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Solvent-dependent 4^4 square grid and $6^4.8^2$ NbO frameworks formed by Cu(Pyac)$_2$ (bis[3-(4-pyridyl)pentane-2,4-dionato]copper(II))†

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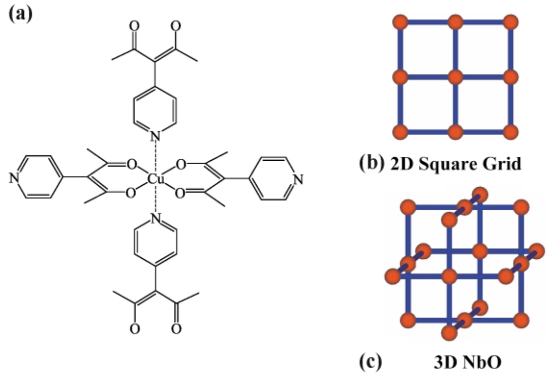
The title compound crystallizes from anhydrous solvents in a simple square-grid topology, but when water is present, crystals form with an unusual interpenetrated 3D NbO topology whose pores contain hydrogen-bonded solvent molecules.

There has been extensive interest in metal–organic frameworks because of their potential applications in materials science. As the bulk properties of these materials are closely related to their structures, it is important to understand the factors such as coordination geometries of metal ions and the resulting secondary inorganic building blocks, spatial arrangements of organic building blocks, interpenetration, anions and solvents, that control their topologies.[1] Among these factors, the effects of solvents have been demonstrated in many examples, but they are difficult to rationalize, mainly because their roles are quite complicated: they can act as ligands or guest molecules, and they can also participate in weak interactions such as hydrogen bonding, either among themselves or with the frameworks.[2]

We have been interested in metal-β-diketonate supramolecules for their "host"–"guest" chemistry.[3] In our effort to incorporate metal-β-diketonate moieties into metal–organic frameworks so as to make open sites available for Lewis base binding, we began with the pre-constructed secondary building block Cu(Pyac)$_2$ (PyacH = 3-(4-pyridyl)pentane-2,4-dione).[4] CuL$_2$ (HL = β-diketone) complexes are normally square-planar,[3,5] but they can accommodate one or two axial ligands. Thus, the Cu^{2+} in Cu(Pyac)$_2$ can be further coordinated by two pyridine nitrogens in nearby Cu(Pyac)$_2$ units, leading to formation of self-assembled Cu(Pyac)$_2$ frameworks. In these frameworks, the "Cu(Pyac)$_4$" moiety is a square planar node (*i.e.* the two chelating and two monodentate ligands form a square-planar arrangement about Cu; see Scheme 1a). Frameworks based solely upon square planar nodes can have several topologies: the two-dimensional 4^4 square grid (Scheme 1b), the three-dimensional $6^4.8^2$ NbO (Scheme 1c), the $6^5.8$ CdSO$_4$, the so-called 'dense' $7^5.9$ and the unusual $4^2.8^4$ topologies.[6,7,10] Among these, the 4^4 square grid is common,[1c] while the other four are very rare.[8–11] Because of the Jahn–Teller effect, we expected that the coordination of the pyridine nitrogens to the Cu^{2+} in Cu(Pyac)$_2$ frameworks would be weak, so that Cu(Pyac)$_2$ frameworks could be re-assembled in different solvents. We report herein two types of self-assembled Cu(Pyac)$_2$ frameworks, *i.e.* 2D 4^4 square grid and 3D $6^4.8^2$ NbO, crystallized from different solvents. Both structures contain the solvents as guest molecules. However, the presence of water favors the formation of the more open NbO framework, whereas solvents with weaker intermolecular interactions within themselves favor the square grid structure with its more isolated cavities.

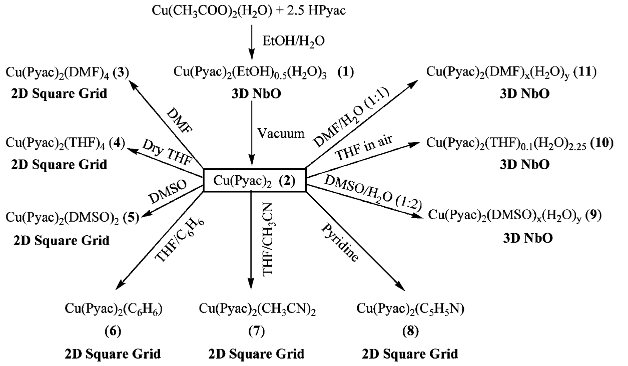


Scheme 1 (a) Square planar "Cu(Pyac)$_4$" node (formed by complexation of Cu(Pyac)$_2$ with two N donors from adjacent Cu(Pyac)$_2$ molecules), and schematic illustrations of its 2D square grid (b) and 3D NbO (c) frameworks.

As shown in Scheme 2, reaction of an aqueous solution of Cu(CH$_3$COO)$_2$(H$_2$O) with an ethanolic solution of HPyac[12] at room temperature readily produces green crystals of Cu(Pyac)$_2$(EtOH)$_{0.5}$(H$_2$O)$_3$ (**1**) in 69% yield. The solvent guest molecules are largely removed from **1** under vacuum, making the nearly dehydrated "building block" Cu(Pyac)$_2$ (**2**). Crystallization of **2** from DMF, dry THF, DMSO, THF–C$_6$H$_6$, THF–CH$_3$CN, and pyridine yields Cu(Pyac)$_2$(DMF)$_4$ (**3**, 89% yield), Cu(Pyac)$_2$(THF)$_4$ (**4**, 86%), Cu(Pyac)$_2$(DMSO)$_2$ (**5**, 92%), Cu(Pyac)$_2$(C$_6$H$_6$) (**6**, 95%), Cu(Pyac)$_2$(CH$_3$CN)$_2$ (**7**, 92%), and Cu(Pyac)$_2$(C$_5$H$_5$N) (**8**, 23%) respectively; crystallization from DMSO–H$_2$O (1 : 2), THF in air and DMF–H$_2$O (1 : 1), on the other hand, produces Cu(Pyac)$_2$(DMSO)$_x$(H$_2$O)$_y$ (**9**, ~90% yield), Cu(Pyac)$_2$(THF)$_{0.1}$(H$_2$O)$_{2.25}$ (**10**, 95%) and Cu(Pyac)$_2$(DMF)$_x$(H$_2$O)$_y$ (**11**, ~90%).†‡ Among these species, only compound **10** was reported in the previous study of Cu(Pyac)$_2$, but its topology was not discussed.[4]

Crystals of the Cu(Pyac)$_2$ solvates turn opaque in air over a period of minutes to hours, due to partial solvent loss. Complete loss of solvent occurs at higher temperatures, as shown by thermogravimetric analysis; for **1**, **3**, **4**, **6** and **10**, this occurs at 124, 133, 88, 131 and 143 °C respectively. The desolvated Cu(Pyac)$_2$ then decomposes at ~220 °C.

Compounds **3–8** are two-dimensional 4^4 square grid frameworks, while **1** and **10** are three-dimensional doubly interpenetrated $6^4.8^2$ NbO frameworks. The representative square grid of ~10 × 10 Å in these two-dimensional 4^4 square grid frameworks is shown in Fig. 1 for compound **6**. Two DMSO, one C$_6$H$_6$, two CH$_3$CN and one C$_5$H$_5$N guest solvent molecules



Scheme 2 Syntheses of self-assembled Cu(Pyac)$_2$ frameworks.

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† Electronic supplementary information (ESI) available: microanalyses of **1**, **2**, **6** and **10**. See http://www.rsc.org/suppdata/cc/b3/b305457h/

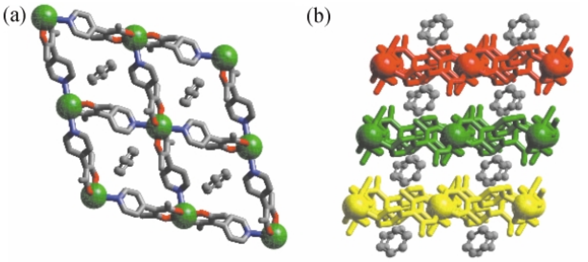

Fig. 1 2D square grid framework of $Cu(Pyac)_2(C_6H_6)$ (**6**). (a) View of one square-grid layer, showing benzene guest molecules; Cu atoms green. (b) Side view of three layers (color), showing orientation of benzene guests (gray) between the layers.

per square-grid unit are enclathrated between the square-grid $Cu(Pyac)_2$ layers in **5**, **6**, **7** and **8** respectively, with interlayer Cu···Cu separations of 7.65, 7.56, 7.42, and 7.43 Å. Compounds **3** and **4** have very similar square-grid structures, but with larger numbers of solvent molecules and correspondingly larger Cu···Cu separations, 8.92 and 9.30 Å respectively. In compounds **1** and **10**, two identical slightly distorted NbO frameworks (Fig. 2a) are interpenetrated with each other (Fig. 2b). Despite this interpenetration, these compounds retain one-dimensional pores of about 7 Å diameter (Fig. 2c) which are filled with solvent molecules (EtOH and H_2O, and THF and H_2O respectively).

The NbO structure is not self-dual. Thus, a second identical framework cannot be placed exactly at the center of the unit cell shown in Scheme 1(c), and a perfectly interpenetrated NbO structure is not possible.[13] It has been proposed that this feature of the NbO structure makes it a desirable topology for porous metal–organic frameworks.[8b] However, we find that structures **1** and **10** do contain interpenetrated NbO networks. This is accomplished by displacing the second net by ($\frac{1}{4}$, $\frac{1}{4}$, $\frac{1}{4}$) relative to the first.

In the 2D square grid frameworks of compounds **3–8**, the solvent guest molecules have no specific interactions with one another; while in the 3D NbO frameworks, the solvent guest molecules of EtOH and H_2O in compound **1**, and THF and H_2O in compound **10**, form hydrogen-bonded aggregates. These solvent guest molecules are disordered in **1** and **10**, which makes detailed rationalization of their structures difficult. However, we believe that it is these hydrogen-bonded aggregates which support the interconnected one-dimensional pores in the 3D NbO $Cu(Pyac)_2$ frameworks. This hypothesis is supported by the fact that crystallization from DMF, dry THF or DMSO yields square-grid products (**3**, **4** and **5** respectively; see Scheme 2), whereas crystallization from DMSO–H_2O (1 : 2), THF in moist laboratory air, and DMF–H_2O (1 : 1) yields hydrated NbO-type products (**9**, **10** and **11** respectively).

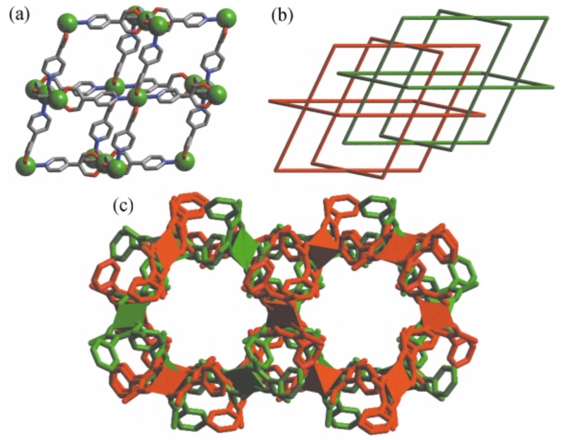

Fig. 2 NbO framework (a), double interpenetration (b) and 1D channel (c) in the 3D doubly interpenetrated NbO framework of $Cu(Pyac)_2(EtOH)_{0.5}(H_2O)_3$ (**1**). (For clarity, in (a) the methyl groups of the Pyac ligands were omitted.)

The present results suggest that the hydrogen-bonded aggregates among guest solvent molecules themselves play an important role in stabilizing the pores of metal–organic frameworks. We are now studying the use of $Cu(Pyac)_2$ and related building blocks in the construction of heterobimetallic supramolecular materials.[14]

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Notes and references

‡ *Crystal data* for **1**: Trigonal, $R\bar{3}c$, a = 22.604(2), c = 22.964(3) Å, V = 10161.3(2) Å^3, Z = 18, D_c = 1.465 g cm^{-3}, μ = 1.013 mm^{-1}, R_1 ($I > 2\sigma(I)$) = 0.043, wR_2 (all data) = 0.143. For **3**: Monoclinic, $P2_1/c$, a = 8.923(1), b = 14.891(2), c = 13.602(2) Å, β = 100.563(7)°, V = 1776.6(4) Å^3, Z = 2, D_c = 1.324 g cm^{-3}, μ = 0.670 mm^{-1}, R_1 ($I > 2\sigma(I)$) = 0.034, wR_2 (all data) = 0.090. For **4**: Monoclinic, $P2_1/c$, a = 9.301(4), b = 14.216(6), c = 14.281(8) Å, β = 93.881(15)°, V = 1883.7(15) Å^3, Z = 2, D_c = 1.242 g cm^{-3}, μ = 0.629 mm^{-1}, R_1 ($I > 2\sigma(I)$) = 0.063, wR_2 (all data) = 0.199. For **5**: Monoclinic, $P2_1/n$, a = 7.654(1), b = 10.553(2), c = 16.470(3) Å, β = 102.058(10)°, V = 1301.0(4) Å^3, Z = 2, D_c = 1.461 g cm^{-3}, μ = 1.041 mm^{-1}, R_1 ($I > 2\sigma(I)$) = 0.036, wR_2 (all data) = 0.087. For **6**: Monoclinic, $P2_1/n$, a = 7.563(1), b = 9.582(2), c = 16.085(3) Å, β = 96.213(11)°, V = 1158.8(4) Å^3, Z = 2, D_c = 1.416 g cm^{-3}, μ = 0.978 mm^{-1}, R_1 ($I > 2\sigma(I)$) = 0.036, wR_2 (all data) = 0.097. For **7**: Monoclinic, $P2_1/n$, a = 7.424(1), b = 14.483(3), c = 11.163(2) Å, β = 95.711(10)°, V = 1194.3(4) Å^3, Z = 2, D_c = 1.385 g cm^{-3}, μ = 0.951 mm^{-1}, R_1 ($I > 2\sigma(I)$) = 0.035, wR_2 (all data) = 0.095. For **8**: Monoclinic, $P2_1/n$, a = 7.432(2), b = 9.583(3), c = 16.114(5) Å, β = 95.766(17)°, V = 1141.8(6) Å^3, Z = 2, D_c = 1.440 g cm^{-3}, μ = 0.993 mm^{-1}, R_1 ($I > 2\sigma(I)$) = 0.043, wR_2 (all data) = 0.100. For **10**, we obtained crystals that were the same as those described in ref. 4. For **9** and **11**, the crystals we obtained did not provide high-quality structures; nevertheless, the topology was clearly NbO in both cases, and the structures are very similar to those of **1** and **10**. CCDC 211018–211024. See http://www.rsc.org/suppdata/cc/b3/b305457h/ for crystallographic data in .cif format.

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