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A Three-Dimensional, Noninterpenetrating Metal–Organic Framework with the Moganite Topology: A Simple $(4^2.6^2.8^2)(4.6^4.8)_2$ Net Containing Two Kinds of Topologically Nonequivalent Points

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Self assembly of Cu^{2+} with the multifunctional ligand 2-(4-pyridyl)-thiazole-4-carboxylic acid (Pytac) affords the neutral 3D coordination polymer $[Cu_3(Pytac)_6](H_2O)_{14}$ (hereafter, SZL-1), which has the rare moganite topology. The mineral moganite has a topology that is closely related to the well-known quartz topology, but the two topologies are differentiated by the number of topologically inequivalent nodes. Whereas only one kind of node is present in quartz, two types of topologically inequivalent nodes are present in moganite. The title compound, which has three vertices in its repeat unit, has two types of topologically inequivalent nodes with the overall vertex symbol $(4^2.6^2.8^2)(4.6^4.8)_2$ corresponding to the moganite net. Prior to this report, few metal–organic framework materials (MOFs) have been found to contain more than one type of node, and SZL-1 is the first MOF with the moganite topology.

The crystal engineering of metal−organic frameworks (MOFs) is of great current interest owing to their potential applications as functional solid materials, as well as due to their intriguing variety of architectures and topologies.[1] Structural diversity in MOFs can occur as a result of various processes, including interpenetration, interweaving, or supramolecular isomerism,[2] whereby simple 3- or 4-coordinate building blocks may generate an astonishingly large number of structures with different topologies. A particularly useful approach that facilitates the analysis, comparison, and design of complicated network structures is the reduction of multidimensional structures to simple node-and-connection reference nets.[1−3] This approach was pioneered many years ago by Wells,[4] who analyzed and classified a great number of nets. Today, nets having "simple, high-symmetry" structures[5] are believed to be the most plausible targets for synthetic design strategies. Interestingly, among the high-symmetry nets, a few structures predominate. For example, diamond nets (6^6) with the highest point symmetry ($-43m$)[6] dominate the 4-connected net structures, while coordination polymers with the net topologies of $CdSO_4$ ($6^5.8$),[7] NbO ($6^4.8^2$-a),[8] $SrAl_2$ ($4^2.6^3.8$),[9] quartz,[10] and dual quartz ($7^5.9$)[11] have been widely observed; additional less common network structures have been identified as well.[12]

All these nets are linked by the common feature of containing nodes (or vertices) with only one kind of point symbol (vertex symbol). In other words, all the nodes are topologically equivalent irrespective of the metal coordination environment. The existence of nets containing nodes with the same connectivity but with more than one kind of point symbol were predicted by Wells long ago.[4] However, the importance of this type of net, serving as a "blueprint" for the design of new MOFs, is not yet fully appreciated.[13]

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(1) (a) Janiak, C. *Dalton Trans.* **2003**, 2781. (b) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 1461. (c) Su, C.-Y.; Goforth, A. M.; Smith, M. D.; Pellechia, P. J.; zur Loye, H.-C. *J. Am. Chem. Soc.* **2004**, *126*, 3576.

(2) (a) Batten, S. R. *CrystEngComm* **2001**, *18*, 1. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M. *Coord. Chem. Rev.* **2003**, *246*, 247. (c) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629. (d) Su, C.-Y.; Goforth, A. M.; Smith, M. D.; zur Loye, H.-C. *Inorg. Chem.* **2003**, *42*, 5685.

(3) O'Keeffe, M.; Eddaoudi, M.; Li, H. L.; Reineke, T.; Yaghi, O. M. *J. Solid State Chem.* **2000**, *152*, 3.

(4) (a) Wells, A. F. *Further studies of three-dimensional nets*; American Crystallographic Association (distributed by Polycrystal Book Service): New York (Pittsburgh, PA), 1979. (b) Wells, A. F. *Three-dimensional nets and polyhedra*; Wiley: New York, 1977.

(5) Friedrichs, O. D.; O'Keeffe, M.; Yaghi, O. M. *Acta Crystallogr.* **2003**, *A59*, 22.

(6) Evans, O. R.; Xiong, R. G.; Wang, Z. Y.; Wong, G. K.; Lin, W. B. *Angew. Chem., Int. Ed.* **1999**, *38*, 536.

(7) Barnett, S. A.; Blake, A. J.; Champness, N. R.; Wilson, C. *Chem. Commun.* **2002**, 1640.

(8) Eddaoudi, M.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2002**, *124*, 376.

(9) Carlucci, L.; Ciani, G.; Macchi, P.; Proserpio, D. M.; Rizzato, S. *Chem.—Eur. J.* **1999**, *5*, 237.

(10) Sun, J. Y.; Weng, L. H.; Zhou, Y. M.; Chen, J. X.; Chen, Z. X.; Liu, Z. C.; Zhao, D. Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 4471.

(11) Carlucci, L.; Ciani, G.; Macchi, P.; Proserpio, D. M. *Chem. Commun.* **1998**, 1837.

(12) (a) Munakata, M.; Ning, G. L.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Horino, T. *Inorg. Chem.* **1998**, *37*, 5651. (b) Tong, M.-L.; Chen, X.-M.; Batten, S. R. *J. Am. Chem. Soc.* **2003**, *125*, 16170.

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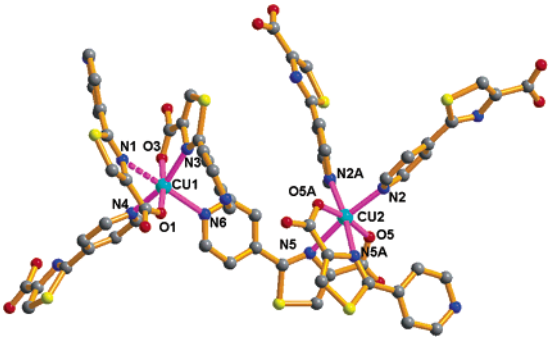

Figure 1. Portion of the extended structure of SZL-1 showing the coordination geometry of the two independent Cu atoms.

O'Keeffe has noticed the potential significance of one such 4-connected net having the moganite topology,[3] which is closely related to the quartz topology. Moganite, a mineral which was first characterized in 1992,[14] has *Cmmm* symmetry in its simplest structure with only three vertices in the repeat unit. O'Keeffe has identified cadmium cyanide as having the moganite topology, an aspect that was not recognized in its original structure paper.[15] Herein we report the single crystal structure of a self-assembled 3D framework with the moganite topology, $[Cu_3(Pytac)_6](H_2O)_{14}$ (Pytac = 2-(4-pyridyl)thiazole-4-carboxylic acid), termed SZL-1. SZL-1 has the vertex symbol $(4^2.6^2.8^2)(4.6^4.8)_2$ which, to the best of our knowledge, has never been documented for a MOF.

The synthesis of SZL-1 can be accomplished using any one of a large number of Cu^{2+} sources (see Supporting Information). Single crystal X-ray diffraction studies[16] revealed that the asymmetric unit contains two crystallographically unique Cu centers and three Pytac ligands. One of the Cu atoms (Cu2) is located on a C_2 rotational axis while the other (Cu1) occupies a general position. The ligand bridges the two Cu atoms via chelation of the thiazole nitrogen and a carboxylate oxygen on one end and via bonding of the pyridyl nitrogen on the other end, as shown in Figure 1. The uncoordinated carboxylate oxygen atom engages in hydrogen bonding with solvated water molecules and may play a role in directing the network topology. Both Cu atoms are in a distorted octahedral coordination environment, CuN_4O_2; however, for Cu1, one of the Cu−N bond distances is significantly longer than the rest.

If, for reasons of classifying the net, we define each chelate ring as a single point of connection to Cu (making each Pytac ligand effectively a bidentate linker), then both Cu atoms become 4-connected nodes. The framework can be represented simply by connecting the Cu nodes according to the connectivity defined by the Pytac bridging ligand, yielding a rare 3D net with the moganite topology, as shown in Figure 2. There are two kinds of nodes: Cu1 at 8*f* (Wyckoff letter) and Cu2 at 4*e* in a ratio of 2:1. Figure 2a is a representation of the most symmetrical form of the net. When viewed down the *c*-axis, one can identify a 2D layer composed of 4-gons and 6-gons sharing edges or vertices. Such a layer exists in the SZL-1 framework, although it is undulating rather than planar. The 3D net is generated by alternatingly connecting Cu1 (not Cu2) nodes to those in adjacent layers above and below. In addition, 8-gons can be identified in the projection shown in Figure 2b; these rings represent the largest circuit of the three essential rings that define the topology of SZL-1 (Figure 2c). The long (Schäfli) notation is $4.8_6.6.6.6.6$, for the Cu1 node and $4.4.6_2.6_2.8_4.8_4$,[3] for the Cu2 node, giving the net the symbol $(4.4.6_2.6_2.8_4.8_4)(4.8_6.6.6.6.6)_2$ which can be represented by the short symbol $(4^2.6^2.8^2)(4.6^4.8)_2$.

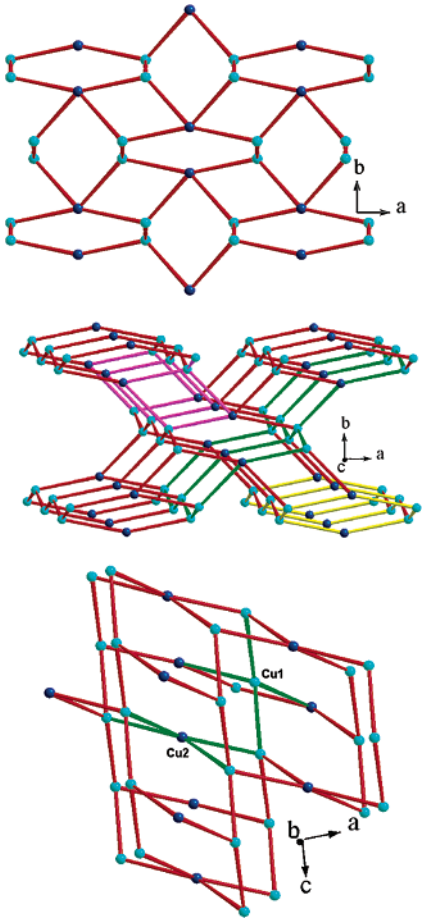

Figure 2. The $(4^2.6^2.8^2)(4.6^4.8)_2$ net of SZL-1 in its most symmetrical form (top), three shortest circuits determining the topology (middle), and a convenient view of the vertices for both kinds of nodes (bottom). The two type of nodes and shortest circuits are differentiated by color.

It is worth noting that moganite, a newly recognized mineral, is closely related to quartz, which is the second most abundant crystalline material in the Earth's crust and one of considerable technological importance. A detailed schematic comparison between quartz and moganite is given in Figure 3. The quartz net contains only topologically equivalent nodes with a Schäfli notation of $6.6.6_2.6_2.8_7.8_7$. Apparently, there are no 4-gons in the quartz structure that are comparable with those found in the moganite net. Instead, the nodes constituting 4-gons in moganite exhibit a helical arrangement

(13) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Rizzato, S. *J. Chem. Soc., Dalton Trans.* **2000**, 3821.
(14) Miehe, G.; Graetsch, H. *Eur. J. Mineral.* **1992**, *4*, 693.
(15) Abrahams, B. F.; Hoskins, B. F.; Robson, R. *J. Chem. Soc., Chem. Commun.* **1990**, 60.
(16) Crystal data for SZL-1: $C_{54}H_{58}Cu_3N_{12}O_{26}S_6$, M = 1674.10, monoclinic, space group $C2/c$, a = 24.9202(10) Å, b = 18.7433(7) Å, c = 14.6524(6) Å, β = 103.510(1)°, V = 95.7400(10) Å^3, T = 150 K, Z = 4, 6046 independent reflections measured, final R1 = 0.0415 and wR2 = 0.1014.

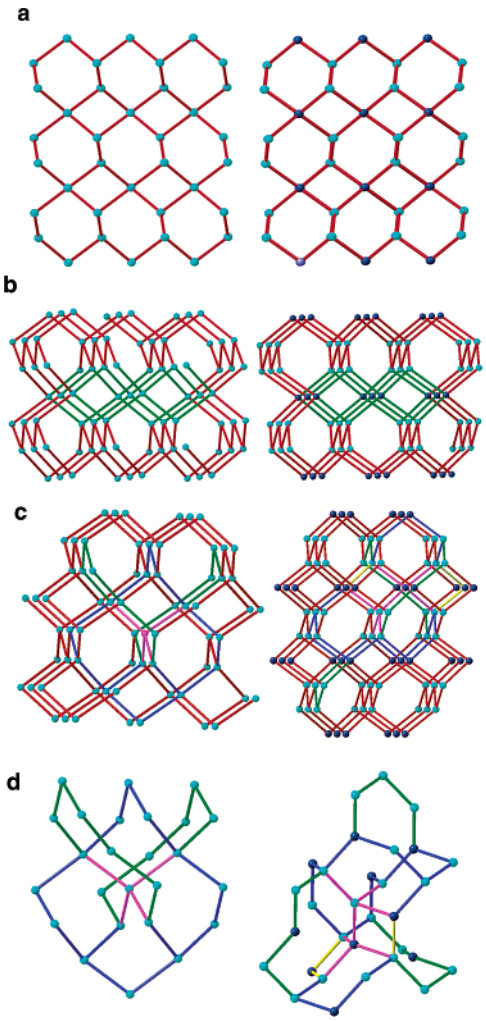

Figure 3. (a) The quartz (left) and moganite (right) nets are shown in their most symmetrical form; (b) helical arrangement of the nodes in quartz and 4-gons in moganite; (c) highlighted shortest circuits that define the topology; (d) and a convenient view of the essential circuits of each vertex.

in quartz, changing the circuit from 4 to 8. However, both quartz and moganite nets contain only three vertices in the repeat unit, one more than is found in the simplest 4-connected net (diamond and $CdSO_4$) topologies.[3] A 3D coordination polymer related to the present structure is the so-called MOF-112 framework.[17] This net possesses the same space group, *C*2/c, but the vertexes lie at 4*a*, 4*c*, and 4*d*. The three vertices in the repeat unit have either square planar or tetrahedral coordination, and these vertices are present in the ratio 1:2. However, the topology of MOF-112 is dramatically different from the present case, as is shown in the Supporting Information as Figure S1.

(17) Eddaoudi, M.; Kim, J.; Vodak, D.; Sudik, A.; Wachter, J.; O'Keeffe, M.; Yaghi, O. M. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4900.

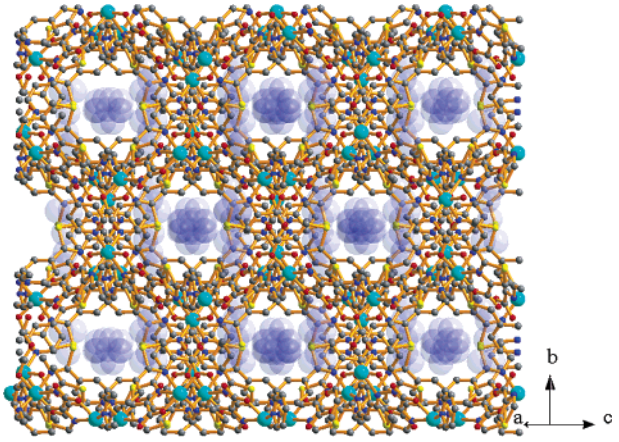

Figure 4. Crystal packing down [101] showing guest molecules in the channels.

SZL-1 accommodates a total of 14 guest water molecules per formula unit that reside in channels. The most important channel extends along the (101) direction as shown in Figure 4. A PLATON program analysis suggests that there is approximately 1542 $Å^3$ accessible to solvents, or 22.7% of the crystal volume. Thermogravimetric analysis indicates that most of the guest molecules are removed over the temperature range 95−135 °C with an observed weight loss of 14%, close to the calculated value of 15%. The framework is thermally stable up to 245 °C, where an abrupt weight loss signals framework collapse and decomposition of the organic components.

In summary, we have synthesized and characterized a new 3D MOF, SZL-1, with the moganite net structure. In contrast to the well-known uninodal 3D coordination frameworks, this net differs significantly from the otherwise simple net types by containing two kinds of topologically nonequivalent nodes with only three vertices in the repeat unit. The present case demonstrates that topological analysis is a useful tool for the description and comparison of natural and artificial networks, and that the enumeration of new topologies and identification of previously unrecognized networks remains an important task in crystal engineering.

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Supporting Information Available: Preparation of SZL-1, schematic representation of MOF-112, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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