

A Molecular Railroad with Large Pores: Synthesis and Structure of $\text{Ni}(4,4'\text{-bpy})_{2.5}(\text{H}_2\text{O})_2(\text{ClO}_4)_2 \cdot 1.5(4,4'\text{-bpy}) \cdot 2\text{H}_2\text{O}^\dagger$

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The construction of open supramolecular coordination networks from molecular building blocks has yielded a diverse family of crystalline materials having unprecedented pore size, shape, and function.¹ At least three factors have contributed to the proliferation of these porous solids. First, the availability of a large number of functionalized organic compounds and metal complexes has allowed the design of cationic, anionic and neutral porous frameworks having wide-ranging compositions.² Second, the ability to access these materials in their crystalline form has permitted their full-structural characterization and the study of their framework stability.³ Third, uncovering their unusual molecular sieving and ion-exchange properties has been an impetus for further exploration of their structure/function relations.⁴ One of the outstanding challenges to designing coordination solids with large pores has been the formation of interpenetrated networks. Generally, this has resulted in more condensed structures having either very small pores or no pores at all. In an effort to establish strategies aimed at preventing interpenetration, and the design of solids with large pores, we have achieved a cationic $\text{Ni}(4,4'\text{-bpy})_{2.5}(\text{H}_2\text{O})_2$ noninterpenetrated railroadlike network, where large pores of $11 \times 11 \text{ \AA}$ dimensions exist despite the tendency of such networks to self-include; instead, the pores are found to be occupied by hydrogen-bonded hydrated anions and 4,4'-bipy-

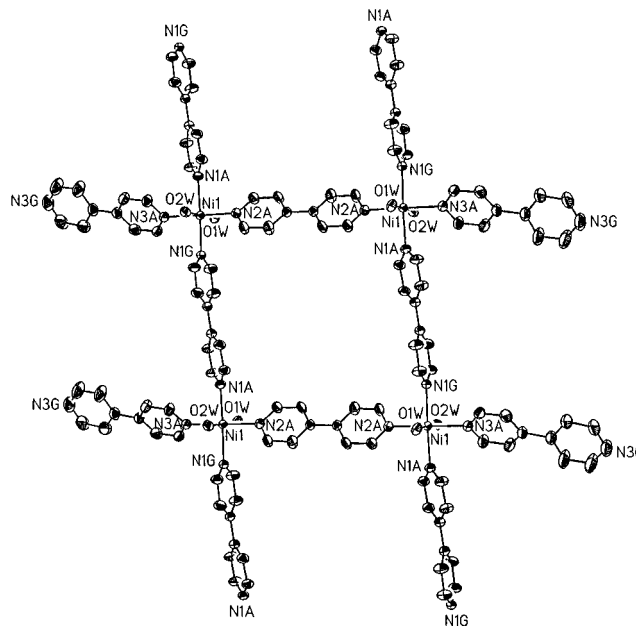


Figure 1. The building unit present in the extended solid-state structure of $\text{Ni}(4,4'\text{-bpy})_{2.5}(\text{H}_2\text{O})_2(\text{ClO}_4)_2 \cdot 1.5(4,4'\text{-bpy}) \cdot 2\text{H}_2\text{O}$ shown with the non-hydrogen atoms represented by thermal ellipsoids drawn to encompass 50% of their electron density. Atoms labeled with additional letters are related by symmetry to those with the same number designation. All hydrogen atoms have been omitted for clarity.

ridine guests. The synthesis and structure of this compound are described herein.

An aqueous mixture (6 mL) of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.624 g, 1.71 mmol) and 4,4'-bpy (0.80 g, 5.12 mmol) was placed in a stainless steel vessel and heated to 140 °C for 10 h. The resulting large blue parallelepipedal crystals were collected and washed with distilled water (15 mL \times 3) and ethanol (10 mL \times 2) to give 0.95 g (78% yield based on 4,4'-bpy) of product. This solid was formulated as $\text{Ni}(4,4'\text{-bpy})_{2.5}(\text{H}_2\text{O})_2(\text{ClO}_4)_2 \cdot 1.5(4,4'\text{-bpy}) \cdot 2\text{H}_2\text{O}$ by elemental microanalysis and structurally characterized by X-ray single-crystal diffraction.^{5,6} The structure is constructed from the building units shown in Figure 1. Here,

[†] Dedicated to the memory of Nathan Everett Olson (1973–1997).

- See, e.g.: (a) Lu, J.; Paliwala, T.; Lim, S. C.; Yu, C.; Niu, T.; Jacobson, A. J. *Inorg. Chem.* **1997**, *36*, 923. (b) Losier, P.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2779. (c) Venkataraman, D.; Lee, S.; Moore, J. S.; Zhang, P.; Hirsch, K. A.; Gardner, G. B.; Covey, A. C.; Prentice, C. L. *Chem. Mater.* **1996**, *8*, 2030. (d) Yaghi, O. M. In *Access in Nanoporous Materials*; Pinnavaia, T. J., Thorpe, M. F., Eds.; Plenum: New York, 1995; p 111. (e) Robson, R.; Abrahams, B. F.; Batteen, S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J. In *Supramolecular Architecture: Synthetic Control in Thin Films and Solids*; Bein, T., Ed.; American Chemical Society: Washington, DC, 1992; Chapter 19. (f) Iwamoto, T. In *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Oxford: New York, 1991; Vol. 5, p 177. (g) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546. (h) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (i) MacGillivray, L. R.; Subramanian, S.; Zaworotko, M. J. *J. Chem. Soc., Chem. Commun.* **1994**, 1325. (j) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *J. Chem. Soc., Chem. Commun.* **1994**, 2755.
- See, e.g.: (a) Bowes, C. L.; Ozin, G. A. *Adv. Mater.* **1996**, *8*, 13. (b) Yaghi, O. M. In *Metal Containing Polymeric Materials*; Pittman, C. U., Carraher, C. E., Culbertson, B. M., Zeldin, M., Sheets, J. E., Eds.; Plenum: New York, 1996; p 219. (c) Zaworotko, M. J. *Chem. Soc. Rev.* **1994**, 283.
- In addition to crystallization methods involving the usual dissolution/precipitation (a), hydrothermal (b) and aqueous (c) and nonaqueous (d) gel methods have been employed for the achievement of coordination solids in the form of single crystals. See e.g.: (a) Holden, A.; Morrison, P. *Crystals and Crystal Growing*, MIT Press: Cambridge, MA, 1982. (b) Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1995**, *117*, 10401. (c) Yaghi, O. M.; Li, G.; Groy, T. L. *J. Solid State Chem.* **1995**, *117*, 256. (d) Yaghi, O. M.; Li, G.; Li, H. *Mater. Chem.* **1997**, *9*, 1074.
- (a) Yaghi, O. M.; Davis, C. E.; Li, G.; Li, H. *J. Am. Chem. Soc.* **1997**, *119*, 2861. (b) Gardner, G. B.; Kiang, Y.-H.; Lee, S.; Asgaonkar, A.; Venkataraman, D. *J. Am. Chem. Soc.* **1996**, *118*, 6946. (c) Yaghi, O. M.; Li, H.; Groy, T. L. *J. Am. Chem. Soc.* **1996**, *118*, 9096. (d) Ramprasad, D.; Pez, G. P.; Toby, B. H.; Markley, T. J.; Pearlstein, R. M. *J. Am. Chem. Soc.* **1995**, *117*, 10694.

- Anal. Calcd for $\text{C}_{40}\text{H}_{40}\text{N}_8\text{O}_{12}\text{Cl}_2\text{Ni}$: C, 50.34; H, 4.22; N, 11.74; Ni, 6.15. Found: C, 50.39; H, 4.15; N, 11.97; Ni, 6.07.

- Single crystals of for $\text{Ni}(4,4'\text{-bpy})_{2.5}(\text{H}_2\text{O})_2(\text{ClO}_4)_2 \cdot 1.5(4,4'\text{-bpy}) \cdot 2\text{H}_2\text{O}$ were analyzed at $20 \pm 1 \text{ }^\circ\text{C}$: Triclinic, space group $P1$ with $a = 7.990(2) \text{ \AA}$, $b = 11.387(4) \text{ \AA}$, $c = 25.210(8) \text{ \AA}$, $\alpha = 78.31(3)^\circ$, $\beta = 81.35(2)^\circ$, $\gamma = 78.42(3)^\circ$, $V = 2185.9(12) \text{ \AA}^3$, $Z = 2$, $d_{\text{calcd}} = 1.452 \text{ g}\cdot\text{cm}^{-3}$; $\mu_a(\text{Mo K}\alpha) = 0.637 \text{ mm}^{-1}$. Data were collected on a Siemens R3m/V autodiffractometer using graphite-monochromated Mo $\text{K}\alpha$ radiation and full 1.60° wide ω scans to a maximum of $2\theta = 50^\circ$, giving 7750 unique reflections. The structure was solved by (SHELXL-PC V.5.03) direct methods, and the resulting structural parameters were refined by least-squares techniques to a standard discrepancy index $R = 0.0452$ and $R_w = 0.0879$ for 5696 reflections with $F > 4 \sigma(F)$. Anisotropic thermal parameters were refined for all non-hydrogen atoms, and fixed thermal parameters were used for included hydrogens. The two crystallographically independent perchlorates were statistically disordered around one C_3 axis with two preferred orientations for the oxygen atoms.

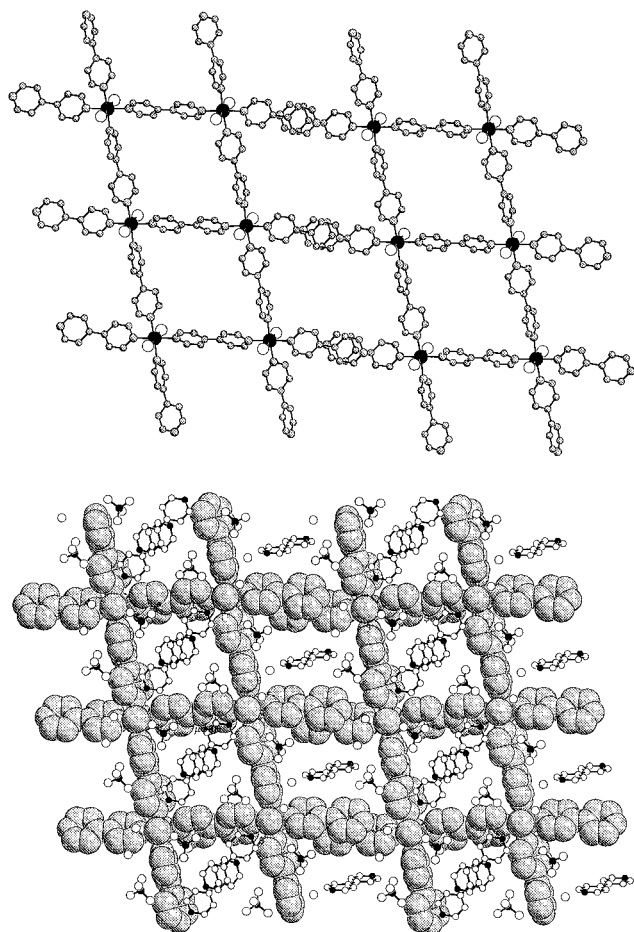


Figure 2. Views of the solid-state structure of $\text{Ni}(4,4'\text{-bpy})_{2.5}(\text{H}_2\text{O})_2(\text{ClO}_4)_2 \cdot 1.5(4,4'\text{-bpy}) \cdot 2\text{H}_2\text{O}$ along the a -axis. (a, top) The π - π overlap of two adjacent 4,4'-bpy ligands of the railroadlike units to form an extended porous layer (Ni, large dark; N and C, shaded; O, open); (b, bottom) channels thus formed, where 4,4'-bpy, perchlorate, and water reside. (The Ni-bpy framework is shown in space-filling shaded representation, while the guests in the channels are shown in stick-and-ball representation with C and O, open, and Cl and N, dark.) For clarity, the hydrogen atoms have been omitted and only one orientation of the disordered perchlorate is shown.

four Ni(II) centers Ni1 are separated by 4,4'-bpy spacers to give a large square arrangement, where each metal adopts an octahedral geometry and is bound equatorially to four 4,4'-bpy ligands (N1, N2, and N3) and axially to two water ligands (O1W and O2W). Three of the 4,4'-bpy (N1 and N2) act as doubly bridging ligands, where two (N1) are responsible for extending these squares along the crystallographic b -axis to form the railroadlike topology. The fourth 4,4'-bpy (N3) acts as a terminal ligand and extends the structure into the crystallographic c -axis by using a π - π interaction (3.777(4) Å) with an identical 4,4'-bpy ligand of an adjacent railroadlike unit resulting in a porous sheet structure as shown in Figure 2a. In the crystal, these sheets are stacked in registry along the crystallographic a -axis to give an extended one-dimensional channel network having 11×11 Å pores, as shown in Figure 2b. The channels are occupied by 4,4'-bpy (N4 and N5), perchlorate (Cl1, Cl2, O1, and O2), and water (O3W and O4W) guests (not shown) that are hydrogen-bonded to each other

(O3W-O4W, O2,N5 = 2.735(2), 2.760(2), 2.819(2) Å) and to the water ligands bound to the Ni(II) centers (O1W-O4W, O1 = 2.716(2), 2.734(2) Å; O2W-O4W, N4 = 2.807(2), 2.744(2) Å).

We believe that hydrogen-bonded guest aggregates, such as those observed here, prevent self-interpenetration by occupying the large voids in the structure. Also, as we have shown in earlier studies that liberating water from such aggregates results in high mobility of the guest ions thereby allowing for their exchange without destruction of the framework. To investigate the ion-exchange properties of this materials, a thermal gravimetric analysis study was performed on a 24.76 mg crystalline sample. It reveals an initial weight loss of 4.9% at 70 °C corresponding to the loss of 2.5 water molecules per formula unit (calculated, 4.7%), and three continuous DTG peaks at 120, 157, and 220 °C to give a total loss of 41.6% of the sample weight, which corresponds to the loss of a total of approximately four water and two 4,4'-bpy guests (calculated, 40.3%). All coordinated 4,4'-bpy is lost gradually as the temperature approaches 325 °C. Thus, a microcrystalline sample (200 mg) was heated to 70 °C under 0.08 Torr pressure for 1 h to remove the guest water. The resulting partially dehydrated solid was immersed in an aqueous NaPF_6 solution (0.20 M) for 15 min and then filtered off and thoroughly washed with water and air dried. The infrared spectrum of this material clearly shows the disappearance of an intense ClO_4^- peaks (1150–1091 cm^{-1}) and the appearance of an equally intense PF_6^- peaks (848 and 565 cm^{-1}) indicating that the material has undergone ion-exchange. This compound remains crystalline upon ion-exchange as indicated by the sharp peaks observed in the X-ray diffraction pattern of the exchanged material.

The railroad 1-D motif observed here constitutes a novel member of metal-4,4'-bpy extended networks, where structures described in terms of the diamond^{1i,j,7 a} and α - ThSi_2 networks,^{3b,7b,c} as well as hexagonal^{7d} and square grids^{1a,b,e,h,7e}, and ladder^{1b} motifs have been prepared and structurally characterized. Close examination of these structures readily reveals the utility of 4,4'-bpy as a rigid and bifunctional rodlike spacer in building extended networks with large pores. In addition, it appears that, in the absence of large inclusions, in the form of molecules, ions or aggregates thereof, the resulting structures have the tendency to be highly interpenetrated. The compound described here demonstrates the importance of intramolecular guest interactions in providing viable space-filling entities, which, due to their bulk, are effective in prohibiting interpenetration of very open supramolecular networks.

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Supporting Information Available: Tables of crystallographic data for $\text{Ni}(4,4'\text{-bpy})_{2.5}(\text{H}_2\text{O})_2(\text{ClO}_4)_2 \cdot 1.5(4,4'\text{-bpy}) \cdot 2\text{H}_2\text{O}$, including a crystal structure analysis report, positional parameters and thermal parameters, and interatomic distances and angles, and an ORTEP diagram (13 pages). Ordering information is given on any current masthead page.

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