β-sheet recognition in the non-interpenetrated and interpenetrated two-dimensional coordination networks containing cavities†

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Two types of secondary building units of CuI (Cu₂I₂ and Cu₄I₄) were shown to generate 2D-coordination networks of (4,4)-topology (non-interpenetrated and interpenetrated) with *exo*-bidentate ligands that contain diamide as spacer.

The rational design and syntheses of coordination polymers have given an impetus to property oriented crystal engineering and supramolecular chemistry.[1] In the last decade several coordination polymers with predefined functional properties, particularly porosity, have been explored.[2] In most of the studies the ligands used are the *exo*-bidentate pyridyl ligands which have either phenyl (rigid) or alkyl (flexible) groups as spacers.[3] The interactions between these spacers are edge-to-face or face-to-face aromatic or hydrophobic interactions which are not strong enough to hold the layers together. To date there are only a few examples in which the layered coordination polymers are held together by strong hydrogen bonds.[4] Accordingly we selected ligand **1** in order to design coordination networks in which the spacer, diamide, is capable of forming a β-sheet hydrogen bond pattern (**I**).[5] Further, the ligand is flexible and capable of exhibiting conformational isomerism due to the free rotation around sp³ H₂C–CH₂ bonds.
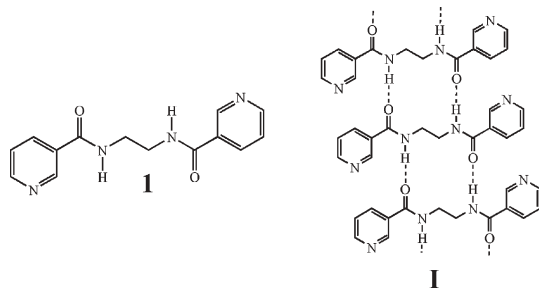
Besides the selection of the ligand, the proper choice of metal atom, counter anion and solvent molecules are also important aspects to get the required coordination network that contains a β-sheet pattern. In this work we have selected CuI as a suitable metal salt considering the following facts: CuI is capable of forming four connected nodes and the counter anion, I⁻, does not interfere in the formation of a hydrogen bond pattern and also strongly binds to the Cu-atom to form a variety of aggregates or secondary building units (SBU) which further leads to the formation of higher dimensional networks. Accordingly in the present work, the reaction of CuI with the ligand **1** resulted in two types of 2D-networks of (4,4) topology which are different in many aspects. For example, one is composed of SBU-I[6] and forms a non-interpenetrated 2D-network with elliptical cavities that are occupied by guest molecules. While the other is composed of SBU-II[7] and forms a 2D-network that is doubly interpenetrated in a parallel fashion. Interestingly, both the networks exhibited a β-sheet hydrogen bond pattern.

The diffusion of a CH₃CN solution of CuI into a CHCl₃–EtOH solution of ligand **1** resulted in the single crystals of the two types of complexes $[(Cu_2I_2)(1)_2 \cdot (CHCl_3)_3]_n$ (**2**) and $[(Cu_4I_4)(1)_2]_n$ (**3**).[8] The single crystal analysis of the complex **2** revealed the formation of a non-interpenetrated 2D-network containing cavities of elliptical shape. Whereas the structure of **3** indicates the formation of doubly interpenetrated network.

In the crystal structure of **2**, the CuI forms a SBU-I in which each Cu is connected to two I-atoms and two pyridyl moieties in a tetrahedral fashion [Cu–I: 2.610(1); 2.654(1) Å; Cu–N 2.079(7)] Å.‡ Further, the two Cu-atoms of SBU-I are connected to each other with a distance of 2.721(3) Å. The ligand **1** joins SBU-I units with a distance of 15.9 Å such that there is a formation of a 2D-network of (4,4)-topology containing elliptical cavities (Fig. 1a). The cavities have the shortest axis of 15.6 Å and longest axis of 30 Å. These 2D-layers pack on each other with a small interlayer separation in an offset fashion *via* β-sheet hydrogen bonds [N···O: 2.882(9) Å and N–H···O: 158°] and form continuous channels which are occupied by guest molecules (Fig. 1b and 1c). The channels are elliptical and the size of the channels is roughly half (7.8 × 15 Å) of the size of the cavities of the 2D-network (15.6 × 30 Å). However, the guest molecules are heavily disordered and the proportion of the guest, three CHCl₃ molecules per SBU-I, was estimated using elemental and TGA analyses.[9] The calculated guest occupied volume in the crystal lattice is 37%.[10,11] Further, the N–C–C–N torsion angle of **1** in **2** is 180°, indicating the linearity and *anti* conformation of the ligand (Fig. 1d).

The crystal structure of **3** reveals the formation of SBU-II which can act as an approximate tetrahedral node (Fig. 2a).§ The four Cu-atoms of SBU-II form a tetrahedron *via* Cu···Cu interactions [2.595(1), 2.722(1) 2.709(2) and 2.729(2) Å] and I-atoms do not cap the faces but four edges of the tetrahedron through Cu–I bonds [2.580(1), 2.609(1), 2.554(1) and 2.581(1) Å] such that two opposite edges of the tetrahedron are left free. Further, the I-atoms make short non-bonded contacts with the third Cu-atom [3.196(1); 2.990(1) Å].[12] The ligands **1** join the SBU-II units with a distance of 13.116 Å such that it forms a 2D-network containing square cavities with diagonal-to-diagonal distances of 18 and 22 Å.
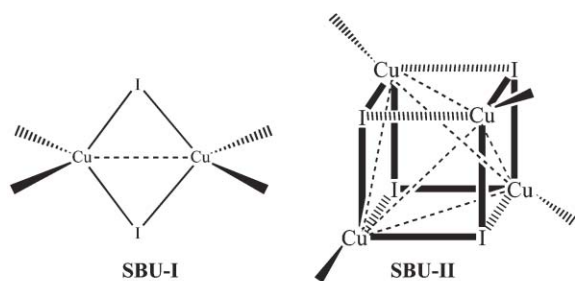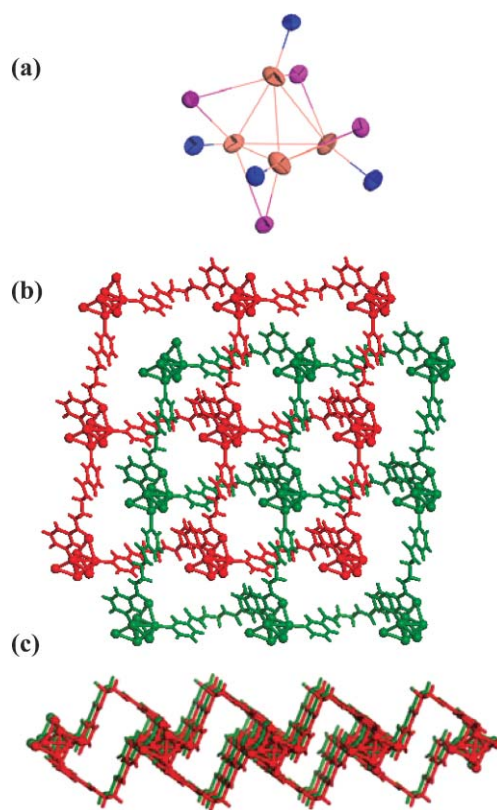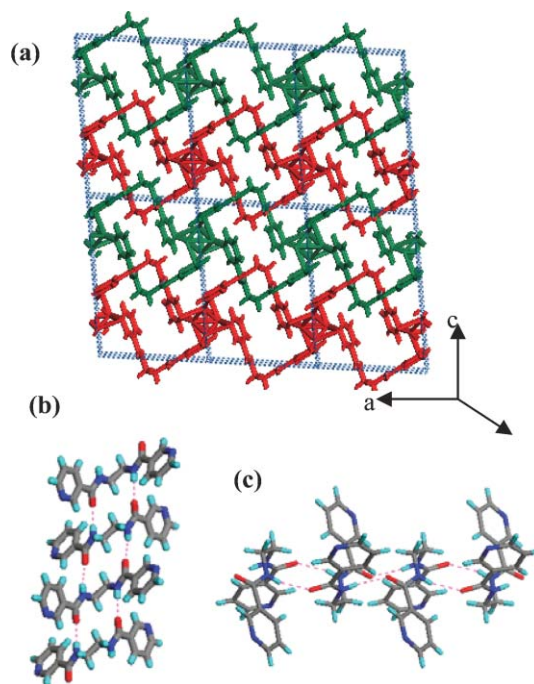
Fig. 1 Illustrations of the crystal structure of **2**: a) part of the 2D-network (C = grey, N = blue, O = red, Cu = brown and I = magenta); packing of the 2D-networks b) view along *a*-axis and c) view along *b*-axis. Alternate layers are coloured in red and green. Please note the hydrogen bonds between the layers; d) *β*-sheet network.

Fig. 2 Illustrations of the crystal structure of **3**: a) ORTEP drawing of SBU-II; two-fold interpenetration of 2D-networks in a parallel fashion; b) view along *c*-axis; c) view along *a*-axis. The interpenetrated networks are shown in two different colours.

Two of these networks interpenetrate in a parallel fashion *via* aromatic interactions between pyridyl moieties (Fig. 2b and 2c).[13] However the networks are highly corrugated as they are constituted by tetrahedral nodes and a non linear conformation of the ligand. Unlike in the structure of **2**, here the ligand adopts the gauche conformation with an N–C–C–N torsion angle of 60° to provide the arc type geometry. The doubly interpenetrated networks interdigitate into the adjacent layers *via* a *β*-sheet hydrogen bond pattern [N···O, N–H···O: 2.929(6) Å, 165° and 2.952(6) Å, 163°] (Fig. 3).

It is noteworthy that the *β*-sheet network was not observed in the crystal structures of phenyl or 2-pyridyl analogues of the ligand **1**.[14] To demonstrate the importance of selection of the right metal salt, we carried out a similar reaction between $Cu(NO_3)_2$ and **1** that resulted in the complex $[Cu(\mathbf{1})(H_2O)_4 \cdot (NO_3)_2]_n$, **4**. The crystal structure of **4**, reveals the formation of a 1D-coordination

Fig. 3 a) Packing of interpenetrated layers in the crystal structure of **3**, note the interdigitation of interpenetrated layers. Alternate layers are colored in red and green; *β*-sheet network observed in **3**: b) view along *a*-axis and c) view along *c*-axis.
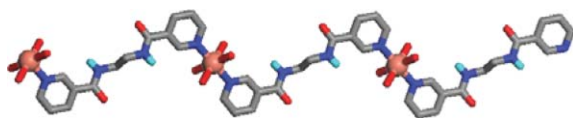
Fig. 4 One-dimensional network exhibited in the crystal structure of **4**. Only H-atoms corresponding to amide groups are shown.

network[15] in which the Cu-atom has octahedral geometry as it is connected to two ligands, in *trans* fashion, and four H_2O molecules (Fig. 4).¶ However, the 1D-chains in **4** are not combined together through a β-sheet pattern as the H_2O molecules and NO_3 anions interfere in the self recognition of the ligands.

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Notes and references

‡ The single crystal data was collected on a Bruker-Nonius Mach3 CAD4 X-ray diffractometer that uses graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) by the ω-scan method. The structures were solved by direct methods and refined by least square methods on F^2 using SHELX-97.[16] Non-hydrogen atoms were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model. Crystal data for **2**: Monoclinic, $C2/m$, $a = 9.649(2)$ Å, $b = 15.559(3)$ Å, $c = 15.163(3)$ Å, $\beta = 91.96(3)°$, $V = 2275.1(8)$ Å^3, $Z = 2$, $D_c = 1.868$ g cm^{-3}, 1404 reflections out of 2064 unique reflections with $I > 2\sigma(I)$, $1.34 < \theta < 24.97°$, final R-factors $R_1 = 0.0649$, $wR_2 = 0.1885$. The CHCl$_3$ molecules are heavily disordered. Eight peaks corresponding to CHCl$_3$ were found and refined as C-atoms. However, the plot of these peaks did not suggest any chemically recognized species. Therefore the structure was further refined using the platon-squeeze option. The final R-factors $R_1 = 0.0485$, $wR_2 = 0.1467$. Elemental analysis: found: C, 28.62; H, 2.21; N, 8.96%; calcd: C, 29.07; H, 2.42, N, 8.75%. CCDC 253151. See http://www.rsc.org/suppdata/cc/b5/b500666j/ for crystallographic data in .cif or other electronic format.
§ Crystal data for **3**: Monoclinic, $P2/c$, $a = 11.312(2)$ Å, $b = 10.012(2)$ Å, $c = 16.597(3)$ Å, $\beta = 97.25(3)°$, $V = 1864.7(6)$ Å^3, $Z = 4$, $D_c = 2.320$ g cm^{-3}, 2520 reflections out of 3078 unique reflections with $I > 2\sigma(I)$, $2.03 < \theta < 24.97°$, final R-factors $R_1 = 0.0405$, $wR_2 = 0.1101$. Elemental analysis: found: C, 25.97; H, 1.82; N, 8.61%; calcd: C, 25.80; H, 2.15; N, 8.60%. CCDC 253152.
¶ Crystal data for **4**: Monoclinic, $P2_1/n$, $a = 10.214(2)$ Å, $b = 7.125(1)$ Å, $c = 14.425(3)$ Å, $\beta = 99.98(3)°$, $V = 1033.9(4)$ Å^3, $Z = 2$, $D_c = 1.702$ g cm^{-3}, 1543 reflections out of 1815 unique reflections with $I > 2\sigma(I)$, $2.27 < \theta < 24.97°$, final R-factors $R_1 = 0.0444$, $wR_2 = 0.1333$. CCDC 253153.

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