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The Topology of Three-Dimensional 4-Connected Nets: Classification of Zeolite Framework Types Using Coordination Sequences

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Coordination sequences provide a practical numerical scale for expressing the degree of similarity of three-dimensional 4-connected nets found in zeolite structures when weighted mean values are used for topologically heterogeneous nets. Values of coordination sequences limited to 5 terms have been determined for nearly all of the known zeolite framework types. They are shown to be useful for classifying zeolite frameworks on purely topological grounds and also for finding the maximum possible space group symmetry in more difficult cases.

Introduction

The tetrahedral frameworks of zeolite structures consist of 4-coordinated T-atoms (usually Si and Al) and bridging oxygen atoms. With at least 38 firmly established structure types (which are topologically distinct per definitionem) and a near-infinite number of hypothetical framework types, the zeolites provide a sizeable number of representative examples of 4-connected nets which by their nature are also geometrically permissible.

Zeolite frameworks can be thought to consist of finite or infinite (i.e. chain- or sheet-like) component units. The existing classification is essentially based on secondary building units (*1, 2*). These are finite units which have been derived under the assumption that the entire framework is built of *one* kind of units only. The secondary building units containing up to 16 T-atoms, which have been found to occur repeatedly in various types of known zeolite frameworks, are shown in Fig. 1. Many of the frameworks can be generated from several different secondary building units. In addition to these, crystallographic as well as chemical criteria are then more or less consciously used to define a family of structures which is not entirely satisfactory in view of the *topological* nature of the structure type concept.

Criteria and notations akin to Schläfli-symbols for polyhedra, which have been developed and applied extensively by Wells in studies of three-dimensional nets (cf. *3*), have not so far been used to any appreciable extent for characterizing zeolite-type nets. This seems understandable in view of the relative complexities of most of these nets. It must be noted here that the nets occurring in zeolites are generally non-uniform, i.e. the shortest circuits (rings of T-atoms) from any point or T-atom are not all equal n-gons whereas the connectedness is invariably 4.

A topological concept, which is readily applicable to zeolite-type nets and has so far been largely overlooked, is that of coordina-

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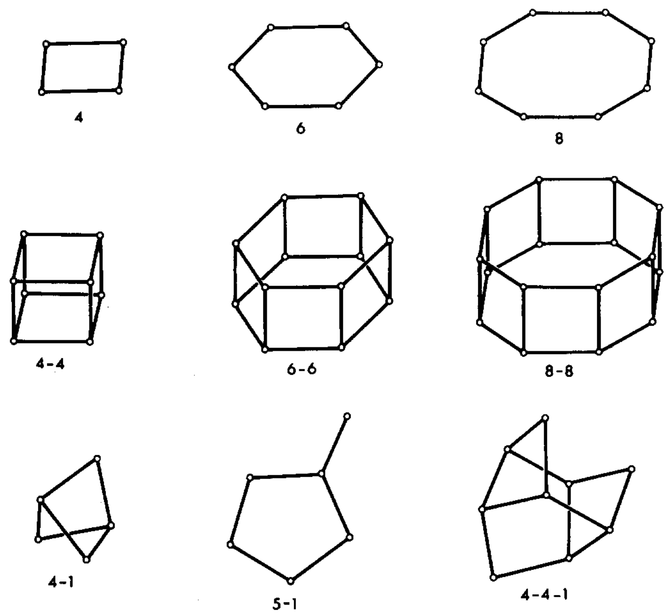

FIG. 1. Secondary building units in zeolite frameworks.

tion sequences (CSQ) or "Wachstumsreihen" as first described by Brunner and Laves (*4*). The same concept was, under the name "Kaskadenfolgen," subsequently introduced by Fischer (*5*) as a criterion in his derivation of homogeneous sphere-packings pertaining to cubic lattice complexes. In the present work CSQ are primarily investigated with a view to broadening the basis for the topological classification of non-uniform 4-connected nets as represented by zeolite frameworks.

Coordination Sequences of the Established Zeolite Structure types

The concept of CSQ is illustrated by way of the two-dimensional 3-connected and homogeneous net shown in Fig. 2. In this example an arbitrarily chosen atom (or point) A is connected to $N_1 = 3$ atoms B. These neighboring atoms are then linked to N_2 additional atoms C lying further out. The translational symmetry of the net is reflected in the sequence of numbers $\{N_k\}$, i.e. the CSQ thus defined, which becomes evident when the differences of successive N_k-values in the example are considered.

It can readily be seen that for an n-connected net

$$N_k \leq n(n-1)^{k-1}.$$

The maximum values of $\{N_k\}$ for the 4-connected nets of T-atoms in zeolite structures (e.g.) are thus

4 12 36 108 324 . . .

Small rings in the structure lower these values substantially. The CSQ for each T-atom in a zeolite structure depend only on the topology of the framework, but not on the actual symmetry, cell dimensions and other structural data. Topologically equivalent T-atoms yield identical CSQ. A necessary condition which is applicable to any two nets or subsets of points of a net, and which is quite useful, is the following: If $\{N_k\}_a \neq \{N_k\}_b$ then a and b are topologically non-equivalent.

In many zeolite framework types the T-atoms are topologically equivalent (homo-

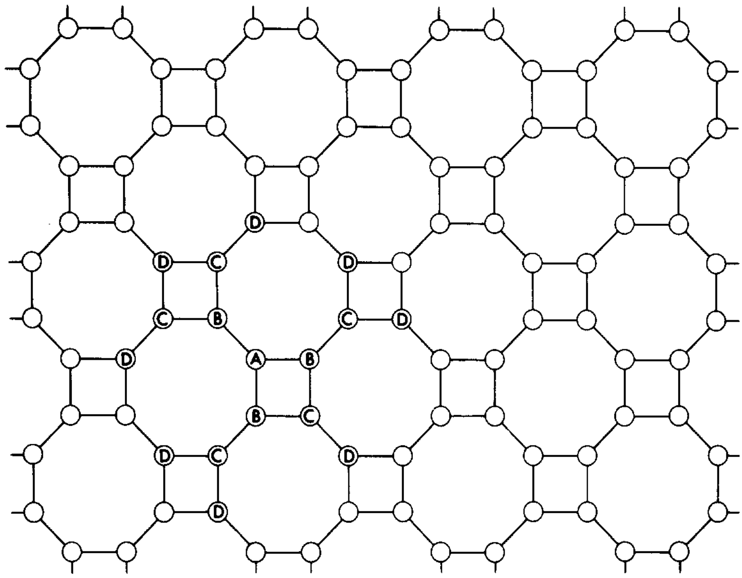

FIG. 2. Coordination sequence for a two-dimensional homogeneous net as an example:

$\{N_k\}$	3	5	8	11	13	16	19	21	...
$\{N_k - N_{k-1}\}$	2	3	3	2	3	3	2		...

geneous nets). In others, there are as many as 12 topologically distinct T-atoms (heterogeneous nets) as shown in Table I. In addition to the values of Q, the number of topologically distinct points, Table I also contains the maximum (topological) symmetries and the type designations of the presently known zeolite networks. Illustrations of these can be found in recent surveys on zeolite structures (*2, 6*). Topologically heterogeneous nets can be assigned weighted mean values $\{\bar{N}_k\}$, the weights being given by the respective number of T-sites per unit cell.

Values of $\{N_k\}$ up to $k = 5$ were determined for all topologically homogeneous and a representative number of heterogeneous zeolite nets. This was done for the most part with the aid of a special computer program in which all the T-sites within a sphere of 14 Å radius around the reference site (encompassing all points up to $k = 5$) were examined using essentially crystallographic criteria. Determinations of N_k-values above N_5 become very time-consuming and the respective results tend to be rather prone to errors unless extraordinary precautions are taken. For the present purposes, CSQ limited to $k \leq 5$ appeared in general to be quite adequate, however. The results are given in Tables II and III.

The values of $\{N_k\}$ for the various T-sites in a particular heterogeneous net do not differ appreciably as a rule as can be seen from Table II. All the zeolite-type nets considered in this work have been listed in Table III in ascending order of $\{\bar{N}_k\}$. It is noteworthy that the spectrum of $\{\bar{N}_k\}$ is almost continuous. Some recognizable gaps (indicated in Table III) occur, however, signifying different families of structure types as is evident from the secondary building units as well as other considerations based on models. Closely related framework structures invariably yield very similar CSQ. For four pairs of closely related frameworks, RHO/LTA,[1] KFI/GME, ERI/OFF and MER/PHI, even a complete match of $\{\bar{N}_k\}$ up to $k = 5$ is observed. In these instances the

[1] For full type names see Table I.

TABLE I

ZEOLITE STRUCTURE TYPES, WITH NUMBER OF TOPOLOGICALLY INEQUIVALENT T-ATOMS (Q) AND MAXIMUM TOPOLOGICAL SPACE GROUP SYMMETRY (TSG)

Type code	Full name	Q	TSG [b]	Type code	Full name	Q	TSG [b]
ABW	Li-A(BW)[a]	1	$Imam$	LEV	Levyne	2	$R\bar{3}m$
AFG	Afghanite	3	$P6_3/mmc$	LIO	Liottite	4	$P\bar{6}m2$
ANA	Analcime	1	$Ia3d$	LOS	Losod[a]	2	$P6_3/mmc$
BIK	Bikitaite	2	$Cmcm$	LTA	Linde Type A[a]	1	$Pm3m$
BRE	Brewsterite	4	$P2_1/m$	LTL	Linde Type L[a]	2	$P6/mmm$
CAN	Cancrinite	1	$P6_3/mmc$	MAZ	Mazzite	2	$P6_3/mmc$
CHA	Chabazite	1	$R\bar{3}m$	MER	Merlinoite	1	$I4/mmm$
DAC	Dachiardite	4	$C2/m$	MFI	ZSM-5[a]	12	$Pnma$
EDI	Edingtonite	2	$P\bar{4}2_1m$	MOR	Mordenite	4	$Cmcm$
EPI	Epistilbite	3	$C2/m$	NAT	Natrolite	2	$I4_1/amd$
ERI	Erionite	2	$P6_3/mmc$	OFF	Offretite	2	$P\bar{6}m2$
FAU	Faujasite	1	$Fd3m$	PAU	Paulingite	8	$Im3m$
FER	Ferrierite	4	$Immm$	PHI	Phillipsite	2	$Cmcm$
GIS	Gismondine	1	$I4_1/amd$	RHO	Rho[a]	1	$Im3m$
GME	Gmelinite	1	$P6_3/mmc$	SOD	Sodalite	1	$I\bar{4}3m$
HEU	Heulandite	5	$C2/m$	STI	Stilbite	4	$Fmmm$
KFI	ZK-5[a]	1	$Im3m$	THO	Thomsonite	3	$Pmma$
LAU	Laumontite	3	$A2/m$	YUG	Yugawaralite	2	$C2/m$

[a] No known natural representative of this structure type (synthetic species only).

[b] Non-standard settings have been chosen for some space groups to facilitate comparison with observed space group symmetry (subgroup relationships).

structural differences lie primarily in the stacking of larger blocks associated with changes in translational symmetry, and it seems likely that some higher terms in $\{\bar{N}_k\}$ will differ at least slightly.

Illustrative examples demonstrating the usefulness of CSQ for classifying zeolite framework types are BRE and MAZ. BRE clearly belongs to the heulandite–stilbite family of structure types (*1*) which is in full agreement with the CSQ whereas on the basis of secondary building units alone this is by no means apparent. Similarly MAZ has very little in common with the mordenite family of structure types, as the secondary building units would indicate, but is obviously more closely related to the frameworks with similar CSQ.

The lower terms of $\{\bar{N}_k\}$ in particular are indicative of the relative abundance of small rings. None of the known zeolite framework types contain any 3-membered rings. $\bar{N}_2$ is less than 12 (the maximum value) when 4-membered rings are present. FER and BIK, for both of which $\bar{N}_2 = 12$, contain no 4-membered rings, whereas for THO, EDI and NAT at the head of Table III (having the lowest $\bar{N}_2$ values) the relative number of 4-membered rings reaches a maximum. Moreover, $\bar{N}_3$ for the latter framework types is comparatively high because there are only 4- and 8- but no 5- or 6-membered rings in these structures.

A comparison of $\{\bar{N}_k\}$ with the number of T-atoms per 1000 Å^3 in Table III shows that denser structures generally lead to higher N_k-values. This applies in particular to higher terms of $\{\bar{N}_k\}$ which could be used to define a "topological density" for the following reasons. The number of points in a fixed volume is essentially a density. The volume V_k is that of a

TABLE II

COORDINATION SEQUENCES IN ZEOLITE FRAMEWORKS WITH TOPOLOGICALLY NON-EQUIVALENT T-SITES

Structure type	Number of T-sites/unit cell	N_1	N_2	N_3	N_4	N_5	Structure type	Number of T-sites/unit cell	N_1	N_2	N_3	N_4	N_5
THO	4	4	8	18	34	50	BRE	4	4	10	20	37	61
	8	4	9	19	33	50		4	4	11	23	37	54
	8	4	9	19	35	52		4	4	11	18	37	62
EDI	2	4	8	18	32	52	YUG	8	4	10	22	39	61
	8	4	9	19	35	52		8	4	11	22	39	61
NAT	4	4	8	18	36	56	HEU	8	4	10	19	37	58
	16	4	9	19	35	52		8	4	10	20	34	62
PHI	16	4	9	18	32	48		8	4	11	21	35	61
	16	4	9	18	32	50		8	4	11	23	39	55
OFF	12	4	9	17	30	50		4	4	12	18	34	62
	6	4	10	20	32	46	EPI	8	4	11	24	42	63
ERI	24	4	9	17	30	50		8	4	12	20	39	66
	12	4	10	20	32	46		8	4	12	22	37	64
LTL	24	4	9	17	29	46	MOR	8	4	11	24	39	54
	12	4	10	21	35	49		8	4	11	24	39	60
LAU	8	4	10	19	32	52		16	4	12	20	37	64
	8	4	10	19	33	53		16	4	12	22	38	60
	8	4	10	20	33	51	DAC	4	4	11	24	39	63
LOS	12	4	10	20	34	52		4	4	11	24	41	59
	12	4	10	20	34	54		8	4	12	20	37	63
MAZ	24	4	10	20	35	55		8	4	12	22	39	65
	12	4	10	21	36	53	FER	8	4	12	20	35	67
STI	16	4	9	17	35	57		16	4	12	21	39	66
	32	4	10	20	34	57		4	4	12	23	40	66
	16	4	11	20	36	57		8	4	12	27	43	62
	8	4	12	18	34	58	BIK	8	4	12	23	43	71
BRE	4	4	10	20	36	61		4	4	12	26	42	66

shell containing the points N_k. In metric terms the relative fluctuations of the shell volumes V_k of various nets decrease with increasing k and, more importantly, the shells corresponding to higher N_k's comprise an increasingly representative sample of the net.

Further properties and characteristics of CSQ have been investigated for tetrahedral framework structures by Brunner (*7*). It should also be mentioned that $\{\bar{N}_k\}$ can at least qualitatively be related to radial distribution (*8*) and pair distribution functions (*9*).

Maximum Topological Symmetry

CSQ can be a potential aid for establishing the maximum topological symmetry of a net. In the great majority of cases the actual space group symmetry of zeolite framework structures is considerably lower than the topological symmetry **G** because of geometrical constraints, chemical requirements and other reasons. The observed or apparent space group **A** is generally a subgroup of **G** but the determination of the latter can nevertheless be fairly difficult. The higher symmetry corresponding to **G** is

TABLE III

CLASSIFICATION OF ZEOLITE FRAMEWORKS ACCORDING TO COORDINATION SEQUENCES $\{\bar{N}_k\}$

Structure type	$\bar{N}_1$	$\bar{N}_2$	$\bar{N}_3$	$\bar{N}_4$	$\bar{N}_5$	Secondary building units[b]							Observed number of T-atoms/ 1000 Å^3
THO	4	8.80	18.80	34.00	50.80							4-1	14.4[c]
EDI	4	8.80	18.80	34.40	52.00							4-1	14.5[c]
NAT	4	8.80	18.80	35.20	52.80							4-1	14.5[c]
FAU[a]	4	9	16	25	37	4	6			6-6			12.7
RHO[a]	4	9	17	28	42	4	6	8			8-8		12.9
LTA[a]	4	9	17	28	42	4	6	8	4-4				14.6
CHA[a]	4	9	17	29	43	4	6			6-6			14.3
KFI[a]	4	9	17	29	45	4	6	8		6-6			14.6
GME[a]	4	9	17	29	45	4	6	8		6-6			14.7
GIS[a]	4	9	18	32	48	4		8					14.7[c]
MER[a]	4	9	18	32	49	4		8			8-8		16.0
PHI	4	9.00	18.00	32.00	49.00	4		8					15.8
OFF	4	9.33	18.00	30.67	48.67		6						15.5
ERI	4	9.33	18.00	30.67	48.67	4	6						15.6
LTL	4	9.33	18.33	31.00	47.00		6						16.4
LAU	4	10.00	19.33	32.67	52.00		6						17.7
SOD[a]	4	10	20	34	52		6						17.2
LOS	4	10.00	20.00	34.00	53.00		6						15.8
CAN[a]	4	10	20	34	54	4	6						16.7
MAZ	4	10.00	20.33	35.33	54.33	4						5-1	16.1
ANA[a]	4	10	20	39	60	4	6						18.6
ABW[a]	4	10	21	36	54	4	6	8					19.0
STI	4	10.22	19.11	34.67	57.11							4-4-1	16.9
BRE	4	10.50	20.25	36.75	59.50	4							17.5
YUG	4	10.50	22.00	39.00	61.00	4		8					18.3
HEU	4	10.67	20.44	36.00	59.33							4-4-1	17.0
EPI	4	11.67	22.00	39.33	64.33							5-1	18.0
MOR	4	11.67	22.00	38.00	60.33							5-1	17.2
DAC	4	11.67	22.00	38.67	63.00							5-1	17.3
FER	4	12.00	22.33	39.11	65.33							5-1	17.7
BIK	4	12.00	24.00	42.67	69.33							5-1	20.2

[a] homogeneous nets, [b] shown in Fig. 1, [c] in expanded state.

frequently by no means evident from a set of refined coordinates nor from a model both of which are usually subject to geometrical requirements. As an example, the relevant data for bikitaite (*10*) given in Table IV show how the CSQ can help to recognize the topological equivalence of points and hence the maximum symmetry **G**. The CSQ in this example indicate that T_1 and T_2 could be topologically equivalent, and T_3 would therefore mark a special position. A simple

TABLE IV

REPORTED POSITIONS OF T-ATOMS IN BIKITAITE BASED ON SPACE GROUP $P2_1$

	Atomic coordinates[a]			N_1	N_2	N_3	N_4	N_5
T_1	0.096	0.104	0.865	4	12	23	43	71
T_2	0.508	0.106	0.800	4	12	23	43	71
T_3	0.937	0.381	0.874	4	12	26	42	66

[a] rounded-off values taken from (*10*) and changed to first setting.

model will then show that T_3 could possibly have point symmetry $mm2$ which leads to orthorhombic symmetry and space group Cmcm with

$$T_{1,2} \text{ in } 8g(m)\ x, y, \tfrac{1}{4}; \bar{x}, y, \tfrac{1}{4}$$

$$T_3 \text{ in } 4c(mm)\ 0, y, \tfrac{1}{4}$$

for a model of the net having maximum topological symmetry. (Note also the changes in origin and axial system which represent a further common difficulty.)

The possible applications of the maximum topological symmetry are manifold. The subgroup relation $\mathbf{A} \subset \mathbf{G}$ is a useful basis for elucidating possible twinning operations. In the present context, **G** can of course provide an easy proof that certain T-atoms are topologically equivalent simply by showing that they are crystallographically equivalent with respect to operations of **G**.

Conclusions

The concept of CSQ has proved very useful in this study as it broadens the basis for classifying zeolite structure types on purely topological grounds. The values of $\{\bar{N}_k\}$, which are generally calculable by computer, provide a numerical scale for evaluating the degree of similarity among members of these 4-connected nets. Perhaps not so much importance should be attached to recognizable gaps in the $\{\bar{N}_k\}$ values for the various frameworks although they give indication of different families of structure types.

CSQ are also a potential aid in determining the maximum topological space group symmetry, a basic characteristic of a net, the usefulness of which is frequently overlooked. CSQ have several properties which help to characterize the various 4-connected nets and thus merit further investigations.

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