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A novel two-dimensional rectangular network. Synthesis and structure of $\{[Cu(4,4'\text{-bpy})(pyz)(H_2O)_2][PF_6]_2\}_n$ (4,4′-bpy = 4,4′-bipyridine, pyz = pyrazine)

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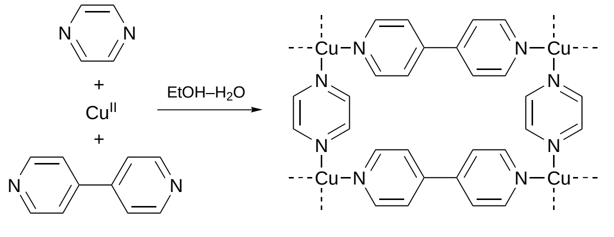
The complex $\{[Cu(4,4'\text{-bpy})(pyz)(H_2O)_2][PF_6]_2\}_n$ comprising two-dimensional rectangular grids with each cavity enclosed by two 4,4′-bipyridine (4,4′-bipy) and two pyrazine (pyz) ligands, which superpose in an off-set fashion to give smaller rectangular channels, has been prepared and characterized by single-crystal X-ray structural analysis.

Considerable research effort has been focused on the crystal engineering of supramolecular architectures organized by coordinate covalent or hydrogen bonding.[1,2] So far a number of one-, two- and three-dimensional infinite frameworks have already been generated with linear N,N′ bidentate spacers.[3–9] However, the above-mentioned frameworks are virtually all formed by only one type of bridging ligand; only three infinite frameworks containing two different types of ligand as edges have been reported,[9,10] and two of them are triply interpenetrating frameworks. We have initiated a synthetic strategy for the preparation of non-interpenetrating open-frameworks with variable cavities or channels, in which the rod-like rigid spacers such as 4,4′-bipyridine (4,4′-bpy), pyrazine (pyz) and related species are chosen as building blocks.[11] In the present work, we report the preparation and crystal structure of a novel two-dimensional rectangular grid constructed simultaneously by 4,4′-bpy and pyz ligands, namely $\{[Cu(4,4'\text{-bpy})(pyz)(H_2O)_2][PF_6]_2\}_n$ **1**.

Complex **1** was synthesized by self-assembly of Cu^{II} ions with 4,4′-bpy and pyz ligands, as shown in Scheme 1. An alcoholic solution (10 cm^3) of pyz (0.080 g, 1.0 mmol) was added dropwise to a stirring aqueous solution (5 cm^3) of $Cu(NO_3)_2{\cdot}6H_2O$ (0.296 g, 1.0 mmol) at 50 °C for 15 min. An alcoholic solution (10 cm^3) of 4,4′-bpy (0.156 g, 1.0 mmol) was then added and followed by $NaPF_6$ (0.336 g, 2.0 mmol). The resulting blue solution was allowed to stand in air at room temperature for 5 d, yielding deep blue block crystals (65% yield). The elemental analysis and IR spectrum confirmed the formula of **1**.† It is noteworthy that no product of square grids based on $Cu(4,4'\text{-bpy})_2$ or $Cu(pyz)_2$ has been observed, which could in principle be produced in the reaction.



(the aqua ligands are omitted)

Scheme 1

X-ray crystallography ‡ has established that complex **1** is made up of a two-dimensional rectangular network and PF_6^- anions. As illustrated in Fig. 1, each layer consists of perfectly ideal planar rectangles with a Cu^{II} ion, a 4,4′-bpy and a pyz at each corner and side, respectively, two pyridyl rings of each 4,4′-bpy ligand are twisted by 66.5(1)°. The inner rectangular cavity is hydrophobic and has dimensions of 6.83 × 11.15 Å, which are comparable to those of related compounds.[4b,10] The Cu^{II} ion has an elongated octahedral geometry with two pyridyl [Cu–N 2.045(3) Å] and two pyz groups [Cu–N 2.036(3) Å] at the equatorial positions and two water molecules [Cu–O 2.445(3) Å] at the axial positions (Fig. 1). The off-set superposition of each pair of adjacent layers by half of the longer edges divides the voids into smaller rectangular channels (*ca.* 5.6 × 6.8 Å) as

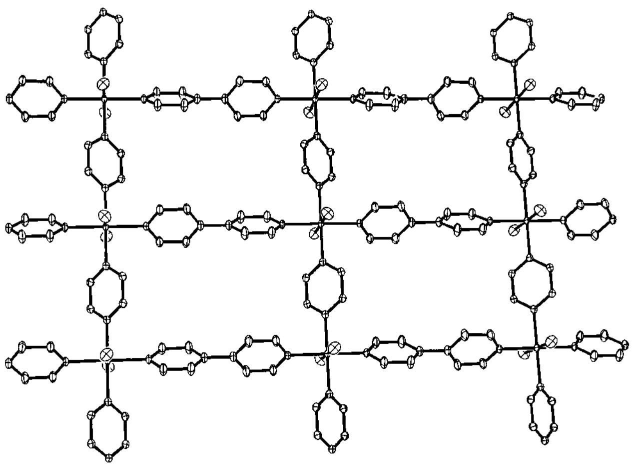


Fig. 1 An ORTEP[14] drawing (at 35% probability level) of the rectangular units in complex **1**

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† (Found: C, 27.10; H, 2.45; N, 9.15. Calc. for $C_{14}H_{16}CuF_{12}N_4O_2P_2$ **1**: C, 26.88; H, 2.58; N, 8.96%). IR data ($\tilde{\nu}/cm^{-1}$): 3620s, 3557m, 3423m (br), 3135w, 3071w, 1644s, 1609vs, 1539w, 1496w, 1426s, 1222s, 1173w, 1124m, 1075s, 1018w, 835vs (br), 646m, 561vs, 477m.

‡ Crystal data for complex **1**: $C_{14}H_{16}CuF_{12}N_4O_2P_2$, $M = 625.79$, orthorhombic, space group *Ibam* (no. 72), $a = 14.756(3)$, $b = 11.149(2)$, $c = 13.656(3)$ Å, $U = 2246.6(8)$ Å^3, $Z = 4$, $D_c = 1.850$ g cm^{-3}, $\mu = 1.234$ cm^{-1}. Data collection ($2.8° \leqslant \theta \leqslant 26.7°$) was performed at 293 K on a Siemens P4 diffractometer (Mo-Kα, $\lambda = 0.710\,73$ Å). The structure was solved with direct methods (SHELXTL-PC)[12] and refined with full-matrix least-squares technique (SHELXL 93)[13] to final $R1$ value of 0.0469 for 87 parameters and 1164 unique reflections with $I \geqslant 2\sigma(I)$ and $wR2$ of 0.1495 for all 1184 reflections. CCDC reference number 186/800.

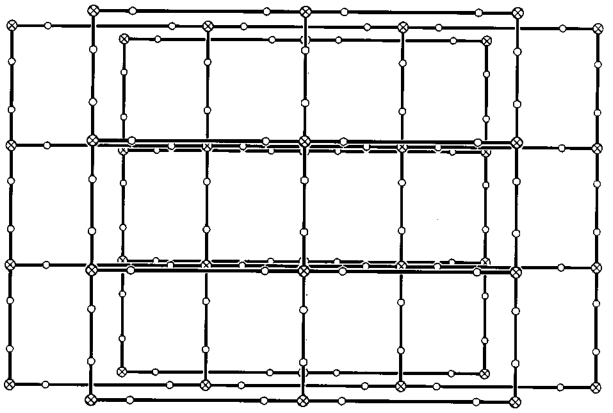

Fig. 2 Top view showing the rectangular channels in complex **1**. Carbon and hydrogen atoms are omitted for clarity, the 4,4′-bpy and pyz molecular rods are shown as single bold lines

shown in Fig. 2, which are similar to those found in A-zeolites and Pentasil zeolites.[15] The PF$_6^-$ anions are located in these channels, and each PF$_6^-$ anion forms two accepter hydrogen bonds with two adjacent aqua ligands [O · · · F 2.848(4) Å]. It is noteworthy that complex **1** is to our knowledge the first example of a two-dimensional framework that is sustained by the self-assembly of two different types of linear bidentate N,N′-donor ligands.

Although the porous structures with designable pore sizes are in principle achievable *via* crystal engineering, interpenetration or self-inclusion commonly occur in these frameworks with voids of large volume, thereby reducing the pore size.[4a,5,8a,9] The self-assembly of these frameworks is also highly influenced by factors such as the solvent system,[1a] template[8c,11,16] and steric requirement of the counter ion;[17] the failure to prepare molecular rectangles containing 4,4′-bpy and pyz edges is thus not surprising.[3] In this sense, the exploration of the synthetic strategies and routes is therefore a long-term challenge. Much work is required to extend the knowledge of the relevant structural types and establish proper synthetic strategies leading to the desired species. The isolation of complex **1** suggests the possibility of constructing similar rectangular frameworks with divalent metal salts and two types of ligand under the appropriate conditions.

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