

Topological relations between three-periodic nets. II. Binodal nets

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The *TOPOS* program package was used to generate all subnets of 3- to 12-coordinated binodal nets taken from the Reticular Chemistry Structure Resource database. 38 304 binodal nets with novel topologies were revealed and stored in the TTD collection. A new invariant, the adjacency matrix of the shell graph of a node, is proposed to distinguish the node local topology. With this invariant, the first six examples of binodal-*quasi*-uninodal nets were discovered. 4604 organic and metal-organic frameworks were analyzed to find examples of the topologies generated. It was shown that many edge-transitive nets as well as unknown topologies occur in crystal structures.

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1. Introduction

Topological descriptions of crystal structures as a whole are becoming increasingly popular in modern crystal chemistry. One of the most natural, simple and powerful models to be used in this field is the *net* (Klee, 2004; Eon, 2005; Delgado-Friedrichs & O'Keeffe, 2005). This model usually ignores the geometrical parameters of an atomic array (such as interatomic distances and bond and torsion angles) and focuses on the overall structure connectivity (Wells, 1977; Öhrström & Larsson, 2005; Carlucci *et al.*, 2007). The initial geometrical data (the space-group symmetry, unit-cell dimensions and atomic coordinates) together with knowledge of the chemically relevant interactions are sufficient to build the net. As this experimental information is the most reliable, the resulting net can also be considered to be one of the most robust topological descriptors for the structure. A further advantage of this approach is that the net concept can easily be coded, as realized in several computer packages [*Gavrog Systre* (<http://www.gavrog.org>), *Olex* (<http://www.olex2.org>), *TOPOLAN* (<http://www.adam.ntu.edu.sg/~mgeorg>), *TOPOS* (<http://www.topos.ssu.samara.ru>)] and databases [EPINET (Euclidean Patterns in Non-Euclidean Tilings, <http://epinet.anu.edu.au/>), RCSR (Reticular Chemistry Structure Resource, <http://rcsr.anu.edu.au/>), TTD and TTO (*TOPOS*, Topological Databases and Topological Types Observed, <http://www.topos.ssu.samara.ru>)]. Using these tools a crystal chemist can now easily separate and identify nets.

If we ignore incommensurate and quasicrystal phases, the structure of a crystal is three-periodic and hence can be described by a three-periodic graph, *i.e.* a graph with translational symmetry in exactly three independent directions. Thus three-periodic nets are of special interest in crystal chemistry [the notion *graph* is wider than *net*; a net is an *n*-periodic simple (without loops and multiple edges) undirected

connected graph] (Delgado-Friedrichs *et al.*, 2005). Incidentally, nets with a lower periodicity, well known to mathematicians (Grünbaum & Shephard, 1987), have been studied much less in crystal chemistry (Koch & Fischer, 1978; O'Keeffe & Hyde, 1980; O'Keeffe, 1992).

O'Keeffe has gathered many nets crucial for crystal chemistry since the beginning of the century in the RCSR database (Ockwig *et al.*, 2005; O'Keeffe *et al.*, 2008). This work has encouraged systematic investigations of crystal-structure topologies in organic, inorganic and metal-organic compounds (Blatov *et al.*, 2004; Baburin *et al.*, 2005, 2008*a,b*; Blatov & Peskov, 2006; Baburin & Blatov, 2007; Baburin, 2008). Most of the results of these studies are collected in the TTD database, although the number of structures processed is less than 5000. However, this now allows one to draw some conclusions about the occurrence of various topologies. Thus, in valence-bonded interpenetrated inorganic and metal-organic frameworks, as well as in single metal-organic frameworks, the three most preferred topological motifs¹ are **dia** (4/6/c1), **pcu** (6/4/c1) and **srs** (3/10/c1) (Blatov *et al.*, 2004; Ockwig *et al.*, 2005; Baburin *et al.*, 2005). In organic molecular crystals with hydrogen-bonded single networks the results are similar: **dia**, **pcu**, **sxd** (6/3/o1) and **hex** (8/3/h4) (Baburin & Blatov, 2007); for hydrogen-bonded coordination compounds they are **pcu**, **bcu** (8/4/c1), **hex** and **dia** (Baburin, 2008; Baburin *et al.*, 2008*a,b*). Thus, nature chooses the same topological motifs; moreover, all of them are sphere packings [*cf.* Koch *et al.* (2006) and references therein].

The question as to why some nets occur more frequently in crystals has still not been answered. O'Keeffe and co-workers (Ockwig *et al.*, 2005; Delgado-Friedrichs *et al.*, 2006, 2007)

¹ Hereafter, the RCSR three-letter symbols (if available) are used to designate net topologies. Fischer's symbols *klm/fn* (Koch *et al.*, 2006) are given for sphere packings along with the RCSR symbols.

assumed that such nets should be topologically the simplest; in particular, they should have a minimal number of inequivalent nodes and/or edges as well as the highest possible symmetry at the nodes (we prefer the term ‘node’ instead of ‘vertex’ for nets). Indeed, the most frequent nets observed for metal-organic frameworks and hydrogen-bonded supramolecular assemblies are *uninodal* (vertex-transitive), *i.e.* have one kind of node, and all but **hex** and **sxd** are *edge-transitive* (with one kind of edge). However, many other uninodal and/or edge-transitive nets are not so abundant, so a close inspection of node symmetries is required to ascertain whether this rule is sufficient. The opposite question is important as well: why do some nets never or rarely occur in nature? To answer this question, the list of natural nets should be extended with artificial nets generated by some tailored methods. In this case, the methods for producing the nets both *ab initio* and in relation to the natural nets are important. The largest project for generating *ab initio* nets is EPINET (Hyde *et al.*, 2006; Ramsden *et al.*, 2009) where three-periodic nets are derived

from two-dimensional hyperbolic tilings irrelevant to real crystal structures. Studying the occurrence of EPINET nets shows how stochastic the realization of topological motifs in crystals is. However, nobody has yet performed such an analysis. The most exciting example of producing artificial nets related to real crystal structures is the Atlas of Hypothetical Zeolite Frameworks [http://www.hypotheticalzeolites.net (Treacy *et al.*, 2004; Delgado-Friedrichs & O’Keeffe, 2005)]. In this case, the generated nets are to obey some geometrical criteria relevant to zeolite structures.

In the first paper of this series, Blatov (2007) proposed one more method for obtaining new nets that are possibly relevant to crystal structures. Starting from a frequently occurring net in a maximum-symmetry Euclidean embedding and considering all possible ways of decreasing the symmetry and coordination of the net, one can obtain all of its subnets with a given number of inequivalent nodes. With a tailored procedure of the *TOPOS* program package, Blatov (2007) collected all 5278 uninodal subnets of the RCSR uninodal nets. Some of

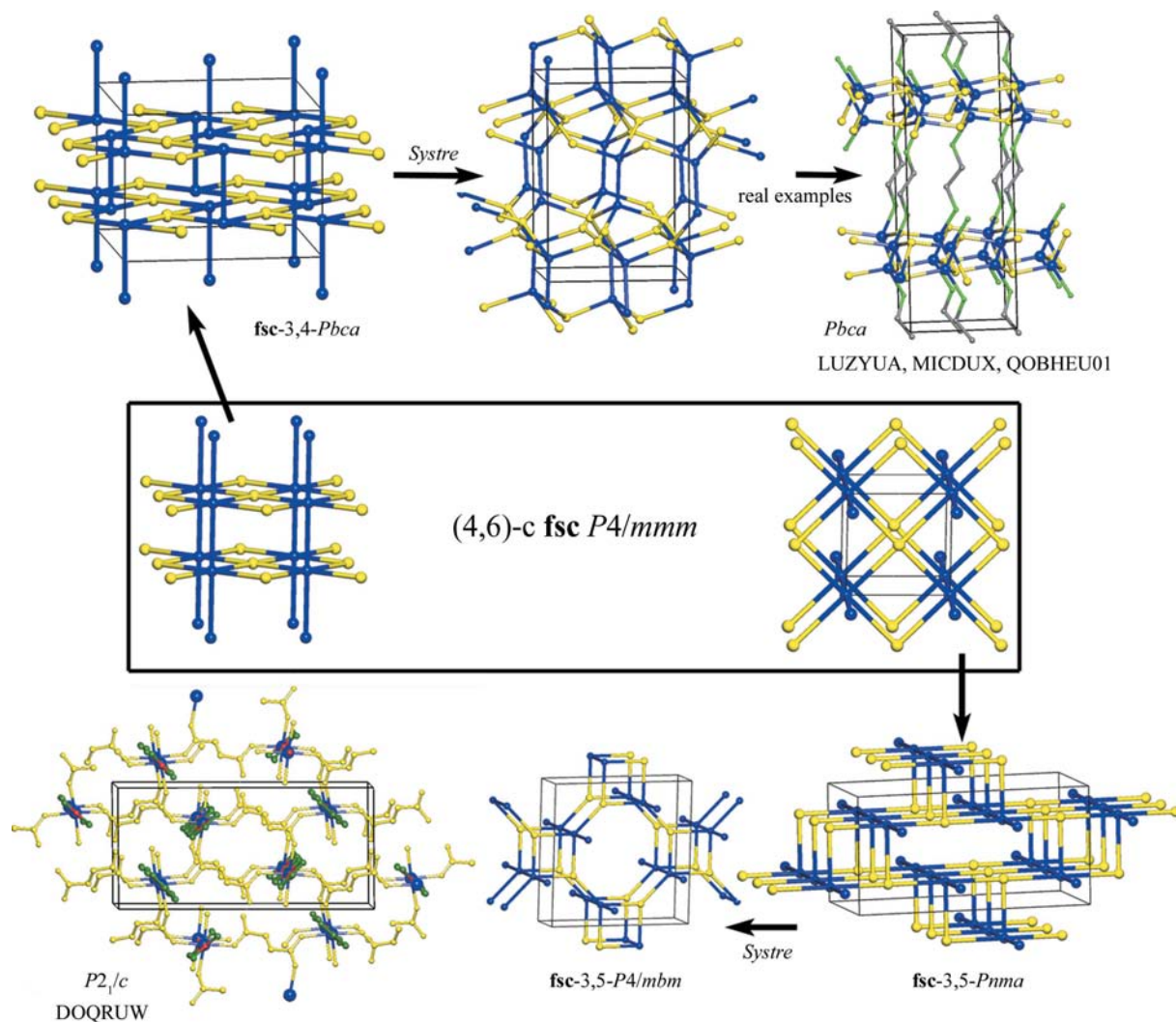


Figure 1

The procedure for deriving two subnets (3,4) and (3,5)-coordinated from (4,6)-**fsc**. For each subnet (top left and bottom right) we also show the *Systre*-optimized embedding (center top and bottom) and one real example [LUZYUA, MICDUX and QOBHEU10 are Zn_2X_2 (ethylenediamine), $X = S, Se, Te$; DOQRUW is $Mn(H_2O)(fumarato)(4,4'$ -bipy)]. See text for further details.

Table 1

The 225 EPINET nets inequivalent to RCSR nets found among the subnets generated.

Node degrees	No.	Net name
3, 3	35	<i>sqc326, sqc946, sqc3051, sqc3053, sqc3058, sqc5599, sqc5600, sqc5601, sqc5602, sqc9243, sqc9247, sqc9248, sqc9250, sqc9252, sqc9264, sqc9267, sqc11250, sqc11253, sqc11254, sqc11255, sqc11257, sqc11261, sqc12871, sqc12874, sqc12881, sqc13759, sqc13771, sqc13774, sqc13776, sqc14290, sqc14292, sqc14293, sqc14294, sqc14297, sqc14298</i>
3, 4	90	<i>sqc74, sqc185, sqc188, sqc476, sqc515, sqc519, sqc522, sqc1255, sqc1374, sqc1383, sqc1388, sqc1425, sqc1426, sqc1427, sqc1429, sqc1431, sqc1436, sqc1441, sqc2196, sqc2205, sqc2209, sqc3681, sqc3705, sqc3852, sqc3853, sqc3880, sqc3881, sqc3890, sqc3895, sqc3896, sqc4674, sqc4709, sqc5594, sqc6667, sqc6855, sqc6856, sqc6930, sqc6934, sqc7386, sqc8168, sqc8169, sqc8170, sqc8171, sqc9849, sqc9903, sqc9904, sqc9912, sqc9916, sqc10089, sqc10093, sqc10103, sqc10603, sqc10611, sqc10615, sqc10660, sqc10667, sqc11155, sqc11240, sqc11241, sqc11249, sqc11984, sqc12015, sqc12018, sqc12019, sqc12020, sqc12028, sqc12029, sqc12251, sqc12269, sqc12277, sqc13150, sqc13541, sqc13993, sqc13996, sqc13997, sqc14002, sqc14004, sqc14015, sqc14016, sqc14018, sqc14019, sqc14134, sqc14135, sqc14139, sqc14149, sqc14150, sqc14389, sqc14390, sqc14396, sqc14397</i>
3, 5	19	<i>sqc138, sqc689, sqc707, sqc1743, sqc1744, sqc2115, sqc2154, sqc2281, sqc2155, sqc5478, sqc5941, sqc7845, sqc7846, sqc8008, sqc8009, sqc8010, sqc8011, sqc8013, sqc12425</i>
3, 6	14	<i>sqc27, sqc251, sqc293, sqc294, sqc892, sqc893, sqc962, sqc2403, sqc2983, sqc2984, sqc2985, sqc5381, sqc8925, sqc11083</i>
3, 8	2	<i>sqc494, sqc7928</i>
4, 4	19	<i>sqc466, sqc967, sqc2186, sqc2188, sqc2189, sqc3818, sqc3848, sqc3868, sqc5553, sqc5567, sqc8092, sqc8105, sqc8112, sqc13484, sqc13489, sqc13496, sqc13497, sqc13505, sqc13511</i>
4, 5	19	<i>sqc278, sqc280, sqc847, sqc932, sqc955, sqc1101, sqc1253, sqc2481, sqc2482, sqc2484, sqc2644, sqc2996, sqc3986, sqc3989, sqc5464, sqc6809, sqc6814, sqc6815, sqc9092</i>
4, 6	12	<i>sqc374, sqc502, sqc645, sqc1245, sqc1730, sqc3754, sqc3793, sqc4582, sqc4588, sqc4595, sqc4596, sqc6738</i>
4, 7	1	<i>sqc1858</i>
4, 8	3	<i>sqc934, sqc1964, sqc1990</i>
5, 5	3	<i>sqc3254, sqc5617, sqc7317</i>
5, 6	3	<i>sqc1067, sqc7877, sqc8329</i>
5, 8	3	<i>sqc1330, sqc6767, sqc6771</i>
6, 8	2	<i>sqc1854, sqc1954</i>

the novel nets were shown to be of potential interest for crystal chemistry. At that time, there were no data for their occurrence and other important RCSR nets, binodal and edge-transitive nets, were not treated. In this paper we will consider these two classes of nets with particular interest in their realization in nature.

2. Generating subnets

To derive all subnets with a given number of inequivalent nodes for a particular net we have used the two-step algorithm proposed by Blatov (2007). Starting from an initial three-periodic net N with a space group G we considered all ways of decreasing its symmetry following the list of all translation-equivalent and class-equivalent subgroups of G that kept the number of inequivalent nodes of N . Then we enumerated all ways of breaking edges in N as well as in its low-symmetry mappings. As a result, nets of different periodicity were obtained; we kept only three-periodic nets. If the resulting subnet had a Euclidean embedding with a higher space-group symmetry [as can be proved with the *Systre* program (Delgado-Friedrichs & O’Keeffe, 2003)], the generating procedure was repeated for the most symmetric mapping of the subnet. In this case, some additional topologies were obtained as subnets of this symmetrized mapping; these could not be derived directly from the initial net. By removing some sets of edges from the initial net we obtain such subnets only in a low-symmetry embedding with a larger number of inequivalent nodes than in the initial net, so an additional step of symmetrization of the subnet embedding is always required. We shall call such subnets *indirectly generated*, unlike *directly generated* subnets produced by one step of the generating

procedure. The number of indirectly generated subnets is rather large, for example among the 5278 uninodal nets with novel topologies described in the first paper of this series (Blatov, 2007) there are 969 such nets (18.3%). However, the role of indirectly generated nets in crystal chemistry seems less important, since a more complex topological transformation leads to such nets (they have a small net relation graph degree, see §4 below). The *TOPOS* program package and TTD collection were used to produce all subnets and to determine their topologies.

In the set of initial nets N we included all 414 binodal nets with a node degree not larger than eight collected in the RCSR database (release of October 2007); among them there are 27 edge-transitive nets (Delgado-Friedrichs *et al.*, 2006; Delgado-Friedrichs & O’Keeffe, 2007). The eight edge-transitive nets with a higher node degree (3,12-coordinated **ttt**; 4,12-coordinated **ftw**, **ith**, **shp**; 6,12-coordinated **alb**, **mge**; 3,24-coordinated **rht**; 4,24-coordinated **twf**) were considered as well. Thus, we have examined all known binodal edge-transitive nets along with the most crystallochemically significant 3–8-coordinated binodal nets, as these coordinations are typical for metal-organic frameworks. Note that the RCSR database contains only 17 binodal nets that are not edge-transitive and have a node degree larger than eight (9–20). [These are (9,20)-**alb-x**, (6,18)-**ast-d**, (12,14)-**bet**, (12,15)-**cla-d**, (5,10)-**fit**, (3,9)-**gfy**, (10,12)-**mbc**, (12,16)-**mge-x**, (8,14)-**reo-d**, (12,12)-**tcj**, (12,12)-**tck**, (12,12)-**tcl**, (12,12)-**tcn**, (10,10)-**tcn**, (10,10)-**tco**, (9,20)-**tsl**, (3,9)-**xmz**. Hereafter the node degrees (n,m) are shown in parentheses before the symbol.]

From these 422 nets all subnets were derived (103 uninodal, which include 20 interpenetrated arrays, and 4024 binodal, of which 133 were interpenetrated), among which we found 3397

Table 2
Binodal-*quasi*-uninodal nets.

Refined unit-cell dimensions and node positions were obtained using *Systre*. The length of contacts between nodes is 1 Å.

Initial net	Transformation sequence and resulting space group	Node degrees, $D (n:N_n)$	Net name, Transitivity $pq†$	a (Å), x_1, x_2	b (Å)/ β (°), y_1, y_2	c (Å), z_1, z_2
cbo-e	$P\bar{a}3$	3, 3 (6:78)	cbo-e-3,3-$P\bar{a}3^{\ddagger}$ 23	4.000 0.2502 0.0418	4.000 0.2918 0.4925	4.000 0.4949 0.2480
mbc	$Cmcm \rightarrow C222_1 \rightarrow P2_12_12 (b, c, a; 1/4, 0, 0)$	7, 7 (1:7)	mbc-7,7-$P2_12_12$ 28	5.297 0.6786 0.4286	1.308 0.2500 0.2500	1.000 0.0027 0.5027
mbc	$Cmcm \rightarrow Cmc2_1 \rightarrow Pca2_1 (-b, a, c; 1/4, 1/4, 0)$	9, 9 (1:9)	mbc-9,9-$Pca2_1$ 29	5.975 0.9408 0.1775	1.000 0.7500 0.7500	1.000 0.2500 0.2500
tcj	$P6_3/mmc \rightarrow Cmcm (-a - b, a - b, c) \rightarrow Pnma (b, c, a) \rightarrow Pna2_1 (a, -c, b)$	9, 9 (1:9)	tcj-9,9-$Pna2_1^{\ddagger}$ 29	1.732 0.6667 0.5000	1.000 0.0000 0.5000	3.266 0.2500 0.5000
tcm	$R\bar{3}m \rightarrow C2/m [(1/3)a - (1/3)b + (2/3)c, -a - b, (1/3)a - (1/3)b - (1/3)c] \rightarrow P2_1/c (-c, -b, -a)$	9, 9 (1:9)	tcm-9,9-$P2_1/c^{\ddagger}$ 2(10)	3.365 0.3840 0.1160	1.000/106.8 0.1839 0.3161	1.982 0.3034 0.4174
tco	$Cccm \rightarrow Ama2 (c, a, b; 0, 0, 1/4) \rightarrow Pna2_1 (0, 1/4, 0)$	9, 9 (1:9)	tco-9,9-$Pna2_1^{\ddagger}$ 29	3.821 0.2790 0.0290	1.000 0.0963 0.2500	1.674 0.2767 0.1259

† p and q are the numbers of different kinds of topologically non-equivalent nodes and edges in the net (cf. Ockwig *et al.*, 2005). ‡ Binodal sphere packing.

topologically distinct nets (82.3%) not contained in the databases EPINET, RCSR and TTD, including 496 indirectly generated nets (14.6%). All the new nets but one correspond to binodal nets; the only novel uninodal subnet is 3-coordinated with vertex symbol [6.12₄.12₄]. No new edge-transitive nets were revealed. To designate subnets we have used **s-d-G-n** symbols (Blatov, 2007), where **s** is the conventional name of the initial net, **d** is a set of ascending integers equal to the degrees of all inequivalent nodes in the subnet, **G** is the space group for the most symmetrical embedding of the subnet and **n** is optional and enumerates non-isomorphic subnets with a given **s-d-G** sequence. For example, the symbol **stc-5,6-C2/m-1** encodes a 5,6-coordinated subnet of the 6,6-coordinated RCSR net **stc**; the highest possible symmetry of the net in Euclidean space is $C2/m$; there are other **stc** subnets with the same symmetry and node degrees; this one is the first net in the list.² Fig. 1 illustrates the procedure for deriving two subnets from (4,6)-**fsc** (see also Table 5 below); both subnets with the embedding of the original net as well as the *Systre*-optimized net are compared with one real example. Here we also show one case where the space group/embedding of the net in *Systre* (**fsc-3,5- $P4/mbm$**) differs from the one directly derived by the removal of some edges (**fsc-3,5- $Pnma$**): moreover the real structures often have another embedding (with

different space group, as for DOQRUW) but the underlying topology is preserved.

We consolidated all the initial nets with their subnets in a *net relation graph* (NRG), which shows pathways linking different topologies (Blatov, 2007). In total there are 4127 nets in the NRG, 3974 single and 153 interpenetrated, 4024 binodal and 103 uninodal, including the 3397 novel nets (82.3%). Most of the known 577 single nets (14.5%) are listed in the RCSR database (334), but there are also 225 EPINET nets (Table 1) and 18 TTD nets not reported among the RCSR nets [AFUQOH, B₂O₃ (high pressure) (34685), CaCl₂ (86209), Cs₂Se (41687), Cu₂S (16550), Cu₃As (100149), ENCDNB01, INIQR, LEJCAE, Mg₂C₃ (71941), NiP (27159), ScD_{0.33} (46032), SiO₂ (56684), SnF₂ (14194), TiSi₂ (96029), two uninodal sphere packings (3/8/c3 and 3/8/t7) and the minimal net 4(3)4]. [If a TTD net occurs in a real structure, it is identified by a refcode or collection code from the Cambridge Structural Database (CSD) or the Inorganic Crystal Structure Database (ICSD), respectively. Sphere packings are considered in detail by Koch *et al.* (2006) and minimal nets by Beukemann & Klee (1992) and Bonneau *et al.* (2004). All the TTD nets are simplified structures of inorganic or metal-organic frameworks; the simplification corresponds to the so-called *standard* representation (see §3).]

We have also treated all ten non-edge-transitive binodal RCSR nets containing 9–12-coordinated nodes; among them there are 12-coordinated close sphere packings [**tcj** (*hc*), **tck** (*hcc*), **tel** (*hhc*) and **tcm** (*hhcc*)]. As expected, the number of subnets for these nets is much larger; many of them have

² The crystallographic data for all 99 new binodal nets mentioned in this paper are available as a *TOPOS* database and a text file in *Systre* input format from the IUCr electronic archives (Reference: EO5002). Services for accessing these data are described at the back of the journal.

combinations of node degrees that are unusual for chemical compounds, for example (7, 8), (9, 11) *etc.* For this reason the remaining seven binodal RCSR nets with node degrees larger than 12 (**alb-x**, **ast-d**, **bet**, **cla-d**, **mgc-x**, **reo-d**, **tsl**) were not considered. Moreover, only directly generated subnets were analyzed for the ten 9–12-coordinated nets and among them there are 34 907 novel topologies. These topologies were not included in the NRG since most of them are not so important for crystal chemistry, otherwise they would have appeared among the subnets generated from the 422 nets in the sample used. Nonetheless, all the $3397 + 34\,907 = 38\,304$ novel topologies have been stored in the TTD collection and are available at <http://www.topos.ssu.samara.ru>. Among them there are 5959 *n*-regular binodal nets (15.5%) with the same coordination for both nodes (273, 586, 639, 1365, 1246, 1181, 468, 178 and 23 nets for the *n*, *n*-coordination, *n* = 3–11 respectively); we may also call them *coordinatively uninodal* or *homocoordinated*. In some exceptional cases *n*-regular binodal nets have a stronger similarity with uninodal nets, as can be seen if we consider other net invariants.

3. Degree of similarity between nodes: the rare binodal-*quasi*-uninodal nets

Following Blatov (2007), to determine the net topology we have used three invariants: (i) the *coordination sequence* $\{CS_k\}$, $k = 1-10$; (ii) the *vertex symbol* collecting the size and number of shortest *rings* (cycles that are not sums of two smaller cycles) meeting at angles of nodes; (iii) the *vertex symbol for cycles* collecting the size and number of shortest

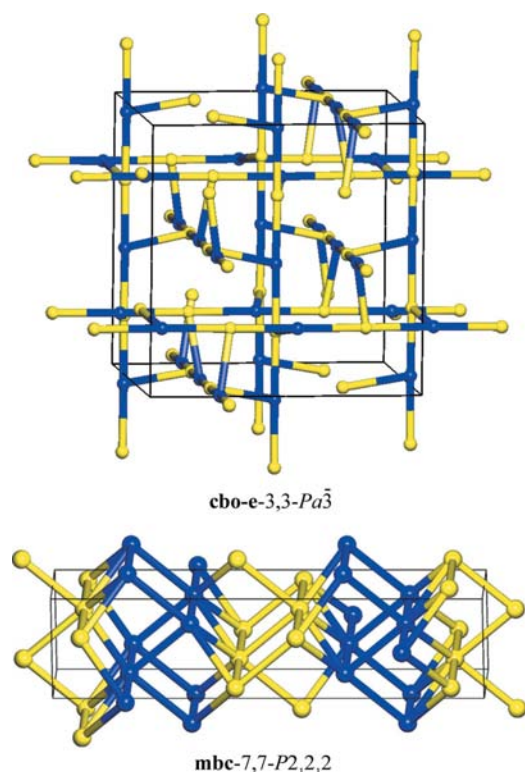


Figure 2
Two examples of the binodal-*quasi*-uninodal nets from Table 2.

cycles in the net. As mentioned by Blatov (2007), no examples of non-isomorphic nets are known with all the invariants equivalent. However, we have discovered six *n*-regular binodal nets with two topologically different nodes that have the same set of the three invariants and so very similar local topologies. Thus, it is reasonable to call them binodal-*quasi*-uninodal; they are gathered in Table 2. We also add the *transitivity pq*, where *p* and *q* are the numbers of different kinds of topologically non-equivalent nodes and edges in the net (*cf.* Ockwig *et al.*, 2005) as a rough measure of the complexity of the net; for example, edge-transitive nets have small transitivity values of 11 or 21.

The topological difference between the nodes in the six nets was found with *Systre*, which uniquely proves the isomorphism of crystallographic nets without collisions (Delgado-Friedrichs & O’Keeffe, 2003). The topological difference can also be demonstrated with one more invariant, the *cycle sequence* (Beukemann & Klee, 1994; Thimm & Klee, 1997), which extends the vertex symbol for cycles to all cycles up to a given size and can be computed with *TOPOS*.³ To study the nets in more detail, and to find a new invariant, we have implemented in *TOPOS* a procedure for searching for any kind of finite subgraph in a net; this procedure was used to compare *shell graphs* for inequivalent nodes. A *shell graph* SG_n is a graph obtained by successive growth of *n* coordination shells around a given node; it consists of $N_n = \sum_{k=1}^n CS_k$ nodes plus the origin and is unambiguously determined by its adjacency matrix. The adjacency matrix of a shell graph is a stronger invariant than the invariants mentioned above; the isomorphism of SG_n for given nodes means that the nodes are topologically equal within the first *n* shells; for complete isomorphism the nodes are topologically equivalent up to $n = \infty$. The degree of similarity (*D*) for the nodes can be expressed as $n:N_n$, where both numbers relate to the largest equal shell graph; the larger both numbers are, the closer the similarity. In this respect, the most similar are the nodes in **cbo-e-3,3- $Pa\bar{3}$** with $D = (6:78)$ (Table 2, Fig. 2), *i.e.* their shell graphs are locally isomorphous within the first six coordination shells and contain $N_6 + 1 = 79$ nodes; the strict similarity in the other nets is limited by the first coordination shell, $n = 1$, $D = (1:N)$. Obviously, the quantity *D* can also be used to compare nets; the larger the *D* values for corresponding nodes of the nets are, the more similar are the nets. Let us emphasize that unlike the invariants relating to cycles, the degree of similarity can be used not only to find the net isomorphism, but also to explore the local topological sameness of nets.

For the moment, binodal-*quasi*-uninodal nets are unknown in crystals; however, binodal nets with a high *D* exist. Probably the most exciting example is the crystal structure of bis(μ_3 -imidazole-4,5-dicarboxylato)-(μ_2 -4,4’-bipyridine)-diaqua-trizinc (XECBOX, Fig. 3*a*) (Lu *et al.*, 2006). Considering Zn atoms and centroids of ligands as nodes we obtain a net (Fig. 3*b*) that can be simplified further by removing dangling water molecules and converting bridge bipyridine and Zn nodes into

³ The cycle sequences computed with *TOPOS* for the six nets are given in the supplementary material.

edges (Fig. 3c). We call this simplified representation of a framework *standard* because it naturally follows the chemical description of coordination compounds made of metals plus ligands, so nodes are assigned both to metals and ligands.

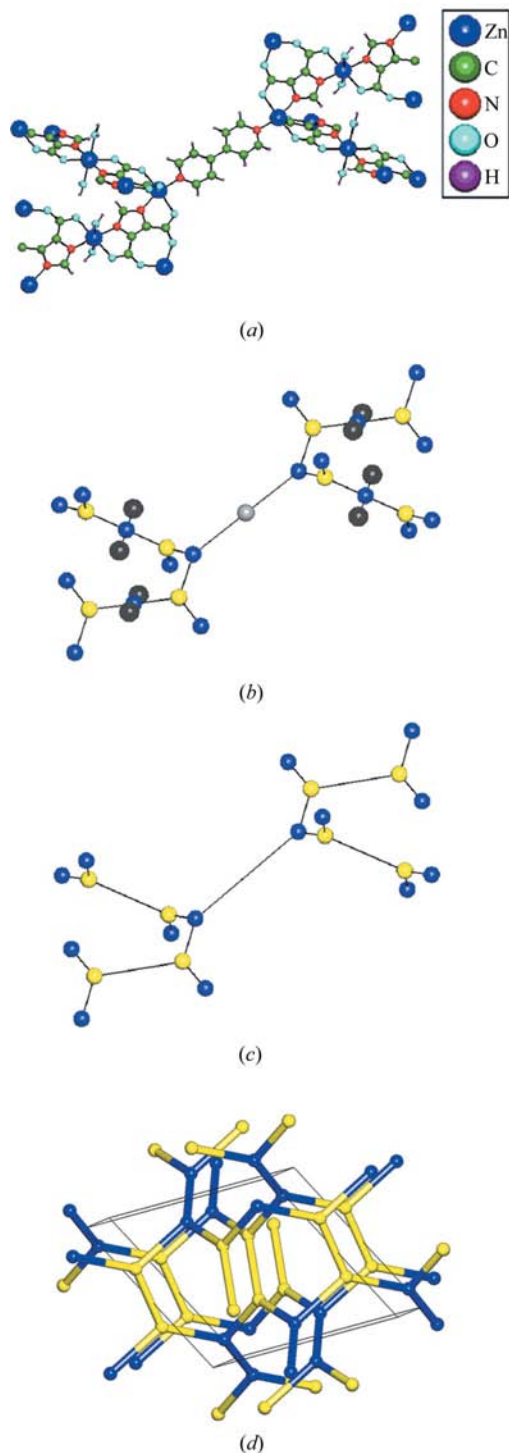


Figure 3
 Different representations of the XECBOX crystal structure. (a) Initial framework; (b) simplified net with the centroids of imidazole-4,5-dicarboxylate (yellow balls), 4,4'-bipyridine (grey ball) and aqua (black balls) ligands; (c) standard representation as **mbc-3,3- $P2_1/c$** obtained from (b) by removing dangling water ligands and contracting bridge bipyridine and Zn nodes into edges; (d) idealized **mbc-3,3- $P2_1/c$** net.

Table 3

The binodal nets with large NRG degrees (>50).

Net	Transitivity pq	Node degrees	NRG degree
cbs	26	5, 7	386
<i>sqc374</i>	26	4, 6	250
alb †	21	6, 12	228
fsg (<i>sqc10</i>)†	24	4, 6	187
cbs-5,6-$Cmmm$	26	5, 6	184
cbs-4,7-$Cmmm$	26	4, 7	175
stc ‡	23	6, 6	169
lib ‡	24	6, 6	144
crs-d (<i>sqc870</i>)	22	4, 8	134
hbr ‡	23	8, 8	124
cor-e ‡	28	7, 7	102
seh ‡	22	6, 8	102
cbs-5,6-$Pmma$	27	5, 6	99
fit-e ‡	23	7, 8	98
cbs-5,6-$Pmna$	27	5, 6	96
nbo-x-d	22	8, 8	95
cbs-4,7-$Pmna$	27	4, 7	92
cbs-4,7-$Pmma$	27	4, 7	89
fsx	23	5, 6	88
<i>sqc1067</i> ‡	24	5, 6	83
fsc (<i>sqc11</i>)†	22	4, 6	78
crb-e ‡	23	6, 6	73
stc-5,6-$C2/m-1$ ‡	25	5, 6	73
stc-5,6-$C2/m-2$ ‡	25	5, 6	73
cbs-4,5-$Cmmm$ ‡	25	4, 5	71
scu (<i>sqc170</i>)†‡	21	4, 8	68
rho-e ‡	24	6, 6	65
neb-e ‡	24	6, 6	62
gis-e ‡	24	6, 6	59
<i>sqc280</i>	25	4, 5	58

† Occurs in crystal structures. ‡ Binodal sphere packing.

Standard representations can be obtained by *TOPOS* in an automated mode. The resulting net is 3,3-coordinated binodal with nodes corresponding to imidazole-4,5-dicarboxylate ligands and Zn atoms. It is among the NRG nets and can be derived from the (10,12)-**mbc** net, hence the symbol is **mbc-3,3- $P2_1/c$** . Both vertex symbols (for rings and for cycles) for the two nodes are [10.10.10₃], but coordination sequences differ starting from the eleventh shell, so the net is not binodal-*quasi*-uninodal. However, $D = 9:702$, so the nodes are locally strongly similar, up to the ninth shell, and play almost the same role in the net.

4. Topological relations between binodal nets

As mentioned by Blatov (2007), the crystallochemical significance of a net is reflected in the role that the net plays in the NRG. If other factors are equal, the nets with large NRG degrees have a higher probability of occurring in nature because they are related to many other nets and have a lot of ways to be transformed to/from other topologies. In Table 3 the single nets with the largest NRG degrees (>50) are collected and in Fig. 4 we show the embeddings for the first six. Note that, compared to uninodal nets (Blatov, 2007), interpenetrated arrays are not as significant in the NRGs of binodal nets; the largest degree (40) belongs to (3,6)-**sit** twofold interpenetrated.

As for uninodal nets, the occurrence of binodal nets depends on the node degree; the most frequent combinations

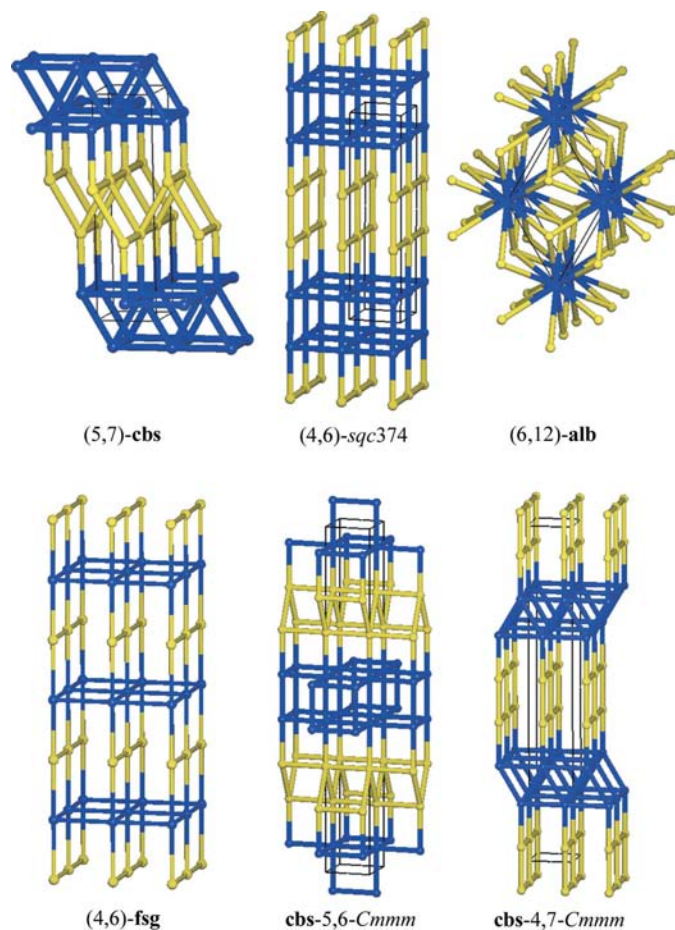


Figure 4
Six *Systre*-idealized nets with highest NRG degree taken from Table 3.

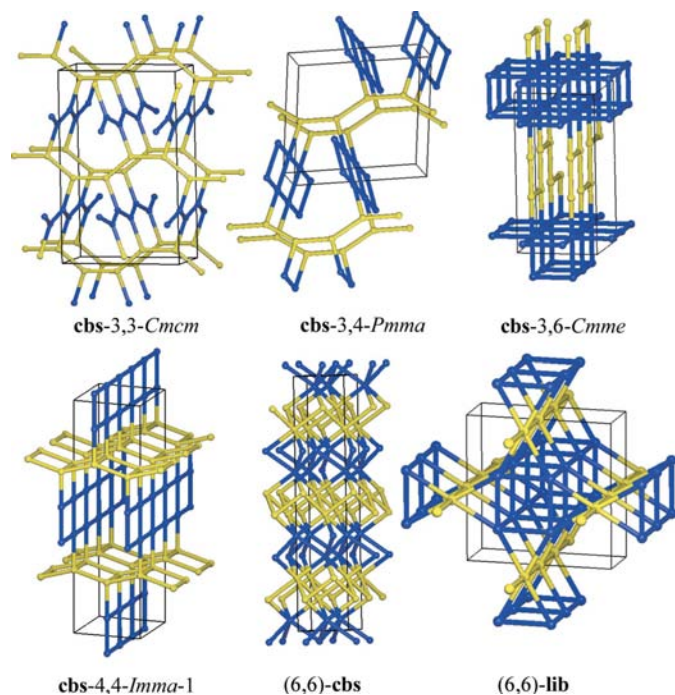


Figure 5
Six selected representatives of 3, 4 and 6-coordinated nets from Table 4.

typical for metal-organic frameworks correspond to small node degrees of 3, 4 or 6. Many nets in Table 3 have other node degrees, therefore in Table 4 we collect the first ten nets with the largest NRG degrees for some typical coordinations and in Fig. 5 we show one net for each coordination. Note that among the nets in Tables 3 and 4 there are many binodal sphere packings, *i.e.* embedding of the type 1a or 1b (Delgado-Friedrichs & O’Keeffe, 2005). Let us emphasize that unlike uninodal sphere packings, which have been intensively studied for years [Koch *et al.* (2006) and references therein], polynodal sphere packings have not been considered in the literature, although some of them are collected in the RCSR database. There are obvious correspondences between nets in Tables 3 and 4: many nets with novel topologies are subnets of the nets with a large NRG degree, such as **cbs**, **fsc**, **fsg**, **seh**, **stc**. Thus, some nets can be crystallochemically significant *indirectly*: the nets themselves do not occur in nature, but their subnets do. At the same time, some nets with a large NRG degree do not

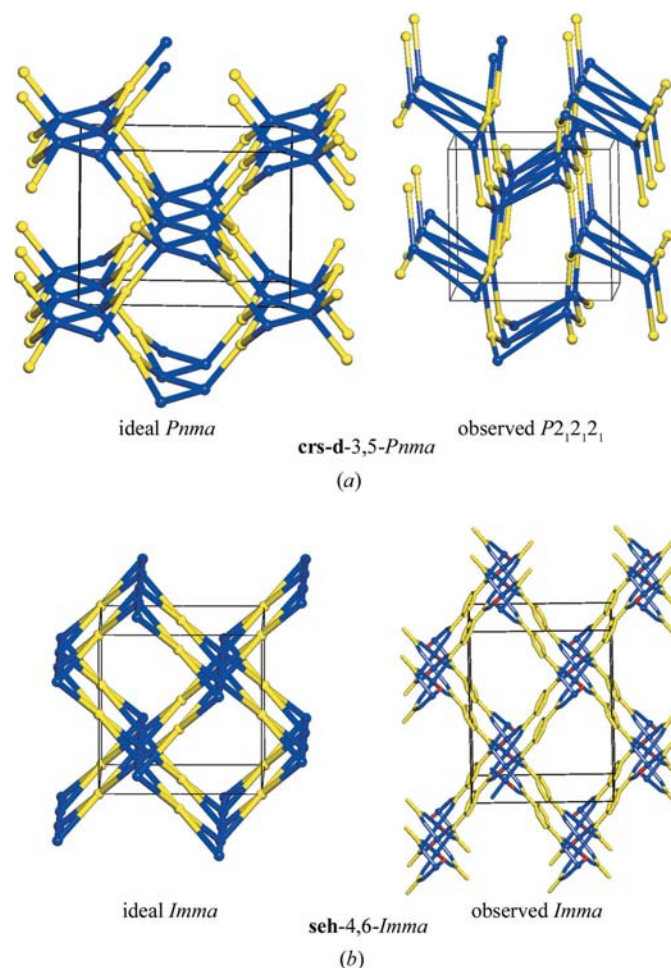


Figure 6
(a) The ideal **crs-d-3,5-*Pnma*** net with the one observed in four (cobalamine) $X(\text{LiCl})_2$, $X = \text{N}^{3-}$, Cl^- , NO_3^- , CN^- (refcodes GIZYOD, GIZYUJ, HUSPAM, WIKXUJ); the 5-coordinated node represents the cobalamine and the 3-coordinated node represents the Li. (b) The ideal **seh-4,6-*Imma*** net with the one observed in two $M(\text{OH})(1,4\text{-benzenedicarboxylato})$ complexes, $M = \text{Cr}^{3+}$, Al^{3+} (refcodes MINVUA, SABVUN; the bridging oxygen is shown in red).

Table 4

A selection of binodal nets with node degrees 3, 4 or 6.

Node degrees 3, 4 or 6 are typical for coordination compounds. The ten nets with the largest NRG degree for each class are listed.

Net	Transitivity <i>pq</i>	NRG degree	Net	Transitivity <i>pq</i>	NRG degree	Net	Transitivity <i>pq</i>	NRG degree
3,3-coordinated (3-regular) nets			3,6-coordinated nets			4,6-coordinated nets		
cbs -3,3- <i>Cmcm</i> †	24	28	cbs -3,6- <i>Cmme</i> †	27	37	<i>sqc</i> 374	26	250
baf -3,3- <i>I4/mmm</i> †	23	27	ant †‡	22	27	fsg (<i>sqc</i> 10)‡	24	187
baf -3,3- <i>Imma</i>	24	26	cbs -3,6- <i>Cmmm</i> -1	25	20	fsc (<i>sqc</i> 11)‡	22	78
cbs -3,3- <i>C2/m</i> -2†	25	23	cbs -3,6- <i>Cmmm</i> -2	26	19	stc -4,6- <i>P3m</i> 1†	23	46
bbe -3,3- <i>Imma</i> †	23	22	mge -3,6- <i>I4</i> 122	22	18	stc -4,6- <i>R3m</i>	23	46
cbs -3,3- <i>Pmma</i> †	25	21	rtl †‡	22	16	cbs -4,6- <i>Pmma</i>	26	36
iph †	23	21	<i>sqc</i> 251	25	16	cbs -4,6- <i>Pmmm</i>	26	33
fsg -3,3- <i>Fddd</i> †	23	17	<i>sqc</i> 2983	25	16	cbs -4,6- <i>Imma</i>	27	33
nof †	23	17	cbs -3,6- <i>Cmcm</i> -1	26	15	fsd (<i>sqc</i> 61)†	23	32
fry -3,3- <i>C222</i> †	25	16	cbs -3,6- <i>Cmcm</i> -2	26	15	<i>sqc</i> 502†‡	22	32
3,4-coordinated nets			4,4-coordinated (4-regular) nets			6,6-coordinated (6-regular) nets		
cbs -3,4- <i>Pmma</i>	25	38	cbs -4,4- <i>Imma</i> -1†	26	19	stc †	23	169
cbs -3,4- <i>Cmmm</i> -1	25	28	cbs -4,4- <i>Cmcm</i> †	26	16	lib †	24	144
cbs -3,4- <i>Cmmm</i> -2	24	25	baf †	25	15	crb -e†	23	73
fry †	25	24	ful †	27	14	rho -e†	24	65
tfi (<i>sqc</i> 515)†‡	22	23	mog -e-x-z-4,4- <i>I4/mmm</i> †	24	14	neb -e†	24	62
bbe -3,4- <i>Cmmm</i> †	23	22	bcp †	24	13	gis -e†	24	59
cbs -3,4- <i>Cmme</i> †	25	20	bcq (<i>sqc</i> 941)†	24	13	sta †	22	48
cbs -3,4- <i>Fmmm</i> †	25	18	fvq †	27	13	stb †	22	48
<i>sqc</i> 1255	24	18	mot (<i>sqc</i> 29)‡	22	13	nia †‡	21	39
<i>sqc</i> 185†	22	18	pts (<i>sqc</i> 183)†‡	21	13	mhg †	25	29

† Binodal sphere packing. ‡ Occurs in crystal structures.

Table 5

Seventy-six metal-organic frameworks with the (4,6)-coordinated **fsc** and derived new topologies.

Topology	Transitivity <i>pq</i>	No.	Refcode from CSD
fsc	22	25	AGPYRZ01, DEKHEH, DEKHUX, DEQVIF, DOYLAE, DOYLIM, EJAXAO, GIFKAH, GIFKEL, GIFKIP, IGAHED, KAHPUK, KONYOB, NARCUF, OLOKEF, RABGUS, RABHAZ, RABHIH, SARNEF, SOVHAM, SOVHIU, SOVHOA, TEHLUO,† WACJUG, ZURQOS
fsc -3,4- <i>Pbca</i>	24	10	EXEMAV, HACPOR, LUZYUA, MICDIL, MICDUX, QESPIO, QOBHEU01, VAMWAI, VAMWEM, XAGTEE
fsc -3,5- <i>P4/mbm</i>	23	9	DOQRUW, EVOMOR, HAOAER, LARMUN, NETFAU, NETFEY, OBUFEX, OGEYII, YAHPEP
fsc -3,4- <i>Imm2</i>	23	8	EJOZAE, EJOZEI, GACQUX, IRIWEL, OJOBIY, SANBOZ, SANBUF, XUHSOI
fsc -3,4- <i>Pnma</i>	24	6	ESIGES, LEGGIO, LOPSI, LOPSOY, NAXMAB, PEPBAO
fsc -4,5- <i>Cmmm</i>	22	4	NIVWIY, OCUSIP, XEHFUL, XOMCIL
fsc -3,5- <i>Pbcm</i>	24	3	MIYZEZ, XARNOU, XARPAI
fsc -3,4- <i>Pbcn</i> -2	24	2	JOVDON, VODSEM
fsc -3,5- <i>Cmce</i> -2	24	2	AXIMUP, BARJIO
fsc -3,4- <i>C2/c</i>	24	1	NERMON
fsc -3,4- <i>I4</i> 1/amd	23	1	LEGHIP
fsc -3,4- <i>Iba</i> 2	24	1	MAYYER
fsc -3,4- <i>Pbcn</i> -1	24	1	ACUXAY
fsc -3,4- <i>Pbcn</i> -3	24	1	ECIVOB01
fsc -3,5- <i>C2/c</i>	25	1	TEDDOW
fsc -3,5- <i>Cmce</i> -1	24	1	KIBCAA

† Obtained by 'cluster representation'.

produce crystallochemically significant subnets of novel topology; among them there are *sqc*374, **lib** and **hbr**.

5. Occurrence of the binodal nets in metal-organic frameworks

For the moment, there are no comprehensive data on the occurrence of binodal nets in crystal structures. Ockwig *et al.*

(2005) listed examples of *n*-regular binodal nets and found more than one example for the 3-coordinated (3-regular) nets **nof** and **noj**, 4-coordinated **pts** and **mog**, 5-coordinated **nok** and 6-coordinated **nia**; four of them, **nof**, **pts**, **nok** and **nia**, are among the significant NRG nets (see Table 4; indeed **nok** occupies the fourth place among the 5,5-coordinated nets). To assess the occurrence of other binodal nets, the total file of crystallographic data on inorganic and metal-organic frame-

Table 6

Eleven hydrogen-bonded and 102 metal-organic frameworks with topologies of some new subnets derived from nets with a large NRG.

The refcodes for hydrogen-bonded frameworks are given in italics.

Topology	Transitivity <i>pq</i>	No.	Refcode from CSD†
alb -3,6- <i>C2/c</i>	23	1	SUYGAU‡
alb -3,6- <i>P4₂/mnm</i>	22	3	HENYUV, HESVOR, SAQYOZ
alb -4,8- <i>P4₂/mmc</i> §	21	1	PUWDAM
alb -4,8- <i>P2₁/c</i>	24	3	LIOXAT, MAQDUD, RORQOE
alb -4,8- <i>Pbcn</i>	24	4	JESCEQ, MUQSIA, MUQSOG, MUQSUM
alb -4,8- <i>Pnma</i>	24	1	WUTLOM
alb -5,10- <i>P2₁/c</i>	25	2	EQUWIW, IWERAD
bbe -3,4- <i>Cmmm</i>	23	4	<i>IBIJAF</i> , JUPFOR, <i>RUJVAT</i> , <i>YUTCEV</i>
cbs -3,3- <i>C2/m-1</i>	25	1	AXUDUS
cbs -3,3- <i>Pmna</i>	25	1	UJUXOM
cbs -4,4- <i>Imma-2</i>	25	1	DOSJAW
crb -e-3,4- <i>P4₁2₁2</i>	25	1	HATZOS
crs -d-3,5- <i>Pnma</i>	23	8	<i>DODWEY</i> , GIZYOD, GIZYUJ, HUSPAM, RARYIT,‡ RARYOZ,‡ RARYUF,‡ WIKXUJ
fit -e-4,4- <i>C2/m</i>	24	1	QEJDIS
fsg -3,4- <i>C2/c</i>	25	1	NIBNAO
fsx -4,5- <i>P2₁2₁2</i>	25	3	DEHBIC, MAYXUG, MAYYAN
fsx -4,5- <i>R3m</i>	23	3	<i>HYXBUR10</i> , YETPOD, YETRAR
fsx -3,4- <i>C2/c-1</i>	24	1	RUFLIN
fsx -3,4- <i>C2/c-2</i>	24	1	MEVBIZ
fsx -3,4- <i>Pccn</i>	24	1	PENZUE
fsx -4,5- <i>P6₃/mmc</i>	23	1	LECHUX
fsx -4,5- <i>C2/c</i>	25	1	LOQVOC
fsx -4,5- <i>Cmce-1</i>	24	1	YALYIU
fsx -4,5- <i>Cmce-2</i>	24	1	ACUTOI
nbo -x-d-4,4- <i>C2/m</i>	24	1	QEQSIP
nbo -x-d-4,4- <i>I4₁/amd</i>	23	1	DEQFOU
nia -4,4- <i>Pbca</i>	24	3	<i>CEJRUE</i> , NEHMET, WINJOS
nia -5,5- <i>P2₁/c</i>	25	3	<i>FELRUJ</i> , IZAVUA, QAJLAP
seh -4,6- <i>Imma</i>	22	25	AHEFAU, EBITUF, FEJHOS, GUSNEN, GUXQEV, IDIWIB, IDIWOH, MAYJOM, MINVOU, MINVUA, NENXIO, PARPII, PARPUU, PEPLAY, PEPLEC, PEPLIG, PEPLOM, SABVOH, SABVUN, SABWAU, VELVEO, WESYAV, WESYEZ, YAXBOP, YAXBUV
seh -3,5- <i>Cmc2₁</i>	23	6	BAHGUN, QERZUI, RIGGIY, UFUMUD, UFUNAK, UFUNIS
seh -3,5- <i>P2₁/c</i>	24	6	ACUBOP, BIDZAO, DEGSIS, NEGDOT, NENDEQ, PEXSOB
seh -3,5- <i>P4₂2₁2</i>	23	6	<i>BUYROCI0</i> , <i>DIWFIY</i> , <i>QUKJEL</i> , WEWTOI, <i>WOGFED</i> , XALXIS
seh -3,5- <i>Pbca</i>	24	2	MAPFOY, QAMNOI
seh -3,5- <i>Pna2₁</i>	24	1	LUNVUL
seh -4,6- <i>P2₁/c-1</i>	25	1	CUCITD01
seh -4,6- <i>P2₁/c-2</i>	25	1	IKEWIE
seh -4,6- <i>P2₁/c-3</i>	25	1	LELXAC
seh -5,7- <i>P2₁/c</i>	26	1	INIZAG
<i>sqc</i> 502-4,5- <i>P4₂/mnm</i>	23	2	MUTNAQ, TEGMOH
<i>sqc</i> 502-3,5- <i>P4₃2₁2</i>	25	1	ACAZEK
sta -4,4- <i>Cccm</i>	22	1	EMAYUM
stb -4,4- <i>P2/c</i>	24	1	VASBUN (2)
stb -5,6- <i>C2/m</i>	23	4	IDAGOK, IDAGUQ, JEVTAG, XAKXAJ

† For interpenetrated arrays the number of nets is given in parentheses. ‡ Obtained by 'cluster representation'. § Net with collisions.

works should be processed. This would be a large task; here we consider only some examples of the NRG binodal nets found in organic and metal-organic frameworks. To find the examples reported in Tables 5–7 we have automatically generated the standard representations for 2131 three-dimensional metal-organic polymeric frameworks and 2473 hydrogen-bonded organic and metal-organic frameworks: their net topology identifications are currently contained in the TTO collection. If the standard representation gives unknown topology, we applied a newly designed *TOPOS* procedure for an automated search for clusters of nodes in augmented or decorated nets. After contracting such clusters to their centroids, the resulting net contains only the centroids of the clusters and edges connecting them; we will call this *cluster*

representation (details on the procedure will be discussed in a future publication).

According to Table 3, many binodal nets with mixed coordination play a significant role in the NRG. Among them there are 4,6-coordinated nets not considered by Ockwig *et al.* (2005). Examples for the *sqc*374 net are still unknown, but we have found two **fsg** nets of hydrogen-bonded organic molecules (JIKHOA and THYMDN01), as well as two organic hydrogen-bonded (WELMEF and a threefold array in TIJKOM) and 25 metal-organic frameworks with the **fsc** topology (Table 5 and Fig. 1). It is important that many novel binodal nets derived from **fsc** have been revealed among crystal structures as well. This fact proves that the **fsc** motif plays a significant role in metal-organic frameworks.

Table 7

Four hydrogen-bonded and 152 metal-organic frameworks with topologies of binodal edge-transitive nets.

The refcodes for hydrogen-bonded frameworks are given in italics.

Topology	Node degrees	No.	Refcode†
alb	6, 12	1	YADQUO
bor (<i>sqc975</i>)	3, 4	1	TOJLOT (2)
cys	3, 6	2	PEXFAA, RIZXUT
flu (<i>sqc169</i>)	4, 8	12	CAZLEV, GAKSOB, JEXPEI, JEXPUY, MEWNAD, NAZDAU, NUXLUN, NUXMEY, TOBHAT, TOJVUJ, VADQAS, YUGJEP10‡
gar (<i>sqc11070</i>)	4, 6	1	VEJZAM
nia	6, 6	17	AFOJEK, AHIJOO, BIVWAE, BMSLAG, ERUPEM, FOFGUD, HAZBOA, JETNIF, JETNOL, KOVYAV, MOYBIL, NIDQEX, NIDQIB, OFIRUQ, PIQSOX, RAQVIP, YEYMIY
pth	4, 4	4	GELVEZ, GELVID, SIYXIH, WIXJIW
pto (<i>sqc5591</i>)	3, 4	2	WILRAK, WILREO
pts (<i>sqc183</i>)	4, 4	84	AJAXOY, AQEQES, AQEQIW, ARUTIQ,‡ AVITUU, AVIVAC, AVIVEG, AVIVIK, AVIVUW, BALLOP (2), BEBCOB, BECRUX, BEDJEA, BEGJUT, BOCKOT, CEVVEF, CEVVIJ, COHGPY, DAYMAS, DEKJAF, DIFCEB,‡ EGUHET, EGUHOD, ETOQIN, ETOQOT, FAZRAA, FENROG, <i>FEZPUV</i> , FIJDAE, FITMAW, HICRUG, HUQMOV, HUTZAX, IFABIA01, JEDJUY, KAPHOZ, LARBOW, LAXNII, LIDEGL, LIVTEP, MELKOD, MEMGAN, MEZSAL, MIMRAB, NATNOM, NIKDAM, NIKDEQ, NIKDIU, NINHOH, OCETEW, OFUWIV02, PANMOH, PAVLOO, PAVLUU, PAVMAB, PEQWAK, PIZIAJ (2), PIZJEN, RAHTAV (2), RAMHUI, REHRAY, SAQYIT, SIVJAI, SUCCUR01, SUDBOI, TECFEM, UCUTIW, UFUKUB01, UGUQOC, UKAYIO, VOZHEX, WASVES,‡ WAZCAB, WEKXAM, WAWGOQ (2), WEBHEQ (2), WOZKUR, XATNIP, YARYEV, YARYIZ, YEMLOS, ZEZGOA, ZUWMIN, ZZZGSA02
pyr	3, 6	10	CUXKEL, ITAPAU,‡ KEYYET,‡ KIBXEZ, KIBXID, KIBXOJ, LEMNOH, QEYWUN, QIGBIR,‡ YUBRUI
scu (<i>sqc170</i>)	4, 8	8	EVUDAA, <i>ICIFEF</i> (2), <i>ICIFIJ</i> (2), MECMEN, MEWNEH, NUXMAU, <i>RAXMOT</i> (2), RICGOA
soc	4, 6	3	IXIPEK,‡ IXIPIO,‡ IXIPOU‡
spn	3, 6	1	ICIZEZ
stp	4, 6	10	GUFWIN, GUFWUZ, ILIFUE, ILIGAL, ILIGEP, ITAHEQ, SERJOP, SERJUV, SERKAC, SERKEG

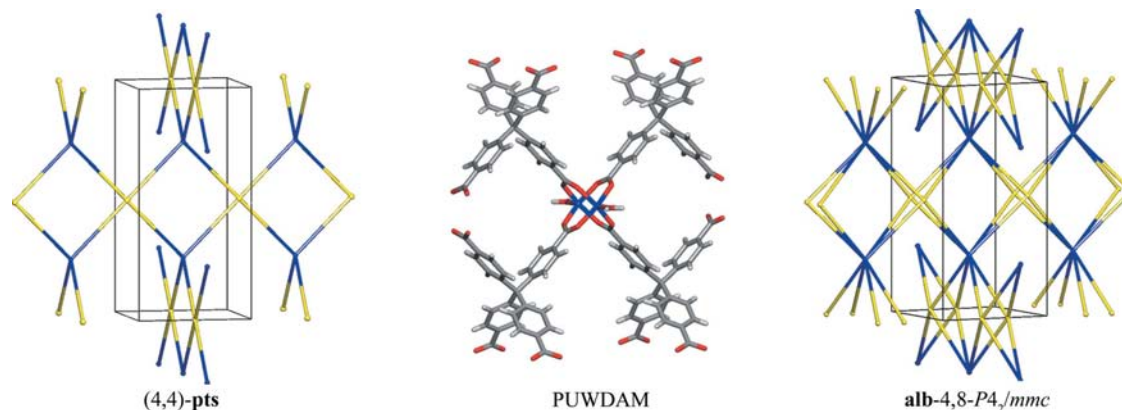
† For interpenetrated arrays the number of nets is given in parentheses. ‡ Obtained by 'cluster representation'.

Some nets with large NRG degrees have still not been found in crystal structures, but their subnets can be rather frequent (Table 6 and Fig. 6). It is relevant to note that all frequently occurring nets from Tables 3–6 have small (21–24) transitivities, which is in agreement with the ideas of Ockwig *et al.* (2005). The nets producing many subnets from Tables 5 and 6, such as **fsc**, **fsx** and **seh**, also obey this condition. Note an interesting example of a novel edge-transitive net but with collisions (**alb**-4,8- $P4_2/mmc$), which is closely related to (4,4)-**pts**, another edge-transitive net (see Fig. 7) [for more on nets

with collisions see Carlucci *et al.* (2007) and Delgado-Friedrichs & O'Keeffe (2003)].

Table 7 contains all known examples of binodal edge-transitive nets [13 out of 27 3–8-coordinated nets as well as (6,12)-**alb**] in metal-organic frameworks. Thus, the data confirm the assumption of Delgado-Friedrichs *et al.* (2006, 2007) about the importance of edge-transitive nets for crystal chemistry.

Many nets from Tables 3 and 4 have not been found in crystal structures so far, but not all known crystal structures


Figure 7

The two possible descriptions of the metal-organic framework observed in the crystal structure of PUWDAM, Zn_2 [tetrakis(4-carboxyphenyl)methane]: on the left is the usually chosen edge-transitive (4,4)-**pts** net [nodes: $Zn_2(COO)_4$ paddle wheel and the tetrahedral ligand]; on the right a different simplification that gives **alb**-4,8- $P4_2/mmc$, a rare edge-transitive net with collisions (nodes: the octa-oxygen donor ligand as 8-coordinated and the Zn as 4-coordinated).

have been topologically investigated. Moreover, there are obviously other useful parameters related to the net global topology besides the node coordination, coordination figure, net transitivity and NRG degree mentioned by O'Keeffe *et al.* (2000), Ockwig *et al.* (2005) and Blatov (2007). Attention should be drawn to local topological features and to symmetry relations in the net (Baburin & Blatov, 2007).

6. Concluding remarks

Our results show that the method for deriving subnets using space-group–subgroup relations is most general and, in principle, can be successfully applied to generate nets of any coordination. Many of the resulting subnets occur in crystal networks; the topological motifs that are important for crystal chemistry can be found by analysis of the experimental crystal data stored in electronic topological databases, taking into account the information on net–subnet relations. In fact, this approach opens a new phase in the development of crystal science: the search for overall structure correlations on the basis of all experimental data collected by structural chemistry. An important task at this stage is to extract the occurrence of nets in all crystal structures; a detailed analysis of the occurrence will be presented in a future article.

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