

Metal assisted self-assembled nano sized porous 2-D structures incorporating malonic acid dihydrazide and melamine

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Abstract The solids $\text{Cu}(\text{MADH})_2 \cdot \text{Cl}_2 \cdot 2\text{TAT} \cdot 9\text{H}_2\text{O}$ and $\text{Zn}(\text{MADH})_2 \cdot \text{Cl}_2 \cdot 2\text{TAT} \cdot 2\text{H}_2\text{O}$ (MADH = malonic acid dihydrazide and TAT = melamine) characterized by spectroscopic and elemental analysis, have been investigated by transmission electron microscope. Microstructure at high magnification revealed the supramolecular assembly of MADH and TAT into a mesh structure in presence of Cu(II) metal ions and tubular structure with intermittent openings on the tube walls and Y- junctions for Zn(II) complex. The mesh structure of the Cu(II) complex has uniformly spaced 40–50 nm long and 20–30 nm wide openings, while the diameter of the tubular structure of the Zn(II) complex is 50–200 nm. The assembly of the supramolecular structure is attributed to H-bonding and the different architectures of the assembly with different metal ions to the difference in waters of crystallization. The potential of the complex for gas adsorption was also investigated.

In supramolecular systems, metal ions have been exploited as a template in the construction of novel materials especially for the reorganization of compo-

nents together through H-bonding. Such interactions have potential applications in the design of metal-based drugs [1]. However, slight modifications in the skeletal structure of such systems have shown drastic changes in their conducting properties. In this context, non-covalent interactions including H-bonding have been exploited in the development of synthetic supramolecular materials like grids [2], boxes [3], rods [4], tubes [5], as well as interlocked systems [6] earlier. Very recently Mishra et al. [7] have observed that malonic acid dihydrazide (MADH) assembled with melamine (TAT) in the presence of Cu(II) and Zn(II) salts led the supramolecular systems of the compositions $\text{Cu}(\text{MADH})_2 \cdot \text{Cl}_2 \cdot 2\text{TAT} \cdot 9\text{H}_2\text{O}$ and $\text{Zn}(\text{MADH})_2 \cdot \text{Cl}_2 \cdot 2\text{TAT} \cdot 2\text{H}_2\text{O}$ and have characterized these structures by spectroscopic techniques in addition to their elemental and mass studies [7]. However, the architecture of the self-assembly into a particular geometrical arrangement could not be studied. It was therefore necessary to look into the morphology of these assembled systems using transmission electron microscopic study and motivated the present study.

The complexes were prepared using a procedure reported earlier [7] by the addition of the selected MADH (2.0 mM) in methanol separately to 1.0 mM of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}/\text{ZnCl}_2$ solution in methanol.

Empirical composition of the complexes as determined by their elemental analysis showed the presence of monomeric unit (M/Z; 812.5 for Cu(II) complex and 661.3 for Zn(II) complex). However, peaks observed also at higher mass showed aggregated nature of the system, which was also supported by the hump-up observed in the X-ray diffraction of the complexes. Upon heating, the complexes shrunk initially at 80 °C, but decomposition started only after 200 °C.

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The presence of the water molecules in these two complexes was identified by their IR spectrum which showed broad peak centered between 3460 and 3450 cm^{-1} . ESR spectrum of the Cu(II) complex in solid state showed g_{\parallel} and g_{\perp} values at 2.6 and 2.3, respectively indicating that unpaired electron of the Cu(II) lies in dx^2-y^2 orbital. This complex also showed a normal magnetic moment value μ_{eff} 2.4 BM discarding any Cu–Cu interaction.

Before microscopic examination, the powders of the complexes were sonicated in methanol separately. The sonicated powder suspended in methanol solution was dispersed on holey carbon grid and was taken to transmission electron microscopy (TEM) study by JEOL 200CX TEM. Microscopy was carried out at a low accelerating voltage of 100 kV and low beam currents to avoid damage due to high electron flux.

C(II)-complex microstructure

Rectangular mesh type structure with perforations was observed in TEM and a typical structure is shown in Fig. 1. The corresponding diffraction pattern is shown in Fig. 2. These perforations in the structure are uniformly spaced with 40–50 nm length and 20–30 nm width. Some areas showed clustering of Cu(II) with dark contrast. These clusters varied in size ranges from 100 nm–1 μm . These structures have grown to varied sizes based on a particular length to width ratio. Typical ratios are in the range of 12–14.

Figure 2 shows the electron diffraction pattern from the Cu(II) complex. The ultra-fine scale microstructure of the sample is responsible for the occurrence of broad rings in the pattern, in lieu of sharp rings expected from a polycrystalline material. These rings also exhibit intensity maxima characteristic of texture (due to the

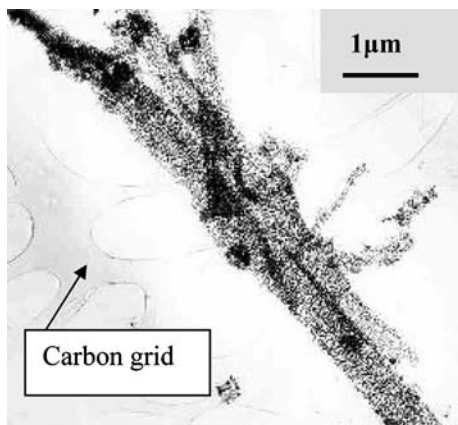


Fig. 1 Rectangular mesh structures of Cu(II) complex

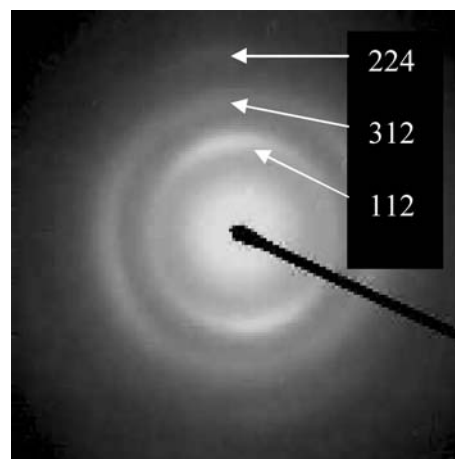


Fig. 2 Electron diffraction pattern of Cu(II) complex

high length to width ratio and crystallographic orientation of these meshes). Some ambiguity exists in indexing the pattern because of the disappearance of the low radius initial rings under the brightness of the transmitted beam. Therefore, the diffraction pattern is indexed to a tetragonal lattice on the basis of the X-ray pattern obtained in the earlier study [8].

Zn(II)-complex microstructure

A tubular structure with perforations on the surface of the tubules was observed in this case as shown in Fig. 3. Y-junctions of the tubes were also noticed at many areas. The wall thickness of the tube varied along its length. These tubules generally have diameters in the range of 50–200 nm. Further, the tubules have opened up at many locations along their length. (Fig. 3)

The mesh structure in the Cu(II) complex can be explained with the help of Fig. 5 and 6. The whole

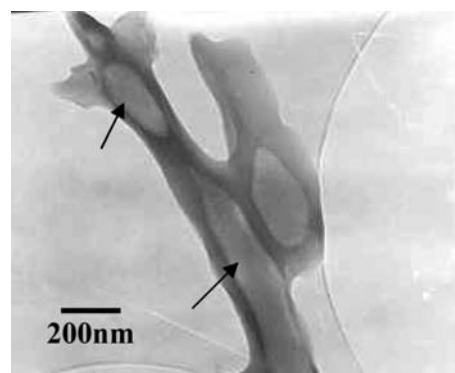


Fig. 3 Zn(II) complex showing Y-tube structure. Arrows show openings on the surface of tubule

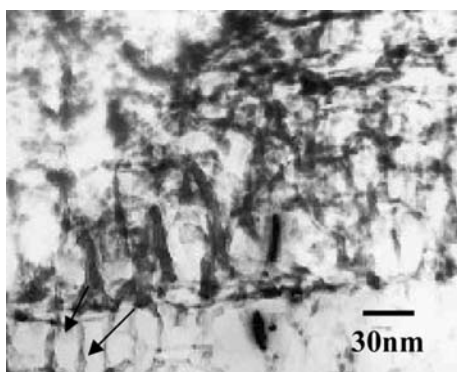


Fig. 4 Magnified view of Cu(II) complex. Arrows indicate cavities

open skeletal structure framework in the assembled state along all directions could develop large size cavity as shown in Fig. 7. The high length to width ratios of these structures can be attributed to the rapid assembly of the complex along a single axis, and a hindered growth in the other directions as proposed below in Fig. 5b.

The walls of this mesh structure could further be porous with an approximate pore size of 0.5 nm. This could be because of H-bonding between carbonyl groups of malonic acid and amino part of TAT which leads to the development of these smaller size pockets

in the self-assembled structure as proposed earlier by Mishra et al. [1] (Fig. 5a). However, these pores are not imaged in the high resolution microstructure of the complex shown in Fig. 4.

As modeled in Fig. 5a, it was observed that replacement of Cu(II) by Zn(II) lead to two different ways of assembling the same components viz. MADH and TAT. Further the number of molecules of water of crystallization in the two complexes after drying was also observed to be different in each case. The water of crystallization in the Zn(II) complex was found to be 0.5 H₂O while the Cu(II) complex showed a water of crystallization of 9H₂O. Probably, this difference in number of molecules of water in the two complexes is leading to the two different architectures—the lesser number leading to the folding of the chain into a tubule in the shorter direction i.e. perpendicular to the direction of preferred axis of molecular assembly(Fig. 6).

In this context, it would not be out of place to mention that such assembled supramolecular systems could be future candidate materials for the recognition of ions or molecules of variable sizes at a time, especially in individual application where particles of various sizes have to be absorbed or desorbed as per requirement. However, this surmise calls for deeper investigation. On a preliminary scale when the smoke of tobacco was passed over a pellet of this complex

Fig. 5 (a) Self-assembly of the Cu(II) complex—After Mishra et al[1]. (b) Probable mechanism of assembly that produced high length-to-width ratios giving rise to long mesh structures shown in Fig. 1

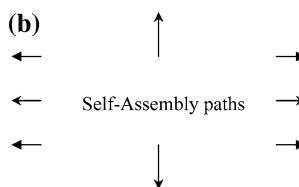
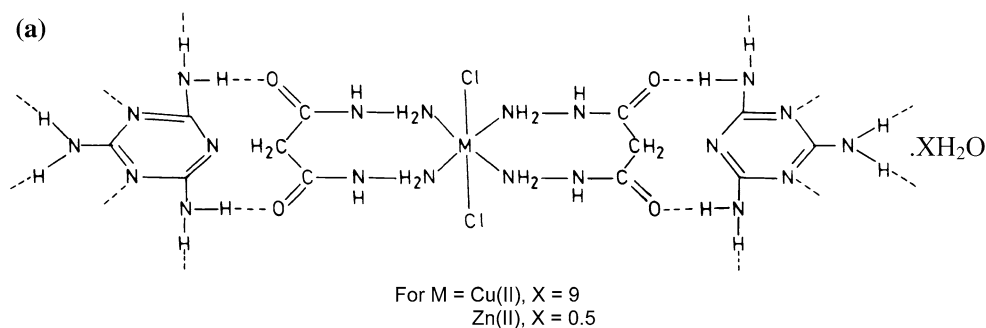
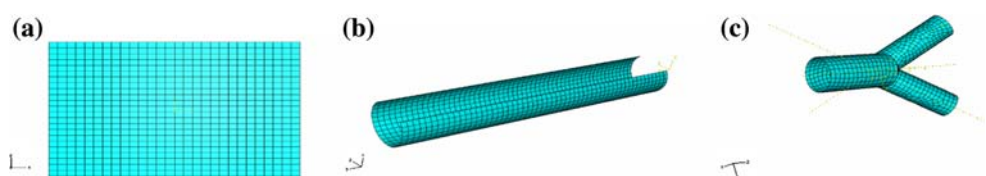


Fig. 6 The mesh (a), curling of mesh into a tubule (b) and Y-junctions of tubules (c) of the assemblies



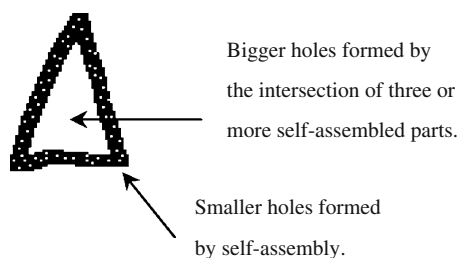


Fig. 7 Bigger and smaller holes formed during assembly

(Cu(II)) it indicated the presence of CO and NO peaks in IR spectrum of the complex (A probable case of gaseous sensing). Further experiments are on the way to explore the effect of other metal ions on the architecture of the assembly and the potential of these assemblies as gas absorbers.

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