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The Reticular Chemistry Structure Resource (RCSR) Database of, and Symbols for, Crystal Nets

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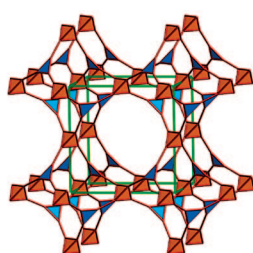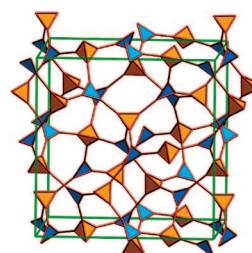
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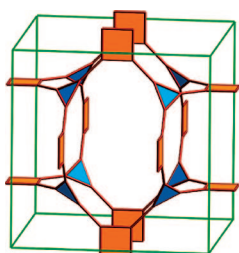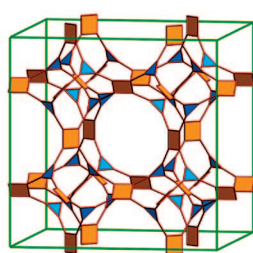
pto-a   tbo-a   bor-a   ctn-a

During the past decade, interest has grown tremendously in the design and synthesis of crystalline materials constructed from molecular clusters linked by extended groups of atoms. Most notable are metal−organic frameworks (MOFs), in which polyatomic inorganic metal-containing clusters are joined by polytopic linkers. (Although these materials are sometimes referred to as coordination polymers, we prefer to differentiate them, because MOFs are based on strong linkages that yield robust frameworks.) The realization that MOFs could be designed and synthesized in a rational way from molecular building blocks led to the emergence of a discipline that we call *reticular chemistry*.

MOFs can be represented as a special kind of graph called a periodic net. Such descriptions date back to the earliest crystallographic studies but have become much more common recently because thousands of new structures and hundreds of underlying nets have been reported. In the simplest cases (e.g., the structure of diamond), the atoms in the crystal become the vertices of the net, and bonds are the links (edges) that connect them. In the case of MOFs, polyatomic groups act as the vertices and edges of the net.

Because of the explosive growth in this area, a need has arisen for a universal system of nomenclature, classification, identification, and retrieval of these topological structures. We have developed a system of symbols for the identification of three periodic nets of interest, and this system is now in wide use. In this Account, we explain the underlying methodology of assigning symbols and describe the Reticular Chemistry Structure Resource (RCSR), in which about 1600 such nets are collected and illustrated in a database that can be searched by symbol, name, keywords, and attributes. The resource also contains searchable data for polyhedra and layers.

The database entries come from systematic enumerations or from known chemical compounds or both. In the latter case, references to occurrences are provided. We describe some crystallographic, topological, and other attributes of nets and explain how they are reported in the database. We also describe how the database can be used as a tool for the design and structural analysis of new materials. Associated with each net is a natural tiling, which is a natural partition of space into space-filling tiles. The database allows export of data that can be used to analyze and illustrate such tilings.

Introduction

Since the earliest days of crystallography crystal structures have been described in terms of *nets* in which atoms are the vertices and the bonds are the links (*edges*) between them. The interest in nets developed particularly with the study of coordination polymers beginning some 75 years ago. In coordination polymers typically a transition metal (M) ion is linked by a polytopic coordinating ligand such as bipyridine (bpy) to form salts such as $M(bpy)_2Cl_2$ with a charged continuous periodic framework $M(bpy)_2$. The underlying topology of the structure is described by a periodic net in which atoms are again the vertices, but now the edges correspond to the linkers joining the two edges. Considerable effort, most notably by A. F. Wells,[1] has been devoted to describing the structures of such nets.

The past decade has seen an explosive increase in synthesis and characterization of crystalline materials with frameworks in which building blocks are joined by covalent bonds. Most notable are *metal—organic frameworks* (MOFs) in which typically polyatomic inorganic metal-containing clusters are linked by polytopic linkers. In the archetypical MOF, MOF-5, OZn_4 cationic clusters are linked by the benzene dicarboxylate (bdc) anion to form a continuous cubic neutral framework of composition $Zn_4O(bdc)_3$.[2] Such materials are sometimes referred to also as coordination polymers; however, we prefer to differentiate them because MOFs are based on strong (typically metal—oxide) linkages, which result in robust frameworks. In the present context, the important point is that the underlying topology of a MOF framework is likewise that of a net, now with vertices as well as edges corresponding to clusters of atoms; thousands of new MOFs and hundreds of previously unreported nets have been described.

The realization that MOFs particularly could be designed and synthesized in a rational way from molecular building blocks[3] led to the emergence of a discipline that we term *reticular chemistry*.[4] Central to that discipline is the hypothesis that there are a relatively small number of *default* nets for a given choice of geometry of molecular building units.[5] Analysis of the existing data for MOFs has confirmed this hypothesis.[6] However, there has been no generally agreed system of nomenclature of nets or a systematic descriptive catalog of their structures. In this Account, we describe our efforts in this regard and describe a database designed to facilitate reticular chemistry. This last is called the *Reticular Chemistry Structure Resource* (RCSR).

Periodic nets are a special kind of graph, and some of the methods of graph theory are relevant to their description.[7]

Unfortunately many terms used by chemists have quite different meanings in graph theory and other areas of geometry; here we use the terms in the sense generally understood by chemists. Readers unfamiliar with these aspects might refer to the reference cited.[7]

Symbols for Nets

In the matter of names or symbols for nets, there is an unfortunate proliferation. A ubiquitous three-connected net is variously known as "Laves net", "(10,3)*a*", "*Y**", "3/10/c1", "K_4 crystal. "labyrinth graph of the *G* surface", and "$SrSi_2$ net". We have developed a set of symbols, which we call RCSR symbols, modeled on those used to specify a zeolite framework type.[8] Thus the framework of the zeolite known as sodalite has the zeolite code **SOD**. This is an important four-connected net that arises in many contexts in crystal chemistry and elsewhere, and we assign it the RCSR symbol **sod** (lower case, bold). Other common four-connected nets are those of diamond and the framework of the quartz form of silica. These are assigned symbols **dia** and **qtz**, respectively. The symbol for the three-connected net referred to at the beginning of the paragraph is **srs**. There are two cases where zeolite codes and RCSR symbols have different letters. The net of the zeolite framework **BCT** has RCSR symbol **crb** (it is the B net in CrB_4); **bct** refers to the 10-connected body-centered tetragonal lattice. The net of zeolite framework **ABW** has RCSR symbol **sra** (it is the Al net in $SrAl_2$). Every structure in RCSR has a unique symbol but, as explained below, may have an "other symbol" that is useful to facilitate searches and to call attention to structural relationships.
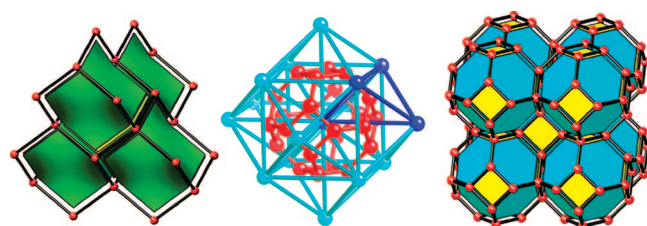
Simple common nets like **dia** (Figure 1) give rise to derived nets, and it is convenient and informative to signify that by one or more extensions to the basic symbol. Specifically, the following extensions are defined:

- **a** refers to the *augmented* net in which the vertices of the original net are replaced by a group of vertices with the shape of the original coordination figure of the vertex.[5] Thus **dia-a** refers to the net obtained by replacing the original vertices of the **dia** net by a tetrahedron of vertices; see Figure 1.
- **b** refers to the *binary* version of a net with just one kind of vertex (*uninodal*). For example, the binary version of diamond is sphalerite, ZnS (Figure 1). The main reason for making the distinction is that the symmetry of the binary version ($F\bar{4}3m$) is lower than that ($Fd\bar{3}m$) of the parent structure, and this knowledge is helpful to those not familiar with deriving subgroups of space groups.
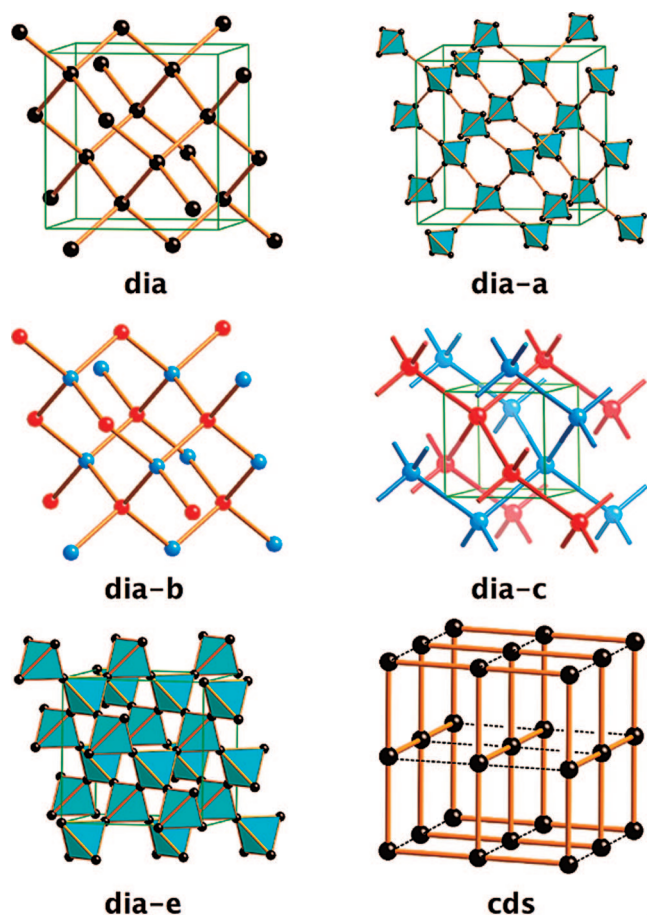
FIGURE 1. The diamond (**dia**) net, some derived nets described in the text, and the **cds** net. In this last, the broken lines indicate distances equal to edge lengths.

FIGURE 2. Part of the diamond (**dia**) net (left) showing natural tiles, which are generalized polyhedra with 10 vertices arranged as in an adamantane cage. In the center, blue spheres and bonds are part of the 14-coordinated extended body-centered cubic (**bcu-x**) net. The outline of one tetrahedron is shown in darker blue. Red spheres center the tetrahedra and are vertices of the dual structure. The right structure is the sodalite net (**sod**) and its natural tiles (truncated octahedra).

- **c** refers to *catenated* nets. **dia-c** is the structure with two interpenetrating but otherwise independent **dia** nets (Figure 1). The reason for making this distinction is that now the pair of nets often has a higher symmetry that is not always obvious (**dia** has symmetry $Fd\bar{3}m$; **dia-c** has symmetry $Pn\bar{3}m$). An elaboration of this idea is to extensions **-c***n* where $n > 2$ indicates that there are n separate interpenetrating nets.
- **d** refers to the *dual* net. For most nets, we can determine a *natural tiling*.[9] The dual of that tiling (see below) carries a net that for shorthand we call the dual net. Some nets have natural tilings that are self-dual. This is the case for the diamond net, so **dia-d** = **dia**.
- **e** refers to the *edge* net. This is obtained by putting new vertices in the middle of the edges of the old net. For a four-connected net such as **dia** or a zeolite net with vertices in tetrahedral coordination, the edge net is a six-connected net formed by a framework of corner-sharing tetrahedra, with the new edges of the net corresponding to the edges of the tetrahedra; see Figure 1. The nets of zeo-

lites are the four-connected nets of the tetrahedral vertices (*T*) with *T-X-T* groups acting as links (*X* is the anion usually an O atom). The net of the *X* atoms is the six-connected edge net of the zeolite net. Thus the net of sodalite anions is **sod-e**.
- **x** refers to *extended* coordination. For example, the net **bcu** is the net defined by links to the eight nearest neighbors of vertices that are at the nodes of a body-centered cubic lattice. Sometimes one wants to consider that structure as 14-connected (first and second neighbors), and then the symbol is **bcu-x**. We remark that **sod-d** = **bcu-x** (see Figure 2).
- **f**, **g**, etc. refer to nets derived from a parent by replacing a vertex by a group of vertices (*decorating*). For example in **dia-j** each vertex is replaced by a cuboctahedron of vertices. This is used sparingly. Notice that the letters of the extension in this instance have no special significance other than to indicate that the net is derived by decoration of a parent net.

Extensions can be repeated or combined as in **sod-a-a** or **dia-a-c**. Symbols with extensions may be "other symbols", thus **dia-e** is an "other symbol" for the net with symbol **crs**. "Other symbols" are useful in searching the database; thus a search for **sod-d** will lead to **bcu-x**. Like symbols themselves, "other symbols" belong to a unique net.

Tilings for Nets

For most nets, there is a unique *natural tiling* in which space is divided into an array of generalized polyhedra.[9] The vertices and edges of the tiling are exactly those of the net (we say that a tiling *carries* a net), and the faces of the tiles are the *essential rings* of the structure. Figure 2 illustrates the natural tiling for the diamond (**dia**), sodalite (**sod**), and extended body-centered cubic (**bcu-x**) nets.

Every tiling has a dual tiling with its associated net. The dual tiling is obtained from the original by placing a new vertex inside the original tiles and joining them by new edges through the tile faces to new vertices inside tiles sharing those faces. The definition is completed by noting that the dual of a dual is the original tiling. The connectivity of a vertex in the new net is equal to the number of faces of the tile of the original net. In particular, a tiling by tetrahedra has a dual in which four tiles meet at a vertex, three at an edge and two at a face. Such structures (*simple tilings*) are particularly important in materials chemistry as they act as the frameworks of clathrates and other important zeolites. We note here that the tiling for **dia** is self-dual and that the tiling for **bcu-x** (a tiling by tetrahedra) and that for **sod** (a simple tiling) are a mutually dual pair.

The RCSR Database

The RCSR database at http://rcsr.anu.edu.au is hosted by the Supercomputer Facility at the Australian National University, Canberra, and is modeled in part after the *Atlas of Zeolite Structure Types*.[8] At time of writing its main part contains data for about 1600 nets. About half of these are nets of uninodal *sphere packings*. By this, we mean that the vertices are all related by symmetry (the net is *vertex transitive* or *uninodal*), and there is an embedding (a realization with unit cell parameters and vertex coordinates) in which all edges are equal in length and are the shortest distances between vertices. The diamond net is the net of a four-connected sphere packing, as are many of the common nets of importance in crystal chemistry. The principle source of data for sphere packings is the work carried out initially by W. Fischer and later with his collaborators E. Koch and H. Sowa. Their enumeration of uninodal sphere packings is complete for cubic,[10] hexagonal,[11] tetragonal,[12] and triclinic[13] symmetries and partly completed for orthorhombic symmetry.[14] Other orthorhombic and monoclinic sphere packings in RCSR have come from the work of V. A. Blatov.[15]

Another group of nets important for reticular chemistry is that with two kinds of vertex (*binodal*) but one kind of edge (*edge transitive*). These have been systematically enumerated and entered into RCSR.[16]

Many four-connected nets come from known crystal structures such as those of zeolites, forms of silica (coesite, keatite, etc.) and framework silicates (feldspar, etc.), and various polymorphs of ice (ice IV, etc.). Nets with other coordination come from other crystal structures. For example (3,6)-connected nets are those of rutile, anatase, etc. Many nets come from new MOFs and related materials. There are no definite criteria for inclusion, but generally preference is for simple (not many different kinds of vertex) high-symmetry structures. An exception to this rule is in nets derived from packing polyhedra. The most complex structure in the database (**rug**) is derived from a packing of just one topological kind of polyhedron. It is triclinic and has 24 different kinds of vertex.

Symmetry, Embeddings, and Topological Properties

Virtually all the nets of interest in crystal chemistry have a combinatorial symmetry that is isomorphic with a space group symmetry, and generally a good embedding is possible with that symmetry although there are exceptions.[17] We recognize several different types of embeddability.[18] The most important is type 1, for which the nets serve as the nets of sphere packings. For such structures, in which the requirement that all edges are equal is insufficient to fix unit cell edges and vertex coordinates, the embedding chosen is that of minimum density subject to the constraint of equal edges. Usually, but not always,[19] this is also a configuration of maximum symmetry.

Surprisingly many nets of relevance to crystal chemistry belong to embeddability type 2. For structures of this type, edges are all equal and are shortest intervertex distances, but there are other equal intervertex distances that do not correspond to edges. The net **cds** (so symbolized because it is the underlying four-connected net in $CdSO_4$) is perhaps the most familiar example; see Figure 1.

There are also nets in which there is no embedding with equal edges; **bcu-x**, mentioned above, is an example (see Figure 2). These are assigned other embeddability types.[18] The RCSR site has an "about" link, which gives details of these.

A typical page of the database is shown in Figure 3. For the chosen embedding, the database gives the space group, unit cell parameters, density (number of vertices per unit volume), and coordinates and site symmetry of all the vertices. The coordinates and site symmetries of the centers of each kind of edge are also reported. Clicking on the thumbnail picture (top left) gives a larger illustration.

A net can be considered a periodic surface of genus *g* if one imagines the edges inflated to finite size. For a net with *v* vertices and *e* edges in the primitive cell $g = 1 + e - v$.[7] For nets with all vertices of the same coordination number, *z*, $g = 1 + (z - 1)v$, so the genus is a measure of the number of vertices in the repeat unit. Accordingly, the genus can be helpful in searching for nets of a certain complexity.

For each vertex, the first ten terms in the *coordination sequence*[20] are given. The *k* term of the coordination
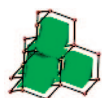
dia

names: diamond, D, 4/6/c1
key words: regular net, uniform net, isohedral tiling, self dual net, quasisimple tiling, good
references: Acta Cryst. A59, 22-27 (2003), Acta Cryst. A60, 517-520 (2004)

embed type	space group	volume	density	genus	td10
1a	Fd-3m	12.3168	0.6495	3	981

unit cell:

a	b	c	alpha	beta	gamma
2.3094	2.3094	2.3094	90.0	90.0	90.0

vertices: 1

vertex	cn	x	y	z	symbolic	Wyckoff	symmetry	order
V1	4	0.125	0.125	0.125	1/8, 1/8, 1/8	8 a	-43m	24

vertex	cs_1	cs_2	cs_3	cs_4	cs_5	cs_6	cs_7	cs_8	cs_9	cs_{10}	cum_{10}	vertex symbol
V1	4	12	24	42	64	92	124	162	204	252	981	6(2).6(2).6(2).6(2).6(2).6(2)

edges: 1

edge	x	y	z	symbolic	Wyckoff	symmetry
E1	0.0	0.0	0.0	0, 0, 0	16 c	-3m

tiling:

tiling	dual	vertices	edges	faces	tiles	D-symbol
[6^4]	dia	1	1	1	1	2

Export 3dt input: dia.cgd

occurrences: [show|hide]

FIGURE 3. The **dia** page from the RCSR.

sequence is the number of vertices separated from the reference vertex by a shortest path of exactly *k* edges. It is a convenient, but unfortunately not unique, fingerprint that can help in identification of a net. A well-known example of a pair of nets with identical sequences is **rho** and **lta** (the nets of zeolites with framework code **RHO** and **LTA**, respectively); there are many others.

For nets with coordination number ≤6, the *vertex symbol*[20] is also given. Vertex symbols come in several flavors. The one given is sometimes called the "long symbol" and records the size and number of shortest rings at each angle. The uninitiated should be aware that as well as different kinds of vertex symbol, there is a plethora of names, such as *point symbol* and *Schläfli symbol,* in use. The vertex symbols used in RCSR are the same as those reported in the *Atlas of Zeolite Framework Types.*[7,21]

Additional Information

As can be seen in Figure 3, in addition to data for the embedding of the net, names are given, and the database can be searched by name. The names for **dia** are "diamond", "D" (it is the *D* lattice complex[22]) and "4/6/c1". The last is the *Fischer symbol*, which is of the form *n/m/zi* for an *n*-coordinated sphere packing in which the shortest ring is an *m*-ring; *z* is a

letter indicating the crystal system (e.g., *c* for cubic, *h* for hexagonal), and *i* is a serial number.[10−14]

References are provided to papers where the properties of the net are discussed. This reference does not necessarily refer to occurrences in crystal structures. Known occurrences as MOFs and related materials in the Cambridge Structural Database (CSD) are given as the CSD letter codes[23] by clicking on "occurrences" at the bottom of the page (see Figure 3).

Also reported are data for the natural tiling of the net.[9] The *signature* of the tiling is the record of face symbols for the tiles. The *face symbol* of a tile in turn is of the form $[M^m.N^n...]$ which indicates that the tile has *m* faces with *M* sides, *n* faces with *N* sides, etc. The tile for the diamond (**dia**) structure (Figure 2) has four six-sided faces and face symbol $[6^4]$.

The numbers of kinds of vertex (*p*), edge (*q*), face (*r*), and tile (*s*), combine to give the *transitivity pqrs*, which is used as a measure of the "regularity" of the net.[24] The five nets with transitivity 1111 (**dia** is one) are called *regular* nets.[25]

Tiles can be subdivided into tetrahedral *chambers* whose vertices are the center of the tile, a vertex, the center of an incident edge, and the center of an incident face. The "D-symbol size" (D-symbol is short for Delaney−Dress symbol[26]) is a measure of the complexity of the tiling and is the number of different (unrelated by symmetry) kinds of chamber. A tiling by cubes with net **pcu** is the only tiling with D-size = 1 (and thus the only *regular tiling*). At the place where these data are reported, one can export a file in a format (coordinates of vertices in faces) that can be read by 3dt; 3dt is a tiling analysis and drawing program written by Olaf Delgado-Friedrichs, and a platform-independent Java version is now available.[27]

Searching the Database

From the home page of RCSR, clicking the link "nets" leads directly to a search page. Here one can search by symbol or by name (or partial name). Note that the database recognizes names that do not appear to the user. For example **dia** is also retrieved using the name "cristobalite" because **dia** is the net of the cristobalite form of silica.

Search can also be made by *keyword*. These are all explained at the Web site via a pop-up associated with each term. We give just a few examples here. *Semiregular nets* are those, other than the regular and quasiregular nets,[25] with one kind of vertex and one kind of edge.[28] *Simple tilings* were defined above. As far as the database is concerned, a *clathrate* structure is a simple tiling by polyhedra with faces that are only four-, five-, or six-sided. A *good* structure in the RCSR context is one either that has high point symmetry (order greater than eight) at the vertices, or in which the shortest nonedge

distance is 1.4 times the edge length. This often acts as a useful filter to reduce the number of structures retrieved in a search to those more likely to be of interest in crystal chemistry. A *rod net* is one in which edges are collinear in one or more directions (so the vertices lie on rods). These are of interest in the design and synthesis of structures based on infinite secondary building units (SBUs).[29]

Finally one can search by attributes such as symmetry, coordination number, and number of different kinds of edge and vertex. These are mainly rather obvious and all explained in popups associated with each term. These all have numerical values (symmetry search is by space group number) and can be searched in a range specified by lower and upper bounds. "td10" is the sum of the first ten terms in the coordination sequence (with, by generally but not universally, agreed convention, an additional one added for the vertex itself) and is a widely used measure of topological density. As illustrated below, a useful way of retrieving nets of relevance to design of potential targets for synthesis is to search for nets with small numbers of kinds of vertex and edge.

It should be noted that the search is AND, so adding more search terms will narrow the field.

Layers and Polyhedra

The database also contains small sections of data (coordinates etc.) for layers (33 entries) and polyhedra (47 entries). The "about" link at the Web site should be consulted on how to use these data. The data for polyhedra are particularly useful for making illustrations using crystal-drawing programs. Layers and polyhedra have unique symbols similar to those for nets. Thus **cub** is the symbol for the cube and **oct** is the symbol for the regular octahedron; **cub-d** (the dual) is an "other symbol" for **oct**, and **cub-a** is the truncated cube with symbol **tcu**. Notice that augmentation is the same as truncation in the case of polyhedra. The reticular chemistry of metal−organic polyhedra (MOPs) has recently been reviewed.[30]

Applications

There are several ways the resource can be used.

a. Information about a Known Topology. Often when a new material is prepared the structure is deconstructed and the underlying topology is determined; we use the freely available computer programs Systre[17,27] and TOPOS.[31] If the topology is known to RCSR, the properties of the net, occurrences, references, tiling data, etc. can be found. Systre is the only program that we know of that produces a signature of a net that is mathematically proven to be unique. It is there-

fore the only program that can say *with certainty* that two nets with different embeddings are the same. With a few pathological exceptions,[32] Systre knows all RCSR nets and can identify them with certainty; conversely, if Systre says a net is new, it is not in RCSR. We do not know at present of two different nets that have identical vertex symbols and coordination sequences, but there are examples (**ana-a** is one) of binodal nets whose distinct vertices do have identical vertex symbols and coordination sequences (out to 50 coordination shells at least).

b. Assistance in Crystal Design.[4] It may be desirable to link SBUs of a given shape (e.g., square, octahedral) by polytopic linkers, again with a given underlying shape. The simplest target topologies are the *default* structures with the minimum number of kinds of vertices and links.[5] For example, one might want to have four-coordinated groups and three-coordinated groups linked together. Searching for nets that have the keyword *heterocoord 34* and two kinds of vertex and one kind of edge yields the four nets **bor**, **ctn**, **pto**, and **tbo**. Examining the augmented nets **bor-a**, **ctn-a**, **pto-a**, and **tbo-a** (illustrated on the title page) shows that the first two correspond to tetrahedral coordination for the four-connected vertex and the second two have planar (square) coordination for that vertex.

c. Identification of Phases. In a recent study in which three-connected and tetrahedral four-connected SBUs were linked, the products had X-ray powder patterns with large cubic unit cells.[33] Modeling crystals with the **bor** and **ctn** nets [see section b above] clearly showed that these were the nets of the observed structures. If this had not been the case, the search could have been extended to other (3,4)-connected nets. This approach should be generally useful when only powder diffraction data are available for materials with large unit cells.

d. As a Source of Information about Three-Periodic Structures in General. For example, in addition to such topics as regular and semiregular nets alluded to above, one can find such things as 18 natural tilings with D-symbol size ≤4 (this is thought to be a complete list), 9 uninodal simple tilings (a complete list), 21 uninodal zeolite nets, 30 binodal zeolite nets, and 28 uniform tilings (a complete list). The last are vertex-transitive (uninodal) tilings of space in which the tiles are all vertex-transitive polyhedra; they all play a prominent role in crystal chemistry. Notice that only for very special symmetrical structures can one realistically claim completeness; the number of, for example, four-connected nets is infinite.

Implementation

The RCSR Web site is written (by S.J.R.) in the web framework "Ruby on Rails" (http://www.rubyonrails.org/). Authored in the "Ruby" language, it incorporates a MySQL database (http://www.mysql.org/) back end with the Object Relational Mapper (ORM) and Model-View-Controller (MVC) paradigms of Rails. Each RCSR structure is given its own homepage and a unique url, to go with its RCSR name. Updates to the database from the moderators, either for new structures or for new information fields, are largely automated, allowing the database to grow as more structures and information about them become available.

Other Databases of Nets

There are other and larger databases of nets. EPINET[34] is an ongoing project in which three-periodic nets are generated by projecting the nets of tilings of the hyperbolic plane onto periodic surfaces in Euclidian space. It currently contains 15 000 nets and is planned to expand greatly in the near future. The database of hypothetical zeolite structures[35] is limited to four-connected nets that would be feasible zeolite nets. It contains over 100 000 unique topologies. The computer package TOPOS[31] is designed to deconstruct crystal structures and determine their underlying topologies. It also analyses the found nets (e.g., determines coordination sequences and vertex symbols). It has a large (66 000 entries) built-in database of nets including all entries in RCSR and EPINET.

BIOGRAPHICAL INFORMATION

Michael O'Keeffe was born in 1934 in Bury St Edmunds, England. He received B.Sc. in chemistry (1954), Ph.D. (1958), and D.Sc. (1976) degrees from the University of Bristol where he studied with Professor F. Stone. In 1963, he joined Arizona State University where is now Regents' Professor of Chemistry. His recent research is devoted particularly to the theory of three-periodic structures relevant to development of a taxonomy of such structures and its application to materials design and description.

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