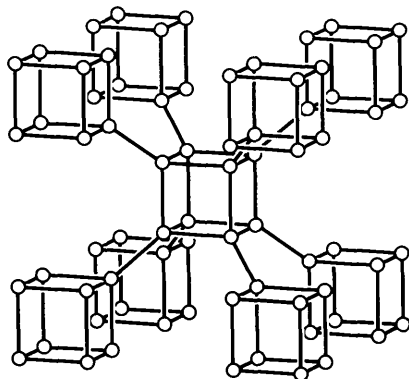


Fig. 2. Net 55 in clinographic projection.

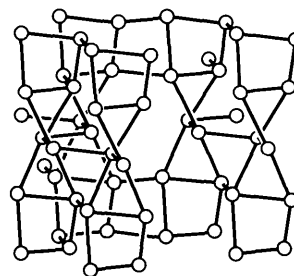


Fig. 3. Net 56 in clinographic projection. c is vertical on the page.

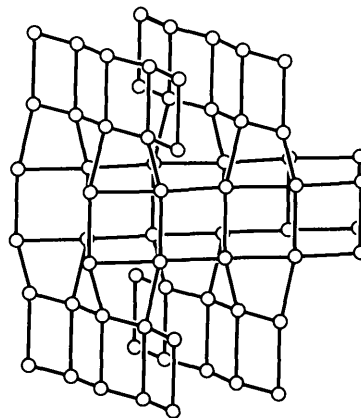


Fig. 4. Net 57 in clinographic projection. c is vertical on the page.

Nets with three 4-rings at each vertex. Nets with three 4-rings meeting at a vertex include the frameworks of

some well known zeolite structures (numbers 46–53, Table 1). Attention is called to the fact that two of them (47 and 48) have identical coordination sequences but are differentiated by the long Schläfli symbol. The remaining nets do not appear to have been found in crystal structures so far, but 55 and 63 were described by Smith (1978); the others I have not found described elsewhere. Net 63 is only included because it is in Smith's (1978) catalog; in its maximum-volume form, it is 5-connected corresponding to square antiprisms linked by additional edges to form a body-centered array (compare no. 55, which is comprised of cubes similarly linked).

Of the new nets, no. 54 (Fig. 1) stands by itself in apparently not being related to other nets. Net 55 (Fig. 2) has been suggested as the structure of a possible metastable form of carbon ('polycubane'), but this

appears unlikely to be the case (Johnston & Hoffmann, 1989).

The remaining nets, nos. 55–62 and 64, form a new and closely knit family characterized by ladders (rods of quadrangles sharing opposite faces) running in two or three directions and linked together by skew quadrangles. They are illustrated in Figs. 3–9. The number of closely related possibilities with just one kind of vertex illustrates how daunting would be the task of system-

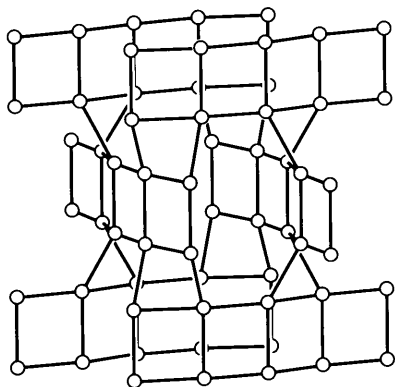


Fig. 5. Net 58 in clinographic projection. *c* is vertical on the page.

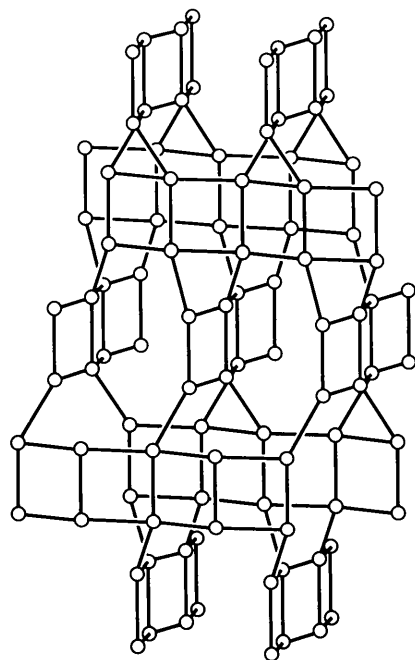


Fig. 6. Net 59 in clinographic projection. *c* is vertical on the page.

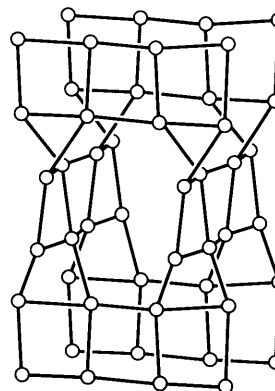


Fig. 7. Net 60 in clinographic projection. *c* is vertical on the page.

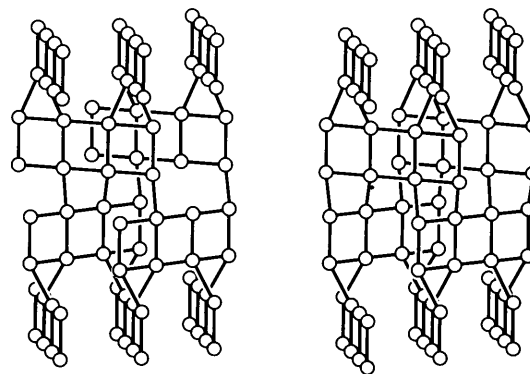


Fig. 8. Nets 61 (left) and 64 in clinographic projection. *c* is vertical on the page.

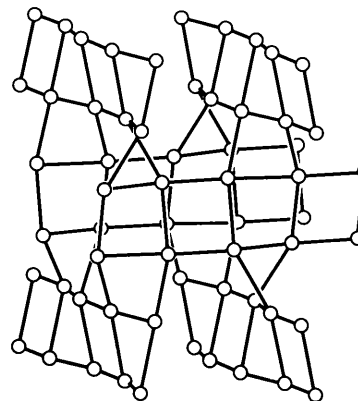


Fig. 9. Net 62 in clinographic projection. *c* is vertical on the page.

atically enumerating nets of this type. Nets 61 and 64 (Fig. 8) provide a nice example of a pair of nets with the same space group and unit-cell dimensions.

In some of these nets, the skew quadrangles approach regular tetrahedra; if the tetrahedra were indeed regular, the nets would become 5-connected and have higher symmetry and higher density. This is perhaps most easily seen for net 60 (Fig. 7). With regular tetrahedra, the symmetry would be $P4_2/mmc$ with $a = 2$, $c = 2 + 2^{1/2}$ and vertices in 8 (o) $0, y, z$ with $y = 1/4$ and $z = 0.1465$. The density is 3% higher. In the conformation listed in Table 2, however, the next shortest distance (d_2 in Table 2) is *ca* 20% longer.

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Dynamical Approach for X-ray Diffraction from Surfaces and Interfaces: Interpretation of Crystal Truncation Rod Using Dynamical Theory

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Abstract

X-ray diffraction from crystal surfaces and interfaces is described within the framework of the dynamical theory. The intensity distributions of specular and non-specular crystal truncation rods are interpreted with this dynamical approach. Difficulties encountered in the ordinary dynamical calculation for these rods are mentioned and the details of the numerical calculation procedure which overcomes the difficulties are given. The coordinates of dispersion surface, linear absorption coefficients and mode excitations of surface diffractions are calculated and the validity of this dynamical approach is discussed.

1. Introduction

Grazing-incidence X-ray diffraction (GIXD) from crystal surfaces and interfaces has been widely used for determining surface crystal structures since 1979 (Marra, Eisenberger & Cho, 1979). These include the structures of Si (111) 7×7 (Robinson, Waskiewicz, Fuoss, Stark & Johnson, 1986), Ge (111) $c 2 \times 8$ (Feidenhans'l *et al.*, 1988), As/Si (100) (Jedrecy *et al.*, 1990), Pb/Si (111) (Grey, Feidenhans'l, Nielsen & Johnson, 1989) and many others (Robinson & Tweet, 1992; Shimura &

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Harada, 1993). Although a crystal surface is a two-dimensional arrangement of atoms, its relative position with respect to the crystal bulk involves the third dimension along the crystal surface normal. To probe this three-dimensional structure, in-plane scan and surface-normal scan are usually employed to gather the structural information parallel and perpendicular to the crystal surface, respectively. The latter, surface-normal scan, is sometimes called crystal-truncation-rod (CTR) scan in the literature (Andrews & Cowley, 1986; Robinson, 1986) because the scan is along the reciprocal rods which are the Fourier transform of a surface-truncated crystal in the reciprocal space (Fig. 1). This CTR scan is also a powerful tool to help solve interface structures on the atomic scale, for example, the structures of NiSi₂/Si (111) (Robinson, Tung & Feidenhans'l, 1988), Si/Si (111) (Robinson, Waskiewicz, Tung & Bohr, 1986) and SiO₂/Si (111) (Kashiwagura *et al.*, 1987). Aside from the crystal structure determination, GIXD together with *in situ* experimental techniques also provides a means of studying surface order-disorder, melting and roughening transitions (Mochrie, Zehner, Ocko & Gibbs, 1990; Held, Jordan-Sweet, Horn, Mak & Feldman, 1989; Dosch, Mailander, Reichert, Peisl &