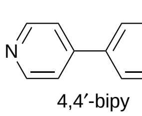
X-Ray crystal structure of $\{Cu[1,2\text{-bis(4-pyridyl)ethane}]_2(NO_3)_2\}_n$: the first example of a coordination polymer that exhibits the NbO 3D network architecture†

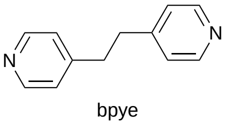
K. Nicole Power, Tracy L. Hennigar and Michael J. Zaworotko*

Department of Chemistry, Saint Mary's University, Halifax, Nova Scotia, B3H 3C3, Canada

The coordination polymer $\{Cu[1,2\text{-bis(4-pyridyl)ethane}]_2(NO_3)_2\}_n$ does not exist as a square grid network, rather it is the first example of a twofold NbO type 3D network. A twofold level of interpenetration does not preclude the presence of 11 × 11 Å channels which contain benzene and methanol guest molecules.

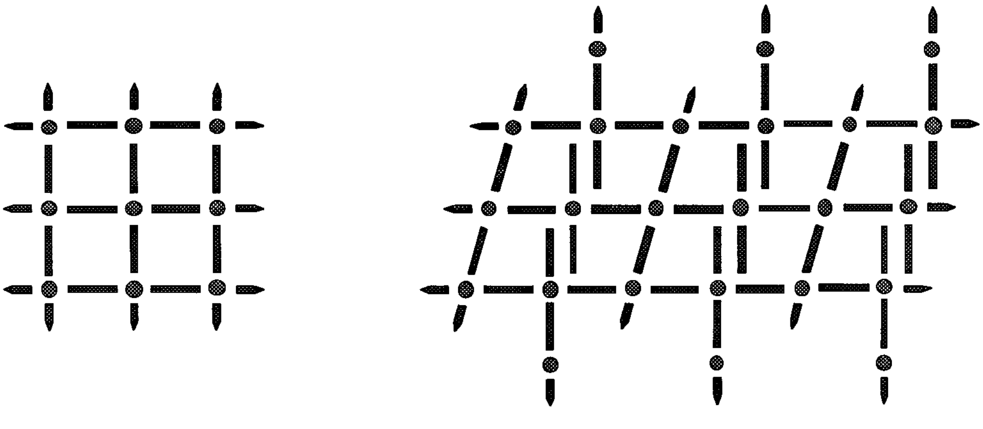
Recent activity in crystal engineering has afforded several examples of coordination polymers which have open framework network structures and therefore have the potential to be functionally related to zeolites.[1–3] The architectures of coordination polymers can be either mineralomimetic or, more commonly, without precedence in naturally occurring solids. If simple linear spacer ligands such as 4,4′-bipyridine (4,4′-bipy) are utilized, the architecture of a coordination polymer is strictly limited by the stoichiometry. For example, a 1 : 1.5 ratio of T-shape, square planar or octahedral metal to 4,4′-bipy affords ladder,[4–7] brick-wall,[4] 3D frame[8,9] or bilayer structures.[7,10] These architectures, which can be regarded as being supramolecular isomers of one another,[7,10] are without precedence in naturally occurring compounds. If one considers a 1 : 2 ratio of square planar or octahedral metal to linear spacer ligand, there would appear to be only two likely supramolecular isomers, square 2D grids or 3D frames (Scheme 1). These supramolecular isomers could occur for either square planar or suitably substituted octahedral complexes. The former has been widely encountered in Hoffman clathrates[11] and 4,4′-bipy sustained networks[12–15] whereas the latter has to our knowledge only hitherto been observed in NbO.[16] In this contribution we report the structure of a copper(II) coordination polymer based upon the spacer ligand 1,2-bis(4-pyridyl)ethane (bpye) which represents, to our knowledge, the first example of a coordination polymer which exhibits the NbO type structure, $[Cu(bpye)_2(NO_3)_2]_n$ **1**.


4,4′-bipy


bpye

Blue crystals of **1** were grown by carefully layering a methanol solution of $Cu(NO_3)_2\cdot 6H_2O$ onto a benzene solution of bpye under ambient conditions. The ligand bpye is capable of adopting either *gauche* or *anti* conformations and can therefore act as either an angular or a linear spacer ligand, respectively.[7] As revealed by single crystal X-ray crystallography, the bpye ligands in **1** are *anti* and they sustain a 3D framework motif with channels of effective cross-section 11 × 22 Å.‡ In the structure there is a single network of **1**.† The large channels in a single framework of **1** facilitate twofold interpenetration with a second independent framework but do not result in a close-packed structure, rather, large square channels with effective cross-sectional area of 11 × 11 Å exist parallel to the crystallographic *a*-axis; these channels contain two ordered benzene molecules and one disordered methanol/benzene molecule per metal centre and crystals appear to lose solvent and crystallinity within minutes of their removal from the mother liquor.†

The coordination geometry around the Cu^{II} moiety can be regarded as pseudo-square planar since the nitrate anions are only weakly coordinated, Cu–O distances being 2.366(4) and 2.486(4) Å, significantly longer than those seen for octahedral Ni^{II} or Co^{II} analogues.[14] Other bond distances are within expected ranges. It is not clear from this study why **1** exists as a 3D NbO type framework rather than a 2D square grid framework of the type commonly exhibited by 4,4′-bipy analogues of **1**.[12–15] Indeed, we have now prepared more than twenty 4,4′-bipy square grid compounds and we have prepared more than ten bpye square grid compounds. The title compound still remains the only one that exhibits the NbO framework. It would not appear that the Jahn–Teller induced distortion from octahedral geometry is a likely factor for the observed structure since, in principle, both square planar and octahedral metal moieties should be able to sustain the NbO network. However, the length of bpye compared to 4,4′-bipy might be a factor. It is


Scheme 1

known that 4,4′-bipy sustained square grid coordination polymers can form close packed structures *via* interpenetration[12] or stable open framework structures through inclusion of aromatic molecules.[13–15] The larger cavity that would be formed by bype might not be as amenable to such behaviour. It should also be noted that bpye inherently possesses conformational flexibility and other supramolecular isomers based upon conformational isomerism[7] are therefore likely for **1**. The factors that affect the generation of supramolecular isomers of **1** and related coordination polymers, in particular the influence of guest and solvent, are currently being investigated further.

We acknowledge Dr C. Campana of Siemens Industrial Automation Ltd. for furnishing the X-ray data and the generous financial support of the NSERC (Canada) in the form of a research grant (M. J. Z.).

Notes and References

* Present address: Faculty of Arts and Science, University of Winnipeg, 515 Portage Avenue, Winnipeg, Manitoba, R3B 2E9, Canada. E-mail: mike.zaworotko@uwinnipeg.ca

† This ChemComm is also available in enhanced multi-media format *via* the World Wide Web: http://www.rsc.org/ccenhanced. Figs. 1 and 2 are shown in the enhanced version.

‡ *Crystal data* for **1**: $C_{41}H_{48}CuN_6O_{8.5}$, orthorhombic, space group *Pccn*, a = 14.7097(18), b = 21.832(3), c = 26.719(3), U = 8580.4(18) Å^3, Z = 8, D_c = 1.281 Mg m^{-3}, λ = 0.709 30 Å, $F(000)$ = 3464. 6639 reflections out of 8443 unique reflections with $I_{net} > 3.5I$ measured at 173 K for a crystal of dimensions 0.2 × 0.3 × 0.4 mm on a Siemens SMART/CCD diffractometer using the θ scan mode ($4 < 2\theta < 52°$) afforded on convergence final R-factors of R_f = 0.114 and R_w = 0.117. Two independent benzene and two independent MeOH guest molecules were observed to have high thermal motion and a third benzene guest was observed to be disordered with a water or methanol molecule. H atoms of the framework were placed in calculated positions (C–H 1.0 Å) whereas H atoms of the disordered guest molecules were not placed. All non-hydrogen atoms were anisotropically refined. The crystallographic calculations were conducted using the NRCVAX program package. CCDC 182/734.

1 D. Venkataraman, G. B. Gardner, S. Lee and J. S. Moore, *J. Am. Chem. Soc.*, 1995, **117**, 11 600.
2 O. M. Yaghi, G. Li and H. Li, *Nature*, 1995, **378**, 703.
3 S. Subramanian and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1994, **35**, 2127.
4 M. Fujita, Y. J. Kwon, O. Sasaki, K. Yamaguchi and K. Ogura, *J. Am. Chem. Soc.*, 1995, **117**, 7287.
5 G. A. Doyle, D. M. L. Goodgame, S. P. W. Hill and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1993, 207.
6 P. Losier and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2779.
7 T. Hennigar, D. C. MacQuarrie, P. Losier, R. D. Rogers and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 972.
8 F. Robinson and M. J. Zaworotko, *Chem. Commun.*, 1995, 2413.
9 O. Yaghi and H. Li, *J. Am. Chem. Soc.*, 1996, **118**, 295.
10 K. N. Power, T. L. Hennigar and M. J. Zaworotko, *New J. Chem.*, in press.
11 T. Iwamoto, in *Inclusion Compounds*, ed. J. L. Atwood, J. E. D. Davies and D. D. MacNicol, Academic Press, London, vol. 1, 1984, ch. 2, pp. 29–57.
12 R. W. Gable, B. F. Hoskins and R. Robson, *J. Chem. Soc., Chem. Commun.*, 1990, 1677.
13 M. Fujita, Y. J. Kwon, S. Washizu and K. Ogura, *J. Am. Chem. Soc.*, 1994, **116**, 1151.
14 J. L. Atwood, T. L. Hennigar, C. M. Hogg, K. T. Holman, P. Losier, L. R. MacGillivray, K. N. Power, R. D. Rogers and M. J. Zaworotko, unpublished work.
15 J. Lu, T. Paliwals, S. C. Lim, C. Yu, T. Niu and A. J. Jacobsen, *Inorg. Chem.*, 1997, **36**, 923.
16 A. F. Wells, *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 4th edn., 1975.

Received in Columbia, MO, USA, 19th May 1997, revised manuscript received 29th October 1997; 7/08943K