A Neutral 3D Copper Coordination Polymer Showing 1D Open Channels and the First Interpenetrating NbO-Type Network**

Xian-He Bu, Ming-Liang Tong, Ho-Chol Chang, Susumu Kitagawa,* and Stuart R. Batten*

The construction of coordination networks with novel topologies and porous structures that provide new sizes, shapes, and chemical environments is of great interest in recent years, due to their intriguing structural diversity and potential for many applications.[1,2] In recent years many porous metal–organic frameworks with unique structures have been obtained and their adsorption properties were widely investigated, however, those with specially shaped channels such as 1D helices are rare.[3] Metal–ligand coordination has been well used in the directed assembly of extended porous metal–organic networks, and one of the key points for such studies is the design or choice of components that organize themselves into desired patterns with useful functions. In this regard, considerable attention has been devoted to the networking ability of isonicotinic acid (**1**) and its derivatives,[4] which are multifunctional ligands potentially able to act as bridging ligands to produce open lattice species with various structural topologies and large pores. In this study, we choose an analogy of **1**, 9-acridinecarboxylic acid (HL), whose coordination chemistry has not been previously investigated, as a bridging ligand to construct new framework materials with novel structures and special properties based on combining its bridging coordination ability with its steric bulk. Although the coordination sites of HL and **1** are very similar, their coordination chemistry are found to be quite different due to the bulk of HL. We report herein a 3D twofold interpenetrating NbO-type network $[\mathrm{Cu_2(\mu_2\text{-}OMe)_2(\mathbf{L})_2\cdot(H_2O)_{0.69}}]_n$ (**2**) with 1D channels.

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[*] Prof. X.-H. Bu
Department of Chemistry
Nankai University
Tianjin 300071 (China)
Fax: (+86) 22-2350-2458
E-mail: buxh@nankai.edu.cn

Dr. M.-L. Tong, Dr. H.-C. Chang, Prof. S. Kitagawa
Department of Synthetic Chemistry and Biological Chemistry
Graduate School of Engineering
Kyoto University
Kyoto 606-8501 (Japan)
Fax: (+81) 75-753-4979
E-mail: kitagawa@sbchem.kyoto-u.ac.jp

Dr. S. R. Batten
School of Chemistry
Monash University
Victoria 3800 (Australia)

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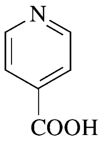

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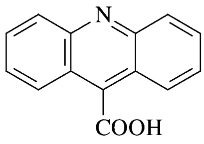

HL

Black crystals of **2** were obtained by the reaction of $Cu(NO_3)_2 \cdot 3\,H_2O$ and HL in MeOH in the presence of Et_3N in fairly strong basic conditions. It is noteworthy that the amount of Et_3N used in the synthetic process is a key point for the formation of **2** because at weak basic or weak acidic conditions, a dinuclear[5a] or a trinuclear Cu^{II} complex[5b] would form.

2 crystallizes in the high symmetry trigonal space group $R\bar{3}$ and consists of $Cu_2(\mu_2\text{-}OMe)_2$ dimers bridged by two-connecting L ligands. Figure 1 a illustrates the coordination environment of center Cu atoms and the fourfold connectivity of the bimetallic unit. Although there are two crystallographically different dimers in the structure, they are both chemically and topologically identical. In the context of the structure, the dicopper dimers constitute so-called secondary building units (SBUs).[6] The copper atoms in each SBU are bridged by two methanolato anions to give $[Cu_2(\mu_2\text{-}OMe)_2]^{2+}$ fragments in which the Cu···Cu distance is 2.992(2) Å. Each copper atom is four-coordinate, with two methanolato oxygen atoms, one carboxylic oxygen atom of L and one nitrogen atom from another L ligand. The Cu_2 unit, which acts as a node, is connected to four others through four bridging L ligands. Each Cu^{II} center coordinates to one L through the pyridyl nitrogen atom, and to another through the carboxylate functional group (Figure 1 a). The coordination of the ligands is such that the pyridyl donors form a *trans* arrangement across the dimer, as do the carboxylate.

The bridging of the SBUs produces an overall 3D network which is spacious enough to contain a second, interpenetrating network. The structure of **2** can be described as two-fold interpenetrating nets with NbO topology, if the dimer is regarded as a four-connecting node (Figure 1 b). To the best of our knowledge, this is the first example of interpenetrating NbO networks.[7] The lack of interpenetrating NbO networks in the literature has recently been attributed to the fact that, unlike other network topologies such as diamond or α-Po, NbO is not a self-dual—that is, it cannot interpenetrate in such a way that it is fully catenated.[7a,8] The interpenetration reported here is that of partially catenated nets, with two of the eight six-membered rings not catenated.[7a,8] The structure of **2** does show, however, that interpenetration is possible for this network topology.

Space-filling views of the structure reveal small channels that run parallel to the *z* axis (Figure 1 c) which contain disordered water molecules (for which a reasonable refinement for the structure was not possible[9]). Calculations from the X-ray structural parameters show that the solvent-accessible void space in the channels is approximately 24 %.[10] The smallest diameter of these channels, after taking into account van der Waals radii, is only about 2.8 Å. However, the observed porosity of the structure (see below) can perhaps be explained by the fact that the channels are not uniform, and are significantly more open in sections. Thus halfway between the narrow sections of the channels lay more open cavities with minimum diameters of about 5.3 Å (and, given its nonspherical shape, larger maximum diameters). No significant channels are observed in any other direction.

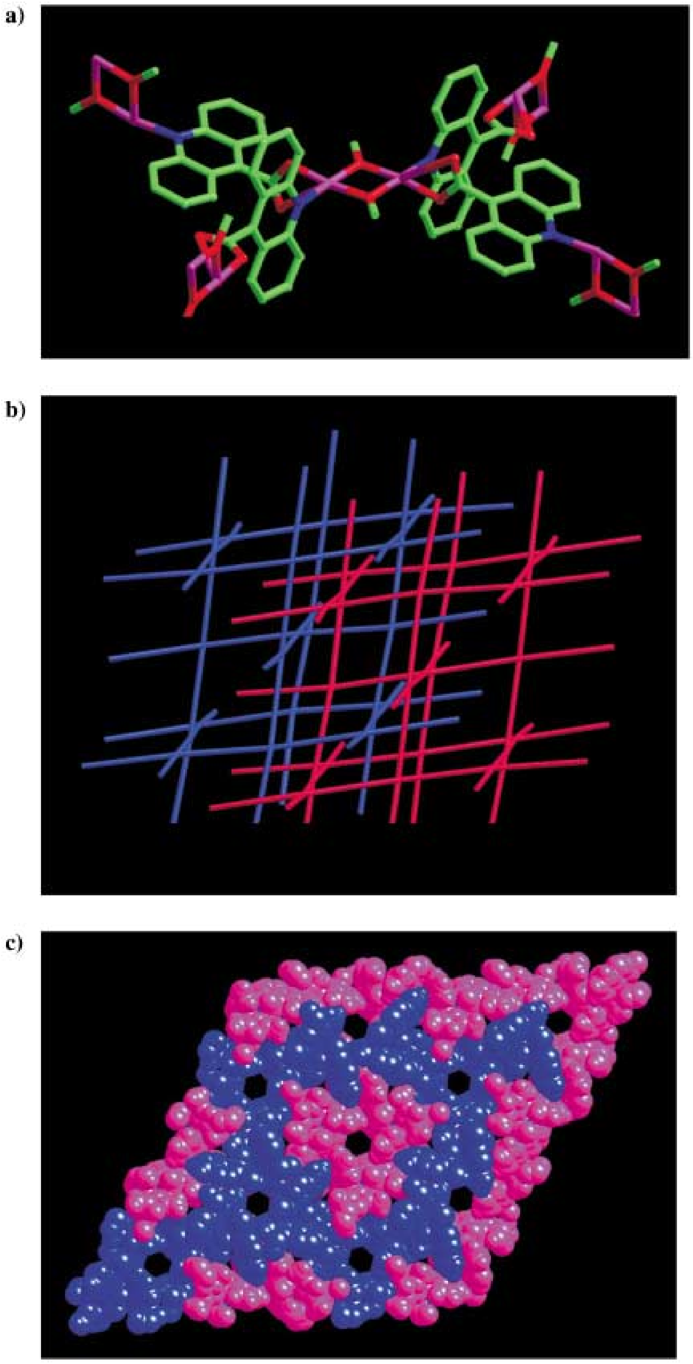

Figure 1. a) The structure of **2**, showing the local coordination geometry. Each $Cu_2(OMe)_2$ dimer is bridged by four L ligands to four other dimers. Green: C; blue: N; red: O; pink: Cu, hydrogen atoms are omitted for clarity. b) The two-fold interpenetrating NbO-type networks, with the nodes representing the $Cu_2(OMe)_2$ dimers, and the links the bridging L ligands. c) Space-filling diagram of the two-fold interpenetrating networks viewed down the *z* axis. Note the 1D channels apparent.

The structure contains numerous intra- and internetwork CH···π and π···π supramolecular interactions that presumably help to stabilize the adopted structure. For example, the rings that form the narrowest part of the channels are stabilized by intranetwork CH···π interactions (Figure 2a). The structure also contains double helices, in which each strand is part of a separate network, which are again stabilized by numerous weak intermolecular interactions (Figure 2b). These double helices run parallel to both the *z* axis and the 1D channels, and pass through the midpoints of imaginary "triangles" whose corners are defined by the 1D channels (as can be seen in Figure 1c).

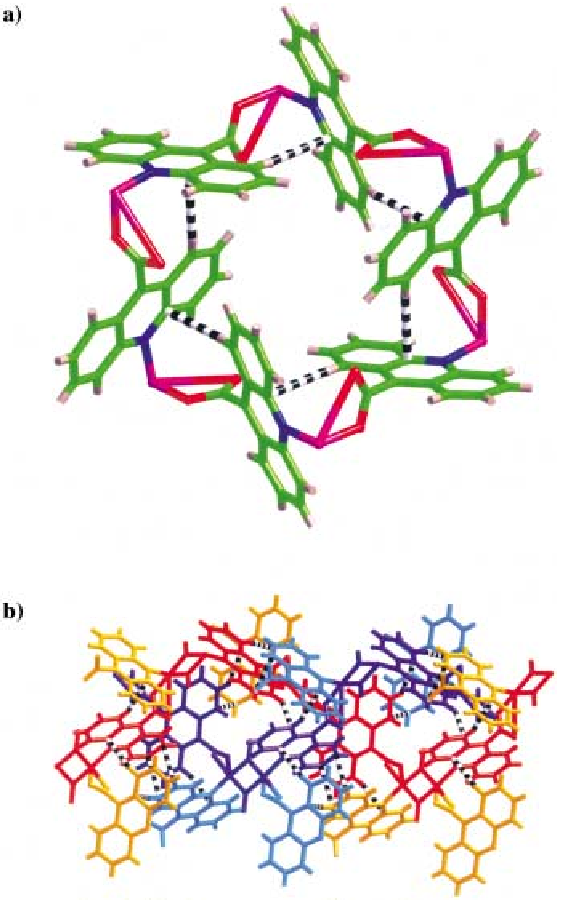

Figure 2. a) A view of the narrowest part of the 1D channels, emphasizing the intranetwork CH···π interactions (shown as black and white striped bonds). b) The double helix motif contained in the structure, with CH···π and π···π interactions depicted as black and white striped bonds. The two strands of the double helix are shown in purple and red, with L appendages to these strands shown in blue and yellow, respectively.

To examine the thermal stability and porous functionality of the synthetic material, the TG analysis and gas adsorption isotherms were carried out. The TG curve shows the release of water molecules below 70 °C. No further weight loss could be observed upon heating up to about. 200 °C, and after this point the compound starts to decompose. Figure 3 shows the isotherms of anhydrous **2** for the adsorption of N_2 and alcohols (EtOH and MeOH) at 77 and 298 K, respectively. A rapid increase in the amount of adsorbed gas is shown by an increase in pressure of up to $0.05\,P_0$, which indicates the diffusion of guest gas molecules into the channels. Approximately 6.0, 3.7 and 4.3 mmol of N_2, EtOH and MeOH, respectively, were adsorbed per 1.0 g of anhydrous sample at a pressure of $0.8\,P_0$. Moreover, adsorption and desorption experiments with MeOH trace the same isotherms, which indicates that the channel structure is retained through this process. Thus, these isotherms are of type **1** according to the IUPAC classification.[11]

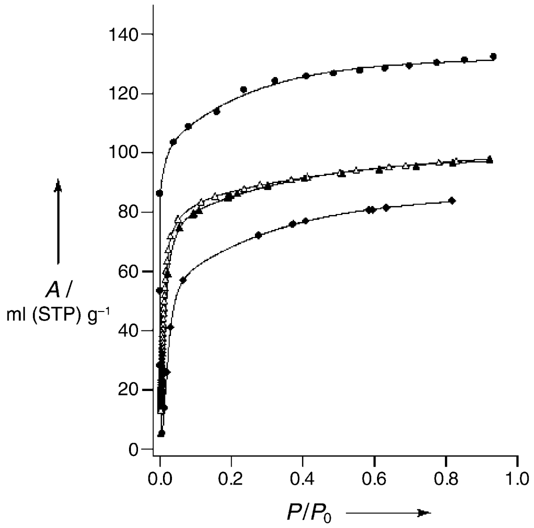

Figure 3. Isomers for the adsorption of N_2 (●) at 77 K and, EtOH (◆) and MeOH (▲) and desortion of MeOH (Δ) on **2** at 298 K. (*A* = absolute adsorption; STP = standard temperature and pressure).

In conclusion, we have successfully constructed a 3D Cu^{II} coordination polymer with 1D channels by using a unique bulky bridging ligand and the key point for the synthetic procedures has been well established. The structure of this complex provides the first two-fold interpenetrating NbO-type network and this result shows that interpenetration is possible for this network topology. The porous properties have been studied and we expect that this coordination polymer will find applications such as in gas separation.

Experimental Section

Synthesis of **2**: $Cu(NO_3)_2{\cdot}3\,H_2O$ (245 mg, 1 mmol) was added to a stirring colorless solution of HL (224 mg, 1 mmol) dissolved in MeOH (100 mL) in the presence of excess Et_3N. After a few minutes, the solution was then filtered and left to stand at room temperature. Black crystals of **2** suitable for X-ray analysis were obtained after several days in about 50 % yield. Elemental analysis calcd (%) for **2**: C 55.90, H 3.44, N 4.35; found: C 51.44, H 3.77, N 3.95. IR (KBr pellet): $\tilde{\nu}$ = 3415s, 2359w, 1615s, 1474w, 1386m, 1321m, 766m, 645m cm^{-1}.

Single-crystal X-ray structure determination on **2**: The data were collected at 298(2) K on a Rigaku mercury CCD diffractometer with graphite-monochromated Mo-K_α radiation. The structure was solved by direct methods by using SHELXS-97 and extended by using Fourier techniques. Crystal data: $C_{60}H_{44}Cu_4N_4O_{13.38}$, $M_r = 1289.15$, rhombohedral, space group $R\bar{3}$, $a = b = 53.643(7)$ Å, $c = 11.920(10)$ Å, $V = 29706(24)$ Å^3, $Z = 18$, $\mu = 13.30$ cm^{-1}, $\rho_{cald} =$

1.297 g cm^{-3}, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, GOF = 1.157, $R1$ ($wR2$) = 0.0709 (0.1934) [10484 observed ($I > 2\sigma(I)$)] for 12944 ($R_{\mathrm{int}} = 0.0973$) independent reflections out of a total of 51565 reflections with 761 parameters. CCDC-210834 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Gas adsorption measurements: The sorption isotherm measurements of nitrogen and alcohol (MeOH and EtOH) were performed at 77 and 298 K, respectively, by using BELSORP18 (BEL inc) automatic volumetric adsorption equipment. A known weight (100–200 mg) of the as-synthesized sample was placed in the quartz tube, then, prior to measurements, the sample was dried under high vacuum at 373 K for 10 h to remove the solvated water molecules. The adsorbate was dosed into the sample tube, then the change of the pressure was monitored and the amount of adsorption was determined by decrease in pressure at the equilibrium state.

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Keywords: carboxylate ligands · coordination polymers · copper · microporous materials · N ligands

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[1] For recent reviews, see: a) O. R. Evans, W. Lin, *Acc. Chem. Res.* **2002**, *35*, 511; b) L. H. Gade, *Acc. Chem. Res.* **2002**, *35*, 575; c) B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629; d) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319; e) D. Braga, *J. Chem. Soc. Dalton Trans.* **2000**, 3705; f) R. Robson, *J. Chem. Soc. Dalton Trans.* **2000**, 3735; g) C. Piguet, J.-C. G. Bünzli, *Chem. Soc. Rev.* **1999**, *28*, 347; h) A. J. Blake, N. R. Champness, P. Hubberstey, W.-S. Li, M. A. Withersby, M. Schröder, *Coord. Chem. Rev.* **1999**, *183*, 117.

[2] For examples: a) G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray, J. D. Cashion, *Science* **2002**, *298*, 1762; b) R. Kitaura, S. Kitagawa, Y. Kubota, T. C. Kobayashi, K. Kindo, Y. Mita, A. Matsuo, M. Kobayashi, H.-C. Chang, T. C. Ozawa, M. Suzuki, M. Sakata, M. Takata, *Science* **2002**, *298*, 2358; c) M. Oh, G. B. Carpenter, D. A. Sweigart, *Angew. Chem.* **2003**, *115*, 2072; *Angew. Chem. Int. Ed.* **2003**, *42*, 2026; d) H. Zhao, M. J. Bazile, Jr., J. R. Galán-Mascarós, K. R. Dunbar, *Angew. Chem.* **2003**, *115*, 1045; *Angew. Chem. Int. Ed.* **2003**, *42*, 1015; e) L. Pan, H. Liu, X. Lei, X. Huang, D. H. Olson, N. J. Turro, J. Li, *Angew. Chem.* **2003**, *115*, 560; *Angew. Chem. Int. Ed.* **2003**, *42*, 542; f) L. Carlucci, G. Ciani, D. M. Proserpio, F. Porta, *Angew. Chem.* **2003**, *115*, 331; *Angew. Chem. Int. Ed.* **2003**, *42*, 317; g) M. Eddaoudi, J. Kim, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2002**, *124*, 376; h) E. Lee, J. Kim, J. Heo, D. Whang, K. Kim, *Angew. Chem.* **2001**, *113*, 413; *Angew. Chem. Int. Ed.* **2001**, *40*, 399; i) X.-H. Bu, W. Chen, S.-L. Lu, R.-H. Zhang, D.-Z. Liao, W.-M. Bu, M. Shionoya, F. Brisse, J. Ribas, *Angew. Chem.* **2001**, *113*, 3301; *Angew. Chem. Int. Ed.* **2001**, *40*, 3201; j) T. J. Prior, D. Bradshaw, S. J. Teat, M. J. Rosseinsky, *Chem. Commun.* **2003**, 500.

[3] a) Y. Cui, S. J. Lee, W. Lin, *J. Am. Chem. Soc.* **2003**, *125*, 6014; b) O. R. Evans, H. L. Ngo, W. Lin, *J. Am. Chem. Soc.* **2001**, *123*, 10395; c) G. J. E. Davidson, S. J. Loeb, *Angew. Chem.* **2003**, *115*, 78; *Angew. Chem. Int. Ed.* **2003**, *42*, 74; d) S. Masaoka, S. Furukawa, H.-C. Chang, T. Mizutani, S. Kitagawa, *Angew. Chem.* **2001**, *113*, 3933; *Angew. Chem. Int. Ed.* **2001**, *40*, 3817.

[4] For recent examples: a) O. R. Evans, R.-G. Xiong, Z. Wang, G. K. Wong, W. Lin, *Angew. Chem.* **1999**, *111*, 557; *Angew. Chem. Int. Ed.* **1999**, *38*, 536; b) K. S. Min, M. P. Suh, *Eur. J. Inorg. Chem.* **2001**, 449; c) M. E. Chapman, P. Ayyappan, B. M. Foxman, G. Y. Yee, W. Lin, *Cryst. Growth Des.* **2001**, *1*, 159; d) L. R. MacGillivray, R. H. Groeneman, J. L. Atwood, *J. Am. Chem. Soc.* **1998**, *120*, 2676; e) J. Y. Lu, A. M. Babb, *Chem. Commun.* **2001**, 821; **2002**, 1340; f) R. Gheorghe, M. Andruh, A. Müller, M. Schmidtmann, *Inorg. Chem.* **2002**, *41*, 5314; g) S.-i. Noro, S. Kitagawa, M. Yamashita, T. Wada, *CrystEngComm* **2002**, *4*, 162.

[5] Crystal data: a) The dinuclear complex: $C_{58}H_{40}Cu_2N_4O_{10}$, $M_r = 1080.02$, triclinic, space group $P\bar{1}$, $a = 10.060(8)$ Å, $b = 10.676(8)$ Å, $c = 11.793(10)$ Å, $\alpha = 90.987(8)°$, $\beta = 110.288(11)°$, $\gamma = 94.560(9)°$, $V = 1182.9(16)$ Å^3, $Z = 1$, $\mu = 9.68$ cm^{-1}, $\rho_{\mathrm{cald}} = 1.516$ g cm^{-3}, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, GOF = 0.996, $R1$ ($wR2$) = 0.0506 (0.1288) [2667 observed ($I > 2\sigma(I)$)] for 3661 ($R_{\mathrm{int}} = 0.0201$) independent reflections out of a total of 4129 reflections with 338 parameters; b) The trinuclear complex: $C_{90}H_{72}Cu_3N_6O_{18}$, $M_r = 1716.16$, cubic, space group $Pa\bar{3}$, $a = b = c = 19.990(2)$ Å, $V = 7988.0(14)$ Å^3, $Z = 4$, $\mu = 8.67$ cm^{-1}, $\rho_{\mathrm{cald}} = 1.427$ g cm^{-3}, $\lambda(\mathrm{Mo_{K\alpha}}) = 0.71073$ Å, GOF = 1.364, $R1$ ($wR2$) = 0.1129 (0.1996) [1941 observed ($I > 2\sigma(I)$)] for 2335 ($R_{\mathrm{int}} = 0.1319$) independent reflections out of a total of 24814 reflections with 193 parameters. The data are not good enough due to the small size and poor quality of the crystal obtained. The data were collected at 298(2) K on a Rigaku mercury CCD diffractometer with graphite monochromated $\mathrm{Mo_{K\alpha}}$ radiation. The structures were solved by direct method using SHELXS-97 and extended using Fourier techniques.

[6] M. O'Keeffe, M. Eddaoudi, H. Li, T. Reineke, O. M. Yaghi, *J. Solid State Chem.* **2000**, *152*, 3.

[7] a) O. D. Friedrichs, M. O'Keeffe, O. M. Yaghi, *Solid State Sci.* **2003**, *5*, 73; b) An earlier review on interpenetration (S. R. Batten, R. Robson, *Angew. Chem.* **1998**, *110*, 1558; *Angew. Chem. Int. Ed.* **1998**, *37*, 1460) incorrectly described the topology of the hydrogen bonded networks contained in the 1:1 cocrystal of cyanuric acid and biuret as being NbO-related, when in fact they have the $CdSO_4$ topology. Possibly as a result, a number of other papers have made the same error in topological assignment: c) K. N. Power, T. L. Hennigar, M. J. Zaworotko, *Chem. Commun.* **1998**, 595; d) S. S. Kuduva, D. C. Craig, A. Nangia, G. R. Desiraju, *J. Am. Chem. Soc.* **1999**, *121*, 1936; e) J. -H. Fournier, T. Maris, M. Simard, J. D. Wuest, *Cryst. Growth Des.* **2003**, *3*, 535. To our knowledge only a small number of non-interpenetrating NbO networks have been reported: f) T. Niu, X. Wang, A. J. Jacobson, *Angew. Chem.* **1999**, *111*, 2059; *Angew. Chem. Int. Ed.* **1999**, *38*, 1934; g) see ref. [8]. Since acceptance of this work for publication, another report of doubly interpenetrating networks has been published:B. Chen, F. R. Fronczek, A. W. Maverick, *Chem. Commun.* **2003**, 2166.

[8] M. Eddaoudi, J. Kim, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2002**, *124*, 376.

[9] The exact number of water molecules in the crystallographic asymmetry unit cannot determined according to the Fourier electron-densities because of disorder.

[10] The accessible void volume was calculated with the program PLATON by using a probe with a radius of 1.2 Å. A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, C34.

[11] IUPAC, *Pure. Appl. Chem.* **1985**, *57*, 603.