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

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The complex $\{[Cu(4,4'-bpy)(pyz)(H_2O)_2][PF_6]_2\}_n$ 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 twodimensional rectangular grid constructed simultaneously by 4,4'-bpy and pyz ligands, namely {[Cu(4,4'-bpy)(pyz)(H₂O)₂]- $[PF_6]_2$, 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 cm³) of pyz (0.080 g, 1.0 mmol) was added dropwise to a stirring aqueous solution (5 cm³) of Cu(NO₃)₂·6H₂O (0.296 g, 1.0 mmol) at 50 °C for 15 min. An alcoholic solution (10 cm³) of 4,4'-bpy (0.156 g, 1.0 mmol) was then added and followed by NaPF₆ (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



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analysis and IR spectrum confirmed the formula of 1.[†] It is noteworthy that no product of square grids based on Cu(4,4'bpy)₂ or Cu(pyz)₂ has been observed, which could in principle be produced in the reaction.

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



^{† (}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{v} /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) Å³, Z = 4, $D_c = 1.850$ g cm⁻³, $\mu = 1.234$ cm⁻¹. Data collection ($2.8^{\circ} \le \theta \le 26.7^{\circ}$) was performed at 293 K on a Siemens P4 diffractometer (Mo-K α , $\lambda = 0.710$ 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 *R*1 value of 0.0469 for 87 parameters and 1164 unique reflections with $I \ge 2\sigma(I)$ 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 PF₆⁻ 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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