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ARTICLE TYPE

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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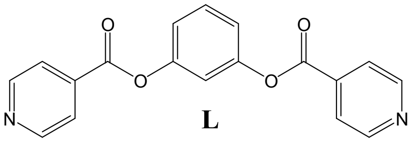
The reactions of a flexible bidentate ligand 1,3-phenylene diisonicotinate (L) with Cu(I/II) salts afforded coordination polymers with varied dimensionalities and guest inclusion capabilities. Complexation of L with CuI resulted in a 2D-network with (4,4) topology and inclusion of guest molecules such as $CHCl_3$, bromobenzene, nitrobenzene and benzonitrile. The treatment of L with $Cu(PF_6)_2$ and $Cu(ClO_4)_2$ resulted in one-dimensional network containing M_2L_2 macrocycles and a 4-fold interpenetrated three dimensional network having quartz topology respectively. The 1D-networks included $CHCl_3$ as guests and interpenetrated 3D-network includes tetrahedral water clusters.

Coordination polymers 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 had 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 play 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 bis(pyridyl) ligands containing secondary amides and phenyl or alkyl groups $-(CH_2)_n-$ as backbone.[6] These studies revealed that CPs containing ligands with shorter spacers such as $-(CH_2)_2-$ or $-(CH_2)_4-$ exhibit versatility in producing 1D chains containing cavities, open 2D-networks, chiral 2D-networks and interpenetrated 2D-networks (both parallel and perpendicular mode). 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 group and others have explored the network geometries of ethanediyl bis(isonicotinate) with Cu(I) halides and $AgNO_3$.[7,8] It was observed that diverse types of 1D-chains were afforded depending on the use of solvents. 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 were demonstrated by Hosseini group.[10] A set of ester-pyridine ligands containing various spacers (hexaethylene glycol, 1,1'-spirobi(indane), dibromo fluorine, *iso*mannide, (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 angular bis-pyridyl 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]



L

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 CH_3CN solution of CuI into a MeOH solution containing ligand **L** and liquid aromatic guest resulted in bright orange coloured crystals of complexes $\{(Cu_2I_2)(\mathbf{L})_2.2(\text{guest})\}_n$, **1**-**4**, containing $CHCl_3$ (**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 *P*2(1)/*c* while **2**-**4** crystallized in *P*2(1)/*n* space group (Figure.1). The asymmetric unit of all contain one unit of each Cu(I), iodide, ligand **L**, and guest molecule. The Cu(I) and I^- form Cu_2I_2 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 C_6-ring in all 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 differ, they point in opposite direction in **1** while they are on the same side in **2**-**4** (Figure.2a).

Interestingly, the Cu-Cu distance in Cu_2I_2 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 the structures, the Cu_2I_2 SBU acts as four connected planar node with four units of **L** are linked to it and results a 2D network of (4,4) topology containing rhomboidal cavities of dimension 12.6x32.8 Å^2. The layers 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 *b*-axis (Figure.1e). These helices contain elliptical channels that are occupied by a column of guest molecules (Figure.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 *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 (Figure.1f). In **1**, the Cu(I) SBU's 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 (Figure.2). Although the geometry of 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-C_2H_4-NH- in place of -O-C_6H_4-O- of **1** was shown by us to form similar type of 2D-layers with Cu_2I_2 SBU.[6a] These layers found to include only $CHCl_3$/$CHBr_3$ molecules as a guest across the layers but not within the layer as was shown here.

The reactions of **L** with Cu(II) 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 $\{[Cu(\mathbf{L})_2(H_2O)_2)]\cdot 2(PF_6)\cdot(CHCl_3)\}_n$, **5**, and $\{[Cu_3(\mathbf{L})_6(H_2O)_3)(ClO_4)_6]\cdot 14(H_2O)\}_n$, **6**, respectively, in MeOH-H_2O-$CHCl_3$ solvent system.

The crystal structure analysis of **5** reveals that it crystallized in monoclinic *C*2/*c* space group and the asymmetric unit is constituted by one unit of each Cu(II), **L**, PF_6 ion, half chloroform and coordinated water molecules (Figure.3). The Cu(II) centres adopt 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 the complex **1**, however it resulted in the formation of 1D-network containing M_2L_2 macrocycles which facilitated given the angular nature of the ligand. The $CHCl_3$ molecule is situated at the centre of M_2L_2 macrocycles. The 1D-networks are linked to 2D-network via O-H···O hydrogen bonds between coordinated H_2O and O=C of ester group (Figure.3b). We note here, 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 (3.56Å) aromatic interactions. It is found that these cavities in 1D-chain are suitable only for $CHCl_3$, unlike **1-4**, as the reactions with other guest molecules failed to produce crystalline materials.

Complex **6** crystallizes in C_2 space group (Figure 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 H_2O (Cu-O 2.267(10) Å) lies 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 exhibits very weak interaction (2.649 Å) and removed during final refinement, due to very high thermal motion, using PLATON squeeze option. The three ligands almost have similar conformational geometries with 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 tetrahedral building block. The depiction of Cu(II) 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. Despite of 4-fold interpenetration, the structure contains three types of channels: two channels were filled by water tetramers and the third one is filled by anions which hydrogen bond to coordinated water. It is interesting to mention here that the water tetramers 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 solid state were recorded at room temperature. **L** shows peaks at 267 and 300 nm (Figure 5a). Complex **1** shows broad absorption in the range 250-550 nm with three intense peaks at 268, 352 and 520 nm. 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). Further solid state luminescence study, at the excitation wavelength of 325 nm, was carried out on complexes **1**-**3** at room temperature (Figure 5b) to notice 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 luminescent emission of these complexes can be attributed to strong cuprophlic 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 iodide-to-copper charge transfer transition (XMCT, X=halogen).[15]

In conclusion, exo-bidentate bis-pyridyl ligand **L** was shown to form coordination networks of versatile topologies with Cu(I/II) salts. The networks observed here includes 1D chain with cavity occupied by anion and $CHCl_3$ guest molecules, two-dimensional (4,4) network with elliptical channels which are occupied by variety of guest molecules, and three-dimensional 4-fold interpenetrated network with quartz topology which accommodates water tetramers. The angular nature of the ligand imparted some helicity in to the two-dimensional and three-dimensional networks.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Details of synthesis procedures and characterizations of complexes by IR spectra, XRPD and TGA data. See DOI: 10.1039/b000000x/

‡ Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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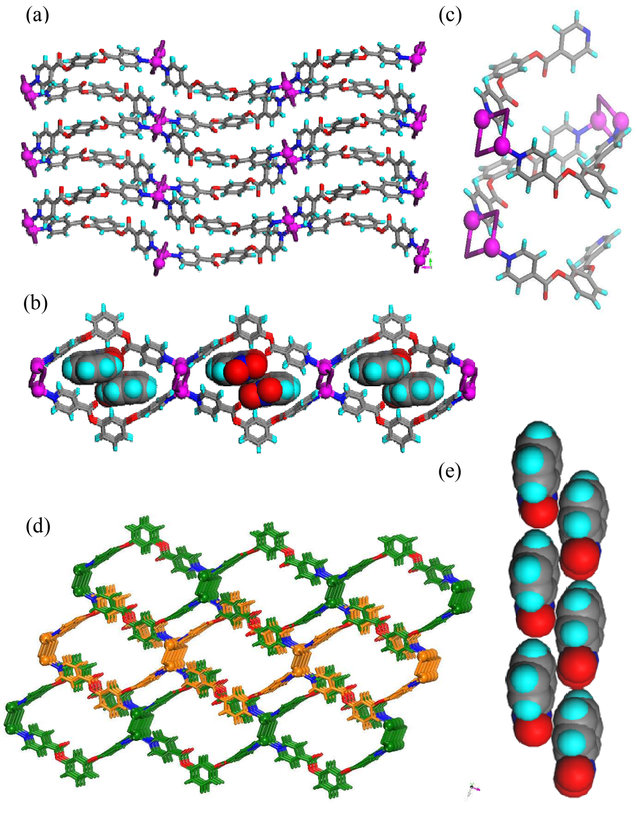


Figure 1. Illustrations for the crystal structure of **2**: 2D layer of (4,4)-topology: (a) top view, guest molecules were not shown; (b) side view along b-axis, guest molecules were shown in space filling mode; (c) helical nature of the layer; (d) packing of layers via aromatic and ester-ester interactions;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

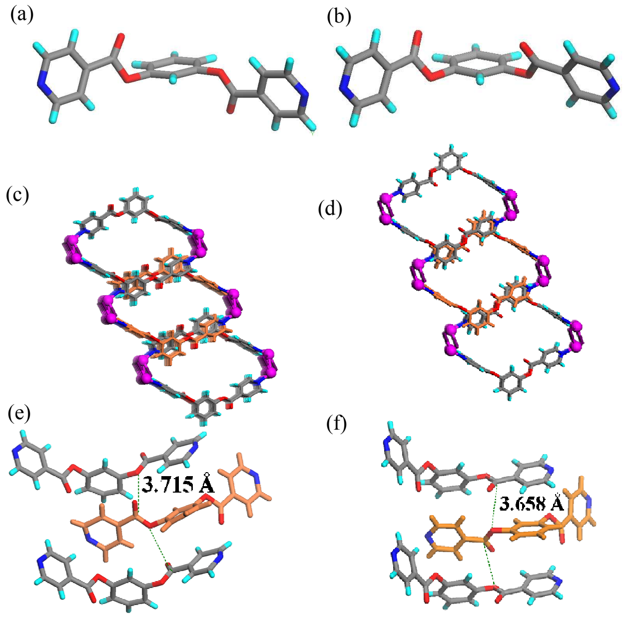


Figure 2. Comparisons of the crystal structures of **1** & **2**-**4**: geometry of **L** in (a) **1**; (b) **2**-**4**, notice the difference in ester group orientations. Interior environment remains same through interdigitation of layers in (c) **1** & (d) **2**-**4**. Interdigitation through aromatic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

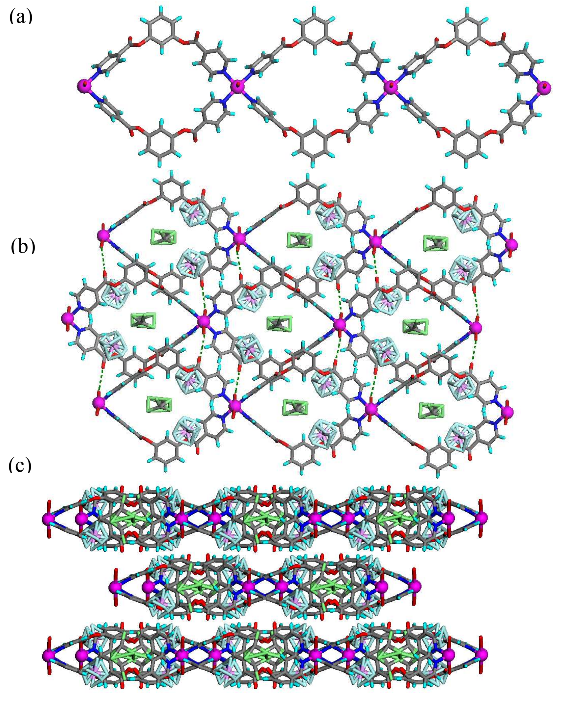


Figure 3. Illustrations for the crystal structure of **5**: (a) 1D-chain containing M_2L_2 macrocycles and rectangular cavities; (b) 2D-layer formed by the joining of 1D-chains via O-H···O hydrogen, (c) side view of packing of the 2D-layers.

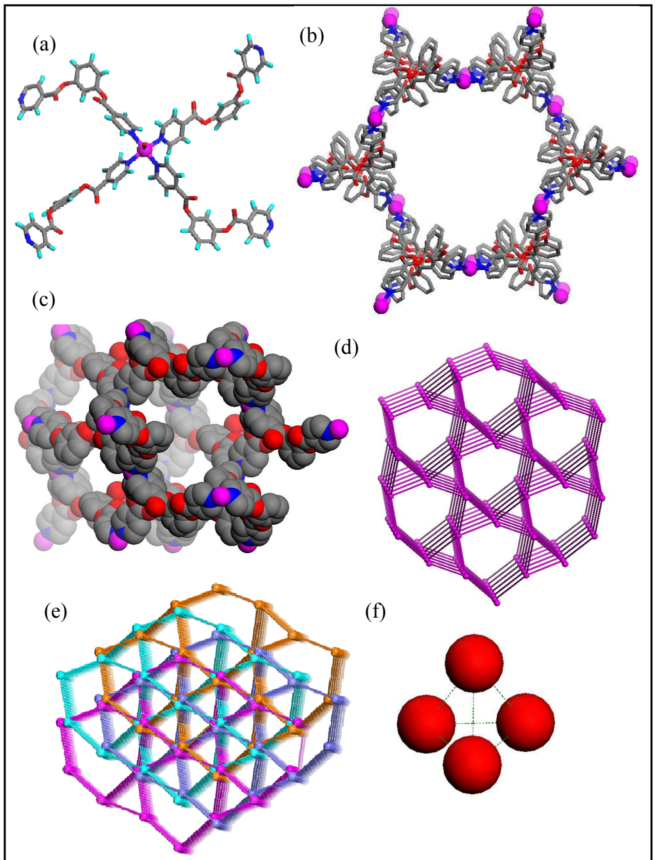


Figure 4. Illustrations for the crystal structure of **6**: (a) coordination geometry around Cu(II) ions; 3D-network with cage like nature (b) cylinder mode; (c) space filling mode, (d) depiction of quartz topology by reducing Cu(II) to nodes and ligands to node connections (e) 4-fold interpenetration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

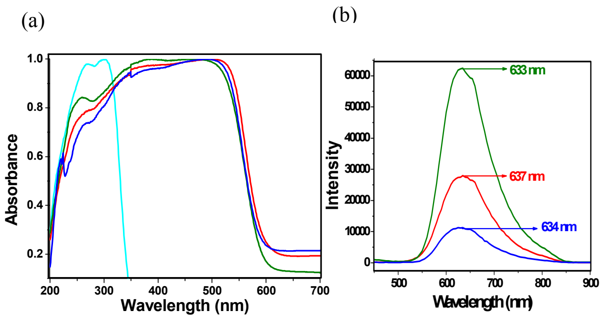
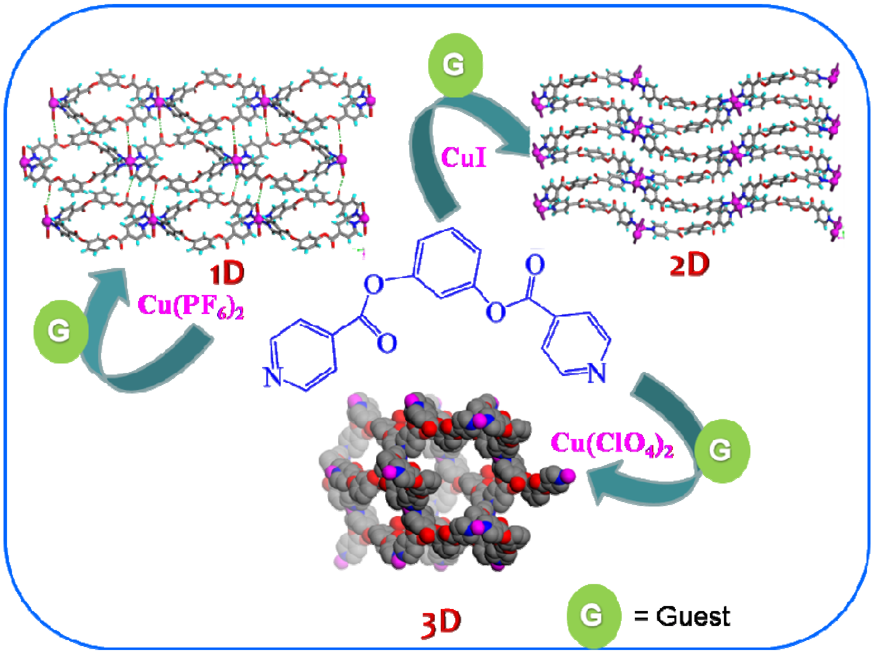


Figure 5. Optical properties of **L** (cyan), **1** (red), **2** (green), **3** (blue): (a) UV-vis reflectance spectra, (b) luminescence spectra.


G
CuI
2D
1D
Cu(PF6)2
G
O
O
O
O
N
N
Cu(ClO4)2
G
3D
G = Guest