Open Square-Grid Coordination Polymers of the Dimensions 20 × 20 Å: Remarkably Stable and Crystalline Solids Even after Guest Removal[**]

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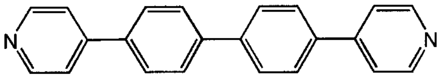
The synthesis of coordination polymers using 4,4′-bipyridine (4,4′-bpy, **1**) and transition metal ions has thus far produced several novel networks with a high degree of porosity.[1, 2] Among all the networks, square-grid polymers are of particular importance due to their predictable pore sizes and selective inclusion of guest molecules. The first square-grid complex $[\{Zn(\mathbf{1})_2(PF_6)_2\}_n]$ was reported by Robson et al. in 1990; it is interpenetrated and thus nonporous.[3] In 1994 we prepared the noninterpenetrated square-grid complex $[\{[Cd(\mathbf{1})_2(H_2O)_2](NO_3)_2\}_n]$.[4] Despite the simple structural design, however, **1** has not been replaced by analogous structural units that are significantly longer. A few structures with a longer ligand Py-X-Py (Py = 4-pyridyl, X = CH_2CH_2, CH=CH, or C≡C) have been reported; however, these ligands are longer than **1** by only 2 Å.[5] Herein we show that noninterpenetrated square-grid networks can be obtained with the larger ligand **2**, which is 8.5 Å longer than **1**.



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Treatment of **2** with $Ni(NO_3)_2$ (1:2 ratio) gives an extraordinarily big square-grid polymer with dimensions of about 20 × 20 Å. Surprisingly, the grid framework thus obtained is so stable that the crystals *after removal of the guest* were analyzed by single-crystal X-ray diffraction.[6]

The single crystals of the complex of **2** were grown by layering a solution of $Ni(NO_3)_2$ in MeOH over a solution of **2** in *o*-xylene and isolated in 80 % yield. The crystal structure of this complex revealed the formation of a noninterpenetrated square-grid polymer **3**. The Ni atom resides in a distorted

$[\{[Ni(\mathbf{2})_2(NO_3)_2]\cdot 4(o\text{-xylene})\}_n]$ **3**

octahedral environment with four pyridyl groups at the equatorial positions and two nitrate groups at the apical positions. The guest molecules occupy 58 % of the crystal volume. The square cavity has dimensions of 19.9 × 20.0 Å. Each cavity is occupied by six *o*-xylene molecules: two of them that are parallel to the grid plane lie within the cavity, while the other four that are perpendicular to the grid plane exist partly outside the cavity (Figure 1a).

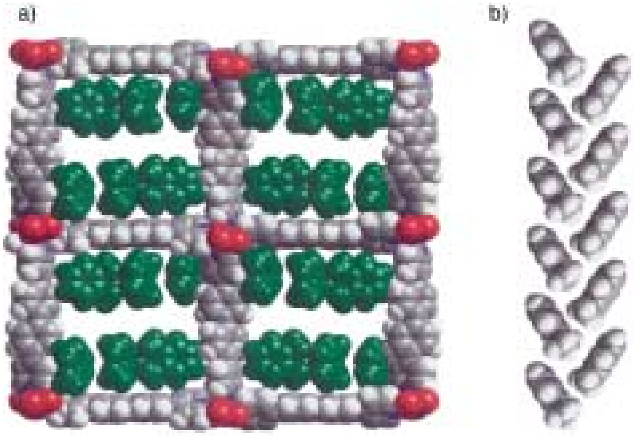

Figure 1. Square-grid network (a) and one-dimensional column of *o*-xylene in complex **3** (b).

Besides the formation of big square cavities, another important feature of this structure is the packing of the grids that creates big rectangular channels (ca. 10 × 20 Å; Figure 2), which are occupied by a one-dimensional (1D) column of guest molecules (Figure 1b). The two-dimensional (2D) layers in **3**, unlike those in metal–(4,4′-bipyridine) square grids that have a large interlayer separation (6–8 Å), display a very short interlayer separation of 4.5 Å, and the ligands of adjacent grids interact with each other through edge-to-face aromatic interactions. For instance, the distance between the plane of the C_6 ring of the ligand of one layer and the edge of the C_5N ring of the ligand from the neighboring layer is as short as 3.4 Å. The guest molecules interact with each other through Me⋯Me (C⋯C 3.940 Å) interactions and Me⋯π interactions (distance from C of Me group to plane of C_6 ring of neighboring molecule: 3.631 Å). The aromatic moieties of the guest also interact with the host through edge-to-face aromatic interactions.

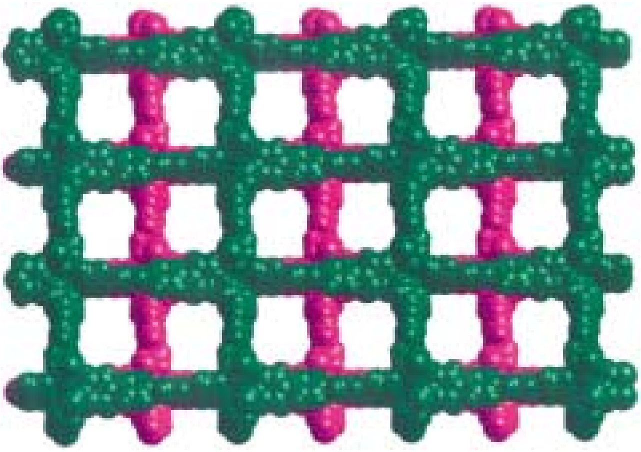

Figure 2. The packing of the grids showing the formation of rectangular channels (ca. 20 × 10 Å) in **3**. Alternate layers are represented by identical colors.

The existence of uniform channels and the short interlayer separation prompted us to study the stability of the structure after removal of guest molecules. Thermogravimetric analysis

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of **3** indicated that the framework maintains its integrity up to 300 °C, while the guest is liberated between 70 and 150 °C. Most surprisingly, the stability of the framework *after guest removal* was confirmed by single-crystal and powder X-ray diffraction studies. The single-crystal X-ray analysis of a sample of **3** from which the guest had been removed, which was prepared by heating the crystals at 150 °C under reduced pressure (100 mmHg) for 3 h, resulted in a sample with very similar cell constants and the same space group as **3**.[7] The crystal structure of the guest-free grid complex was essentially identical with that of **3** except for the loss of the guest. The powder X-ray diffraction spectra of the sample without the guest was also identical with that of **3** except for the absence of two peaks at 2θ values of 10.9° and 22.37° (Figure 3).

The ligand **2** formed a similar noninterpenetrated square-grid complex **4** when benzene was used in place of *o*-xylene.

$$[\{[\mathrm{Ni}(\mathbf{2})_2(\mathrm{NO_3})_2]\cdot 5(\mathrm{C_6H_6})\cdot 2(\mathrm{CH_3OH})\}_n] \qquad \mathbf{4}$$

Although the packing of the grids is identical in both complexes, the square grids in **4** are much less symmetrical than those in **3**.[8] Interestingly, the 2D layer in complex **4** was built up of two crystallographically independent squares **A** and **B**. The square cavities of **A** are occupied by five benzene molecules, while those of **B** are occupied by five benzene and two MeOH molecules (Figure 4a).[9] Both **A** and **B** are slightly distorted and have dimensions of about 19.85 × 19.87 Å and 19.94 × 19.87 Å, respectively. The big rectangular channels are occupied by a 1D column of guest molecules (Figure 4b). The 1D column is formed by the combination of benzene and MeOH molecules through the layers of the grid sheets. All the benzene molecules in the column interact with each other and also interact with the walls of the channels through edge-to-face aromatic interactions (3.5–4.5 Å). The length of the repeating unit of the 1D column is equivalent to that of the long axis of the unit cell (49.646 Å). The lower symmetry of the grid compared to **3** can be attributed to the lower symmetry in guest–guest interactions: benzene, being a symmetrical molecule, shows less selectivity in guest–guest interactions and forms a more unsymmetrical 1D column with inclusion of MeOH, whereas *o*-xylene, being an unsymmetrical molecule, shows more selectivity in guest–guest interactions and forms a very symmetrical 1D column (Figure 2b). The asymmetric unit of the crystal contains three MeOH molecules: two of them interact with each other (O···O 2.68 Å), while the other interacts with nitrate ion (O···O 2.77 Å).

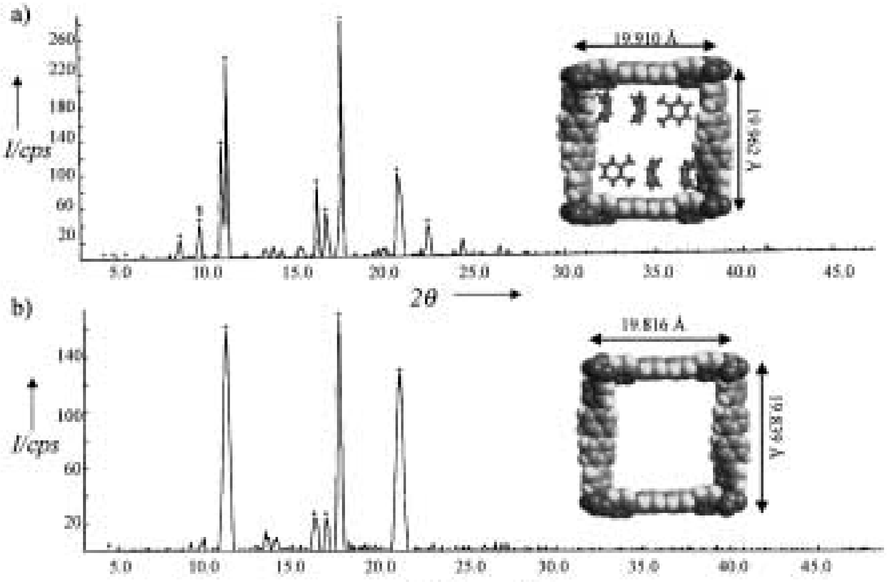

Figure 3. Powder X-ray diffraction spectra and single-crystal X-ray structures for **3** with guest (a) and without guest (b). The grids from the corresponding single-crystal X-ray diffraction analysis are also shown. The differences in grid dimensions are minimal after guest removal.

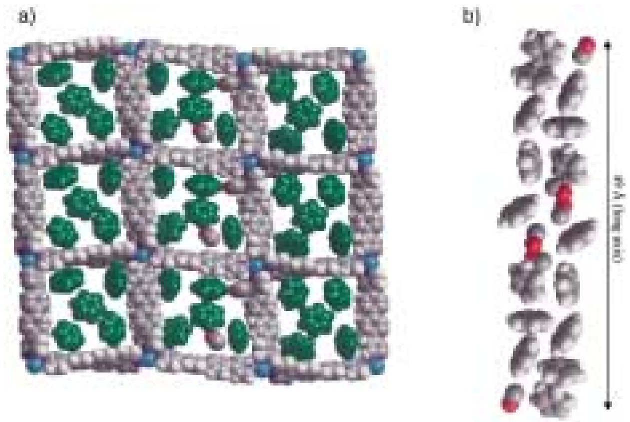

Figure 4. a) The square grid network in complex **4**. The square cavities in consecutive columns display different arrangements of guest molecules. There are two types of distorted squares: One includes five benzene molecules (square **A**), while the other includes five benzene molecules and two methanol molecules (square **B**). b) Representation of the one-dimensional column of benzene and MeOH molecules.

Experimental Section

2: 2-(4-Pyridyl)-4,4,5,5-tetramethyl-1,3-dioxaboralone: 4-Bromopyridine (38 mmol, 6 g) in dry $\mathrm{Et_2O}$ (300 mL) was slowly added to *n*BuLi (1.5 M in hexane, 46 mmol, 30 mL) at −78 °C. After 30 min $\mathrm{B(OBu)_3}$ (46 mmol, 10.6 g) was added and the temperature was raised slowly over two hours to room temperature. Pinacol was added to this solution, and then after 10 min AcOH was added. The resulting crude ester was crystallized from cyclohexane (yield: 5.0 g, 64 %). A mixture of the above ester (0.8 g, 3.9 mmol), 4,4′-dibromobiphenyl (0.4 g, 1.3 mmol), $\mathrm{K_3PO_4}$ (1.7 g, 7.8 mmol), and $[\mathrm{Pd(PPh_3)_4}]$ (0.15 g, 0.13 mmol) in dioxane (40 mL) was refluxed under an Ar atmosphere for three days. After removal of the dioxane, the resulting mass was worked-up with $\mathrm{CHCl_3}$–$\mathrm{H_2O}$ and crystallized from $\mathrm{CHCl_3}$–methanol (yield: 0.27 g, 67 %).

3: The single crystals of **3** were prepared by layering a solution of $\mathrm{Ni(NO_3)_2\cdot 6\,H_2O}$ (6 mg) in MeOH (5 mL) onto a solution of **2** (12.6 mg) in *o*-xylene (15 mL). After the solution had been allowed to stand for seven days, the crystals formed were isolated in 80 % yield by filtration. Monoclinic, *C*2/*c*, $a = 27.187(3)$, $b = 19.963(2)$, $c = 12.685(4)$ Å, $\beta = 106.923(2)°$, $V = 6585.9(12)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.235\ \mathrm{g\,cm^{-3}}$, 5932 unique reflections out of 7770 with $I > 2\sigma(I)$, $1.29 < \theta < 27.98°$, final *R* factors $R_1 = 0.067$, $wR_2 = 0.2054$. Elemental analysis: calcd: C

74.57, H 5.93, N 6.87; found: C 73.58, H 5.69, N 7.06. These results indicate the loss of 0.5 *o*-xylene per metal: calculated values for $[Ni(\mathbf{2})_2(NO_3)_2 \cdot 3.5(o\text{-xylene})]$: C 73.85, H 5.77, N 7.18.

Crystal data for **4**: The crystals were prepared in the same way as above but benzene was used instead of *o*-xylene. However few crystals were obtained with some powdery material (in 15% yield). Monoclinic, $P2_1/n$, $a = 13.570(2)$, $b = 19.874(3)$, $c = 49.646(7)$ Å, $\beta = 96.815(3)^\circ$, $V = 13294(3)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.237$ g cm^{-3}, 23360 unique reflections out of 68329 with $I > 2\sigma(I)$, $1.32 < \theta < 25^\circ$, final R factors $R_1 = 0.1561$; $wR_2 = 0.3795$. The data for both **3** and **4** were measured on a Siemens SMART/CCD diffractometer (Mo$_{K\alpha}$ radiation $\lambda = 0.71073$ Å) at 193 K. An empirical absorption correction was applied by using the SADABS program. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-141218 (**3**), and CCDC-141217 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[1] Only eight polymeric structures were published before 1990 for reactions of **1** with transition metals, while from 1990 to 1998 about 70 polymeric structures were published. Statistics were taken from Cambridge Structural Database: Version 5.17 (197481 Structures, April, 1999 release): F. H. Allen, O. Kennard, *Chemical Des. Autom. News* **1993**, *8*, 31.

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[6] a) Quite recently a three-dimensional coordination polymer was characterized following removal of guest molecule by single-crystal X-ray diffraction: H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276; b) for zeolite analogues see: D. W. Breck in *Zeolite Molecular Sieves*, Wiley, New York, **1974**.

[7] Crystal data for **3** after removal of guest molecule: monoclinic, $C2/c$, $a = 26.234(5)$, $b = 19.839(3)$, $c = 13.236(2)$ Å, $\beta = 109.514(4)^\circ$, $V = 6493(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 0.818$ g cm^{-3}, 2541 unique reflections out of 7718 with $I > 2\sigma(I)$, final R factors $R_1 = 0.1943$, $wR_2 = 0.4494$, largest difference peak and hole 2.126 and -0.764 e Å^{-3}. Elemental analysis suggests that the crystal absorbed water from atmosphere: calcd for $[Ni(\mathbf{2})_2(NO_3)_2] \cdot 1.5(H_2O)$: C 63.94, H 4.27, N 10.17; found: C 64.17, H 3.90, N 9.96.

[8] The data collection for **4** at room temperature resulted in different cell constants and space group as well as disordered ligands and nitrates. All the benzene molecules were located with relatively high thermal motions in comparison to those found for the low-temperature structure, but the MeOH molecules could not be located at this temperature. Monoclinic, Cm, $a = 12.731(7)$, $b = 19.912(9)$, $c = 13.902(7)$ Å, $\beta = 96.544(1)^\circ$, $V = 3501(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.129$ g cm^{-3}, 3846 unique reflections out of 5211 with $I > 2\sigma(I)$, final R factors $R_1 = 0.0887$; $wR_2 = 0.2166$.

[9] One of the MeOH molecules which is close to the corner of a square interacts with benzene through a C–H···O hydrogen bond (H···O, 2.522 Å; C···O 3.441 Å; C–H···O 169.8°). The square **B** (diagonal–diagonal distances: 26.067 and 30.099 Å) is more distorted than square **A** (diagonal–diagonal distances: 27.911 and 28.270 Å).

The Electrical Properties of Gold Nanoparticle Assemblies Linked by DNA[**]

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Electron transport through DNA has been one of the most intensely debated subjects in chemistry over the past five years.[1] Some scientists claim that DNA is able to transport electrons efficiently, while others believe it to be an insulator. In a seemingly disparate field of study, a great deal of effort has been devoted to examining the electrical properties of nanoparticle-based materials.[2–5] Indeed, many research groups have explored ways to assemble nanoparticles into two- and three-dimensional networks and have investigated the electronic properties of such structures. However, virtually nothing is known about the electrical properties of nanoparticle-based materials linked with DNA.

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