5320 *Inorg. Chem.* **2001,** *40,* 5320−5321

$[Ni(4,4'\text{-bpy})_2(H_2PO_4)_2]\cdot C_4H_9OH\cdot H_2O$: a Novel Metal Phosphate That Exhibits Interpenetration of 2D Net into 3D Framework

Yau-Chen Jiang,[†] Yu-Chen Lai,[†] Sue-Lein Wang,[*,†] and Kwang-Hwa Lii[*,‡,§]

Department of Chemistry, National Tsing Hua University, Hsinchu, Taiwan, R.O.C., Department of Chemistry,
National Central University, Chungli, Taiwan, R.O.C., and Institute of Chemistry, Academia Sinica, Nankang, Taipei, Taiwan, R.O.C.

Received June 6, 2001

The construction of coordination polymers based on metal−bridging ligand building blocks is an area of great activity because of their fascinating structural diversity and potential applications as function materials.[1,2] A study of the literature about transition metal supramolecular architectures shows that the most extensively studied bridging ligand is 4,4′-bipyridine (4,4′-bpy), and a wide range of infinite frameworks including diamondoid, grid, ladder, brick, railroad, and octahedral building blocks have been generated with 4,4′-bpy or its extended analogues.[1] In some cases, the frameworks generate spacious voids, cavities, and channels, which are usually occupied by solvent molecules. In other cases, interpenetrating structures are formed in which the voids associated with one framework are occupied by one or more independent infinite substructures of the same chemical composition and with the same topology.[3] Examples of interpenetrating 3D frameworks derived from the diamond structure appear to be the most common type. To our knowledge, an example of interpenetrating nets of the same chemical composition but with different topology is hitherto unknown. In this contribution we report the synthesis and crystal structure of a nickel(II) phosphate containing the bridging ligand 4,4′-bpy, which exhibits an unprecedented type of interpenetration involving a 2D square net and a 3D $CdSO_4$-type framework of the same chemical composition.

Blue plate crystals of $[Ni(4,4'\text{-bpy})_2(H_2PO_4)_2]\cdot C_4H_9OH\cdot H_2O$, **1**, were obtained in a yield of 81% by heating a reaction mixture of $NiSO_4\cdot 6H_2O$ (1 mmol), $NH_4H_2PO_4$ (10 mmol), 4,4′-bpy (4.6 mmol), H_2O (9 mL), and 1-butanol (3 mL) in a Teflon-lined acid digestion bomb at 120 °C for 1 day followed by quenching to room temperature by removing the autoclave from the oven. The powder X-ray diffraction pattern of the bulk product is in good agreement with the calculated pattern based on the results from single-crystal X-ray diffraction. Elemental analysis of the bulk product confirmed the stoichiometry of **1** (Found: C, 43.02; H, 4.87; N, 8.59. Calcd for $C_{24}H_{32}N_4NiO_{10}P_2$: C, 43.86; H, 4.91; N, 8.52%). It appears that 1-butanol is crucial to the formation of **1**. When pure water and a mixture of water/ethylene glycol (9/3 mL) were used instead of water/1-butanol, we isolated two 4,4′-bpy square net compounds, $[Ni(4,4'\text{-bpy})_2(H_2PO_4)_2]\cdot(4,4'\text{-bpy})_2\cdot 3H_2O$ (**2**) and $[Ni(4,4'\text{-bpy})_2(H_2PO_4)_2]\cdot(4,4'\text{-bpy})_2\cdot C_2H_6O_2\cdot H_2O$ (**3**), respectively.[4] The structures of the 2D nets in **2** and **3** are similar to those in $[Cd(4,4'\text{-bpy})_2(NO_3)_2]$ and $[Cu(4,4'\text{-bpy})_2(H_2O)_2]\cdot(ClO_4)_4\cdot(4,4'\text{-}H_2bpy)$.[5,6] Although such square nets have been widely encountered in 4,4′-bpy sustained networks, **2** and **3** are the first examples of metal phosphates. As revealed by single-crystal X-ray crystallography,[7] the structure of **1** consists of independent and an interpenetrating 2D square net and 3D net of the same chemical composition (Figure 1). The 2D net is constructed from $[Ni(4,4'\text{-bpy})_2]^{2+}$ grids based on the (4,4) topology, with each $Ni(1)^{II}$ site additionally coordinated to two $H_2PO_4^-$ groups which project above and below this plane. The coordination geometry around the $Ni(2)^{II}$ moiety in the 3D net is the same as that in the 2D net. The nickel atoms in the former

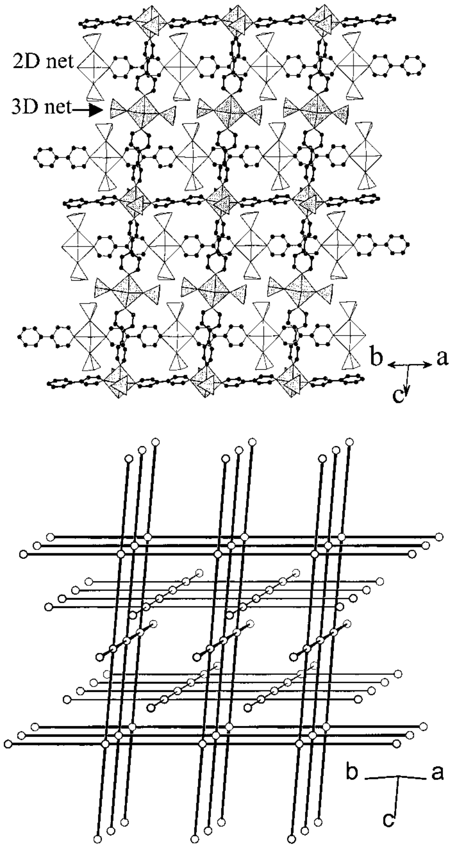

Figure 1. (a) Structure of **1** viewed along the [110] direction. The 1-butanol and water molecules are omitted for clarity. Average bond distances: Ni(1)−N = 2.124(2) Å, Ni(1)−O = 2.047(2) Å, Ni(2)−N = 2.125(2) Å, and Ni(2)−O = 2.108(2) Å. (b) Schematic representation of two interpenetrating nets in **1** viewed in a direction approximately parallel to [110]. The circles represent the Ni atoms. Each line connecting neighboring Ni atoms is a 4,4′-bpy ligand. The thin lines represent the 2D square net, while the thick lines represent the 3D $CdSO_4$-type framework.

---

[*] To whom correspondence should be addressed. E-mail: liikh@cc.ncu.edu.tw.

[†] National Tsing Hua University.

[‡] National Central University.

[§] Academia Sinica.

(1) Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2638, and references therein.

(2) Batten, S. R. *Curr. Opin. Solid State Mater. Sci.* **2001**, *5*, 107, and references therein.

(3) Batten, S. R.; Robson, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1460, and references therein.

(4) Jiang, Y.-C.; Lai, Y.-C.; Wang, S.-L.; Lii, K.-H. unpublished research.

(5) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151.

(6) Tong, M.-L.; Ye, B.-H.; Cai, J.-W.; Chen, X.-M.; Ng, S. W. *Inorg. Chem.* **1998**, *37*, 2645.

10.1021/ic0106017 CCC: $20.00

are each connected through 4,4′-bpy bridges to four neighbors, two in the same orientation and the other two with a 90° rotation along the connection. This structure belongs to the rarely observed $CdSO_4$ structure type.[8] To our knowledge, {Cu[1,2-bis(4-pyridyl)ethane]$_2$(NO_3)$_2$} is the only other example in the area of coordination polymers which can also be ascribed to the $CdSO_4$ structure type.[9,10] In addition to the presence of a rarely observed 3D framework type, compound **1** is also the first coordination polymer that exhibits interpenetration of a 2D net into a 3D framework. The smaller cavity that is formed by 4,4′-bpy in **1** might not be amenable to two-fold interpenetration of $CdSO_4$-type framework as observed in {Cu[1,2-bis(4-pyridyl)ethane]$_2$(NO_3)$_2$}. The $CdSO_4$-type network based on the spacer ligand 4,4′-bpy appears to facilitate interpenetration of 2D square nets instead. The 2D net is hydrogen bonded to the 3D framework either directly (PO(3)H···O(8)P = 1.74 Å) or through the water and 1-butanol molecules of solvation (PO(2)H···O(10)H_2 = 1.77, C_4H_9OH···O(8)P = 1.85, H(10)OH(10′)···OHC_4H_9 = 1.83 Å). Hydrogen bonding may also play an important role in the stability of this interpenetrating network.

In conclusion, the structure reported here reveals a new type of interpenetration and a rarely observed 3D framework type. It is also the first example of a metal−4,4′-bpy−phosphate system that exhibits interpenetrating networks. A small change of solvent in the hydrothermal synthesis has a surprising effect on the preferential formation of a 3D rather than 2D network. The inclusion of 1-butanol molecules appears to be necessary for the formation of **1**. Other changes in reaction variables, such as temperature and pH value, could also have a profound influence on the reaction outcome. The synthesis of other supramolecular isomers based on 4,4′-bpy and phosphate has intrigued us. Can we avoid interpenetration and achieve a polymorph with a single $CdSO_4$ network? Further work on this theme is in progress.

Acknowledgment. We thank the National Science Council and Chinese Petroleum Corp. for financial support and a reviewer for valuable comments.

Supporting Information Available: Crystallographic data for [Ni(4,4′-bpy)$_2$(H_2PO_4)$_2$]·C_4H_9OH·H_2O in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0106017

---

(7) Crystal data for **1**: $C_{24}H_{32}N_4NiO_{10}P_2$, blue plate crystal of dimensions 0.35 × 0.30 × 0.08 mm, $T = 295$ K, monoclinic, space group $C2/c$, $a = 15.1902(7)$, $b = 16.8168(8)$, $c = 22.680(1)$ Å, $\beta = 97.214(1)°$, $V = 5747.8(5)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.519$ g cm^{-3}, $\lambda = 0.71073$ Å, $\mu = 8.48$ cm^{-1}, 7029 unique reflections with $I > 2\sigma(I)$ ($2\theta_{max} = 56.6°$, R(int) = 0.0358), GOF = 1.032, $R1 = 0.0395$ and $wR2 = 0.1107$. H atoms of the phosphate groups and guest water molecule were located from difference Fourier maps, whereas H atoms of 4,4′-bpy and 1-butanol were placed in calculated positions. The final cycles of least-squares refinement included atomic coordinates and anisotropic thermal parameters for all non-hydrogen atoms. The atomic coordinates and isotropic thermal parameters for all hydrogen atoms in H_2PO_4 groups and H_2O molecules were fixed. Diffractometer: Siemens SMART CCD (Mo Kα radiation, graphite monochromator). Structure refinement: *SHELXTL* (Sheldrick, G. M., Version 5.1, Siemens Analytical X-ray Instruments, Madison, WI, 1998). Absorption correction: *SADABS* (Sheldrick, G. M., University of Göttingen, 1995).

(8) O'Keeffe, M. *Z. Kristallogr.* **1991**, *196*, 21.

(9) Power, K. N.; Hennigar, T. L.; Zaworotko, M. J. *Chem. Commun.* **1998**, 595.

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