Assembling one-dimensional coordination polymers into three-dimensional architectures via hydrogen bonds

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Abstract. The reactions of *bis*(pyridylcarboxamido)alkanes (amides) and *bis*(3-pyridyl)alkanediamides (reverse amides) with copper(II) and zinc(II) in the presence of various anions resulted in one-dimensional polymeric crystalline complexes with or without guest inclusion. The crystal structure analyses of these complexes reveal that the one-dimensional networks observed here are of three types: simple linear chain, chains with wavy nature and chains containing cavities. The self-complementary amide groups of the ligands assembled these coordination networks into higher dimensional architectures via N–H···O hydrogen bonds.

Keywords. Coordination polymers; hydrogen bonds; self-assemblies; β -sheet; guest inclusion.

1. Introduction

Crystal engineering is aimed at the designing periodic structures of desired supramolecular organization and has potential applications in the field of magnetism, conductivity, sensors, nonlinear optics, host–guest chemistry, catalysis, separation science, gas storage and so on.^{1–3} The concepts of crystal engineering are based on understanding and exploiting the intermolecular interactions. There are several crystal engineering studies on metal–organic hybrid materials that are purely based on coordination bonds and also on organic materials that are purely based on hydrogen bonds.⁴ However, the utilization of hydrogen bond supramolecular synthons in assembling metal–organic frameworks is relatively less explored area of research. The combination of these two aspects is expected to result in more control over the network geometries and therefore the properties. The aim of the present work is to apply the supramolecular synthon approach for assembling the coordination networks by designing the ligands containing functional groups which are capable of forming the hydrogen bond synthons and the coordination bonds (scheme 1). The coordination networks of these ligands are expected to fulfill the following objectives: (i) introduces the functional groups into the polymeric networks; (ii) these functional groups help in fine tuning the nature of the

cavities to accommodate wide range of guest molecules; (iii) self recognition synthons act as communicators and assembles polymeric networks into various novel architectures.

Recently we have explored the recognition patterns of amides and reverse amide ligands (**1–3**) and found that amides and reverse amides, which have the same combination of functional groups at the molecular level, behave very differently at supramolecular level. It was shown in case of amide analogues that even in the presence of pyridine groups; the amide groups form amide-to-amide hydrogen bonds whereas in case of reverse amide analogues, pyridine group exhibits interference in amide-to-amide hydrogen bonds and disrupts the amide-to-amide recognition pattern.⁵

In our previous studies using ligands **1**, **2** and **3** we have also shown that Cu(II) salts are capable of forming various open 2D-networks, chiral 2D-networks, interpenetrated 2D-networks (both parallel and perpendicular mode) and 3D pseudo diamondoid (6⁵8-topology) networks.⁶ In several instances these networks exhibit recognition through amide-to-amide hydrogen bonds namely β -sheet hydrogen bonding pattern. Here we discuss our results on one-dimensional networks of **1**, **2** and **3** with Cu(CH₃COO)₂, Cu(NO₃)₂, Cu(SCN)₂, CuSO₄, ZnI₂ and Cu(ClO₄)₂.

Among polymeric networks, the one-dimensional networks are of the simplest coordination polymers observed with bidentate ligands.⁷ The primary reason

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Scheme 1. Exobidentate ligands with *bis*(amido)alkane spacer; β -sheet networks.

Scheme 2. 1D-networks with exobidentate ligand.

for the formation of 1D-chains may be due to the presence of other competing ligands such as anions, H_2O or solvents in the reaction of the bidentate ligand with the metal centre. Various possible geometries are known for 1D-networks with linear rigid bidentate ligands: linear,⁸ zigzag,⁹ helical,¹⁰ ladder,¹¹ molecular antenna,¹² railroad¹³ and 1D-chains with cavities¹⁴ (scheme 2). The formation of these networks depends on the ligand to metal ratio, coordination environment of the metal centre and influence of counter anions and guest/solvent molecules. The role of these amide groups in assembling

the one-dimensional coordination networks and the effect of various factors such as counter anions and solvent molecules on the occurrence of amide-to-amide hydrogen bonds will be presented here.

2. Experimental

2.1 Materials

All the reagents and solvents employed were commercially available and used as supplied without further purification. $\text{Cu}(\text{NO}_3)_2$, $\text{Cu}(\text{OAc})_2$, CuSO_4 ,

ZnI₂, NaSCN, Cu₂(CO₃)₂ and perchloric acid were obtained from Merck Co. Cu(ClO₄)₂ was prepared from Cu₂(CO₃)₂ and perchloric acid. The ligands were prepared according to the previously reported procedures.⁵

2.2 Physical measurements

FTIR spectra were recorded with an NEXUS-870 instrument, Thermo Nicolet Corporation. Elemental analyses were obtained with a Perkin Elmer instrument, series II, CHNS/O analyzer 2400. TGA data were recorded with a Perkin Elmer instrument, Pyris Diamond TG/DTA (N₂).

2.3 Syntheses of complexes

The complexes **4–7**, **9** and **10** were prepared by adopting the layering technique. The complexes **8** and **11** were prepared by direct mixing of ligand with metal in the presence of aromatic guest molecules.

2.3a Synthesis of complex 4 by layering: The ligand **1a** (54.0 mg, 0.2 mmol) was taken in CHCl₃–EtOH (10 : 1) solvent (5.5 mL). An ethanolic solution (1.0 mL) of Cu(NO₃)₂·6H₂O (24.1 mg, 0.1 mmol) was slowly layered over the ligand solution. The slow diffusion of the components resulted in the formation of blue coloured crystals after one week. Yield: 36.1%; Elemental analysis: C₂₈H₄₄N₁₂O₂₄Cu₂ (1059.8): Calculated: C 31.73%, H 4.18%, N 15.86%; Found: C 30.60%, H 4.09%, N 15.58%.

2.3b Syntheses of complex 5 and 6: Complexes **5** and **6** were prepared in similar way by the reaction of ligand **1b** with Cu(OAc)₂ and ZnI₂, respectively. Complex **5**: Yield: 28.7%; Elemental analysis: C₂₂H₂₆N₄O₉Cu₁ (553.5) Calculated: C 47.69%, H 4.69%, N 10.11%; Found: C 47.13%, H 4.76%, N 10.60%. Complex **6**: Yield: 20.3%; Elemental analysis: C₁₈H₁₈N₄O₄I₂Zn₁ (673.1): Calculated: C 32.09%, H 2.67%, N 8.31%; Found: C 32.16%, H 2.58%, N 8.35%.

2.3c Syntheses of complex 7: The ligand **2a** (54.0 mg, 0.2 mmol) was taken in CHCl₃–EtOH (10 : 1) solvent (5.5 mL). An ethanolic solution (1.0 mL) of Cu(ClO₄)₂·6H₂O (37.0 mg, 0.1 mmol) was slowly layered over the ligand solution. The slow diffusion of the components resulted in the

formation of purple coloured crystals after one week. Yield: 61.1%; Elemental analysis: C₃₈H₄₂Cl₈Cu₁N₈O₁₄ (1181.94): Calculated: C 38.58%, H 3.55%, N 9.47%; Found: C 38.46%, H 3.51%, N 9.39%.

2.3d Synthesis of complexes 8: Ethanolic solution (20 mL) of Cu(ClO₄)₂·6H₂O (370.15 mg, 1.0 mmol) was added to a stirred solution (30 mL of EtOH) of ligand **1a** (540 mg, 2.0 mmol) and naphthalene (2.56 g, 20 mmol). This resulted in the formation of a blue precipitate. After 15–20 min of stirring, 20 mL of water was added. The blue precipitate became soluble and a clear solution was obtained. This solution was filtered and kept for slow evaporation. Blue coloured crystals were formed after one week. For the inclusion of liquid aromatic guest molecules, 20 mL of the corresponding liquid was taken in place of naphthalene.

8•Naphthalene (8a): Yield: 83.7%; Elemental Analysis: C₃₈H₄₄N₈O₁₆Cl₂Cu₁ (1003.5): Calculated: C 45.48%, H 4.38%, N 11.17%; Found: C 46.06%, H 4.44%, N 11.43%.

8•Toluene (8b): Yield: 76.1%; Elemental Analysis: C₃₅H₄₄N₈O₁₆Cl₂Cu₁ (967.2): Calculated: C 43.45%, H 4.55%, N 11.50%; Found: C 43.65%, H 4.37%, N 11.35%.

8•Ethylbenzene (8c): Yield: 80.6%; Elemental analysis: C₃₆H₄₆N₈O₁₆Cl₂Cu₁ (980.5): Calculated: C 44.05%, H 4.69%, N 11.42%; Found: C 43.40%, H 4.66%, N 11.51%.

8•Anisole (8d): Yield: 73.0%; Elemental analysis: C₃₅H₄₄N₈O₁₇Cl₂Cu₁ (982.5): Calculated: C 42.74%, H 4.47%, N 11.39%; Found: C 43.18%, H 4.39%, N 11.41%.

2.3e Synthesis of complex 9 by layering: Ethanolic solution of ligand (2 mL) **3a** (27 mg, 0.1 mmol) was layered over aqueous solution (5 mL) of Cu(ClO₄)₂·6H₂O (12.48 mg, 0.05 mmol). After 15 days green coloured crystals were formed at the interface of the two layers. Yield: 27.40%.

2.3f Synthesis of complex 10 by layering: Complex **10** was prepared in similar way as of **9** by the reaction of ligand **3b** with CuSO₄. Yield: 43.23%; Elemental analysis: C₁₆H₃₀N₄O₁₂SCu (566.04): Calculated: C, 33.95%; H, 5.34%; N, 9.90%; Found: C, 34.38%; H, 5.07%; N, 10.0%.

2.3g Synthesis of complex 11 by direct mixing: 63.6 mg (0.2 mmol) of **3c** was dissolved in 3 mL of

DMSO. To this solution methanol (2 mL) solution of $\text{Cu}(\text{NO}_3)_2$ (24.16 mg, 0.1 mmol) and NaSCN (16.21 mg, 0.2 mmol) was added. After a week, green coloured crystals were formed. Yield: 54.64%; Elemental analysis: $\text{C}_{24}\text{H}_{26}\text{N}_6\text{O}_4\text{S}_4\text{Cu}$ (654.31): Calculated: C, 44.05%; H, 4.01%; N, 12.84%; Found: C, 44.42%; H, 4.18%; N, 12.35%.

2.3h X-ray crystal structure determination: The single crystal data for **4–6** and **7–9** were collected on a Bruker–Nonius Mach3 CAD4 and CCD APEX-2 X-ray diffractometers, respectively, that uses graphite monochromated $\text{MoK}\alpha$ radiation ($\mu = 0.71073 \text{ \AA}$). The structures were solved by direct methods and refined by least square methods on F^2 using SHELX-97.¹⁷ In the structure **7**, perchlorate ions are somewhat distorted and disordered, therefore Cl-atoms are refined anisotropically and O-atoms are refined isotropically. Further the solvent molecules which accounts for 23% of crystal volume could not be located, therefore Platon.¹⁸ squeeze option was used for the final refinement. Otherwise, non-hydrogen atoms in all the structures were refined anisotropically and hydrogen atoms were fixed at calculated positions and refined using a riding model. PLATON is used for the calculations guest available volumes. The crystal structures **5**, **6** and **9–11** were deposited in the Cambridge data centre (depository numbers: CCDC 755602–755606).

3. Results and discussion

The complexes were synthesized either by direct mixing of the components or by the layering procedure. The complexes **4–6** are prepared by layering ethanolic solution of corresponding metal salt over the $\text{CHCl}_3/\text{EtOH}$ solution of ligands **1**. Whereas the complexes **7** and **8** were prepared by direct mixing of the ligand and $\text{Cu}(\text{ClO}_4)_2$ in EtOH and water. The complexes **9** and **10** were prepared by layering methanolic solution of **3a** and ethanolic solution of **3b** over the aqueous solution of $\text{Cu}(\text{ClO}_4)_2$ and CuSO_4 , respectively. The complex **11** was obtained by direct mixing of **3c**, $\text{Cu}(\text{NO}_3)_2$ and NaSCN in DMSO and MeOH.

The crystal structures of complexes **4–11** were determined and analysed in terms of coordination network geometries, recognition of networks through amide hydrogen bonds and effects of anions and guest molecules. The complexes **4–6** and **9–11** show the formation of 1D-chains but these 1D-chains differ from each other in many ways. The complexes **7** and **8** form 1D-chain with cavities for guest inclusion and have 1 : 2 metal to ligand ratio. The pertinent crystallographic details, bond lengths around metal centre and geometrical parameters of strong hydrogen bonds involving amides are given in tables 1, 2 and 3 respectively. In the following section the crystal structures of complexes **4–11** will be discussed in detail.

3.1 Crystal structures of complexes of amides

3.1a NO_3^- Included channels resulted from the packing of 1D chains: In complex **4**, the Cu(II) centre is octahedrally coordinated to two ligand (**1a**) units which occupy the axial positions while four water molecules occupy the equatorial positions (table 2, figure 1a). The alkyl spacer of the ligand adopts perfect *anti* conformation (N–C–C–N torsion 180°) which resulted in the linear geometry of the ligand (figure 1a). The packing of the chains is governed by the hydrogen bonded interactions of amide spacers of the ligand **1a** with the NO_3^- anions and water molecules. The NO_3^- anions form hydrogen bonds with amide $-\text{NH}$ and coordinated H_2O ($\text{O} \cdots \text{H} \cdots \text{ONO}_2$: $1.90 \text{ \AA}$, $2.702(4) \text{ \AA}$, 157° ; $1.81 \text{ \AA}$, $2.660(4) \text{ \AA}$, 175° , figure 1a). The chains are further packed via hydrogen bond interactions between the amide ($\text{C}=\text{O}$) of one chain and coordinated H_2O of another chain (figure 1b). The packing of the layers resulted in the formation of channels which are occupied by NO_3^- anions (figures 1b and c).

3.1b 1D Chain with wave-like features: In complex **5**, the Cu(II) centre adopts square pyramidal coordination geometry. The two ligand (**1c**) units occupy the two equatorial sites in a *trans* fashion, the other two equatorial sites are occupied by acetate anions and one water molecule is coordinated at the

Table 1. Crystallographic data and structure refinement parameters for complexes **5**, **6** and **9–11**.

Complex	5	6	9	10	11
Formula	C ₂₂ H ₂₆ Cu ₁ N ₄ O ₉	C ₁₈ H ₁₈ Zn ₁ N ₄ O ₄ I ₂	C ₂₈ H ₃₀ Cl ₂ Cu ₁ N ₈ O ₁₃	C ₁₆ H ₃₀ Cu ₁ N ₄ O ₁₂ S	C ₂₄ H ₂₆ Cu ₁ N ₆ O ₄ S ₄
M. wt.	554.01	673.53	821.04	566.04	654.29
System	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>P2/c</i>	<i>Aba2</i>	<i>P2/c</i>	<i>P2(1)/n</i>
<i>a</i> (Å)	26.836(5)	12.302(3)	35.565(3)	13.1933(2)	11.8971(1)
<i>b</i> (Å)	6.4400(1)	7.1400(1)	26.508(3)	7.9300(1)	14.8682(1)
<i>c</i> (Å)	15.407(3)	13.683(3)	9.486(3)	25.363(3)	16.4846(2)
α (°)	90	90	90	90	90
β (°)	115.85(3)	114.78(3)	90	115.41(4)	92.989(3)
γ (°)	90	90	90	90	90
<i>V</i> (Å ³)	2396.3(1)	1091.17	8943.1(2)	2396.8(6)	2912.0(5)
<i>Z</i>	4	2	8	4	4
Den. (mg/m ³)	1.536	2.050	1.220	1.569	1.492
GOF on <i>F</i> ²	1.019	1.181	1.370	1.048	0.967
<i>R</i> ₁ (<i>I</i> > 2σ(<i>I</i>))	0.0715	0.0459	0.0726	0.0466	0.0786
<i>wR</i> ₂ (on <i>F</i> ² , all data)	0.2282	0.1348	0.1924	0.1457	0.1981

For crystallographic data of **4**, **7** and **8** please see the reference⁶

Table 2. Bond lengths around M(II) centre in complexes **4–11**.

Complex	M(II)–N (Å)	M(II)–H ₂ O (Å)	M(II)–Anion (Å)
4	2.032(3)	2.022(2); 2.245(3)	None
5	2.011(5)	2.373(7)	1.977(4); 2.922(4)
6	2.055	None	2.547
7	2.022(4)	None	2.668(6)
8a	2.066(3); 2.095(3)	2.414(3)	None
8b	2.052(4); 2.083(4)	2.403(4)	None
9	1.997(9) 1.982(1) 2.040(1) 2.053(9)	2.471(1)	2.774(2)
10	2.015(2) 2.027(3)	2.286(3) 1.987(2) 2.677(3)	1.960(2)
11	2.019(5) 2.028(5)	2.464(5)* 2.703(5)*	1.943(7) 1.962(7)

*DMSO coordination

axial site. The phenyl ring and the two pyridyl rings of the ligand **1c** are coplanar (figure 2a). The combined effects of rigid spacer of the ligand **1c**, 3-pyridyl group and the coordination of the ligands at the equatorial position of the metal centre resulted in the formation of wave-like 1D chain (figure 2b).

These 1D chains are packed via hydrogen bonded interactions between the coordinated H₂O molecules and acetate anions to form a 2D layer (O–H...OAc: 1.89(8) Å, 2.789(6) Å, 165(8)°; 1.82(8) Å, 2.761(7) Å, 173(5)°, figure 2b). These 2D-layers are further packed in a staggered fashion via C–H...O

hydrogen bonds between amide C=O and pyridyl –CH group (figures 2c and 2d). The –NH of the amide groups is involved in hydrogen bonded interactions with free H₂O molecules that are present in the crystal lattice (figure 2b).

3.1c Packing of 1D chains via β -sheet type pattern: In complex **6**, the Zn(II) centre adopts tetrahedral coordination environment with two units of **1c** and two I[–] anions. The geometry of the ligand **1c** is different from the previous complex. Unlike in complex **5**, the geometry of **1c** in **6** is non-coplanar

Table 3. Geometrical parameters of strong hydrogen bonds of amide in complexes 4–11.

Complex	Type ¹	H...A (Å)	D...A (Å)	D–H...A (°)
4	O(1W)–H(2W)···O(11) ^a	1.92	2.800(4)	159
	O(2W)–H(4W)···O(11) ^b	2.01	2.747(3)	145
	N(12)–H(12)···O(103) ^c	2.15	2.987(4)	163
5	N(12)–H(12)···O(2W) ^d	2.18	3.034(7)	170
	C(15)–H(15)···O(16) ^e	2.34	3.089(8)	137
6	N(10)–H(10)···O(1W) ^f	1.99	2.831(8)	166
	O(15)···O(1W) ^g		2.726(8)	
7	N(21)–H(21)···O(16) ^h	2.04	2.818(6)	150
8a	N(31)–H(31)···O(104) ⁱ	2.30	3.083(7)	151
	N(32)–H(32)···O(104) ^j	2.47	3.096(8)	130
	O(1W)–H(11W)···O(16) ^k	2.06(6)	2.765(6)	169(8)
9	O(1W)–H(12W)···O(26) ^l	2.10(6)	2.868(6)	169(6)
	N(12B)–H(12C)···O(31B) ^m	2.54	3.128(1)	127
	N(12B)–H(12C)···O(102) ⁿ	2.14	2.88(4)	145
	N(22A)–H(22A)···O(200) ^o	2.26	3.110(2)	171
	N(22B)–H(22C)···O(32B) ^p	2.01	2.867(1)	177
10	N(22B)–H(22B)···O(101) ^q	1.957	2.796(5)	165
11	N(12A)–H(12A)···O(2M) ^r	2.30	3.010(7)	140
	N(12B)–H(12C)···S(100) ^s	2.72	3.500(6)	151

¹Symmetry operators: (a) $1/2 + x, 3/2 - y, 1/2 + z$; (b) $3/2 - x, 1/2 + y, 3/2 - z$; (c) $3/2 - x, 1/2 + y, 3/2 - z$; (d) $-x, 1 + y, 1/2 - z$; (e) $-1/2 - x, -1/2 + y, 1/2 - z$; (f) x, y, z ; (g) $x, 1 + y, z$; (h) $-1/2 + x, -1/2 - y, z$; (i) $x, -1 + y, 1 + z$; (j) $x, -1 + y, 1 + z$; (k) $-1 - x, -y, 1 - z$; (l) $1 + x, 1 + y, -1 + z$; (m) $1/2 - x, y, 1/2 + z$; (n) $1/2 - x, y, -1/2 + z$; (o) $x, 1/2 + y, 3/2 + z$; (p) $1/2 - x, y, -1/2 + z$; (q) $1 - x, 1 - y, -z$; (r) $1 + x, y, z$; (s) $-1 + x, y, z$.

Figure 1. Illustrations for crystal structure of complex 4: (a) 1D chain, which shows the hydrogen bonds between the amide group and NO₃ anion; packing of the chains resulted in channels occupied by NO₃ anions; (b) top view and (c) side view; NO₃ anions are shown in space fill mode and the middle layer was shown in light colour.

as the plane of the phenyl ring is perpendicular to those of the two pyridyl rings (figure 3a). The 1D-chains are linked by the hydrogen bonded interactions between the amide groups and the H₂O molecules to form a 2D-layer (figure 3c). This resulted in the formation of pattern which is similar to the β -sheet type. The H₂O molecules are acting as mediator/connectors between the -NH and C=O of the amide groups. These 2D-layers are further packed via aromatic interactions between the phenyl group and the pyridyl groups (figure 3d).

3.1d 1D Chain with rhomboidal cavities assembled via β -sheet hydrogen bonds: In complex 7, the Cu(II) centre adopts octahedral environment with four ligand units at equatorial sites and ClO₄ anions at axial sites. The ethyl spacer of the ligand 2a exhibits *gauche* conformation, both the amide moieties of the ligand are *anti* to each other. This results in arc-like ligand geometry, which joins the Cu(II) centers and form 1D chain with rhomboidal cavities of dimensions 13.0 Å × 12.3 Å (figure 4a). The rhomboidal cavities are occupied by CHCl₃ dimers, which are held together by Cl...Cl interactions (3.641 Å, 3.920 Å) (figure 4b). These dimers fit in the cavities such that C–Cl moieties lie within the cavities while C–H groups point out of the

Figure 2. Illustrations for the crystal structure of **5**: (a) geometry of ligand **1c** in the complex; (b) packing of wave-like 1D chains to form 2D layer; (c) side view of the packing of the 2D layers via C–H...O hydrogen bonds, free water molecule shown in space fill mode; (d) C–H...O hydrogen bonds network between the ligands.

Figure 3. Illustrations for the crystal structure of **6**: (a) geometry of the ligand **1c** in the complex; (b) 1D chain; (c) packing of the 1D chains via β -sheet type hydrogen bonds to form a 2D-layer; (d) side view of the layers, which shows the packing of the layers via aromatic interactions.

cavities. The C–H groups of these dimers are further bonded to coordinated ClO_4^- via C–H...O hydrogen bonds (2.600 Å, 3.445 Å, 144.43°).

These chains form a layer via C–H...O hydrogen bonds between pyridyl C–H groups and ClO_4^- (C–H...O: 2.646 Å, 3.383 Å, 136.60°). The 2D-

Figure 4. Illustrations for the crystal structure of **7**: (a) 1D chain with rhomboidal cavities; (b) CHCl₃ dimers, which are present in the cavities; (c) packing of the chains via β -sheet hydrogen bonds; (d) β -sheet.

layers pack via interdigitation, which occurs via β -sheet (figures 4c and d). Further this type of packing results in two types of channels, one of which is occupied by CHCl₃ and the other is occupied by EtOH molecules. It is found that these cavities in 1D-chain are suitable only for CHCl₃, as the reactions with other guest molecules failed to produce crystalline materials. Here it is important to note that the previously reported 1D structure of **2a** with Cu(ClO₄)₂ neither contains guest molecules, nor contains β -sheet.¹⁵

3.1e 1D Chains for inclusion of aromatic guests:

The complex **8** also shows the formation of similar type of 1D chain as **7** but there exists some important structural differences. In complex **8**, the axial positions are occupied by H₂O molecules whereas in **7**, ClO₄⁻ anions were present at the axial position. The cavities formed in **8** have rectangular geometry with the dimensions of 10.0 Å × 13.8 Å (figure 5a), whereas in **7** they are almost rhomboidal (13.0 Å × 12.3 Å). Further, the amide moieties in complex **8** are *syn* to each other (figure 5b). In complex **7**, the amide moieties are *anti* to each other. Also one of the important differences between **7** and **8** is that in **7**, the chains interact with each other via β -sheet hydrogen bonds whereas in **8** β -sheet hydrogen bonds are absent. Regarding differences in the nature of the cavities of **7** and **8**, it was observed that

in **7**, the cavities are suitable only for CHCl₃, as the reactions with other guest failed to produce crystalline materials. The cavities in **8** are good enough to accommodate several aromatic guest molecules such as naphthalene, toluene, xylene, anisole, nitrobenzene and ethylbenzene. Also the guest occupied volume of **8** (22%) is much less than that of **7** (22% CHCl₃ + 19% EtOH).

The structure of **8a**, which has naphthalene in the cavities, shows that the naphthalene molecules are sandwiched by four amide moieties of the ligands via π - π interactions (figure 5d). Besides, amide groups are also involved in extensive hydrogen bonding (not amide-to-amide) with the water molecules and the ClO₄⁻ (figure 5c). Accordingly, 1D-chains are joined together by ClO₄⁻ by forming the hydrogen bonds with amide and coordinated H₂O. These layers pack with perfect overlap on each other such that the rhomboidal cavities are converted into channels (figure 5d). Along these channels, the edges of naphthalene molecules interact with each other via π - π interactions (figure 5e). These layers are glued together by O-H...O hydrogen bonds between the C=O of **1a** and coordinated and uncoordinated H₂O molecules.

The full structural analysis has been carried out for one more complex (**8b**) where the toluene acts as a guest. This structure confirms that disordered toluene occupies the cavities in 1D-chain similar to the

Figure 5. Illustrations for the crystal structure of **8a**: (a) 1D chain with naphthalene molecules (space fill mode) included in rhomboidal cavities; (b) ligand geometry in the complex; (c) packing of the chains via N–H...O and O–H...O hydrogen bonds (d) sideways linking of 1D chains; (e) top-bottom linking of 1D-chains; (f) column of naphthalene molecules, which are accommodated in channels.

Figure 6. Toluene molecules in complex **8b**: (a) disordered molecule; (b) column of toluene molecules which are accommodated in the channels of complex **8b**.

naphthalene in **8a** (figures 6a and b). The cell parameters were determined for the other complexes with guest molecules such as anisole, ethylbenzene, *p*-xylene, nitrobenzene, benzonitrile, biphenyl and found that they also have the similar unit cell parameters as **8a** and **8b**. Here, it is interesting to note that using **1a** and $\text{Zn}(\text{ClO}_4)_2$ similar 1D chain that contains smaller guest molecule such as CH_3CN in cavities was reported earlier.¹⁶

3.2 Crystal structures of complexes of reverse amides

3.2a 1D Chain containing rectangular cavities assembled via β -sheet hydrogen bonds: In complex **9**, the Cu(II) centre adopts octahedral environ-

ment and four ligand units occupy the equatorial sites. Unlike in **7** and **8**, the axial sites are occupied by one ClO_4 anion and one water molecule (figure 7a). The ethyl spacer of the ligand **3a** exhibits *gauche* conformation (figure 7b) and the amide moieties in **3a** are placed *syn* to each other. This type of geometry gives an arc-like shape to the ligand which joins the Cu(II) centers to form 1D chain with rectangular cavities of dimensions $14.0 \text{ \AA} \times 11.4 \text{ \AA}$, similar to the one observed in complex **8**. However in **8**, the cavities are occupied by various aromatic guest molecules while in **9** they are occupied by solvent ($\text{H}_2\text{O}/\text{MeOH}$) molecules. Another, important difference between **7**, **8** and **9** is that the packing of the chains: in **7**, both edges of the 1D chains interact with each other via β -sheet hydrogen bonds whereas in **9** one edge of the chain is involved in amide-to-amide hydrogen bond via β -sheet through interdigitation and the amide groups on the other edge are hydrogen bonded to water molecules (figure 7c). While in **8**, no such β -sheet hydrogen bonds were observed.

The packing of these one-dimensional chains along X-axis results in three types of channels, two are of rectangular geometry and one is of triangular geometry. Bigger rectangular cavities are filled by solvent molecules and the other cavities are filled by

Figure 7. Illustrations for the crystal structure of **9**: (a) 1D chain with rectangular cavities; (b) ligand geometry in the complex; 3D-packing of chains; (c) view along the metal atoms; (d) side view, notice that the packing of chains via β -sheets and also only one edge of the network is involved in the β -sheet formation; (e) β -sheet hydrogen bonds.

perchlorate anions (figure 7d). Apart from β -sheet pattern these networks further connected through hydrogen bonds between coordinated perchlorate, water and amide groups. Our efforts to include guest molecules were not successful in obtaining crystalline materials.

3.2b Zig-zag 1D chain: In complex **10**, the Cu(II) centre adopts octahedral coordination geometry and the ligand **3b** exhibits two types of geometries. One (A) contains all anti conformation for butyl spacer whereas the other (B) contains disordered butyl group with anti-gauche-anti conformation (figures 8a and b) and the asymmetric unit contains only half units of A and B as they sit on crystallographic symmetry. The two ligand (**3b**) units occupy the two equatorial sites in a *syn* fashion; one sulphate anion and one water molecule occupy the remaining two equatorial sites. The axial positions are coordinated by water molecules. Due to the *syn* coordination of the ligand to the metal

centre resulted in the formation of zig-zag 1D chain (figure 8c). The geometry of the ligand B gives a curvature to 1D-chain which helps in the interlocking with two of the adjacent chains. The interlocking of the chains in ac-plane generates a two-dimensional layer which is highly corrugated. Generally, several examples of interlocking exist for macro-cycles, 2D-layers and 3D-networks. To our knowledge, this is the first example of 1D-chains with such interlocking. The primary interactions responsible for such interlocking are found to be O–H...O hydrogen bonds between coordinated water and amide carbonyl of A (O...O distance: 2.791 Å) (figure 8d). The pyridine groups also involved in edge to edge aromatic interactions with each other (C...C distances: 3.699 Å, 3.742 Å, 4.035 Å, 4.179 Å). The N–H group of A hydrogen bonds to water molecules (1.949 Å, 167.67°, 2.796 Å) while the N–H groups in B hydrogen bonds to sulphate O-atom (1.958 Å, 164.56°, 2.796 Å). The carbonyl groups of B hydrogen bonds to free water molecules

Figure 8. Illustrations for the crystal structure of **10**: Geometry of the ligand (a) **A** exhibits all anti CH_2 groups; (b) **B** with *anti-gauche-anti* CH_2 groups (disordered); (c) interlocking of adjacent chains; (d) interactions at the interlocking point and (e) the 3D packing of the chains.

($\text{O}\cdots\text{O}$ distances 2.782 Å). The packing of the layers is governed by plethora of strong and weak hydrogen bonds (figure 8e).

3.2c Linear 1D chain: In complex **11**, two independent 1D chains X and Y are present and the Cu(II) centre adopts octahedral coordination geometry in both the chains. The ligand **3c** in chain X is coplanar with the interplanar angle between the amide and pyridyl plane is 7.74° , while in chain Y the **3c** deviates more from planarity with the interplanar angle of 17.76° (figures 9a and b). In both the chains the equatorial position of Cu(II) are occupied by two ligand units and two thiocyanate anions while the axial positions are occupied by DMSO which are disordered in chain-Y.

These chains are interconnected in *ac* plane via $\text{N-H}\cdots\text{O}$ (2.289 Å, 140.55° , 3.003 Å) hydrogen bonds between the amide N-H of chain Y and O-atom of DMSO of chain X (figure 9c). The N-H groups of chain X are connected to the S-atom of

SCN of the chain Y via $\text{N-H}\cdots\text{S}$ (2.732 Å, 150.53° , 3.507 Å; 2.923 Å, 135.97° , 3.649 Å) interactions, several other weak interactions such as edge to face $\text{C-H}\cdots\pi$ interaction between the pyridine and central phenyl ring of **3c** ($\text{C}\cdots\text{C}$ distances 3.6–4.0 Å) exist between the adjacent chains X and Y (figure 9d).

3.3 Thermal gravimetric analyses

Thermo gravimetric analyses have been performed on the complex **8** as it has shown an ability to include several aromatic guest molecules in its cavities. The analyses show that the weight loss observed in complexes of **8** follow the same pattern and does not depend on the type of guest molecules present in the network. When naphthalene is present as guest molecule (**8a**), the 12.6% of weight loss observed till 168°C corresponds to the loss of naphthalene molecules from the network (calculated: 12.7%). The weight loss of 2.5% observed in the temperature range 168 to 210°C corresponds to the

Figure 9. Illustrations for the crystal structure of **11**: Geometry of ligand **3c** in (a) chain-X; (b) chain-Y; (c) interactions between chain-X and chain-Y and (d) 3D packing of chains.

Figure 10. TGA of complexes (a) **8a**; (b) **8b**; (c) **8c**; (d) **11**.

loss of one water molecule (calculated: 2.1%). Further weight loss of 3.8% from 210 to 222°C corresponds to the loss of two molecules of water (calculated: 4.2%) and 2.1% of weight loss in the temperature range of 222 to 253°C corresponds to the loss of remaining one water molecule from the

network (calculated: 2.1%). The network found to collapse after 253°C due to the loss of the ligand molecules (figure 10a).

Similar trend of weight loss was observed with the guest molecules toluene (**8b**) or ethyl benzene (**8c**). The initial weight loss corresponds to the loss

of aromatic guest molecules followed by the loss of the water molecules. In complex **8b**, 11.4% of weight loss at 132°C corresponds to the loss of toluene (calculated: 12.4%). 8.4% weight loss from 132°C to 255°C corresponds to the loss of three H₂O (calculated: 8.3%). The network is stable up to 255°C (figure 10b). In complex **8c**, 14.1% of weight loss at 124°C corresponds to the loss of ethylbenzene (calculated: 13.4%). 6.1% weight loss from 124°C to 241°C corresponds to the loss of three H₂O (calculated: 7.8%). The network is stable up to 241°C (figure 10c).

In complex **10**, 9.35% of the weight loss observed till 61°C corresponds to the loss of three free water molecules from the network (calculated: 9.54%). The weight loss of 9.35% observed in the temperature range of 61 to 255°C corresponds to the loss of three coordinated water molecules (calculated: 9.54%). The complex is stable till 255°C and after that it collapses due to the loss of the ligand molecules (figure 10d).

4. Conclusions

The 1D networks with the ligands **1–3** mainly exhibited three types of geometries: (i) linear chains (**4** and **11**), (ii) wavy chains (**5**, **6** and **10**) and (iii) chains with cavities (**7–9**). The flexibility of the ligand resulted in the formation of arc type ligand geometry, which resulted in the formation of chains with cavities (type iii). Further, the cavities were shown to be included by guest molecules or solvents. The cavities of complex **7** and **9** have exhibited specificity for guest inclusion whereas those in complex **8** exhibited versatility to accommodate wide range of aromatic guest molecules.

The amide groups of the ligands in the complexes assembled the networks into higher dimensionalities. In complexes **4**, **5** and **10**, the anions and H₂O molecules formed hydrogen bonds with the amide groups. In case of complex **6**, the amide groups were involved in hydrogen bonded interactions with itself (β -sheet) and also with water molecules. In complex **7**, the chains were assembled via β -sheet hydrogen bonds while in complex **8** and **11**, the amide groups are hydrogen bonded to anions/solvents. However, in complex **9**, the amide groups exhibit amide-to-amide (β -sheet) as well as amide-to-solvents/anions hydrogen bonds. We note here that the complex **10** contains an unprecedented interlocking for one-dimensional networks.

Acknowledgements

We gratefully acknowledge the financial support from Council of Scientific and Industrial Research (CSIR), Department of Science and Technology (DST)–Fund for Improvement of Science and Technology (FIST) for single crystal X-ray facility. LR thanks Indian Institute of Technology (IIT) (Kharagpur) for research fellowship.

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