Reliable Formation of an Unusual and Chiral Two-Dimensional Network Containing Entanglement of the Ligand in the Presence of Different Anions

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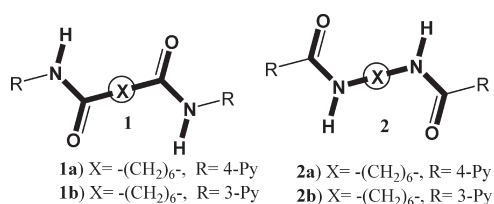
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ABSTRACT: The coordination polymers of the ligand N,N'-bis(4-pyridyl)suberamide (**1a**) with Cu(II) were explored in the presence of anions such as bivalent SO_4^{2-} and SiF_6^{2-} and univalent NO_3^{-1}. It was found that the ligand with Cu(II) ion consistently forms an unusual two-dimensional layer containing (4,4)-topology irrespective of the anions present. In the layer, the alkyl chains are entangled via weak hydrophobic interactions such that the chirality is generated in the layer. The entangled spacers occupy grid cavities with dimensions of 12 × 12 Å. These layers are further linked via hydrogen bonds between amide N—H groups and anions (SO_4^{2-} or SiF_6^{2-}).

The design and synthesis of coordination polymers (CPs) have attracted chemists due to their useful functional properties and intriguing network topologies.[1] Although several thousands of CPs have been explored to date, the predictable and consistent formation of networks is still in its infancy. In most of the cases the network topologies are influenced by several other factors such as metal—ligand ratios, counteranions, metal coordination geometries, pH values, guest molecules, and the solvent of crystallization.[2] The anions in particular play a very important role in tuning the network geometries; the coordinating nature, shape, size, and hydrogen bonding ability of an anion greatly influence the resultant network geometries.[3] Therefore, it is very rare to obtain an identical network topology for a particular metal and ligand in the presence of a diverse set of anions. Here we would like to present such an example in which the ligand **1a** with Cu(II) in the presence of different anions (SO_4^{2-}, SiF_6^{2-} and NO_3^{-1}) consistently forms an unusual two-dimensional chiral layer. The CPs of **2** are well studied by us while those of **1** are much less explored.[4a,4b] In the CPs of **2** the networks were found to recognize each other via β-sheet hydrogen bonds to enhance the dimensionality of the networks (1D → 2D and 2D → 3D).[4c−f] The results of the 3-pyridyl analogue of **1** (**1b**) with Cu(SCN)$_2$ were reported recently by us; these complexes were found to exhibit predictable 2D layers with inter- and intralayer β-sheet hydrogen bonds.[5] The longer alkyl spacer such as -(CH$_2$)$_6$- prefers to interact with itself via hydrophobic interactions and therefore facilitates the formation of similar networks with either **1b** or **2b** in the presence of various guest molecules. In anticipation of similar phenomena, we have started the exploration of CPs of **1a** and **2a** with Cu(II) salts in the presence of various anions.

1a) X= -(CH$_2$)$_6$-, R= 4-Py   **2a)** X= -(CH$_2$)$_6$-, R= 4-Py
1b) X= -(CH$_2$)$_6$-, R= 3-Py   **2b)** X= -(CH$_2$)$_6$-, R= 3-Py

The layering of EtOH solution of **1a** over the aqueous solution of CuSO$_4$ resulted in the crystals of complex {[Cu(**1a**)$_2$(H$_2$O)$_2$].SO$_4$·3H$_2$O·2EtOH}$_n$, **3**. The single crystal X-ray analysis reveals that the crystal system is orthorhombic and the space group is

$P2_12_12_1$.[6] The asymmetric unit is constituted by two ligands, one Cu(II), two coordinated water, three free water, two EtOH molecules, and sulfate ion. The Cu(II) atom has an octahedral coordination geometry with four pyridyl groups at equatorial positions (Cu—N: 2.018, 2.011, 2.018, 2.027 Å) and two H$_2$O molecules at axial positions (Cu—O: 2.504, 2.650 Å) (Figure 1).

The ligands (**1a**) exhibit U-shape geometry as the alkyl chains having amide substitution at both ends adopt gauche−anti−anti−anti−gauche conformations (Figure 1a). It is interesting to note here that the 3-pyridyl analogue (**1b**) exhibited linearity in the crystal structures of its coordination polymers.[5] The U-shape ligands link the metal atoms to give rise to a [4,4]-network in which the cavities are occupied by entangled spacers of **1a** (Figure 1c,d). The grid dimensions are 12.09 × 10.95 Å and the joining of the metal atoms gives a distorted square resembling cyclobutane geometry (Figure 1b) with an interplanar angle of 73.44°. It is worth noting here that the metal-to-metal separation distance would have been as high as ~22.5 Å provided the ligand **1a** is linear with all anti conformations. The entanglement of the ligands is such that the chirality of the layer is maintained. The layer is highly corrugated (Figure 1e) as the Cu(II) atoms of the layer placed in two planes with the plane-to-plane separation 5.3 Å (layer width). The hydrophobic part and CO groups of the layer remain within while the hydrophilic portion (amide N—H groups and coordinated H$_2$O) protrudes out. The layers are linked via a plethora of hydrogen bonding between H$_2$O molecules, anions, and solvated EtOH (Table 1). In particular, the linking of the layers via sulfate ions is interesting as the four O-atoms of sulfate engage in N—H⋯O hydrogen bonds with four amide N—H groups, two each from one layer (Figure 1f). In addition to N—H⋯O, the sulfate ion also engages in C—H⋯O with pyridine C—H and O—H⋯O with EtOH and water molecule. The interlayer separation is 6.454 Å, which was taken as the distance between two nearest neighboring Cu(II) planes of the adjacent layers.

We have further explored the complexation of ligand **1a** with Cu(II) in the presence of the anion SiF_6^{2-} to verify the role of anions in the formation of this unusual layer and also the significance of hydrogen bonds observed with the sulfate anion. The layering of the EtOH solution of **1a** over the aqueous solution of Cu(NO$_3$)$_2$ and (NH$_4$)$_2$SiF$_6$ resulted in the crystals of complex {[Cu(**1a**)$_2$(H$_2$O)$_2$]·SiF$_6$·3H$_2$O·2EtOH}$_n$, **4**.[7] The crystal structure analysis reveals that the layers are identical with considerable differences in the layer thickness (4.66 Å), grid dimensions (11.89 × 10.73 Å), and interlayer distances (7.262 Å) (Figure 2a,b). The layer width was reduced by

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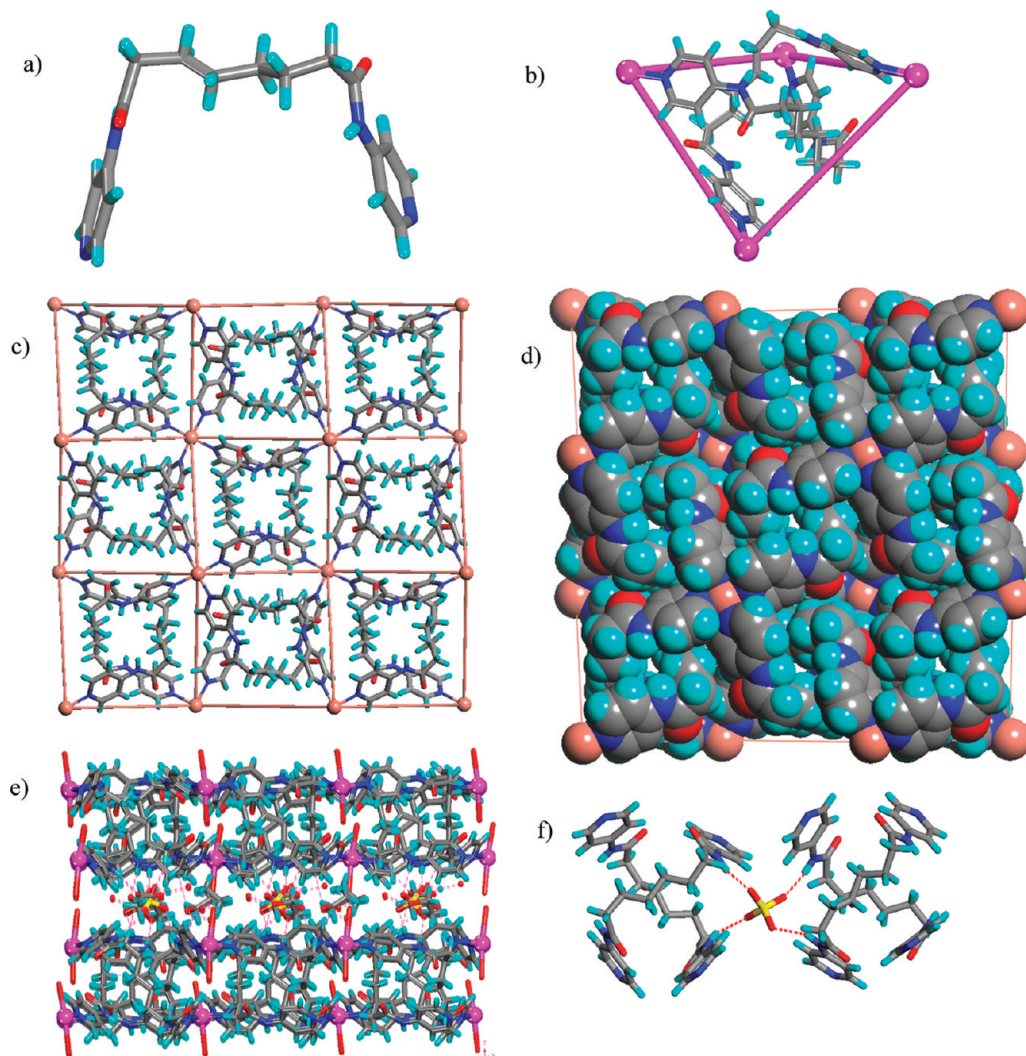
Figure 1. Illustrations for the crystal structure of complex **3**. (a) U-shape geometry of the ligand (notice the gauche−anti−anti−anti−gauche conformation of the alkyl spacer); (b) the building unit of the layer; notice the cyclobutane geometry of Cu(II)$_4$-unit; two-dimensional layer of [4,4] topology (*xy*-plane): (c) cylinder mode (d) space filling mode; note the chirality of the layer; (e) packing of the 2D layers (view along the *xy*-diagonal); (f) hydrogen bonding of sulfate anion with the four amide -NH groups.
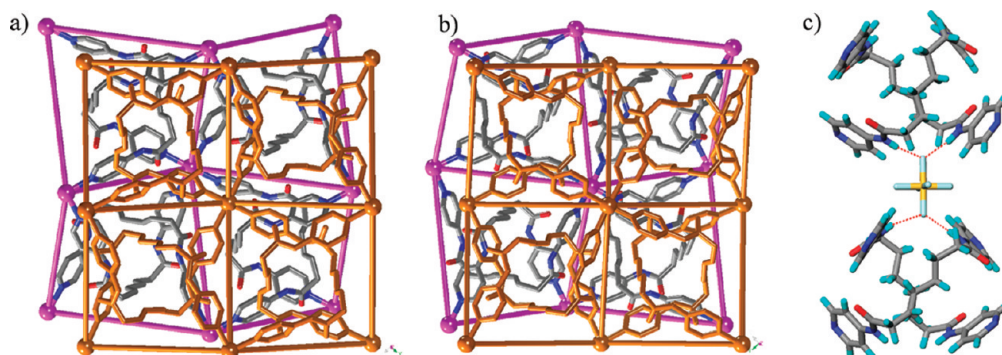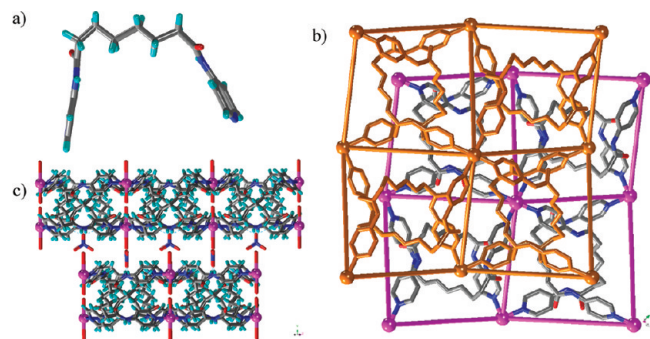

Figure 2. Packing of the [4,4]-networks in complexes: (a) **3** and (b) **4** (*ab* plane); (c) hydrogen bonding of SiF$_6^{2-}$ anion with the four amide -NH groups in complex **4**.

0.66 Å, while the interlayer separation increased by 0.808 Å compared to **3**. The interlayer separation increased due to the bigger size of the anion SiF$_6^{2-}$ compared to the SO$_4^{2-}$ anion. The amide N−H groups link the layers via N−H···F hydrogen bonds with SiF$_6^{2-}$, the F-atoms are bifurcated by two N−H groups from the same layer (Figure 2c). Therefore, the packing of

the layers in **4** is similar to that of complex **3** in which the Cu atoms from the neighboring layers overlap each other. However, unlike in complex **3**, the guest molecules in **4** are found to be disordered and could not be located or modeled. The presence of EtOH and H$_2$O were estimated to be same as in complex **3** by elemental analysis, by TGA, and by comparing guest occupied volumes in

Table 1. Hydrogen Bonding Parameters in the Crystal Structures of 3 and 4

complex	hydrogen bond type	D···A (Å)	D−H···A (°)
3	N−H···O−S	2.827(5)	153.03
		2.857(5)	167.56
		2.881(5)	154.51
		2.753(5)	170.66
	EtO−H···O−S	2.737(5)	
		2.748(6)	
	HO−H···O−S	2.982(5)	
4	N−H···F−Si	2.852(7)	160.98
		2.899(7)	165.62
		2.949(7)	156.61
		2.816(7)	168.72
		3.089(7)	127.98
		3.048(7)	135.08

Figure 3. (a) U-shape geometry of the ligand (notice the gauche−anti−anti−anti−anti conformation of the alkyl spacer); (b) offset packing of the [4,4]-networks (view along the *z*-axis); (c) displaced 2D layers (view along the *xy*-diagonal) in complex **5**. Compare with Figure 2.

both the complexes (24.1% and 25.8% per unit cell volume in **3** and **4**, respectively).[8]

Interestingly, a similar layer structure was found to reproduce even with smaller and flatter anions such as NO_3^-. The crystals of **1a** with $Cu(NO_3)_2$ were found accidentally when we tried to grow the crystals of **1a** with Cu(II) and thiocyanate. This reaction was carried out in a different way as the mixing of $Cu(NO_3)_2$ and NaSCN in H_2O leads to the formation of an insoluble precipitate. The components **1a**, $Cu(NO_3)_2$, and NaSCN were mixed directly in DMF, which resulted in the crystals of $\{[Cu(\mathbf{1a})_2(DMF)_2]\cdot 2NO_3\cdot DMF\cdot 2H_2O\}_n$, **5**.[9] In the crystal structure **5**, one of the anion and solvents of crystallization was found to be disordered, and the absence of SCN^- was identified through the IR spectra.[10] In this complex, the ligand **1a** has a slightly different geometry as the alkyl chain adopts syn−anti−anti−anti−anti geometry (Figure 3a) with torsion angles of 77.89°, 154.33°, 171.26°, 155.17°, and 167.45°. However, the layer geometry, grid dimensions (12.14 × 12.14 Å) and the width (5.481 Å) are almost similar to those of the above complexes. The interlayer separation of 5.99 Å (6.45 Å in **3** and 7.26 in **4** Å) is less than those of the above two complexes given the smaller size of the anion. The crystal structure of **5** has a distinctive packing feature with the offset packing of the layers (Figure 3b,c).

Our efforts to get the complexes of ligand **2a** with various Cu(II) salts were not successful as the components remain in solution in most of the cases. Therefore, we could not test the isostructurality between the complexes of **1a** and **2a**. On the other hand, this isostructurality was clearly proven by us in the complexes of **1b** and **2b**. It is important to note here that the presence of SCN^- was found to be important to obtain the crystals of **5**. We have also found that the ligand **1a** forms a similar type of layer structure with the anion PF_6^-.[11] It is important to mention here that in the complexes of **2** with smaller spacers such

as -$(CH_2)_2$- or -$(CH_2)_4$- the molecules have shown several network variations in identical condition.[4c−f] In some of the complexes the molecule has adopted gauche conformation, but no such entanglement of the ligand was observed before. We attribute the consistent and reliable formation of similar structures in the presence of different anions to the weak hydrophobic interactions between the long spacers. To our knowledge, the geometry and chirality of the two 2D layers observed here is the first of its kind.

Supporting Information Available: Synthesis, elemental analysis, IR, TGA, and crystallographic information of **2**, **3**, and **4**.This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) The single crystal data was collected on Bruker APEX-2 CCD X-ray diffractometer that uses graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) by the hemisphere method. The structures are solved by direct methods and refined by the least-squares methods on F^2 using SHELX-97. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were fixed at calculated positions and refined using a riding model. Crystal data for **3** (CCDC-739966): orthorhombic, $P2_12_12_1$, $a = 14.262(3)$ Å, $b = 14.562(3)$ Å, $c = 23.545(5)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 4890.1(17)$ Å^3, $Z = 4$, $D_c = 1.351$ g cm^{-3}, 7911 reflections out of 9734 unique reflections with $I > 2\sigma(I)$, $1.64 < \theta < 26.16°$, final R-factors $R_1 = 0.0504$, $wR_2 = 0.1351$.

(7) Crystal data for **4** (CCDC-739967): orthorhombic, $P2_12_12_1$, $a = 14.532(2)$ Å, $b = 14.557(2)$ Å, $c = 23.839(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 5042.7(10)$ Å^3, $Z = 4$, $D_c = 1.371$ g cm^{-3}, 5263 reflections out of 9340 unique reflections with $I > 2\sigma(I)$, $1.64 < \theta < 25.50°$, final R-factors $R_1 = 0.0763$, $wR_2 = 0.1918$. The solvent EtOH molecules could not be located, and therefore final refinement was done by using Platon squeeze option.

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(9) Crystal data for **5** (CCDC-739968): orthorhombic, $C222_1$, $a = 15.1320(9)$ Å, $b = 22.948(1)$ Å, $c = 15.4770(9)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 5374.3(5)$ Å^3, $Z = 4$, $D_c = 1.354$ g cm^{-3}, 2798 reflections out of 4965 unique reflections with $I > 2\sigma(I)$, $1.61 < \theta < 25.50°$, final R-factors $R_1 = 0.0818$, $wR_2 = 0.2490$. The solvent DMF and H$_2$O molecules could not be located and therefore final refinement was done by using Platon squeeze option.

(10) CN vibrational stretch of the thiocyanate around 2065 cm^{-1} is absent in the IR of complex **5** (IR is given in Supporting Information).

(11) Cell parameters for Cu(PF$_6$)$_2$ complex: orthorhombic, $P2_12_12_1$, $a = 14.594(4)$ Å, $b = 14.633(4)$ Å, $c = 23.285(7)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 4972.76$ Å^3.