CRYSTAL GROWTH & DESIGN

COMMUNICATION

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Crystal Engineering Using a "Turtlebug" Algorithm: A *de Novo* Approach to the Design of Binodal Metal−Organic Frameworks

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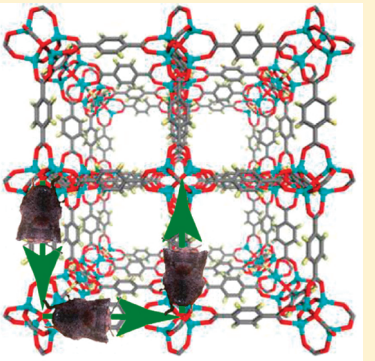
Supporting Information

ABSTRACT: A new series of computer programs that enumerate three-dimensional periodic embedded nets (i.e., representing crystals) is based on an algorithm that can theoretically enumerate all possible structures for all possible periodic topologies. Unlike extant programs, this algorithm employs algebraic and combinatorial machinery developed during the 1980s in combinatorial and geometric group theory and ancillary fields. This algorithm was validated by a demonstration program that found all strictly binodal periodic edge-transitive 3,4-, 3,6-, 4,4-, and 4,6-coordinated nets listed in the RCSR database. These programs could be used in two ways: to suggest new ways for targeting known nets, and to provide blueprints for new chemically feasible nets. They rely on a discrete version of "turtle geometry" adapted for these nets.



INTRODUCTION

The increasingly rapid development of metal organic frameworks (MOFs) or porous coordination polymers (PCPs) over the past two decades has attracted considerable attention from both academic and industrial researchers because they offer unprecedented levels of permanent porosity and exceptional opportunities for design of materials from the molecule up.[1a−n,2a−2k] Furthermore, their chemical and structural diversity offers the possibility of combining porosity with other important properties, such as magnetism, luminescence, semiconductivity, and catalytic activity.[1f−h,m,p−u] The fact that MOFs are amenabled *prior* to design distinguishes them from most other classes of materials and is a consequence of the geometry of their chemical building blocks which manifests itself in the topology of the resulting crystal structures.[3a−g]

"Design" implies a blueprint or some other formal description developed prior to and in fact directing synthesis of the crystal in mind.[2c,d] In this communication, we outline an algorithm for generating such designs, and we present output from two demonstration programs based on this algorithm. To discuss these designs, we employ a formalism variously called (in various communities) an "embedded net" or an "embedded graph" or a "geometric graph" or a "Euclidean graph", among other things; to eliminate ambiguity, we will refer to an *embedded net* as a geometric structure in 3D-space consisting of the following:

- a set of points, which we call *nodes* (although they are often called *vertices*);
- a set of line segments, which we call *edges* (although they are often called *linkers*), each with two nodes as end points.

If an embedded net is employed as a blueprint for a MOF, the nodes would represent positions of atoms or molecular building blocks (MBBs), positioned at specific points in 3D-space, while the edges would represent bonds or molecular linkers between atoms or MBBs, each linking the two end point nodes.

Such a *geometric* (as opposed to topological or combinatorial) representation serves as a *de facto* blueprint for the design of related MOFs because it tells us the shape of MBBs and the range of their possible spatial arrangements; that is, just as a representation is constructed from nodes linked by edges, a MOF can be constructed from metals or MBBs linked by organic ligands.

We should distinguish the geometric notion of an *embedded* net from two other extant notions:

- The *combinatorial* notion of a *net* (or a *graph*), consisting of nodes and vertices and incidence relations between the two, but with no spatial relations. Thus, two nets are *combinatorially equivalent* if there is a one-to-one correspondence between their vertices and a one-to-one correspondence

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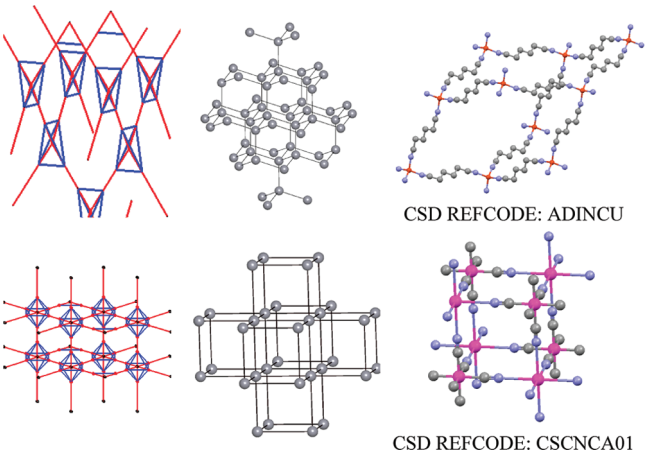

Figure 1. Graphical representation of **dia** (top) and **pcu** (bottom) nets: (left) geometric embeddings generated by the Crystal Turtlebug (in red) showing vertex figures (in blue), (center) embedded nets at a distance, and (right) corresponding examples of crystal structures having **dia** and **pcu** topologies.

between their edges, such that these correspondences preserve the incidences between corresponding nodes and edges.

- The *topological* notion of a *net* (or a *graph*), which is a net with certain spatial relations; we will not discuss topology in this contribution, with the following two exceptions. (1) In the chemical literature, combinatorial equivalence is often called "topological equivalence", a denotation we will not employ, as it conflicts with mathematical nomenclature. (2) Two nets are *homeomorphic* if "chains" of 2-coordinated nodes (with connecting edges) in one net are replaced by single edges or chains of differing lengths in the other; compare the middle and right columns of Figure 1 for examples of embedded nets representing homeomorphic nets.

In fact, some chemical papers refer to a "topology" when what is meant is a "net" as understood above; henceforth, we will use the word "net" instead of "topology". To be precise, we will discuss "embedded nets" as geometric objects and "nets" as combinatorial objects (as understood above). Note that a net can be regarded as a class of combinatorially equivalent embedded nets. For example, the embedded net whose vertices are integer points (i.e., (x, y, z), in which x, y, and z are integers, in Cartesian coordinates in 3D-space) and whose edges bond vertices of distance 1 apart (parallel to the Cartesian coordinate axes) is a geometric representation of the net **pcu** (Figure 1), which has infinitely many other geometric representations. We will frequently be lazy and say that a net is observed or generated when we mean that embedded nets representing that net were observed or generated.

One of the more important databases of nets describing crystal structures, originally developed by O. Yaghi and M. O'Keeffe, is located at the Reticular Chemistry Structure Resource (RCSR) Web site[4a,16] (and we will use RCSR symbols for 3D-periodic nets). The database contains most of the simpler nets that have been observed experimentally. The RCSR database is an important source of nets that can be used as blueprints to design new MOFs. For example, because of the wide availability of appropriate MBBs, two of the most studied and most commonly observed nets for MOF structures are the *diamond* (**dia**) and *primitive cubic lattice* (**pcu**) nets,[3b,2i,10] where **dia** and **pcu** are the symbols assigned to those nets by RCSR. Both nets are represented by embedded nets in which the vertex figures are regular polygons or polyhedra: the vertex figure is a tetrahedron for **dia** and an octahedron for **pcu**. In order to design MOFs having such geometric properties, tetrahedral and octahedral MBBs would be the obvious choice to start with, and there are many examples of such an approach to design.[10] Figure 1 shows the graphical representation of **dia** and **pcu** nets together with examples of structures having those topologies, i.e. being derived from those nets. Structures were obtained as a result of assembly of tetrahedral or octahedral building units—in these cases, single metal coordination nodes. The other important regular nets (their dominant vertex figures in parentheses) include the following: SrSi (**srs**, triangles) (**srs**, **pcu**, and **dia** are especially common[4b]), NbO (**nbo**, squares), and body centered cubic (**bcu**, cubes); in addition, face centered cubic (**fcu**) has cubooctahedral units.

While graphical representations of the molecular or atomic structure of crystals as nets goes back at least to Kepler (if not Leucippus and Democritus), the current thread is more recent, running through the connection between the "periodic" nets and crystal structures described by Wells[2a] and expanded upon by theoretical works, constructions, and surveys such as those by Chung and Klee et al.,[15a,b] Delgado-Friedrich and O'Keeffe,[2b,i,3b,3j] Eon,[2e] Koch and Fischer et al.,[2f−h] Blatov, Baburin, Calucci, Ciani, and Proserpio[3n−q] (see also refs 2j, 2k,4c−4f), and others;[3a−g] this is merely a biased sample of work involving several communities going back to the 1960s.

Roughly speaking, a material is a crystal (in the classical sense) if its atomic or molecular structure can be represented by a 3D-periodic embedded net. In this paper, we consider these embedded nets as potential blueprints for designing the crystals that they might represent. Today, MOF design often starts by manipulating a known net taken from a standard database,[4a,5,6] to obtain a "blueprint" for a new structure.[3a−i] However, geometric methods have been developed to enumerate such nets from scratch. Treacy and Rivin developed an algorithm enumerating tetrahedral nets, using crystallographic groups generated by reflections.[7a,b] Le Bail composed a program which enumerates 3-, 4-, 5-, and 6-coordinated three-dimensional embedded nets.[8] Delgado-Friedrichs, O'Keeffe,Yaghi, and collaborators employed an algorithm based on tiling theory[9a] and have been generating nets, especially edge-transitive nets.[2i,9c−9e] The nets with only one kind of edge ("edge-transitive" nets) are of special importance, as they have topologies most commonly observed so far in MOFs' crystal structures.[2i,3b,3c,9c−9f,10]

The above is only a small sample of current activity, which spans a wide range of approaches from the lifting of nets embedded in hyperbolic 2D-space into Euclidean 3D-space[3k] to systematic or stochastic searches for nets "near" known nets (within some searchable metric space).[3l]

We present here results of net enumeration using programs based on an algorithm motivated by a different approach from those above (although it could be regarded as a formalization of the Le Bail algorithm) involving algebraic and combinatorial developments of the last few decades. The underlying algorithm, called the *Turtlebug* because of its relationship with *turtle geometry*,[14d] is based on an application[12] of geometric group theory[14e] to a model of computational self-assembly.[11a,b] We call the resulting algorithm for generating embedded nets the *Crystal Turtlebug*, and from this algorithm

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we have developed—and are developing—a series of programs for enumerating embedded nets.

The programs we have developed from the *Crystal Turtlebug* algorithm use as their parameters the point groups that generate the configuration figures about the initial vertices and the initial edge(s). One of these programs has enumerated all (strictly) binodal periodic edge-transitive 3,4-, 3,6-, 4,4-, and 4,6-coordinated nets listed in RCSR, while another found feasible, yet apparently unlisted and hence probably novel nets; the algorithm itself can (in theory) enumerate embedded nets representative of all 3D-periodic nets.[12b]

This program and its algorithm are generalizations of an algorithm developed into a working program developed by W. E. Clark, whose program had the theoretical ability to enumerate (embedded representatives of) all uninodal nets.[13] In this contribution, we will present a qualitative description of the algorithm (with additional description in the Supporting Information), and then we will describe some of the nets enumerated by these *Crystal Turtlebug* programs.

CONCEPTS AND DEFINITIONS

Before we begin, it is important to define several terms. This paper lies at the intersection of several fields, but we shall endeavor to stay reasonably close to the nomenclature of (classical!) crystallography, although there will be some exceptions.

- An *isometry* is a mapping of 3D-space to itself that preserves distances and is thus a reflection, a rotation, or a rotational reflection (if it has any fixed points) or a translation, glide reflection, or a screw rotation (if it does not). These are the elements of crystallographic space groups.
- The *symmetries* of an embedded net are those isometries that map nodes of the embedded net to nodes and edges to edges.
- An embedded net is *3D-periodic* if there are three translations along three axes among its symmetries and if any finite ball in 3D-space contains finitely many vertices. We say that a net is 3D-periodic if it is combinatorially equivalent to a 3D-periodic embedded net.
- Two edges of an embedded net are in the same *orbit* if there is a symmetry of that embedded net mapping one to the other. Similarly, two nodes are in the same orbit if there is a symmetry mapping one to the other.
- An embedded net is *uninodal* if there is one orbit of nodes; it is *binodal* if there are two orbits of nodes.
- An embedded net is *edge transitive* if, for any two edges, there is a symmetry sending the first edge to the second.
- A binodal net is *bipartite* if there is no edge connecting two nodes of the same kind. A binodal edge transitive net will not be connected if it is not bipartite. All nets (but one!) in this contribution are bipartite.

Two versions of the program have been developed:

- A *one-edge version* that enumerates (necessarily) bipartite edge-transitive binodal embedded nets. We will call this Version 1/3.
- A *two-edge version* that enumerates bipartite binodal embedded nets with two orbits of edges. We will call this Version 2/3.

The "/3" is to remind us that these are demonstration programs and that a more comprehensive program is desirable.

While these programs enumerate binodal periodic embedded nets, the mathematical formalization[12a−c] based on a variant of the group action rationale[13a,b] of "Bass−Serre" theory[14a−c] (related to the "vector method" of 15a-b) asserts that these programs can be generalized to enumerate embedded nets of crystals of arbitrary complexity. We shall outline how the one-edge version works, but first we need some preliminaries on computational practicalities and on crystallographic point groups, which we will treat qualitatively. We take a very abstract view of the situation, since we will then be in a better position to focus on practicalities.

It should be emphasized that we do not have an algorithm to generate *all* 3D-periodic embedded nets; we only generate representative embedded nets for all 3D-periodic nets. To be precise:

- The collection of all 3D-periodic embedded nets is "uncountable" in the sense that if we enumerated embedded nets, one after another, it would be impossible to enumerate them all even given infinite time: the collection of all 3D-periodic embedded nets is "uncountable". (This is a straightforward exercise in combinatorial set theory.)
- However, the collection of all nets representing 3D-periodic embedded nets is countable, albeit infinite. (One would enumerate quotient graphs,[15b] and the number of quotient graphs is infinite but "countable".) Thus, there is a desire for an algorithm enumerating 3D-periodic embedded nets which would, given infinite time, enumerate representatives of all topologies, i.e., of all nets.

As a practical matter, we would like a computer program that *effectively* implements this algorithm; that is, it should enumerate (geometric representatives of) interesting and important nets fairly quickly. One way to do this is to have the computer program have a bias toward embedded nets of high symmetry, for nets of high symmetry appear to be disproportionately represented among known nets.[4b,10] Since this algorithm is based on symmetries, the fact that we quickly found interesting and important nets using two primitive implementations of it bodes well for future programs.

The claim that this algorithm *eventually* enumerates representatives of all nets of 3D-periodic embedded nets is explored elsewhere,[12a,b] although the rationale is outlined very briefly in this communication (and explored further in the Supporting Information) for the curious reader. However, we will focus on two particular implementations of this algorithm and present empirical evidence that this and related implementations should *effectively* enumerate representatives of interesting and important nets within a reasonable time.

EXPERIMENTAL SECTION

Two programs implementing the algorithm for binodal embedded nets were composed in the programming language Maple (because of its utility in engineering demonstration projects). The program used Cartesian coordinates and, for efficiency, placed nodes on integer points, i.e., points $(x, y,$ and $z)$ in 3D-space such that x, y, and z were integers. Both programs generated embedded nets from two nodes, one at the origin $(0, 0, 0)$ and the other at an integer point (x, y, z), with an edge joining the two nodes.

The first program, which we call *Version 1/3*, is described in the Theoretical Supplement in the Supporting Information. The program enumerated edge transitive embedded nets (i.e., one

Table 1. List of Some Edge Transitive Nets Found by Version 2/3 of the Program[a]

3,4-coordinated nets					4,6-coordinated nets				
TD10	name	d_{min}	D_{min}	point symbol	TD10	name	d_{min}	D_{min}	point symbol
248.14	*	*	1.10	$(4^2.20^4)_3(4^3)_4$**3,4T7**	1100.6	**stp**	1.15	1.31	
819.86	**bor**	1.15	1.73		1188.0	*	*	1.00	$(4^3\cdot6^{12})_2(4^6)_3$**4,6T4**
819.86	**tbo**	1.15	1.37		1228.2	**toc**	1.15	1.15	
894.43	**ctn**	1.57	1.55		1304.0	*	*	0.67	new $(4^3\cdot8^{12})_2(4^6)_3$
905.00	**pto**	1.41	1.41		1463.4	**gar**	1.10	1.10	
2957.3	*	0.44	0.65	new $(12^3)_4(12^6)_3$	1464.2	**iac**	1.10	1.10	
3237.3	*	0.51	0.62	new $(12^3)_4(12^6)_3$	1767	*	*	0.85	new $(4^{15})_2(4^2\cdot8^4)_3$
3245.0	*	0.00	0.63	new $(12^3)_4(12^6)_3$	1931.0	**ibd**	1.00	1.00	
					1988.2	**soc**	1.00	1.00	
					2071.4	**she**	1.00	1.00	
					3441.8	**ifi**	0.65	0.65	

4,4-coordinated net					3,6-coordinated nets				
TD10	name	d_{min}	D_{min}	point symbol	TD10	name	d_{min}	D_{min}	point symbol
584.4	*	*	1.00	new $(4^2\cdot12^4)(4^6)$	721.7	**spn**	0.58	1.41	
785	**lcv**			*uninodal; not found*	807.7	**cys**	*	1.04	known
791.0	**sod**	1.41	1.00		1419.0	**pyr**	1.29	1.29	
933	**ana**			*uninodal; not found*	3079.0	*	0.54	0.63	new $(8^{15})(8^3)_2$
977.0	**pts**	1.15	1.60						
981.0	**dia**	1.63	1.60						
1028.0	**rhr**	1.15	1.00						
1127.0	**lvt**	1.15	1.31						
1137.0	**ssb**	1.15	1.00						
1161.0	**lcs**	1.52	1.00						
1169.0	**nbo**	1.41	1.32						
1198.0	**ssa**	0.82	1.31						
1205.0	**pth**	1.15	1.41						
1231.0	**qtz**	1.41	1.46						
2168.0	*	*	0.60	new, *uninodal*, 8^6					
2249.0	*	0.82	0.82	new $(6^4\cdot10^2)(6^6)$					
2324.0	*	*	0.77	new $(6^2\cdot8^4)(6^4\cdot8^2)$					
3797.0	*	0.58	0.71	new, *uninodal*,					
4593.0	**ssc**	0.65	0.65	$(6^2\cdot8^4)$					

[a] See the Supporting Information for node and edge positions. d_{min} = Systre's minimal nonbonded distance; D_{min} = largest minimal nonbonded distance found by Version 1/3. **lcv** and **ana** are italicized to stress their problematic nature (see text).

orbit of edges) as follows. For each (x, y, z), $-3 \le x, y \le 3$, and $0 \le z \le 3$ satisfying $(x, y, z) \neq (0, 0, 0)$, and each assignment of two point groups (of appropriate order) to the two nodes, it would attempt to generate an embedded net. Thus, it would proceed systematically through up to several thousand initial conditions, attempting to generate an embedded net from each one, and reporting all successes.

In theory,[12b] enumerating each integer point (x, y, z) and generating a net from that point (and the origin) would produce a complete if infinite list of representatives of binodal edge transitive 3D-periodic embedded nets. In practice (or at least in this computer experiment), just checking 195 integer points (x, y, z) satisfying $-3 \le x, y \le 3$ and $0 \le z \le 3$ and $(x, y, z) \neq (0, 0, 0)$ sufficed to generate representatives of all edge transitive *strictly binodal* 3,4-, 4,4-, 3,6-, and 4,6-coordinated nets listed in RCSR[4a] and TOPOS[17] (Table 1). This suggests that, for such a search, generating a sufficiently long list of integer points would often suffice.

To give an idea of how the algorithm works, we describe in the Supporting Information how Version 1/3 would generate (an embedding of) the net **pto**. As in the programs, we use Cartesian coordinates and place the nodes (and edges) in 3D-space in positions with respect to the standard *x*-, *y*-, and *z*-axes. Here is a description of the "search space" for Version 1/3; for a more complete description of Version 1/3, see the Supporting Information.

To generate a net, we first decide that we are working in the lattice of integer points. (If we were generating a hexagonal embedded net, we would work in a hexagonal lattice.) Notice that the point group of this lattice is the maximal point group $m\bar{3}m$. We need the following:

- We must fix the valencies of the two types of nodes. For example, suppose that we decide that we are generating a 4,3-coordinated net.
- We place a node at the origin, (0, 0, 0). For example, suppose that we decide that the node at the origin is to be 4-coordinated.

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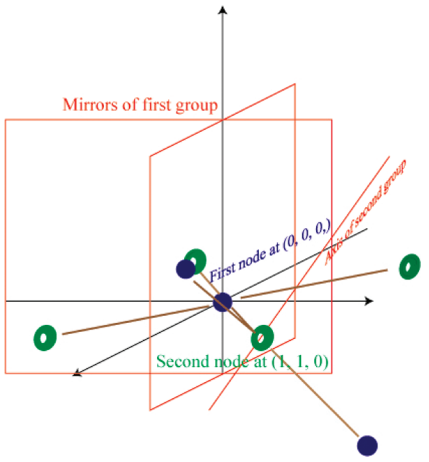

Figure 2. We start with a first (blue) node at the origin and a second (green) node at (1, 1, 0). Two mirrors, on the planes of the *xz*- and *yz*-axes, generate three additional green images of nodes adjacent to the first node. The axis of rotation through (1, 1, 0) generates two additional blue images of nodes adjacent to the second node.

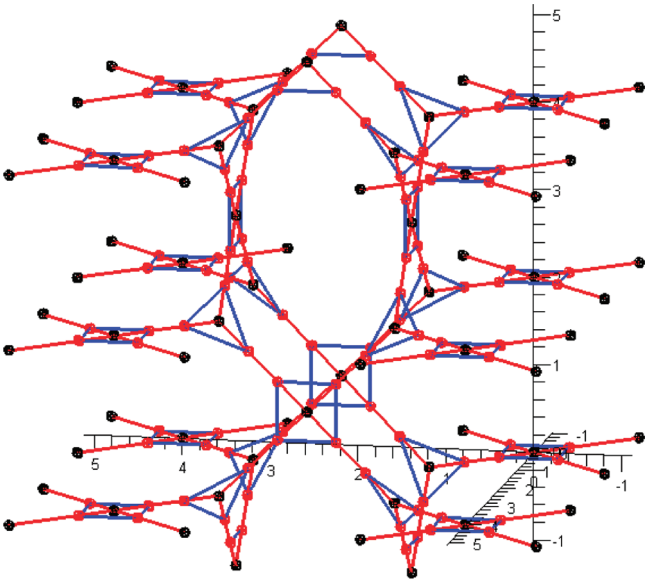

Figure 3. The outputted net for the initial conditions in the 4,3-coordinated example of the text, using the neighbor (1, 1, 0), applying the conjugates described above, and repeatedly iterating until one obtains a complete quotient graph. The first node is at the intersection of the three axes; it is a vagary of the program that it often builds the quotient graph in one direction from the first node rather than in all directions more equally.

- We choose an edge by choosing a point for a node of the other (3-coordinated) kind. Suppose that we chose (1, 1, 0) for the position of the other node, so that the edge is the line segment from (0, 0, 0) to (1, 1, 0), so that the second node is at (1, 1, 0).
- We choose a 4-element point group (which has the origin as a fixed point)—a subgroup of $m\bar{3}m$—to apply to the edge {(0, 0, 0), (1, 1, 0)} to obtain the four edges (and hence the four neighbors) of the first node. For example, suppose we chose the "conjugate" of *mm*2 whose reflecting mirrors are the *xz*- and *yz*-planes. ("Conjugates" are defined and discussed in the Supporting Information.)

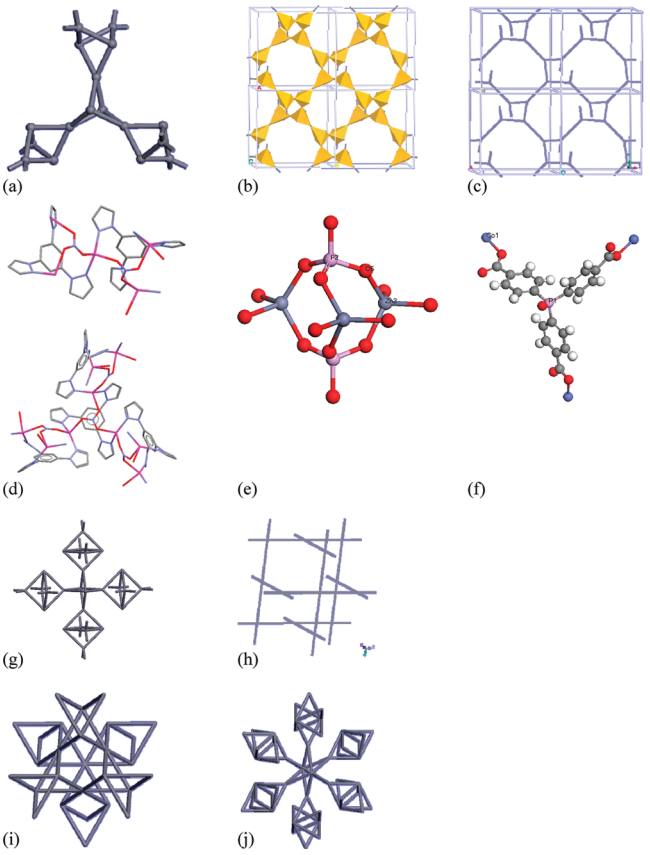

Figure 4. (a and b) Graphical representations of Net 248; (c) graphical representation of the *srs* net; (d) example of structure topologically equivalent to net 248 found in CSD (REFCODE: 3,4T7; (e and f) examples of building block (CSD REFCODE: ACUBEF) and ligand (CSD REFCODE; HOXMUC) amenable to form the structure with 248 topology; (g) graphical representations of Net 584; (h) graphical representation of **nbo** net; (i) graphical representation of Net 1188; (j) graphical representation of Net 1767.

This is the initial position depicted in Figure 2, where the computation begins. In essence, the computation runs by developing the edges and adjacent nodes of every node developed, replicating the operations on the first pair of nodes, until there are enough nodes to characterize a unit cell; e.g. Figure 3. Again, for more, see the Theoretical Supplement in the Supporting Information.

RESULTS AND DISCUSSION

We consider two classes of results.

First of all, for purposes of surveying the landscape, Version 1/3 is more effective because its (infinite!) theoretical search space is apparently more faithfully exemplified by the (finite!) search space employed by the program. So here are several global observations about the results from Version 1/3, including the question of the faithfulness of this exemplification.

- While Version 1/3 did generate all binodal edge transitive nets listed in RCSR, Version 1/3 did not generate all uninodal edge transitive nets listed in RCSR. For example, among the 4-coordinated nets, Version 1/3 did not generate any examples of **ana** or **lcv**. As we shall see in the Theoretical

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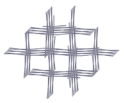
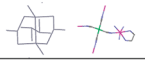
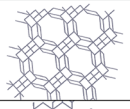
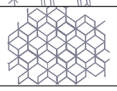
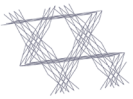
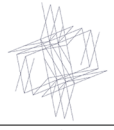
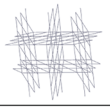
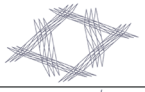
Table 2. Examples of New Nets Found by Version 0.7 of the Program[a]

4,4		***Point symbol***	
1140	new	$(4^2.6^4)(4^2.8^4)$	
1578	new	$(4^2.8^2.10^2)(4^2.8^4)$	
1597	new	$(4^2.8^3.10)(4^2.8^4)$	
1641	Known / 4,4T3	$(6^5.10)(6^5.8)$	
3,6			
845	new	$(4^2.6)_2(4^4.6^4.8^6.10)$	
1059	new	$(4^2.6)_2(4^4.6^2.8^7.10^2)$	
		4,8	
1403	new	$(4^{16}.6^8.8^4)(4^5.6)_2$	
2081	new	$(4^{16}.6^{12})(4^4.6^2)_2$	
2619	new	$(4^{16}.6^{12})(4^4.6^2)_2$	
2656	new	$(4^{16}.6^{12})(4^4.6^2)_2$	
2669	new	$(4^{16}.6^{12})(4^4.6^2)_2$	
2681	new	$(4^3.6^3)_2(4^6.6^{16}.8^6)$	
2690	new	$(4^2.6^4)_2(4^4.6^{24})$	
2829	new	$(4^4.6^2)_2(4^8.6^{16}.8^4)$	
2995	new	$(4^4.6^2)_2(4^8.6^{16}.8^4)$	
3019	new	$(4^{12}.6^{12}.8^4)(4^2.6^3.8)_2$	

[a] See Supporting Information for node and edge positions.

subsection, Version 1/3 would not list **lcv** for any integer point (x, y, z), so this is not a surprise: Version 1 (now under development) will not have the theoretical constraints of Version 1/3, so we do not expect this limitation in Version 1. However, **ana** does not have the combinatorial problem lcv has, and so we would have expected **ana** to appear (as did other uninodal nets such as **dia** and **qtz**). So we expect **ana** to appear for some integer point (x, y, z), and this experiment merely shows that, for such an integer point for obtaining **ana**, at least one of x, y, or z must have an absolute value greater than 3. How much greater is uncertain.

- Version 1/3 found a number of "dense" nets in the sense that the "topological density" (td10 = the mean number of nodes within edge distance 10 of an average node[9h,16a]) is high in the following sense. RCSR lists 47 4,6-coordinated nets, and the one with the highest topological density was **ifi**, with td10 = 3441.8. The majority of the 50 distinct 4,6-coordinated edge transitive nets enumerated by Version 1/3 were not listed in RCSR, and only nine had td10 < 4000, with four having td10 > 20,000.
- Version 1/3 found a few nets that were not *barycentric*[9h,16a] (or *locally stable*) for which Systre would abort an analysis with the message that the inputted embedded net had "vertex collisions" or was "not locally stable". One of these is the td10 = 248 embedded net of Table 1. These nets tended to be of low topological density.
- Version 1/3 did not find any barycentric novel nets of any obvious importance.

In the Supporting Information, we provide CGD files (and Systre output) of the following:

- embedded representatives of all 3,4-coordinated periodic nets found by Version 1/3;
- embedded representatives of all 3,6-coordinated periodic nets found by Version 1/3;
- embedded representatives of all 4,4-coordinated periodic nets found by Version 1/3 of topological density at most 4593;
- embedded representatives of all 4,6-coordinated periodic nets found by Version 1/3 of topological density at most 6240.2.

As Version 2/3 was even hobbled in theory (for logistical reasons) and thus unsurprisingly missed many extant bipartite binodal nets of two orbits of edges, the primary interest of results from Version 2/3 is the interesting novel nets that it found, suggesting that, unlike the binodal edge transitive nets (which appear to have been well-explored prior to this contribution), the binodal bipartite nets of two orbits of edges include much interesting but unexplored territory. Some of the novel nets found by Version 2/3 are described in the discussion or pictured in Figure 4 or Table 2 or listed in the Supporting Information. Version 2/3 searched for binodal nets of *two* orbits of edges; again, because of certain constraints on the program, a comprehensive survey was impractical, so we make no global comments on the results here. Comments on specific novel nets are below. All CGD files for (embedded representatives of) nets in Table 2, and examples of 3,6-, 4,4-, and 4,8-coordinated embedded nets found by Version 2/3 are provided in the Supporting Information, along with TOPOS outputs of some of them.

The two programs found many novel nets, but the nets found that seem to be most feasible from a crystal engineering point of view are nets with topological density TD10 = 248, 584, 1188,

1304, and 1767 (see below and Tables 1 and 2); again, the most feasible novel nets were found by Version 2/3. Note that Nets 248 and 1188 are recognized by TOPOS[17] as having topologies (nets) of structures from the CSD database (Recodes: 3,4T7 and 4,6T4).

- Closer analysis of those five nets reveals an interesting correspondence to well-known nets. The embedded net found of Net 248 is a 3,4-coordinated net with tetrahedral and pyramidal nodes (Figure 4a,b), with chiral symmetry, and with the $I4_132$ space group, and it can be represented as trigonal bipyramids. This is similar to the well-known **srs** net. By applying local rules—connecting centroids of bipyramidal polyhedra—Net 248 can be reduced to **srs**. While Nets 248 and **srs** are distinct, they possess the same chiral symmetry and have the same type of helices.
- Analogous nets are as follows: Net 584 (TD10 = 584.4, Figure 4g,h), which is a 4,4-connected net with tetrahedral and pyramidal nodes. Net 584 can be reduced to an **nbo** type net, and nets 1188 (4,6), 1304 (4,6), and 1767 (4,6) are similarly adjustable (Figure 4i,j).

Again, most of the new nets found are relatively dense (although some look feasible from a crystal engineering point of view). More plausible nets found by Version 2/3 and not listed in the RCSR[4] and TOPOS[17] databases are enumerated in Table 2.

The fact that most of the plausible and new nets found thus far were found by Version 2/3 suggests that in looking at embedded nets with two orbits of edges rather than nets with just one, we are crossing something akin to a contemporary frontier. This also suggests that, for a comprehensive exploration of this frontier, the search space should (at least) involve choosing one of 195 edges, and then one of the 341 remaining edges (in that entire $7 \times 7 \times 7$ box), for a total of 66,495 pairs of edges. This large number of initial conditions to test is another reason for composing a new version of the program.

CONCLUSIONS

Two demonstration programs of the *Crystal Turtlebug* algorithm generate all known edge-transitive binodal nets of four classes of nets of high symmetry, plus several new nets not presented in RCSR[4a] and TOPOS[17] databases. Among the new nets are some that appear feasible from the point of view of crystal engineering. Subsequent programs should be able to generate more complex nets in a reasonable time. Further, in addition to the theoretical point that such a program can enumerate all the infinitely many nets (in its scope) given infinite time—and thus that, in such an enumeration, any given net will *eventually* be enumerated—the results of this preliminary version suggest that a user will not have too long to wait before interesting nets are enumerated.

One limitation of the current program is the restriction of vertices to integer points (or, in the case of embedded nets, images of integer points under a particular linear transformation). While the embedded nets of maximal symmetry fall in this class, most embedded nets generated are not of maximal symmetry. Thus, the output may require additional massaging and/or filtering as well as analysis by other programs.

In order to design these structures, the crystal engineer must analyze the geometry of targeted nets and choose the right MBBs and the right linker ligands. Special attention should be directed to the shape and conformation of the linker ligands. For example, Eddaoudi et al.[1v] showed that it is possible to design a crystal structure by controlling the linker conformation by using 2-bromo-1,4-benzenedicarboxylate instead of 1,4-benzenedicarboxylate. Specifically, when the former is reacted with Cu(II) ions to form "paddlewheel" nodes, a square grid type structure is formed whereas the latter generates an NbO net. The Br substituent causes the adjacent of the carboxylate moiety to be orthogonal to the plane, which in turn causes the paddlewheel nodes to be twisted with respect to each other. *Crystal Turtlebug* programs will generate many embedded nets, which should provide sufficiently many conformations so that some should be suitable for targeted nets. *Crystal Turtlebug* has already produced a number of nets that are novel and nets that were only observed experimentally. One example is the 4,4-connected net 1641 (Table 2); it is composed of square planar nodes and distorted tetrahedral nodes. The net was found by our program but is recognized by TOPOS[17] as having the topology of a structure reported in the CSD database—4,4T3 (Table 2). That validates that variants of net 1641 are indeed feasible to design from a crystal engineering perspective. The analysis of the entire set of new nets is now in progress, and we believe it will result in several novel "feasible to design" nets, and these will be delineated in a future contribution. Meanwhile, a catalogue of embedded nets (as CGD files) is listed in the Supporting Information: comprehensive lists of representatives of nets of particular coordinations and of sufficiently low density found by Version 1/3, and a sample of representatives of novel nets found by Version 2/3 appears as well.

ASSOCIATED CONTENT

Supporting Information. Theoretical information about crystallographic point groups, generating a net, and the rationale; CGD output for some nets; and TOPOS outputs of selected nets. This material is available free of charge via the Internet at http://pubs.acs.org.

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