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1D, 2D and 3D coordination polymers of 1,3-phenylene diisonicotinate with Cu(I)/Cu(II): Cu_2I_2 building block, anion influence and guest inclusions⁺

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The reactions of a flexible bidentate ligand 1,3-phenylene diisonicotinate (L) with Cu(1/11) salts afforded coordination polymers with varied dimensionalities and guest inclusion capabilities. Complexation of L with CuI resulted in a 2D-network with (4,4) topology and inclusion of guest molecules such as CHCl₃, bromobenzene, nitrobenzene and benzonitrile. The treatment of L with Cu(PF₆)₂ and Cu(ClO₄)₂ resulted in a one-dimensional network containing M₂L₂ macrocycles and a 4-fold interpenetrated three dimensional network having quartz topology, respectively. The 1D-networks included CHCl₃ as guests and the interpenetrated 3D-network includes tetrahedral water clusters.

Coordination polymers (CPs) are being studied extensively due to their intriguing structures and applicative aspects such as gas sorption, separation, catalysis, gels and photoluminescence.^{1,2} The synthesis of new ligands and exploration of their coordination abilities to form coordination polymers has developed as an active area of research during the past decade as there is a direct correlation between structures and properties. A large amount of CPs reported to date corresponds to bis(pyridyl) or bis-carboxylate ligands.^{3,4} Although the coordinating groups, pyridine and carboxylate, play a major role in the formation of CPs, the backbone that connects these functional groups plays a more significant role in tailoring the network topologies and geometries and nature of the cavities of the CPs.⁵ We have recently initiated studies on CPs of the bis(pyridyl) ligand containing secondary amides and phenyl or alkyl groups -(CH₂)_n- as a backbone.⁶ These studies revealed that CPs containing ligands with shorter spacers such as -(CH₂)₂- or -(CH₂)₄- exhibit versatility in producing 1D chains containing cavities, open 2D-networks, chiral 2D-networks and interpenetrated 2D-networks (both parallel and perpendicular modes). On the other hand, the ligands with phenyl, hexyl or octyl spacers have consistently formed 2D-networks which are further linked by amide-to-amide hydrogen bonds.

Fromm's group and others have explored the network geometries of ethanediyl bis(isonicotinate) with Cu(I) halides and AgNO₃.^{7,8} It was observed that diverse types of 1D-chains were afforded depending on the solvents used. Further, M(II)halide (Zn, Hg, Co) complexes of the same ligand were also reported to yield iso-structural metallamacrocycles with inclusion of guest molecules.9 Furthermore, the role of spacers containing ester groups which anchor bis-pyridyl moieties in tailoring the network geometries and properties was demonstrated by Hosseini's group.¹⁰ A set of esterpyridine ligands containing various spacers (hexaethylene glycol, 1,1'-spirobi(indane), dibromofluorene, isomannide, (R)-6,6'-dibromo-1,1'-binaphthyl) were synthesized and their combination with different metal salts produced a variety of novel networks including double stranded interwound linear networks,^{10a} double stranded interwoven,^{10b} triple stranded^{10c} and quadruple-stranded helices.^{10d} In this paper, we wish to present our studies on CPs of an angular bispyridyl ligand (L) containing m-phenylene and ester functionalities as a backbone. We note here that the corresponding amide based derivative of L was explored to form CPs and CP based gels, to the best of our knowledge to date no CPs of L are explored. Generally, angular or V-shaped ligands are known to form helical coordination networks with transition metal ions. Studies on CPs derived from N,N'-bis(4-pyridinecarboxamide)-1,3-benzene and its reverse analogue N,N'-bis-(4-pyridyl)isophthalamide with transition metal salts (e.g., Cu(II) and Zn(II)) revealed to yield mainly 1D-networks.11,12



Department of Chemistry, Indian Institute of Technology, Kharagpur 721302, India. E-mail: kbiradha@chem.iitkgp.ernet.in; Fax: +91 3222 282252; Tel: +91 3222 283346 † Electronic supplementary information (ESI) available: Details of synthesis procedures and characterization of complexes by IR spectra, XRPD and TGA data. CCDC 981869–981874. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ce00123k

The ligand 1,3-phenylene diisonicotinate (L) was synthesized by reacting resorcinol with isonicotinic acid in chloroform in the presence of dicyclohexylcarbodiimide (DCC).¹³ The Cu(I) and Cu(II) metal salts were considered for complexation with L as we have shown earlier that related amide containing ligands have more propensity to form crystalline complexes with these salts. The diffusion of a CH₃CN solution of CuI into a MeOH solution containing ligand L and a liquid aromatic guest resulted in bright orange coloured crystals of complexes $\{(Cu_2I_2)(L)_2 \cdot 2(guest)\}_n$, 1-4, containing CHCl₃ (1), nitrobenzene (2), benzonitrile (3) and bromobenzene (4), respectively, as guests. The single crystal X-ray diffraction analyses revealed that all contain 2D-networks, and 1 crystallized in P2(1)/c while 2-4 crystallized in P2(1)/nspace group (Fig. 1). All the asymmetric units contain one unit each of Cu(1), iodide, ligand L, and guest molecules. The Cu(1) and I⁻ form Cu₂I₂ SBU in which each Cu(I) adopts a tetrahedral geometry as two L and two I are coordinated to it. The isonicotinyl planes of ligand L are nearly perpendicular to its central C₆-ring in all of the four complexes (74.96, 83.74; 67.55, 83.66; 70.55, 82.62; 66.69, 86.20°). However, the position of C=O groups differs, they point in opposite directions in 1 while they are on the same side in 2-4 (Fig. 2a).



Fig. 1 Illustrations of the crystal structure of 2: 2D layer of (4,4)-topology: (a) top view, guest molecules were not shown; (b) side view along the *b*-axis, guest molecules were shown in space filling mode; (c) helical nature of the layer; (d) packing of layers *via* aromatic and ester–ester interactions; (e) dimeric column of C–H…O hydrogen bonded nitrobenzene molecules in **2**.



Fig. 2 Comparisons of the crystal structures of **1** & **2**–4: geometry of L in (a) **1**; (b) **2**–4, notice the difference in ester group orientations. Interior environment remains the same through interdigitation of layers in (c) **1** & (d) **2**–4. Interdigitation through aromatic and O==C···O interactions in (e) **1** & (f) **2**–4.

Interestingly, the Cu-Cu distance in Cu₂I₂ SBU was found to be much shorter (2.634 Å) in 1 than the other three (2.854, 2.776 & 2.822 Å) complexes.14 Nevertheless, in all of the structures, the Cu₂I₂ SBU acts as a four connected planar node with four units of L linked to it and results in a 2D network of (4,4) topology containing rhomboidal cavities of dimension 12.6 \times 32.8 Å². The layers are found to be highly corrugated such that there exist continuous channels within the layers. In other words, the 2D-layer can also be described as the joining of 1D-helices which run along the b-axis (Fig. 1e). These helices contain elliptical channels that are occupied by a column of guest molecules (Fig. 1d). Chloroform molecules were not located in 1; however, aromatic guest molecules in 2, 3 and 4 were located and found to form a dimeric column along the *b*-axis via C-H···O (2.799, 3.283 Å), C-H…N (3.566 Å), and C-H…Br (3.838, 3.974 Å), respectively (Fig. 1f). In 1, the Cu(I) SBUs are joined by the ligand with a distance of 16.716 Å.

The layers pack *via* the interdigitation of adjacent helices which occurs through aromatic interactions between the pyridyl moieties and the central phenyl rings (4.299, 4.180 Å) and O=C···O interactions (Fig. 2). Although the geometry of the ligand is different in 1 and 2–4, the interior environment of the channel remains similar given the interdigitation of the layers. The solvent accessible volumes amount to 31.7%, 29.7%, 31.8% and 31.5%, respectively, in 1–4. We note here that previously the amide analogue of 1 which contains –HN–C₂H₄–NH– in place of –O–C₆H₄–O– in 1 was shown to form a similar type of 2D-layers with Cu₂I₂ SBU.^{6a} Those layers were found to include only CHCl₃/CHBr₃ molecules as guests across the layers but not within the layer.

The reactions of L with $Cu(\pi)$ metal salts such as $Cu(PF_6)_2$ and $Cu(ClO_4)_2$ are also investigated to study the network geometries of the resulted materials, guest inclusion properties, anion influence and also to understand the difference between SBU based and non-SBU based complexes. The reaction of L with $Cu(PF_6)_2$ and $Cu(ClO_4)_2$ resulted in the crystals of complexes { $[Cu(L)_2(H_2O)_2]$ ·2(PF₆)·(CHCl₃)}_n, 5, and { $[Cu_3(L)_6(H_2O)_3)$ (ClO₄)₆]·14(H₂O)}_n, 6, respectively, in a MeOH-H₂O-CHCl₃ solvent system.

The crystal structure analysis of 5 reveals that it crystallized in monoclinic C2/c space group and the asymmetric unit is constituted by one unit each of $Cu(\pi)$, L, PF₆ ion, half chloroform and coordinated water molecules (Fig. 3). The Cu(II) centres adopt an octahedral environment with four ligand units at equatorial sites and two water molecules at axial sites. The geometry of the ligand is somewhat similar to the one observed in complex 1; however, it resulted in the formation of the 1D-network containing M2L2 macrocycles which facilitated the angular nature of the ligand. The CHCl₃ molecule is situated at the centre of M2L2 macrocycles. The 1D-networks are linked to the 2D-network via O-H···O hydrogen bonds between coordinated H₂O and O=C of the ester group (Fig. 3b). We note here that a similar type of hydrogen bonding was also observed in the CPs of amide analogues.^{6f} The layers packed on each other via C-H...O and edge-to-face (3.56 Å) aromatic interactions. It is found that these cavities in 1D-chain are suitable only for CHCl₃, unlike 1-4, as the



Fig. 3 Illustrations of the crystal structure of **5**: (a) 1D-chain containing M_2L_2 macrocycles and rectangular cavities; (b) 2D-layer formed by the joining of 1D-chains *via* O-H···O hydrogen bonds, (c) side view of packing of the 2D-layers.

reactions with other guest molecules failed to produce crystalline materials.

Complex 6 crystallizes in C_2 space group (Fig. 4) and the asymmetric unit is constituted by two Cu(II) ions with occupancies of 1 and 0.5, three units of L, anions and water molecules. The Cu(II) centres exhibit two coordination modes: square pyramidal (Cu1) and distorted octahedral geometry (Cu2). The Cu1 and coordinated H₂O (Cu-O: 2.267(10) Å) lie on the glide plane and connected to four units of L in equatorial positions (Cu-N: 1.984(7), 2.032(7) Å). Whereas, the Cu2 exhibits distorted octahedral geometry with two water molecules at axial sites, one of which exhibited a very weak interaction (2.649 Å) and was removed during final refinement, due to very high thermal motion, using the PLATON squeeze option. The three ligands almost have similar conformational geometries with an overall length (N-atom to N-atom) of 13 Å. Although the metal centre has square planar coordination with respect to pyridyl groups, the angular nature of the ligand results in a tetrahedral building block. The depiction of $Cu(\pi)$ centres as nodes and ligands as node-connections reveals that the network has quartz-type topology and the voids of each network are filled by 4-fold interpenetration of such networks.



Fig. 4 Illustrations of the crystal structure of **6**: (a) coordination geometry around Cu(II) ions; 3D-network with cage-like nature: (b) cylinder mode, (c) space filling mode; (d) depiction of quartz topology by designating Cu(II) as nodes and ligands as node connections; (e) 4-fold interpenetration of networks; (f) tetrahedral water cluster incorporated in the channels of 4-fold interpenetrated nets.

Despite the 4-fold interpenetration, the structure contains three types of channels: two channels were filled by water tetramers and the third one was filled by anions which are hydrogen bonded to coordinated water. It is interesting to mention here that the water tetramers are found to exhibit distorted tetrahedron geometries with O···O distances ranging from 2.2 to 3.2 Å.

The UV-vis absorption spectra of the free ligand (L) and complexes 1-3 in the solid state were recorded at room temperature. The spectrum of L shows peaks at 267 and 300 nm (Fig. 5a). The spectrum of complex 1 shows broad absorption in the range 250-550 nm with three intense peaks at 268, 352 and 520 nm. A similar type of absorption behaviour was also observed for the complexes 2 (256, 350, 507 nm) and 3 (263, 350, 510 nm) with a blue shift in all three peaks compared to 1. The blue shift of absorption edges can be correlated with the longer Cu…Cu distances in SBUs of 2 (2.854 Å) and 3 (2.776 Å) compared to 1 (2.634 Å). A further solid state luminescence study, at the excitation wavelength of 325 nm, was carried out on complexes 1-3 at room temperature (Fig. 5b) to determine if there are any apparent differences in their emission properties. An emission (reddish yellow) peak of complex 1 was observed at 637 nm. As for complex 2, it is blue shifted to 633 nm and becomes sharper compared to 1, while complex 3 exhibits emission band at 634 nm which is broader compared to 1. The luminescence emission of these complexes can be attributed to strong cuprophilic interactions observed in the complexes. At room temperature, all three complexes show a low-energy (LE) broad emission centred around 630 nm. Based on the previous reports on the Cu(I) clusters, the LE emissions are assigned to iodideto-copper charge transfer transition (XMCT, X = halogen).¹⁵

In conclusion, the exo-bidentate bis-pyridyl ligand L was shown to form coordination networks of versatile topologies with Cu(I/II) salts. The networks observed here include a 1D chain with a cavity occupied by anion and CHCl₃ guest molecules, a two-dimensional (4,4) network with elliptical channels which are occupied by variety of guest molecules, and a three-dimensional 4-fold interpenetrated network with quartz topology which accommodates water tetramers. The angular nature of the ligand imparted some helicity into the two-dimensional and three-dimensional networks.



Fig. 5 Optical properties of L (cyan), 1 (red), 2 (green), 3 (blue): (a) UV-vis reflectance spectra, (b) luminescence spectra.

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