

A New Self-Penetrating Uniform Net, (8,4) (or 8⁶), Containing Planar Four-Coordinate Nodes

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The analysis of network topology is an important tool in the design and interrogation of crystal structures. A large number of these topologies were elucidated by Wells in his classic monographs on networks.¹ He described a particularly fundamental class of networks, which he called uniform nets. In these networks the shortest circuits are all of the same size. A shortest circuit is defined for each pair of links from a node, and is the circuit with the smallest number of nodes which can be constructed to include the nominated links. A further subclass of uniform nets, which Wells labeled as Platonic uniform nets, are those in which all points are of the same connectivity. These networks can be represented using the (n,p) notation (where n is the number of nodes in the shortest circuit, and p is the connectivity of the node) rather than the usual n^x Schläfli symbol. A number of examples of these special networks were illustrated which are now known (or were shown by Wells) to be displayed by real crystal structures. These contain either three-coordinate nodes (including, for example, (6,3), (12,3), (8,3)-*c*, and various (10,3) nets) or tetrahedral four-coordinate nodes (e.g., (6,4) (diamond)). We report here a coordination polymer which contains a new uniform net, (8,4) (or 8⁶), containing only planar four-coordinate nodes. This net was not recognized by Wells, who goes so far as to state, "We are not aware of the existence of a 4-connected net in which there is a square coplanar arrangement of links at each point and for which the point symbol is n^6 ."² Thus, this net represents the first uniform net to contain only planar four-coordinate nodes, and is the first four-coordinate uniform net not to have the Schläfli symbol 6⁶.

Reaction of NiCl₂·6H₂O (0.119 g, 0.5 mmol) with 3-(3-pyridyl)acrylic acid (pyaraH) (0.149 g, 1.0 mmol) and NaOH (0.04 g, 1.0 mmol) in water (10 mL) at 180 °C for 24 h under hydrothermal conditions yields very fine pale green crystals of α-Ni(pyara)₂(H₂O)₂ (**1**) in ca. 90% yield.³

The structure of **1** contains two crystallographically unique (but chemically similar) Ni atoms and two unique pyara ligands (Figure 1). The ligands bridge between the metals in a linear fashion, with the carboxylate groups coordinating in a monodentate fashion. Each Ni lies on a center of symmetry and is coordinated to two trans pyara via the pyridyl donors (Ni–N = 2.131(2), 2.157(2) Å), two trans pyara via the carboxylate donors (Ni–O = 2.057(1), 2.079(2) Å), and two trans terminal water ligands (Ni–O = 2.097(2), 2.048(2) Å). The uncoordinated oxygen atoms of the carboxylates hydrogen-bond to the coordinated water molecules (H···O = 1.745, 1.756 Å) as shown in Figure 1, and these interactions may play an important role in directing the network topology.

The Ni atoms act as four-coordinate planar centers (the trans water ligands do not bridge). The network can thus be represented topologically simply by the Ni nodes and the connections (bridging

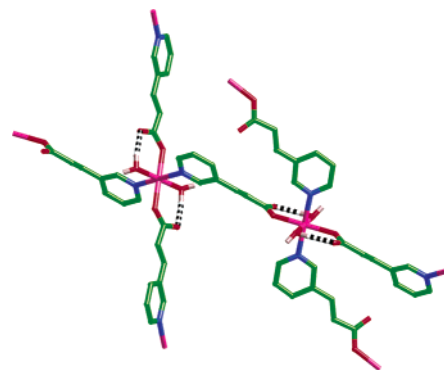


Figure 1. View of the local coordination geometries of the two crystallographically distinct, but chemically similar Ni atoms in the structure of **1**. Hydrogen bonds are denoted by the zebra-striped bond.

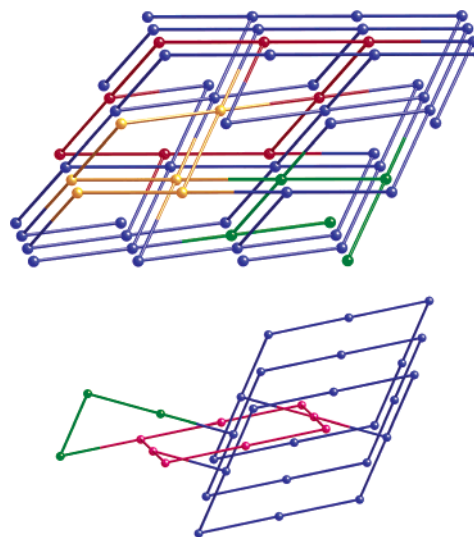


Figure 2. (Top) The (8,4) net in the structure of **1**. Highlighted are a single helix (yellow), one strand of a triple helix (green), and one type of eight-membered shortest circuit (red). (Bottom) Catenation of some of the eight-membered shortest circuits, illustrating that (8,4) is a self-penetrating network.

pyara ligands) between them. Figure 2 reveals the unusual (8,4) network displayed by this structure. The "long" Schläfli symbol for this net is 8₃.8₃.8₃.8₃.8₂.8₂. This net is clearly different from other reported network topologies containing planar centers, such as NbO (Schläfli symbol 6⁴.8²), CdSO₄ (6⁵.8), the quartz dual net (7⁵.9), USF-1, MOF-112, and 4².8⁴.⁵ These nets are illustrated for comparison in the Supporting Information. There are two different node–node distances in the structure reported here (Ni1···Ni2 = 10.00 and 10.73 Å), and the angles about the nodes are not 90° (Ni···Ni···Ni = 71.1° and 108.9° about Ni1; 53.2° and 126.8° about

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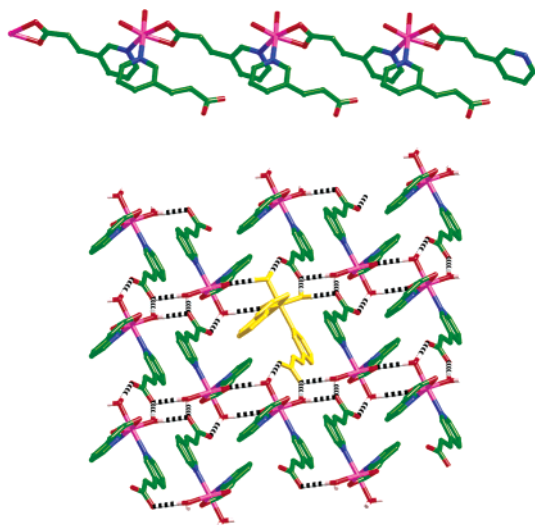


Figure 3. (Top) A single chain in the structure of **2**. (Bottom) Packing diagram, with the chains viewed end-on, showing the interchain hydrogen bonds (one chain highlighted in yellow).

Ni2). The maximum symmetry of the underlying net, however, is orthorhombic *Pnna* (No. 52), with the nodes lying at the origin and symmetry related positions. This net contains only one type of node, but there are two types of links—one connects the node at 0,0,0 to the node at 0,0.5,0.5, and the other connects 0,0,0 to 0.5,1,0. Although a net with 90° angles at all the nodes (i.e., true square-planar geometry) cannot be constructed, a net with equal length links is obtained in *Pnna* if the cell parameters hold to the relationship $c^2 - a^2 = 3b^2$; the length of the links is thus $0.5(b^2 + c^2)^{1/2}$. Because the net has at least two types of links and it is not possible for all the nodes to have 90° angles, it cannot be classed as either a “regular” (all vertices, edges, and angles are equivalent (related by symmetry)) or “quasi-regular” (all vertices and edges (but not angles) are equivalent) net.⁶ This net also cannot be realized as a four-coordinated sphere packing; there are internodal distances between nodes not directly connected by links which are shorter than the link length itself.

An interesting feature of this net is the presence of parallel single and triple helices running through the structure. One example of each are highlighted in Figure 2; there are equal numbers of each hand of each type of helix. Another noteworthy aspect of this structure is the fact that the network is a self-penetrating one. In other words, its shortest circuits are penetrated by rods of the same network (Figure 2). Another uniform network, (12,3), has also recently been shown to be self-penetrating.⁷ Interestingly, this net also cannot be constructed using the highest symmetry nodes (i.e., truly trigonal nodes).

Curiously, when the above-mentioned reaction was carried out at 150 °C for 24 h, deep green crystals of a second polymorph, β -Ni(pyra)₂(H₂O)₂ (**2**), as a single phase were isolated (yield 60%).³ Phase purity of the bulk material was confirmed by comparison of its powder diffraction pattern with that calculated from the single-crystal study.

The structure of **2**⁸ consists of 1D chains of metal centers bridged by pyra ligands which coordinate through both the pyridyl (Ni–N = 2.057(2) Å) and carboxylate (Ni–O = 2.108(2), 2.129(2) Å) functional groups, the latter in a chelating fashion (Figure 3). The remainder of the octahedral metal coordination sphere is composed of two cis-disposed water ligands (Ni–O = 1.996(2), 2.095(2) Å)

and an additional pyra ligand coordinating via the pyridyl group (Ni–N = 2.132(2) Å). Both types of L ligands are anionic, having lost their carboxylate protons. The chains are cross-linked into a 3D net by hydrogen-bonding interactions (H···O = 1.752–1.976 Å) between the water ligands and carboxylate oxygens of adjoining chains, and vice versa (Figure 3).

In summary, we have prepared and characterized the first (8,4) uniform net, containing only planar four-coordinate nodes. We have also shown that the formation of two polymorphs can be directed simply by variation of the reaction temperature. We are extending this controlled hydrothermal method to other metal-ion cases,⁹ and further systematic investigation will focus on the influence of hydrothermal reaction conditions on the diversity of M–pyra networks.¹⁰

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Supporting Information Available: X-ray crystallographic file for the structure determination of **1** and **2** (CIF); calculated and experimental powder diffraction patterns for **1** and **2**, and schematic diagrams of various reported networks containing only planar four-coordinate nodes (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Wells, A. F. *Three-dimensional Nets and Polyhedra*; Wiley-Interscience: New York, 1977. (b) Wells, A. F. *Further Studies of Three-dimensional Nets*; ACA Monograph 8; American Crystallographic Association: 1979.
- (2) Reference 1a, p 14.
- (3) Anal. Calcd for **1** and **2**, C₁₆H₁₆N₂NiO₆: C, 49.15; H, 4.12; N, 7.16. Found for **1**: C, 49.06; H, 4.01; N, 7.05. Found for **2**: C, 49.10; H, 4.06; N, 7.08.
- (4) Crystal data for **1**: C₁₆H₁₆N₂NiO₆, *M* = 391.02, monoclinic, space group *P*₂₁/*c* (No. 14), *a* = 16.784(5), *b* = 5.4457(18), *c* = 17.862(6) Å, β = 105.987(5)°, *V* = 1569.5(9) Å³, *Z* = 4, *D*_c = 1.655 g/cm³, *R*₁ = 0.0419, *wR*₂ = 0.1040.
- (5) (a) O’Keeffe, M.; Eddaoudi, M.; Li, H.; Reinecke, T.; Yaghi, O. M. *J. Solid State Chem.* **2000**, *152*, 3. (b) O’Keeffe, M.; Hyde, B. G. *Crystal structures I: patterns and symmetry*; Mineralogical Society of America: Washington, 1996. (c) Carlucci, L.; Cozzi, N.; Ciani, G.; Moret, M.; Proserpio, D. M.; Rizzato, S. *Chem. Commun.* **2002**, 1354. (d) Moulton, B.; Abourahma, H.; Bradner, M. W.; Lu, J.; McManus, G. J.; Zaworotko, M. J. *Chem. Commun.* **2003**, 1342. (e) 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. (f) Eddaoudi, M.; Kim, J.; O’Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2002**, *124*, 376. (g) Rather, B.; Moulton, B.; Walsh, R. D. B.; Zaworotko, M. J. *Chem. Commun.* **2002**, 694.
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- (8) Crystal data for **2**: C₁₆H₁₆N₂NiO₆, *M* = 391.02, triclinic, space group *P* $\bar{1}$ (No. 2), *a* = 7.6036(5), *b* = 9.6014(6), *c* = 11.8554(6) Å, α = 113.88(1), β = 95.08(1), γ = 95.04(1)°, *V* = 781.00(8) Å³, *Z* = 2, *D*_c = 1.663 g/cm³, *R*₁ = 0.0444, *wR*₂ = 0.1221.
- (9) While preparing this Communication, we obtained iron(II) and cobalt(II) compounds isostructural with **1**. Crystal data for Fe compound: C₁₆H₁₆FeN₂O₆, *M* = 388.16, monoclinic, space group *P*₂₁/*c* (No. 14), *a* = 17.014(3), *b* = 5.4687(7), *c* = 18.043(3) Å, β = 106.106(4)°, *V* = 1613.0(4) Å³, *Z* = 4, *D*_c = 1.598 g/cm³, *R*₁ = 0.0413, *wR*₂ = 0.1093. Crystal data for Co compound: C₁₆H₁₆CoN₂O₆, *M* = 391.24, monoclinic, space group *P*₂₁/*c* (No. 14), *a* = 16.906(3), *b* = 5.4534(9), *c* = 17.948(3) Å, β = 105.986(3)°, *V* = 1590.8(5) Å³, *Z* = 4, *D*_c = 1.634 g/cm³, *R*₁ = 0.0403, *wR*₂ = 0.1040. These will be reported in a subsequent full paper.
- (10) Since submission of this paper, another coordination polymer with (8,4) topology has appeared in the literature: Ma, J.-F.; Yang, J.; Zheng, G.-L.; Li, L.; Liu, J.-F. *Inorg. Chem.* **2003**, *42*, 7531.

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