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An unprecedented interpenetrating structure with two covalently bonded open-frameworks of different dimensionality

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A chemical rearrangement under hydrothermal conditions resulted in an unprecedented interpenetrating structure with two covalently bonded open frameworks of different dimensionality: $\{[Cu_2(IN)_4 \cdot 3H_2O] \cdot [Cu_2(IN)_4 \cdot 2H_2O]\} \cdot 3H_2O$ (IN = isonicotinate).

Interpenetrating network structures have been one of the fascinating subjects in crystal engineering of coordination polymers owing to their attractive new topologies and intriguing structural features.[1–8] Many of these structures have been reviewed recently.[9] Although interpenetrating networks consisting of chemically and topologically different components are rare, Robson and coworkers[10] reported interpenetrating nets of different topology where a single, rhombohedral α-polonium-related net interpenetrates with two types of hydrogen-bonded sheets, one consisting entirely of water and the other of F^- ions and water molecules, while Zaworotko and coworkers[11] synthesized the first example of interpenetrating covalent and non-covalent 2D networks. While some of the interpenetrating structures may be predictable, structural control of metal–organic reactions remains a great challenge, and often, unexpected structures may result. Here we report an unprecedented interpenetrating structure with two covalently bonded open frameworks of different dimensionality formed from a chemical rearrangement under hydrothermal conditions: $\{[Cu_2(IN)_4 \cdot 3H_2O] \cdot [Cu_2(IN)_4 \cdot 2H_2O]\} \cdot 3H_2O$ (IN: isonicotinate) **1**.

The reaction of $Cu(NO_3)_2 \cdot 2.5H_2O$ with nicotinic acid and *trans*-1,2-bis(4-pyridyl)ethylene in a mole ratio of 1 : 1 : 1 under hydrothermal conditions at 140 °C for three days produced dark blue crystals of **1** in 59% yield suitable for single crystal X-ray diffraction analysis.† The structure consists of a covalently bonded three-dimensional (3D) open-channel network and a covalently bonded two-dimensional (2D) open-framework which are mutually interpenetrating. The 3D network contains three crystallographically distinct copper atoms (Fig. 1). Atom Cu(1) is square pyramidal coordinated by two pyridyl groups from two IN units and two carboxylate groups from the other two IN units in a monodentate fashion. A water molecule occupies the remaining site. Atoms Cu(2) and Cu(3) are in octahedral sites surrounded by two water molecules occupying the axial positions, with two pyridyls and two carboxylates from four IN units occupying the equatorial positions. Both Cu(2) and Cu(3) clearly show John–Teller distortion. The square pyramidal and octahedral Cu centers are linked by four two-connected tridentate IN units into a single-net 3D open-channel-network. The large rectangle in the open-channel-network consists of six Cu and six IN units (Fig. 1). The four Cu atoms at each corner of the rectangle display separations of 17.776 × 8.928 Å. The large rectangular channels in the 3D network extend into two directions, perpendicular to each other (Fig. 1). The topology of this 3D network is similar to a single net of tetragonal $CdSO_4$ type suggested by O'Keeffe *et al.*[12] The 2D open-framework consists of two independent copper atoms. Atoms Cu(4) and Cu(5) are in square pyramidal positions (Fig. 2). Each copper atom is coordinated by two carboxylate groups from two IN units in a monodentate fashion, and two pyridyl groups from the other two IN units. A water molecule occupies the remaining apical site. The square pyramidal copper atoms are linked by four two-connected tridentate IN units into a two-dimensional square grid network (Fig. 2). The Cu–Cu lengths in the square grid are 8.871 × 8.862 Å. The 3D and 2D open-frameworks interpenetrate to form an unprecedented mixed-

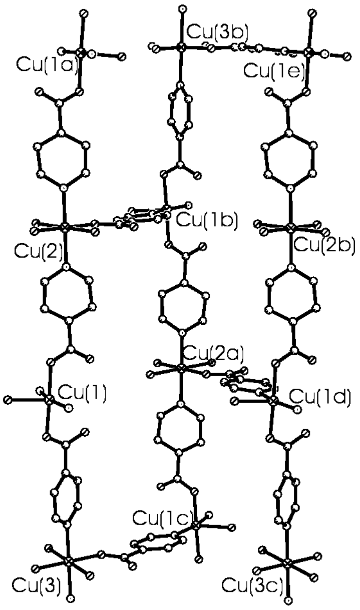

Fig. 1 View of the rectangular open framework in the 3D structure with copper atoms labeled and complete coordination shown.

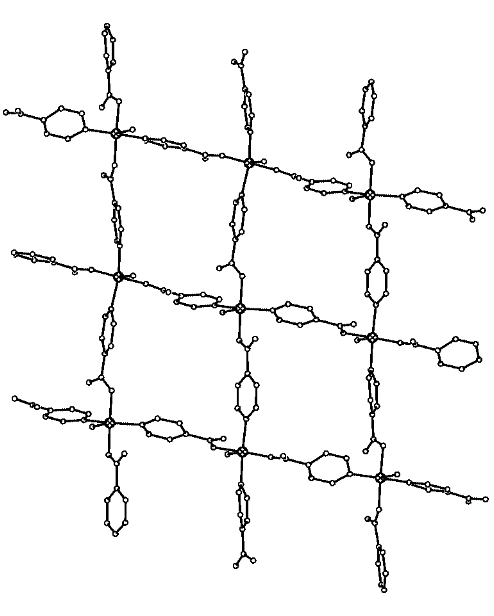

Fig. 2 View of a representative section of the 2D lattice. Note that all Cu atoms have square pyramidal coordination.

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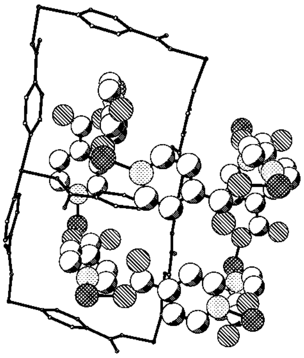

Fig. 3 Interlocked units in the interpenetrating structure. Only two of the four 2D square grids are shown for clarity.

2D–3D structure. The interpenetration is in such a way that each 3D closed-circuit displaying a 'table-frame' shape interlocks with four square grids of a 2D sheet (Fig. 3), so that each rectangular open-channel in the 3D network interpenetrates with two 2D sheets. Although several coordination polymers of isonicotinate and its derivatives have been reported, the structural feature in complex **1** has not been observed.[13] In spite of the interpenetrating networks in **1**, a dozen water molecules are included in a unit cell. Numerous hydrogen-bonding interactions found in the interpenetrating structure link the coordinating water molecules and the carboxylate groups of IN units between the 3D and 2D networks [O(9)···O(13) 2.864 Å, O(9)···O(15), 2.924 Å, O(11)···O(15) 2.865 Å, O(21)···O(4) 2.794 and 2.855 Å]. Thermal analysis indicated that the interpenetrating framework lost water molecules below 150 °C, and started to decompose at *ca.* 275 °C.

The reaction to prepare **1** was conducted *via* a self-assembly process under fairly mild hydrothermal conditions. The interpenetrating structure is stabilized owing to an unexpected chemical rearrangement of the ligand. While the reaction is fully reproducible, many attempts made to produce compound **1** from using isonicotinate instead of nicotinate as starting materials all failed.[14] The chemical rearrangement from nicotinate to isonicotinate under hydrothermal conditions is not well understood, while in other cases, rearrangements under hydrothermal conditions have been observed such as with 2,2-dipyridylamine.[15] The *trans*-1,2-bis(4-pyridyl)ethylene present in the reaction mixture is a necessary component for the preparation of compound **1**. Although the present research results might indicate that structural control of metal–organic reactions and prediction of interpenetrating networks under hydrothermal conditions could be a long-term challenging task in some cases, we are actively seeking clear directions from related investigations as well as searching for other unexpected structures under hydrothermal conditions.

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Notes and references

† *Crystal data* for **1**: M = 1375.10, monoclinic, space group, $P2_1/c$; cell dimensions: a = 22.554(1), b = 11.462(1), c = 21.861 (1) Å, β = 105.645(1)°, U = 5441.6(4) Å^3, Z = 4, D_c = 1.678 g cm^{-3}, μ = 1.635 mm^{-1}, T = 223(2) K. Reflections collected: 25199; independent reflections: 8507 ($R_{(int)}$ = 0.0447). Final R indices [$I > 4\sigma(I)$]: R_1 = 0.0675, wR_2 = 0.1529. Several water molecules were disordered and hydrogen atoms on water molecules could not be located. Additionally, a few of the pyridyl rings were found to be disordered over two different orientations, and these were refined using distance constraints. CCDC 157033.

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14 Reactions using isonicotinate instead of nicotinate produced a mixed-ligand complex: unit cell dimensions: a = 11.839(1), b = 13.377(1), c = 28.522 (2) Å, β = 98.209(1)°. Reactions using only *trans*-1,2-bis(4-pyridyl)ethylene produced very different, poor quality red crystals the structure of which was not obtained.

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