Two Exceptional Patterns of Helical SBUs Found in MOF Structures.

Eugeny V. Alexandrov[‡], Andrey V. Goltsev[‡], Michael O'Keeffe[†*] and Davide M. Proserpio[‡§*]

[†] School of Molecular Sciences, Arizona State University, Tempe AZ 85287, USA.

[‡] Samara Center for Theoretical Materials Science (SCTMS), Samara University, Ac. Pavlov Street 1, Samara 443011, Russia.

[§] Dipartimento di Chimica, Università degli Studi di Milano, Milano 20133, Italy

Abstract: We report the first example of a rod MOF in which the rod axes intersect. It suggests a new area of reticular chemistry in which helical rods that can be linked into frameworks are designed

INTRODUCTION

In a recent study[1] of the structures of metal-organic frameworks (MOFs) with rod-shaped secondary building units (SBUs) many structures were described in which the rod axes were either parallel or were in two different directions (*2-way*). Only one structure with 3-way rod axes was reported.[2] A more-recent study[3] of structures containing rod-like groups found a number with 3- or 4-way rod axes. Of these three qualified as rod MOFs as defined below. One of them[4] (CSD refcode = QANSUV) had the same 3-way pattern of rod axes as in the previously described MOF[1,2] and is not discussed here. However, the other two essentially isostructural examples which we describe in this communication, have a structure of a type which we believe has not been recognized before.

Cubic 3-way and 4-way rod MOF structures are rare in part because with rectilinear rods the cell edge is determined by the spacing between units of the rod; the dimensions of the organic linker joining the rods have to exactly right to fit in the fixed cell size. There is more flexibility in helical rod as the pitch of the helix can be varied to accommodate the linker dimensions as in the MOF structure here described.

We also found a MOF with a second novel structure type involving helical rods on a 2-way rod packing so that the helix axes are not along principal symmetry axes.

STRUCTURE DESCRIPTIONS

The two structures, although described somewhat differently by the authors[5,6] are in fact isoreticular, indeed essentially isostructural (with interchange of Cu and Ag). This observation can readily be verified using the *standard representation* of ToposPro[7]. This method determines the net formed by the links between metal atoms and the centers of the organic linkers with additional links between pairs of metal atoms if they are bonded to the same anion (Figure 1). This process is objective and readily implemented for computer searches for isoreticular structures in large databases. For the two MOFs $[Cu_2(btr)_2]\cdot 2NO_3$ (JONKEE[5], btr= 4,4'-bi-1,2,4-triazole) and $[Ag_2(btr)_2]\cdot 2ClO_4\cdot 3H_2O$ (YIKJUZ[6]) the program gives the same four-nodal 4-coordinated underlying net in standard representation, named 4,4,4,4T73 (Figure S1).

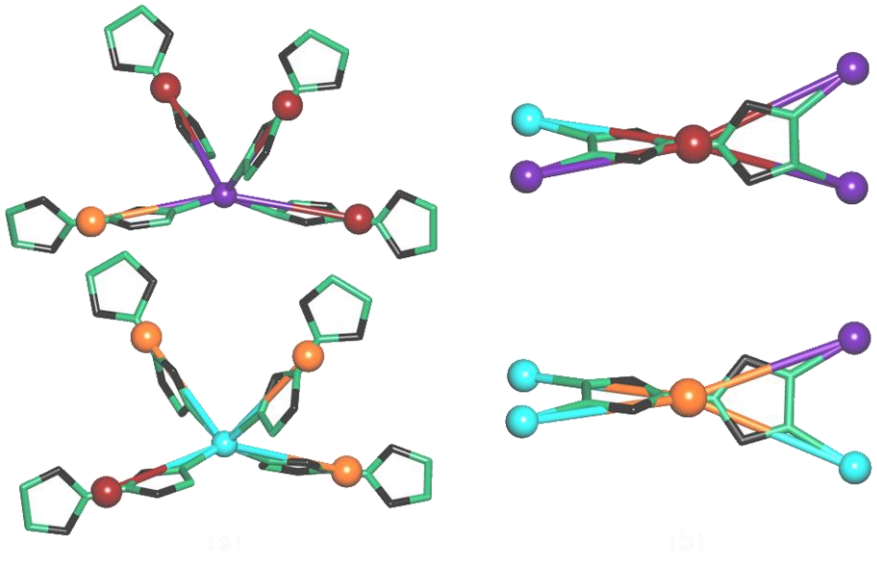


Figure 1. On the left, the environment for the two symmetrical distinct complexing metals M=Cu, Ag (cyan and violet) and on the right for the two ligands (C black, N green).

However, in the theory and practice of reticular chemistry one is concerned with linking polyatomic units (known generally as SBUs) into symmetrical frameworks[8]. In this approach the shape of the metal SBU is determined by identifying *points of extension* that mark the interface between the metal SBU and the organic linker. In the large class of carboxylate MOFs the points of extension are taken as the carboxylate carbon atoms. However, the choice of points of extension, and of how to link them into a shape can be subjective, so is less amenable to computer searches of large databases.

Metal atoms that are joined directly (i.e. not through an organic linker) to a common atom or to a common point of extension are considered to be part of the same metal SBU. SBUs that are infinite in one direction are termed *rod* SBUs.

In the materials that are the subject of this communication Cu(or Ag) atoms are linked by azolate linkers. Each metal is coordinated to four N from four different triazolate rings. Furthermore, the N-N pair is linked to two Cu atoms rather as in carboxylates so the point of extension is chosen as a fictive atom situated between these two bridging atoms as shown in the figure 2.

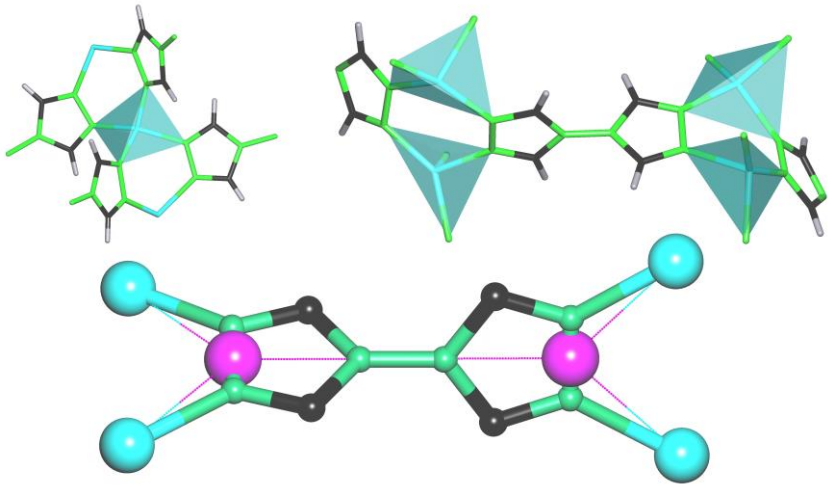


Figure 2. The MN_4 tetrahedral coordination of the metals, and the four coordination of the ligands btr in $[M_2(btr)_2]^{2-}$ (M = Ag, Cu). Hydrogen grey, carbon black, nitrogen green, copper cyan. The larger magenta spheres mark the points of extension.

In this approach, metal atoms joined to the same point of extension are considered as belonging to the same SBU (just as the two Cu atoms in the familiar copper paddlewheel SBU). It follows that the tetrahedron around each metal expands up to the point of extension, defining the infinite SBU as a rod of tetrahedra sharing opposite edges as shown in the sequences

a → b →c in figure 3. These rods form 4_1 or 4_3 helices with 16 tetrahedra per repeat unit.

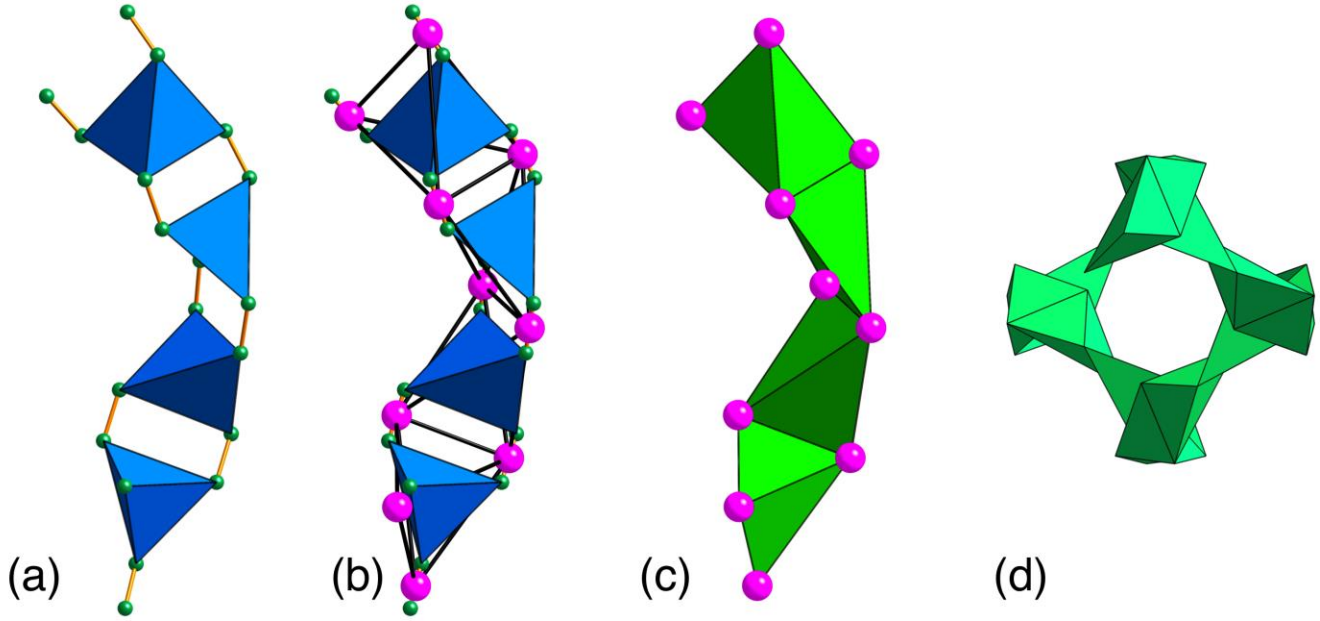


Figure 3. (A) part of a rod of CuN_4 tetrahedra linked by N-N bonds (b) the same with the points of extension (magenta) indicated. (c) the pattern of points of extension as green tetrahedra sharing opposite edges. (d) the rod in (c) projected down the rod axis.

ToposPro provides a way to find rod SBUs in automatic mode using the the "cluster" algorithm that search for clusters by extracting the shortest cycles for each independent bonds in the unit cell.[9] Only short cycles, up to 12 edges, form dense SBUs, where metal atoms can be connected directly through the points of extension. This procedure applied to our structure, shown in Figure 4, finds a bond (circled in black) that belongs to a very large circuit (4a in yellow). Marking such bond as inter-cluster,

divide the structure into infinite 1-periodic SBUs (figure 4b,c) of composition M(btr). It is then possible to expand the tetrahedron to include the N-N pair (or the 1,2,4-triazole ring) so to get the same edge sharing tetrahedra helical chain seen in figure 3c (figure 4c).

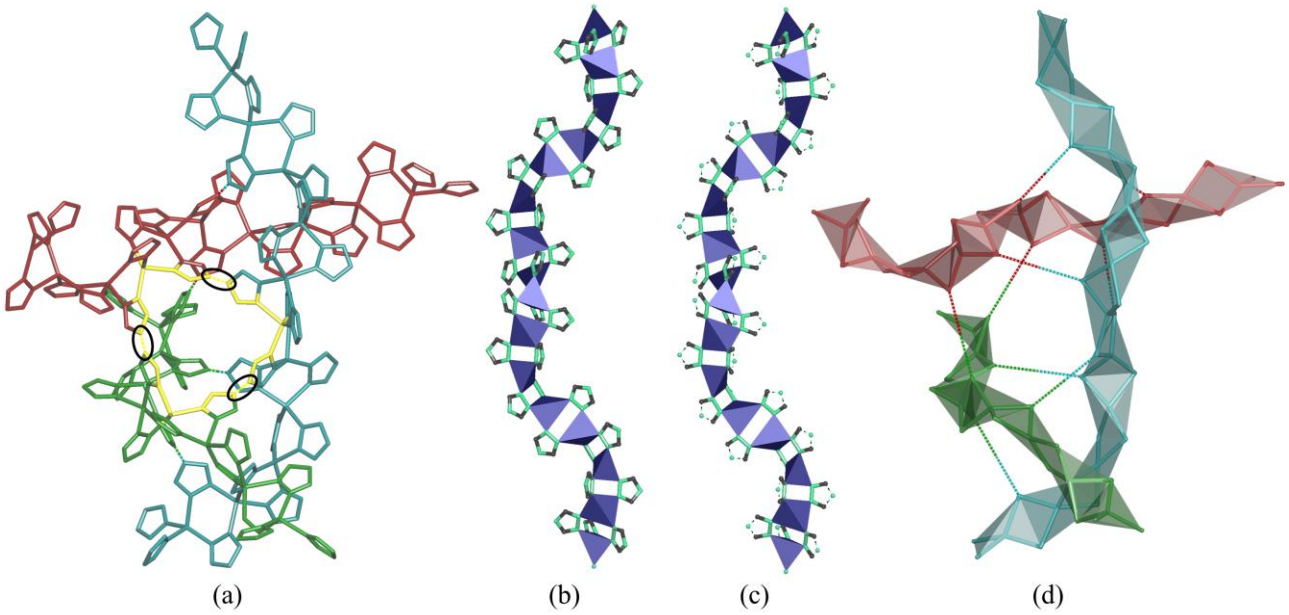


Figure 4. The process of rod SBUs searching: three differently rods are identified by cluster simplification procedure (a), inter-rod bonds are circled in black. The isolated rod (b). The three intersected rods connected by points of extension (c).

Figure 5 shows (a) how the rod axes intersect in pairs and (b) how the rods are linked so their axes are in three mutually-perpendicular directions. The full pattern of rod axes is shown in the figure 6. The pattern of linked intersections is the cubic 4-c net **nbo**.

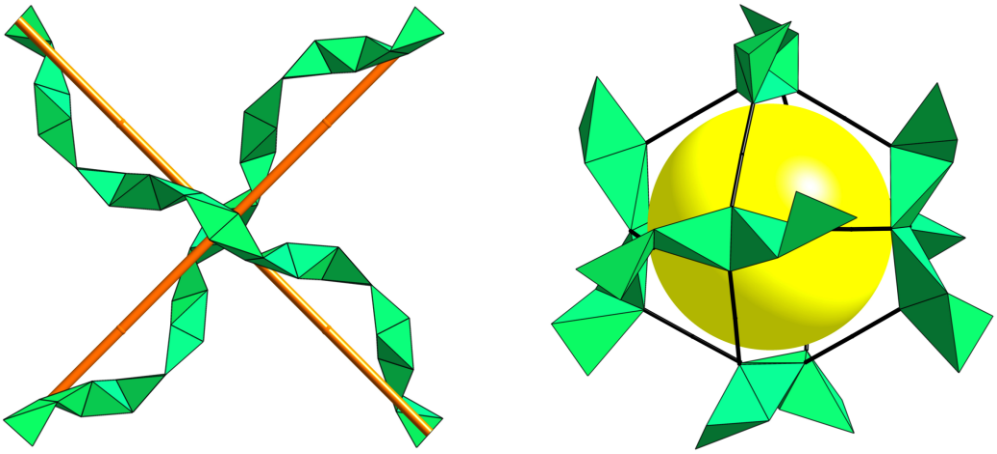


Figure 5. (A) a crossing of two rods. The intersecting yellow cylinders run along the rod axes. (B) a fragment of the structure showing how rods are linked in three directions. Heavy lines represent the organic linker joining rods.

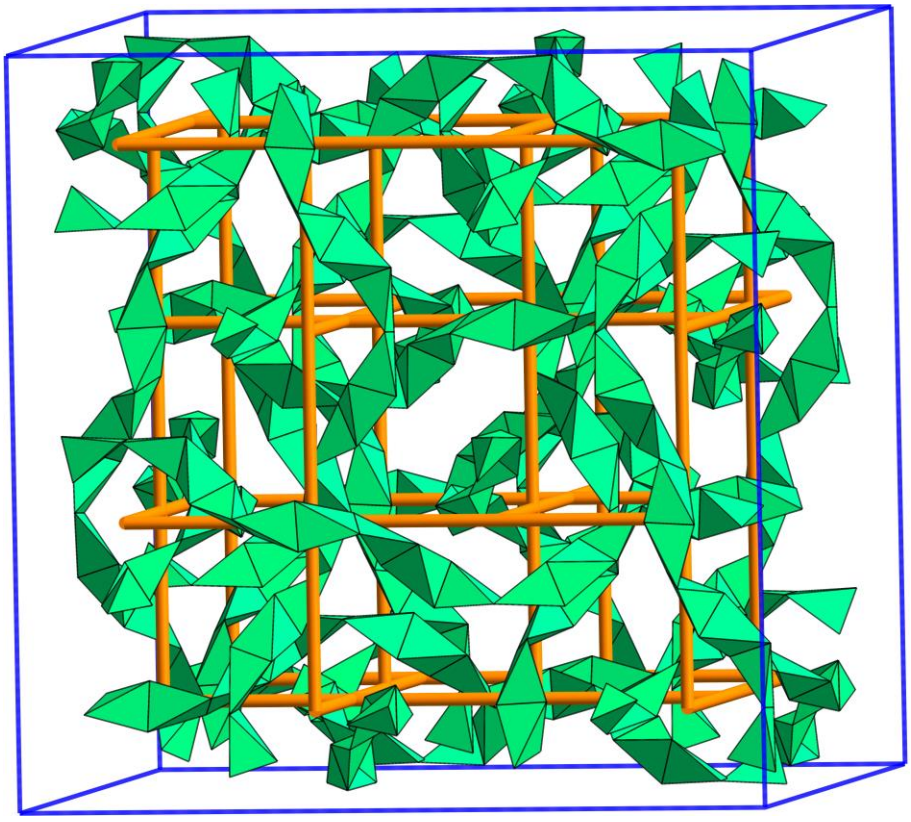


Figure 6. The helical rods (green) in a unit cell of the structure. Yellow intersecting cylinders mark the rod axes and form a **nbo** net. Links between the helical rods are not shown.

To shed light on the question “Which structural features of the two compounds leads to the unusual topology and the helical shape of the rods?” we extracted with ToposPro and CSD 18 3-periodic structures containing 4,4'-bi-1,2,4-triazole ligand. The details of their topological classification are presented in the supplementary. Surprisingly, we found one more rod MOF structure $[Ag(btr)]\cdot PF_6\cdot 0.5CH_3CN$ (HOWPOA[10]), in which the rod SBUs are helical with a period of six tetrahedra of Ag atoms but with the rods spanning only two perpendicular directions (100) and (010) without crossing (Figure 7). The underlying net in standard representation is 4-nodal 4-c net (Figure S3). In this structure, the helices do not create warp-and-woof motifs as in the previous two 3-ways crossing structure. The resulting net is binodal 4-c with point symbol $(5^3.8^3)(5^5.8)_2$. This structure is a rare example of helices with axes in two directions and thus not parallel to principal symmetry axes. The rod packing is the invariant four-layer tetragonal structure[15].

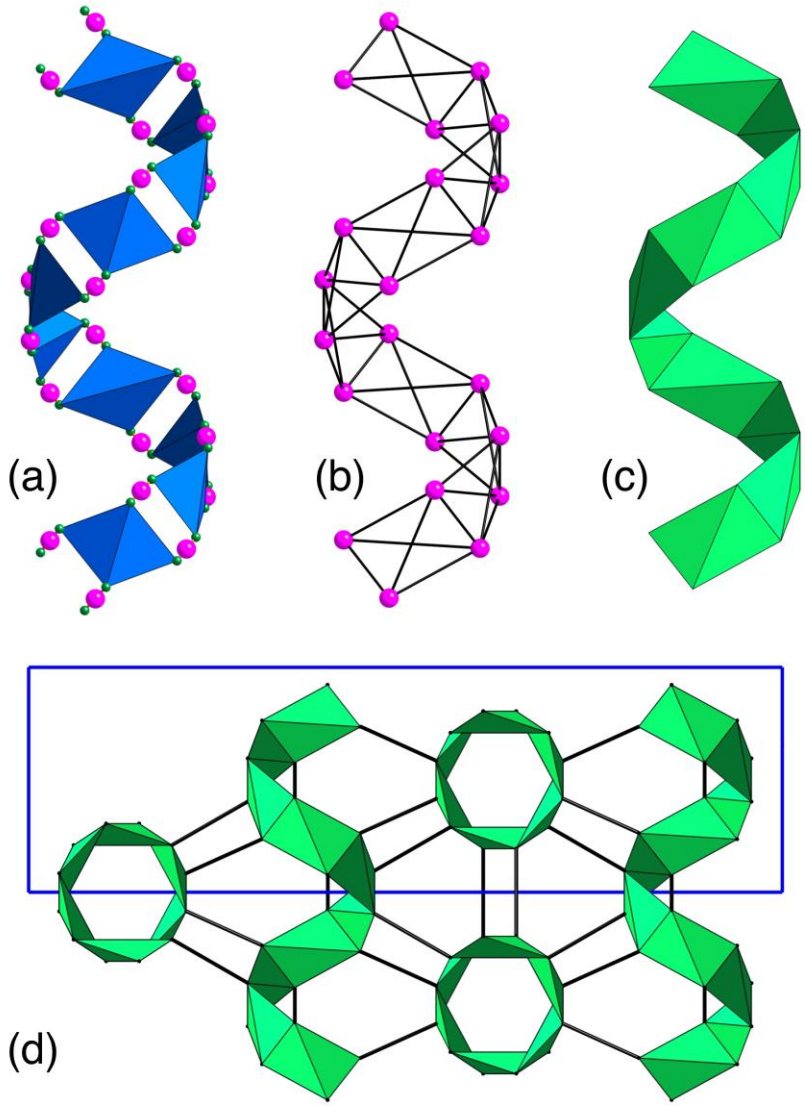


Figure 7. (A) a rod of AgN_4 tetrahedra HOWPOA joined by N-N links/ large magenta balls mark the points of extension. (b) The pattern of points of extension. (c) The pattern in (b) as edge-linked tetrahedra. (d) The pattern of linked helices in HOWPOA shown projected down [100] with **c** horizontal on the page.

INVARIANT LINE SETS

The description of the 14 invariant non-intersecting line sets was given by Rosi *et al* [15]. Corresponding intersecting line sets are now seen to be of interest and these are also listed here in Table 1. The invariant period point sets (lattice complexes) have been known for many years and are in, for example, the *International Tables for Crystallography*. Here *invariant* means that the coordinates are fixed by symmetry. The corresponding invariant (straight) line sets do not appear to be well known. Those with non-intersecting lines correspond to the axes of equal cylinders in contact. For those with intersections the coordinates of the intersections are fixed and taking these points as vertices, line segments between adjacent points as edges, the pattern corresponds to a vertex- and edge-transitive net, and accordingly is in RCSR. In the table below the symbol *pq* refers to a *p*-way patterns with *q* lines meeting at an intersection. Strictly, **rhr** does not belong as the other condition of straight lines is required to determine the coordinates (*x*, *x*, 0) of intersections. Beside the **nbo** pattern here described, also the 2-periodic **sql** net is observed in all the coordination polymers that show warp-and-woof entanglements.[12-16]

CONCLUDING REMARKS

We believe that we report the first example of a rod MOF in which the rod axes intersect. It suggests a new area of reticular chemistry in which helical rods that can be linked into frameworks are designed. The nets, either standard representation or defined by points of extension, for rod MOFs are generally rather complex – in the present case quadrinodal. These nets are included in the supplementary Information in Systre format. The illustrations use the coordinates of points of extension found directly from the crystal structure. Earlier discussions of rod MOFs assumed that the rod axes would not intersect.

Table 1

type	***pq***	**net**	**symmetry**	**coordinates**
square 2-way ,<10>	22	**sql***	*p*4*mm*	0,0
hexagonal 3-way ,<10>	32	**kgm**	*p*6*mm*	½,0
	33	**hxl**	*p*6*mm*	0,0
tetragonal 4-way, <101>	42	**lvt**	$I4_1/amd$	0,0,0
cubic 3-way, <100>	32	**nbo***	$Im\bar{3}m$	½,0,0
	33	**pcu**	$Pm\bar{3}m$	0,0,0
cubic 4-way, <111>	43	**bcs**	$Ia\bar{3}d$	0,0,0
	44	**bcu**	$Im\bar{3}m$	0,0,0
cubic 6-way, <110>	62	**rhr**	$Im\bar{3}m$	⅓, ⅓,0
	63	**hxg**	$Pn\bar{3}m$	0,0,0
	63	**crs**	$Fd\bar{3}m$	0,0,0
	64	**reo**	$Pm\bar{3}m$	½,0,0
	66	**fcu**	$Fm\bar{3}m$	0,0,0

* The observed rod crossing nets

SUPPORTING INFORMATION

Additional figures showing the possible alternative representations of the structures here described and some recommendations for design of the three-way helical rod MOFs.

ACKNOWLEDGEMENTS

EVA and AVG thanks Russian Science Foundation for financial support (Grant N 16-13-10158).

REFERENCES

(1) Schoedel, A.; Li, M.; Li, D.; O'Keeffe, M.; Yaghi, O. M. *Chem. Rev.* **2016**, *116*, 12466–12535.

(2) Colombo, V.; Galli, S.; Choi, H. J.; Han, G. D.; Maspero, A.; Palmisano, G.; Masciocchi, N.; Long, J. R. *Chem. Sci.* **2011**, *2*, 1311–1319.

(3) Goltsev, A. V; Alexandrov, E. V; Blatov, V. A.; Proserpio, D. M. *Acta Crystallogr. Sect. A* **2016**, *72*, s435.

(4) Xiao, J.; Liu, B. Y.; Wei, G.; Huang, X. C. *Inorg. Chem.* **2011**, *50*, 11032–11038.

(5) Gao, Q.; Xu, J.; Cao, D.; Chang, Z.; Bu, X. H. *Angew. Chemie - Int. Ed.* **2016**, *55*, 15027–15030.

(6) Li, X.; Xu, H.; Kong, F.; Wang, R. *Angew. Chemie - Int. Ed.* **2013**, *52*, 13769–13773.

(7) Blatov, V. A.; Shevchenko, A. P.; Proserpio, D. M. *Cryst. Growth Des.* **2014**, *14*, 3576–3586.

(8) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705−714.

(9) Alexandrov, E. V.; Blatov, V. A.; Proserpio, D. M. *CrystEngComm* **2011**, *13*, 3947–3958.

(10) Li, X.; Gong, Y.; Zhao, H.; Wang, R. *Inorg. Chem.* **2014**, *53*, 12127–12134.

(11) Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B.; Keeffe, M. O.; Yaghi, O. M. **2005**, *127*, 1504–1518.

(12) Carlucci, L.; Ciani, G.; A.; Proserpio, D. M. *Coord. Chem. Rev* **2003**, *246*, 247–289.

(13) Carlucci, L.; Ciani, G.; Gramaccioli, A.; Proserpio, D. M.; Rizzato, S. *CrystEngComm* **2000**, *29*, 1–10.

(14) Feng, Y.; Guo, Y.; OuYang, Y.; Liu, Z.; Liao, D.; Cheng, P.; Yan, S.; Jiang, Z. *Chem. Commun.* **2007**, 3643–3645.

(15) Mizzi, J. E.; LaDuca, R. L. *Inorg. Chem. Commun.* **2016**, *70*, 4–6.

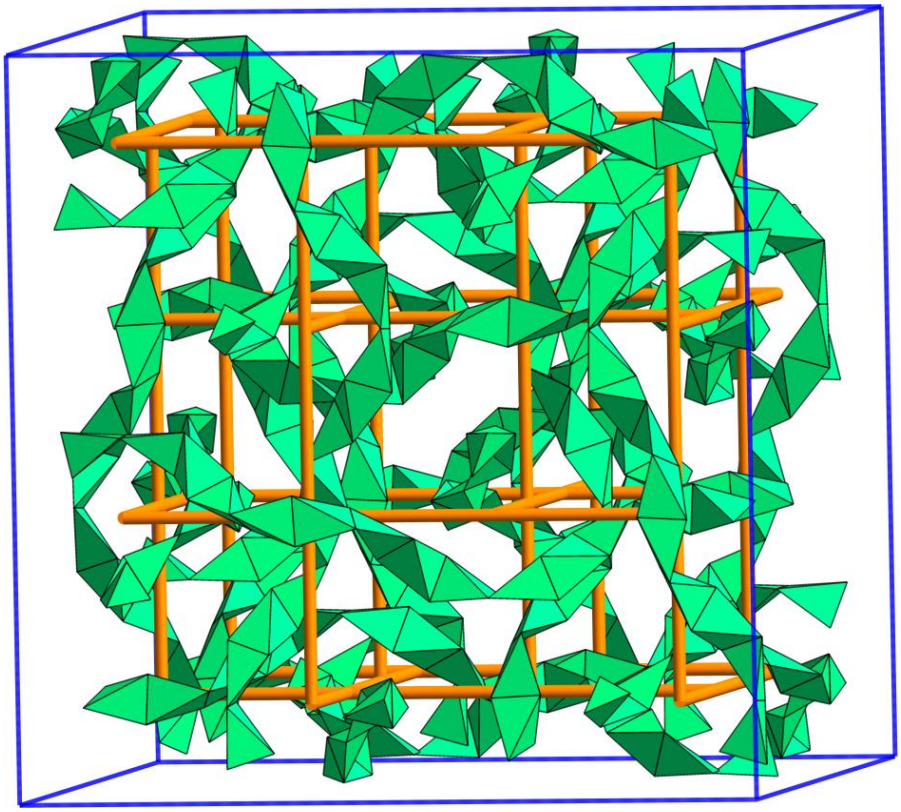
(16) Han, L.; Zhou, Y. *Inorg. Chem. Commun.* **2008**, *11*, 385–387.

For Table of Contents Use Only

Two Exceptional Patterns of Helical SBUs Found in MOF Structures.

Eugeny V. Alexandrov[‡], Andrey V. Goltsev[‡],

Michael O'Keeffe[†*] and Davide M. Proserpio[‡§*]



Synopsis:

We report the first example of a rod MOF in which the rod axes intersect. It suggests a new area of reticular chemistry in which helical rods that can be linked into frameworks are designed