

## An eight-connected metal organic framework based on Cu<sub>5</sub> clusters: Synthesis, structure, magnetic and catalytic properties

Debajit Sarma & Srinivasan Natarajan\*

Framework Solids Laboratory, Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore 560 012, India

Email: snatarajan@sscu.iisc.ernet.in

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A reaction of copper acetate, 5-nitroisophthalic acid in a water-methanol mixture under solvothermal condition results in a new metal-organic framework compound, [Cu<sub>5</sub>(μ<sub>3</sub>-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>{(NO<sub>2</sub>)-C<sub>6</sub>H<sub>3</sub>-(COO)<sub>2</sub>}]<sub>4</sub>.5H<sub>2</sub>O, (**1**). The compound contains Cu<sub>5</sub> pentameric cluster units connected by 5-nitro isophthalate (NIPA) moieties forming a CdCl<sub>2</sub>-like layer, which are further connected by another NIPA moiety forming the three-dimensional structure. The water molecules in (**1**) can be reversibly adsorbed. The removal of water accompanies a change in the colour as well as a structural re-organization. Magnetic studies suggest strong antiferromagnetic correlations between the Cu<sub>5</sub> cluster units. The compound (**1**) exhibits heterogeneous Lewis acid catalysis for the cyanosilylation of imines with more than 95 % selectivity. Compound (**1**) has been characterized by IR, UV-vis, TGA, powder XRD studies.

**Keywords:** Coordination polymers, Metal organic framework, Pentameric clusters, Cyanosilylation, Polycarboxylates, Imines, Copper

The contemporary interest in the design and synthesis of inorganic coordination polymers (also known as metal-organic framework (MOF) compounds) is primarily due to the applications in the areas for gas storage, sensors, magnetism, non-linear optics, luminescence, ion exchange, catalysis, etc.<sup>1</sup> The necessary feature for most of the above applications is to have sufficiently large and permanent porosity available within the framework.<sup>2</sup> These compounds also presents unique possibilities of combining the well developed chemistry of the organic and the inorganic.<sup>3</sup> The inorganic part has been explored for the development of multidimensional molecular based magnets and more recently, the “porous magnets”.<sup>4</sup> The long range magnetic ordering in a material requires considerable orbital overlap between the nearest neighbor metal centers in these compounds. There are intense efforts to synthesize newer compounds possessing metal clusters or -M-O-M-bonds.<sup>5</sup>

Aromatic polycarboxylate ligands have proved to be good building blocks for the assembly of coordination polymers as well as multidimensional supramolecular networks. Several interesting compounds have been reported using the tricarboxylic acid, 1,3,5-benzenetricarboxylate (trimesic acid).<sup>6</sup>

5-Nitro isophthalic acid closely resembles the 1,3,5-benzenetricarboxylic acid. The presence of the nitro-group, however, reduces the symmetry. This acid can function: (i) as a hydrogen bond acceptor and participate in the formation of polymeric networks, (ii) as an electron-donating group, and, (iii) as an enhancer of the crystallization, as the nitro group would aide the crystallizing in the aqueous medium. Despite these advantages, there are only a few reports in the literature on the formation of MOFs using 5-nitro isophthalic acid.<sup>7</sup>

As part of a study to explore the reactivity of 5-nitroisophthalate in the presence of transition metals, we have investigated the formation of new compounds using copper salts. During the course of this study, we have now prepared a new three dimensional compound, [Cu<sub>5</sub>(μ<sub>3</sub>-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>{(NO<sub>2</sub>)-C<sub>6</sub>H<sub>3</sub>-(COO)<sub>2</sub>}]<sub>4</sub>.5H<sub>2</sub>O, (**1**). Compound (**1**) possesses unique pentameric copper clusters, that are held together by nitroisophthalate to form a three-dimensional structure. We report herein, the synthesis, structure and properties of (**1**).

### Materials and Methods

The reagents needed for the synthesis were used as received, i.e., Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O [CDH (India), 98 %],

5-nitroisophthalic acid, [Lancaster (U.K.), 99 %] and methanol CDH (India), 98 %]. The water used was doubly distilled through a Millipore membrane.

#### Synthesis of compound (1)

A mixture containing  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$  (0.060 g, 0.3 mM), 5-nitroisophthalic acid (0.042 g, 0.2 mM), 3 mL methanol and 5 mL of water was heated in a PTFE-lined stainless steel autoclave at 125 °C for 72 h to give light blue crystals of (1) (the yield was ~73 % based on Cu). The product was washed with deionized water under vacuum, and dried at ambient conditions. The IR spectrum was recorded on a KBr pellet (Perkin-Elmer, Spectrum 1000). The IR spectra exhibited typical peaks corresponding to the hydroxyl group, nitro group, carboxylate groups of the compounds (Supplementary Data, Fig. S1). IR (KBr):  $\gamma_{\text{as}}(\text{O}-\text{H}) = 3215 - 3615 \text{ cm}^{-1}$ ,  $\gamma_{\text{s}}(\text{C}-\text{H})_{\text{aromatic}} = 3060$  and  $3095 \text{ cm}^{-1}$ ,  $\gamma_{\text{s}}(\text{C}=\text{O}) = 1618 \text{ cm}^{-1}$ ,  $\delta(\text{H}_2\text{O}) = 1530 \text{ cm}^{-1}$ ,  $\delta(\text{COO}) = 1458 \text{ cm}^{-1}$ ,  $\gamma_{\text{s}}(\text{N}-\text{O}) = 1357 \text{ cm}^{-1}$ ,  $\gamma_{\text{s}}(\text{C}-\text{C})_{\text{skeletal}} = 1085 \text{ cm}^{-1}$ ,  $\delta(\text{CN})_{\text{skeletal}} = 920 \text{ cm}^{-1}$  and  $\delta(\text{CH}_{\text{aromatic}})_{\text{out of plane}} = 780 \text{ cm}^{-1}$ . Anal. (%): Calcd for (1): C, 27.72; H, 2.62; N, 4.04. Found: C, 28.31; H, 3.12; N, 4.62.

#### XRD and single-crystal structure studies

Powder X-ray diffraction (XRD) patterns were recorded on well ground samples in the  $2\theta$  range 5-50° using Cu- $K_{\alpha}$  radiation (Philips X'pert). The XRD patterns indicated that the product is a new material; the pattern being entirely consistent with the simulated XRD pattern generated based on the structure determined using the single crystal X-ray studies (Supplementary Data, Fig. S2).

A suitable single crystal was carefully selected under a polarizing microscope and glued carefully to a thin glass fiber. The single crystal data were collected on a Bruker AXS Smart Apex CCD diffractometer at 293(2) K. The X-ray generator was operated at 50 kV and 35 mA using Mo- $K_{\alpha}$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. Data were collected with  $\omega$  scan width of 0.3°. A total of 606 frames were collected in three different setting of  $\phi$  (0, 90, 180°) keeping the sample-to-detector distance fixed at 6.03 cm and the detector position ( $2\theta$ ) fixed at -25°. The data were reduced using SAINTPLUS<sup>8</sup> and an empirical absorption correction was applied using the SADABS program.<sup>9</sup> The structure was solved and refined using SHELXL97<sup>10</sup> present in the WinGx suit of programs (ver. 1.63.04a).<sup>11</sup> The hydrogen position of the  $\mu_3$ -OH groups and the water molecules in compound (1)

could not be located from the difference Fourier maps. The possible hydrogen positions were arrived at based on the bond valence sum (BVS) calculations for the  $\mu_3$ -OH group.<sup>12</sup> All the hydrogen atoms of the carboxylic acids were initially located in the difference Fourier maps, and for the final refinement, the hydrogen atoms were placed in geometrically ideal positions and held in the riding mode. Restraints for the bond distances were used during the refinement for holding the hydrogen atoms in place of the water molecules. Final refinement included atomic positions for all the atoms, anisotropic thermal parameters for all the non-hydrogen atoms, and isotropic thermal parameters for all the hydrogen atoms. Full-matrix least-squares refinement against  $|F^2|$  was carried out using the WinGx package of programs.<sup>11</sup> Details of the structure solution and final refinements is given in Table 1 and selected bond distances are given in Table 2.

#### Heterogeneous catalytic studies

The reagents for the heterogeneous cyanosilylation experiments, N-benzilidine aniline and trimethylsilyl

Table 1 – Crystal data and structure refinement parameters for the compound,  $\text{Cu}_5(\mu_3\text{-OH})_2(\text{H}_2\text{O})_6\{(\text{NO}_2)\text{-C}_6\text{H}_3\text{-(COO)}_2\}_4 \cdot 5\text{H}_2\text{O}$ , (1)

Empirical formula	$[\text{Cu}_5(\mu_3\text{-OH})_2(\text{H}_2\text{O})_6\{(\text{NO}_2)\text{-C}_6\text{H}_3\text{-(COO)}_2\}_4] \cdot 5\text{H}_2\text{O}$
Formula wt	1386.36
Crystal system	Triclinic
Space group	P-1
<i>a</i> (Å)	10.7739(9)
<i>b</i> (Å)	11.5683(10)
<i>c</i> (Å)	11.5923(8)
$\alpha$ (°)	75.049(7)
$\beta$ (°)	63.522(8)
$\gamma$ (°)	62.599(8)
Volume (Å <sup>3</sup> )	1145.63(16)
<i>Z</i>	2
<i>T</i> (K)	293(2)
$\rho_{\text{calc}}$ (g cm <sup>-3</sup> )	1.992
$\mu$ (mm <sup>-1</sup> )	2.406
$\theta$ range (deg.)	2.39 to 26.00
$\lambda$ (Mo- $K_{\alpha}$ ) (Å)	0.71073
<i>R</i> <sub>int</sub>	0.0434
Reflection collected	12662
Unique reflections	4498
Number of parameters	379
<i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> 1 = 0.0364, <i>wR</i> 2 = 0.0961
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0489, <i>wR</i> 2 = 0.0996
$R_1 = \sum  F_o  -  F_c  / \sum  F_o $ ; $wR_2 = \{ \sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)] \}^{1/2}$ ; $w = 1 / [\rho^2(F_o)^2 + (aP)^2 + bP]$ ; $P = [\max(F_o, O) + 2(F_c)^2] / 3$ , where $a = 0.0548$ and $b = 0.0000$ for (1).	

Table 2 – Selected observed bond distances in the compound, Cu<sub>5</sub>(μ<sub>3</sub>-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>{(NO<sub>2</sub>)-C<sub>6</sub>H<sub>3</sub>-(COO)<sub>2</sub>}<sub>4</sub>.5H<sub>2</sub>O, (1)

Bond	Distances (Å)	Bond	Distances (Å)	Bond	Distances (Å)
Cu(1)-O(1)#1	1.940(2)	Cu(2)-O(3)	1.951(3)	Cu(3)-O(7)#5	1.902(2)
Cu(1)-O(1)#2	1.940(2)	Cu(2)-O(4)#4	1.961(2)	Cu(3)-O(8)#1	1.926(2)
Cu(1)-O(2)#3	1.992(2)	Cu(2)-O(2)	1.972(2)	Cu(3)-O(9)	1.971(3)
Cu(1)-O(2)	1.992(2)	Cu(2)-O(5)	1.991(2)	Cu(3)-O(2)	1.990(2)
Cu(1)-O(10)	2.587(2)	Cu(2)-O(6)	2.383(2)	Cu(3)-O(10)	2.394(3)
Cu(1)-O(10)#3	2.587(2)				

Symmetry transformations used to generate equivalent atoms: #1  $x-1, y, z$ ; #2  $-x+2, -y+1, -z$ ; #3  $-x+1, -y+1, -z$ .

cyanide (Aldrich) were used as received. The reagents were taken in a 100 mL round bottom flask with the freshly distilled DCM solvent. After the addition of the catalyst, copper nitroisophthalate, the mixture was stirred for 6 h at 0 °C in N<sub>2</sub> atmosphere. The product was filtered through Millipore membrane filters to remove the catalyst particles. The supernatant liquid was dried under vacuum to remove the solvent. The product was analyzed and evaluated for the conversion of the reactants.

## Results and Discussion

### Structure of [Cu<sub>5</sub>(μ<sub>3</sub>-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>{(NO<sub>2</sub>)-C<sub>6</sub>H<sub>3</sub>-(COO)<sub>2</sub>}<sub>4</sub>].5H<sub>2</sub>O, (1)

The asymmetric unit of Cu<sub>5</sub>(μ<sub>3</sub>-OH)<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub>{(NO<sub>2</sub>)-C<sub>6</sub>H<sub>3</sub>-(COO)<sub>2</sub>}<sub>4</sub>.5H<sub>2</sub>O, (1) consists of 40 non-hydrogen atoms, of which three Cu<sup>2+</sup> ions are crystallographically independent along with two 5-nitroisophthalate (NIPA), one μ<sup>3</sup>-hydroxyl groups, three coordinated water molecule and three lattice water molecules (Supplementary Data, Fig. S3). One of the Cu<sup>2+</sup> ions Cu(1) occupies a special position (1e) with a site multiplicity of 0.5. Similarly, one of the lattice water molecules [O (100)], also occupies a special position (1b) with a site multiplicity of 0.5. The copper species in (1) forms a pentameric cluster (Fig. 1). The Cu<sub>5</sub> clusters are formed by the connectivity involving two μ<sub>3</sub> hydroxyl groups. The central copper, Cu(1), is also connected with the other copper atom, Cu(2), through a μ<sub>2</sub>-H<sub>2</sub>O molecule. Thus, Cu(1) has an octahedral environment and Cu(2) and Cu(3) have square pyramidal coordination with respect to their oxygen neighbors. The Cu – O distances are in the range of 1.902(2) – 2.587(2) Å (avg. Cu(1) – O = 2.173, Cu(2) – O = 2.052, Cu(2) – O = 2.037Å). The longer Cu – O distances are associated with the μ<sub>2</sub>-H<sub>2</sub>O molecule. The Cu – O bond angles are in the range 79.74(10)–180.00(13)°.

The two nitroisophthalates (NIPA) unit exhibits differences in their connectivity with copper. Thus, NIPA(1) is connected to three Cu<sup>2+</sup> ions through three

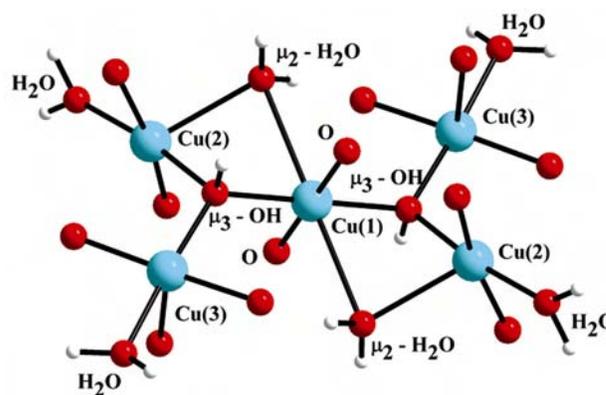


Fig. 1 – The Cu<sub>5</sub> pentameric cluster. Note that the μ<sub>3</sub>-OH group connects all the copper atoms and μ<sub>2</sub>-OH<sub>2</sub> unit connects the two copper centers (see text).

carboxylate oxygen while the fourth carboxylate oxygen along with the oxygen of the nitro group remains non-bonded (Supplementary Data, Fig. S4). The other acid, NIPA(2) is also connected to three Cu<sup>2+</sup> ions, but through one oxygen atom from each of the carboxylate units along with that of the nitro group (Supplementary Data, Fig. S5). The carboxylate connectivity of NIPA(1) with copper results in the formation of a one dimensional ladder along the (1 0 0) axis (Fig. 2). The carboxylate connectivity of NIPA(2), on the other hand, results in a two-dimensional layer ( Fig. 3a). In this layer, each NIPA(2) is connected to six pentameric cluster and each cluster, in turn, is connected to three NIPA(2) unit. The pentameric cluster and the NIPA(2), thus, forms a binodal net (6, 3 net) with a Schläfli symbol of (4<sup>3</sup>)<sub>2</sub>(4<sup>6</sup>.6<sup>6</sup>.8<sup>3</sup>). This net connectivity resembles the bonding observed in the CdCl<sub>2</sub> structure (Fig. 3b). The one-dimensional Cu–NIPA(1) units pillar the layer formed by the Cu–NIPA(2) units forming an overall three-dimensional structure (Fig. 4). One can view the structure as a two-dimensional CdCl<sub>2</sub>-like layer connected through the NIPA(1) unit giving rise to the three-dimensional structure.

CdCl<sub>2</sub>-like layers pillared by the carboxylate units have been observed earlier.<sup>13</sup> In the lanthanum compound,

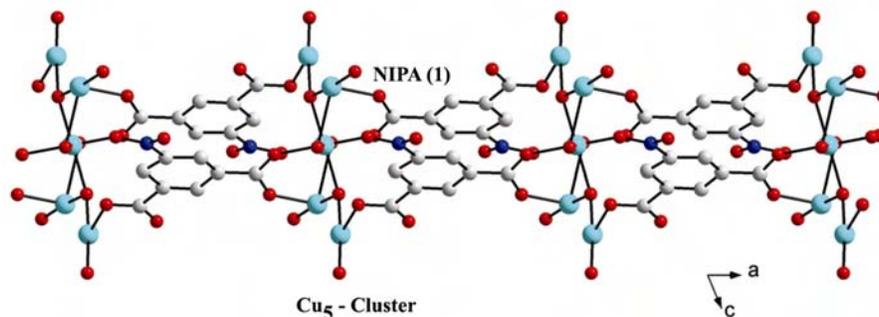


Fig. 2 – The one-dimensional ladder formed by the connectivity between the  $\text{Cu}_5$  and NIPA(1) units.

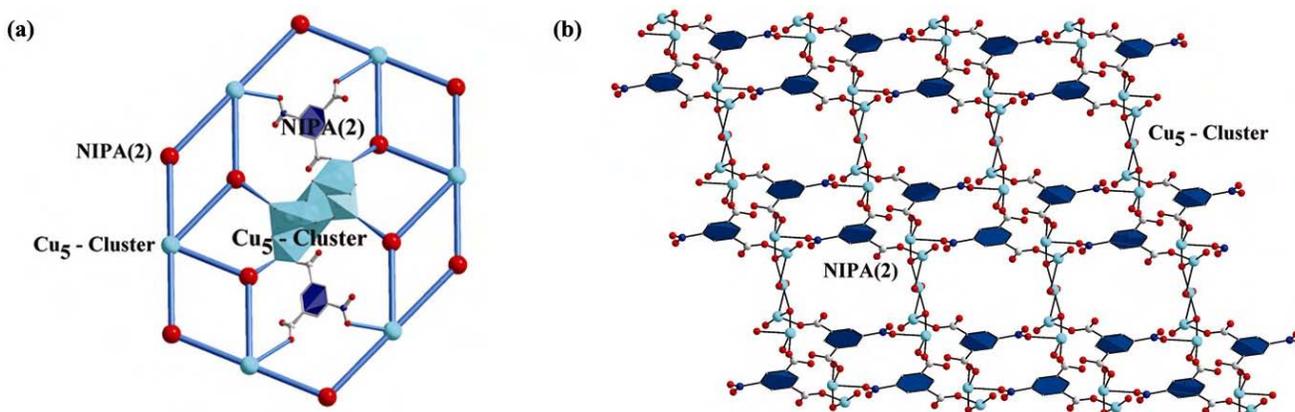


Fig. 3 – (a) View of the two dimensional layers formed by the connectivity between the  $\text{Cu}_5$  and NIPA (2) units. (b) The  $\text{CdCl}_2$ -like layer formed by the NIPA(2) and the  $\text{Cu}_5$  units.

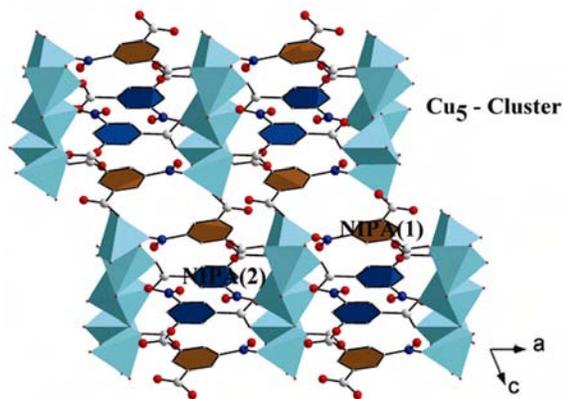


Fig. 4 – The three dimensional structure of (1).

$[\text{M}_2\text{-(H}_2\text{O)}_4][\{\text{C}_5\text{H}_3\text{N(COO)}_2\}_2\{\text{C}_6\text{H}_4\text{(COO)}_2\}]$ ,  $\text{M} = \text{La, Pr, and Nd}$ , the layers are formed by the connectivity between  $\text{M}_2\text{O}_{14}\text{N}_2$  dimers and the pyridine-2,3-dicarboxylate units. This layer is pillared (cross-linked) by the terephthalate unit forming the three-dimensional structure. In (1), the connectivity between the  $\text{Cu}_5$  units and one of the NIPA acids forms the  $\text{CdCl}_2$ -like layers. The second NIPA acid connects the  $\text{Cu}_5$  pentameric units of the adjacent

layer similar to the terephthalate units in  $[\text{M}_2\text{-(H}_2\text{O)}_4][\{\text{C}_5\text{H}_3\text{N(COO)}_2\}_2\{\text{C}_6\text{H}_4\text{(COO)}_2\}]$  (Fig. 5).

The presence of the water molecules, coordinated and lattice water gives rise to  $\text{O-H}\cdots\text{O}$  type hydrogen bond interactions. The important observed  $\text{O-H}\cdots\text{O}$  interactions with  $\text{O}\cdots\text{O}$  contact distances are in the range of 2.652(3) – 2.852(7) and the  $\text{O-H}\cdots\text{O}$  bond angles are in the range of 146 – 172. This suggests that the hydrogen bond interactions are relatively strong.<sup>14</sup> The important hydrogen bond interactions are listed in Table 3. From a cluster connectivity view, each pentameric cluster is connected to eight other clusters and forms an eight connected node (Fig. 6a). A topological analysis of the compound shows that it forms a uninodal eight connected net with  $3^6.4^{18}.5^3.6$  topology (Fig. 6b).

#### Thermogravimetric studies

The thermogravimetric analysis (TGA) (Metler-Toledo) was carried out in oxygen atmosphere (flow rate = 20 mL/min) in the temperature range 30-850 °C (heating rate = 5 °C/min) (Supplementary Data, Fig. S6). The TGA studies indicate that compound (1)

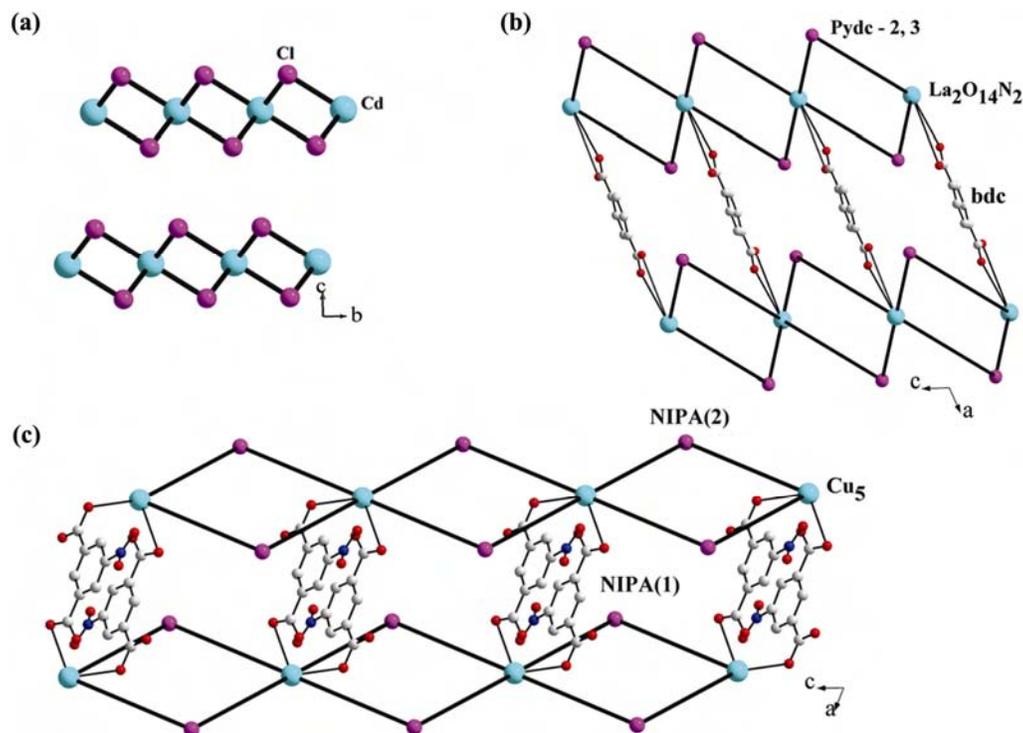


Fig. 5 – (a) The CdCl<sub>2</sub> layer. (b) The CdCl<sub>2</sub>-like layer observed in [M<sub>2</sub>-(H<sub>2</sub>O)<sub>4</sub>][{C<sub>5</sub>H<sub>3</sub>N(COO)<sub>2</sub>}<sub>2</sub>{C<sub>6</sub>H<sub>4</sub>-(COO)<sub>2</sub>}], M=La, Pr, and Nd. (c) The CdCl<sub>2</sub>-like layer observed in (1). The layers are cross-linked by terephthalate units in [M<sub>2</sub>-(H<sub>2</sub>O)<sub>4</sub>][{C<sub>5</sub>H<sub>3</sub>N(COO)<sub>2</sub>}<sub>2</sub>{C<sub>6</sub>H<sub>4</sub>-(COO)<sub>2</sub>}] and NIPA(1) in (1) (see text).

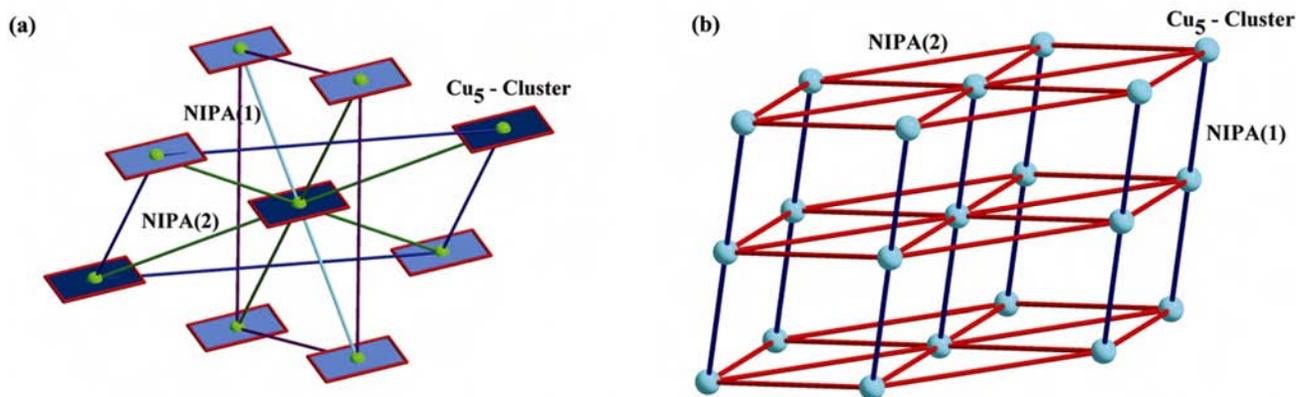


Fig. 6 – (a) The eight-connected net formed by the connectivity between the Cu<sub>5</sub> units. The connectivity involving NIPA(1) and NIPA(2) are shaded differently. (b) The eight-connected net based on the connectivity between Cu<sub>5</sub> and NIPA(1) and NIPA(2) units.

Table 3 – Important H-bonding interactions observed in compound (1)

D – H ... A	D – H (Å)	H ... A (Å)	D ... A (Å)	D – H ... A (°)
O(3)-H(31)...O(11)	0.95(3)	1.82(3)	2.652(3)	146(5)
O(3)-H(32)...O(16)	0.95(4)	1.74(4)	2.678(5)	169(4)
O(9)-H(91)...C(15)	0.95(9)	2.00(8)	2.852(7)	148(8)
O(9)-H(92)...O(300)	0.95(2)	1.82(2)	2.759(5)	172(7)
O(10)-H(101)...O(5)	0.95(3)	1.78(3)	2.697(4)	164(4)

shows an initial weight loss of (~14 %) up to 150 °C, which may be due to the loss of the lattice water molecules and the second weight loss of 53 % at ~305 °C which corresponds to the loss of the carboxylate moieties. The total weight loss of 67 % compares reasonably with the loss of all the water molecules (coordinated and free) and the carboxylate units (calc. 71.3 %). The final calcined product was found to be crystalline by powder XRD and corresponds to CuO (JCPDS: 80-1916).

#### Dynamics of the water molecules

##### Thermal studies

The TGA studies indicated that the water molecules are lost below ~150 °C. This prompted us to examine the possibility of reversible removal and reinsertion of the water molecules. To this end, the TGA setup was modified with a port for introducing the water vapor at appropriate time and temperature. A sample of compound (**1**) was taken in the TGA crucible and heated up to 140 °C in an atmosphere of flowing dry nitrogen (20 mL/min) using a heating rate of 5 °C/min. The sample was cooled and saturated water vapor was introduced into the system for 60 min. During the re-hydration step, compound (**1**) absorbs the water molecules sluggishly, but reach the near original weights taken at the start of the dehydration cycle. Thus, 97 % of the initial weight was observed from the dehydrated weight of 86 % (Fig. 7). Complete absorption of water molecules was observed when the sample was exposed to atmospheric conditions for a longer duration. The reversibility of water uptake was confirmed by repeating the dehydration and rehydration cycles twice. In each case more or less identical behavior was observed. This study confirms that the dehydration–rehydration behavior is fully reversible.

##### Powder XRD studies

To probe the possible structural changes that may accompany the dehydration-rehydration cycles, we carried out *ex-situ* temperature dependent powder XRD studies on compound (**1**). The powder XRD pattern of the fully dehydrated phase of (**1**) (heated at 125 °C for 1 h) indicates a new phase. The single crystalline nature of the compound was lost during the dehydration of (**1**), which prevented the possibility of establishing the structure of the dehydrated phase. The original phase, however, reappears when the sample was kept exposed to the atmospheric condition

for about 15 min. (Supplementary Data, Fig. S7). This suggests that the removal of the water molecules (coordinated and lattice) from (**1**) accompanies a structural re-organization.

##### IR spectroscopic studies

To understand the possible reversible hydration behavior we have carried out IR spectroscopic studies (Perkin-Elmer, Spectrum 1000) of compound (**1**). In addition, we have exchanged the water molecules with D<sub>2</sub>O molecules and investigated the changes by IR spectroscopy. The IR band for water appeared in the region ~ 3215 – 3615 cm<sup>-1</sup> and the D<sub>2</sub>O exchanged sample exhibited two additional bands at ~2455 and ~2425 cm<sup>-1</sup> ( Supplementary Data, Fig. S8). The additional bands correspond to the coordinated and lattice D<sub>2</sub>O stretching vibrations.<sup>15</sup> This study indicates that the water molecules in (**1**) can be replaced by the D<sub>2</sub>O molecule. This also establishes the reversibility of the adsorption of the water molecules (**1**).

It may be expected that the removal of the coordinated water molecules would affect changes at the coordination of the copper centers which is likely to impart some changes in the color of the sample. During the dehydration, we observed that the color of (**1**) changes from blue to green. The blue color reappears after exposure to the atmospheric conditions, as expected (Supplementary Data, Fig. S9).

##### Magnetic studies

The presence of the pentameric copper cluster in (**1**) with two triangles connected through the center could

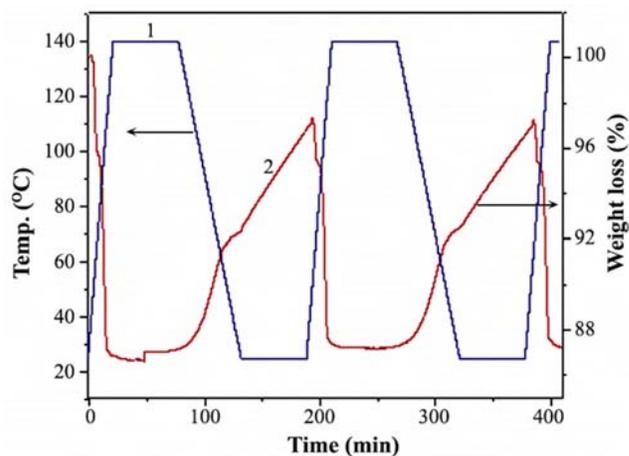


Fig. 7 – The reversible water uptake in (**1**). The blue curve (1) represents the heating and the cooling cycle while the red curve (2) represents the weight loss and weight gain. Note the sluggish weight uptake.

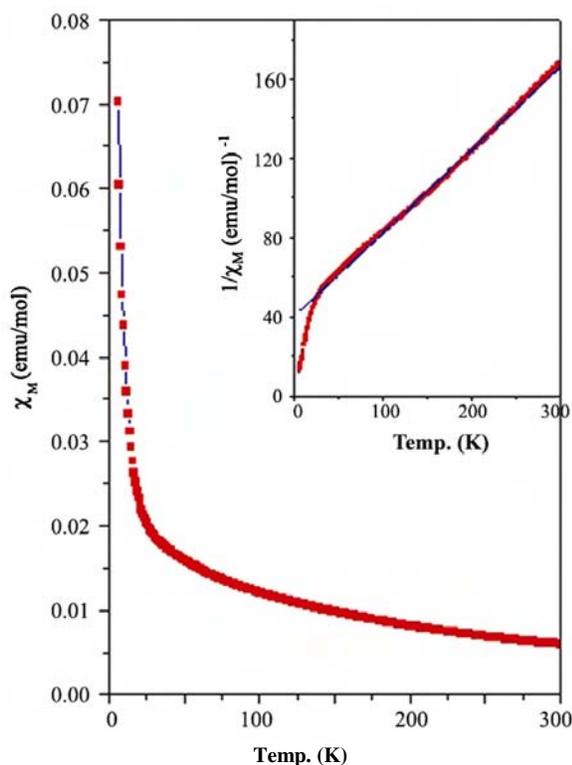


Fig. 8 – Temperature variation of the molar susceptibility ( $\chi_M$ ) for (1). The inset shows the corresponding  $1/\chi_M$  vs  $T$  plots.

give interesting magnetic behavior.<sup>16</sup> The temperature dependent magnetic susceptibility studies were performed on the powdered sample using a SQUID magnetometer (Quantum Design Inc., USA). At room temperature, the  $\chi_M T$  value of (1) is  $1.78 \text{ emu mol}^{-1} \text{ K}$  for five  $\text{Cu}^{2+}$  ions ( $\chi_M T = 0.375 \text{ emu mol}^{-1} \text{ K}$  for a  $S = 1/2$  system, single  $\text{Cu}^{2+}$  ions), which is somewhat lower than the value expected for five non-coupled  $\text{Cu}^{2+}$  ions. The molar magnetic susceptibility,  $\chi_M$ , value of (1) increases slowly from  $0.0059 \text{ emu mol}^{-1}$  at room temperature to a maximum value of  $0.0834$  at  $5 \text{ K}$  (Fig. 8). The field-cooled (FC) and zero-field-cooled (ZFC) measurements did not exhibit any appreciable differences in the magnetic susceptibility behavior upto  $5 \text{ K}$  (Supplementary Data, Fig. S10). A fit of the  $1/\chi_M$  vs  $T$  data in the temperature range  $50 - 300 \text{ K}$  for the Curie-Weiss behavior gave a value for  $C$   $2.39 \text{ emu/mol}$  and  $\theta_p$   $-96.94 \text{ K}$ . The high negative values of  $\theta_p$  indicate that the exchanges between the copper centers are strongly antiferromagnetic.

#### Heterogeneous catalytic studies

Cyanosilylation of aldehydes is used to demonstrate the presence of Lewis acid centers in

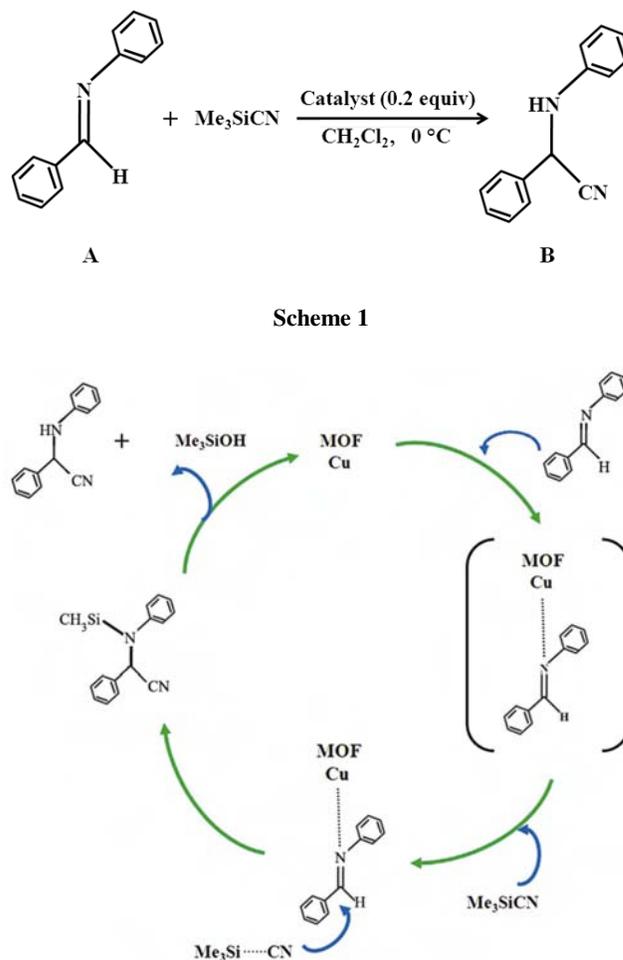


Fig. 9 – Possible mechanism of the Lewis acid catalytic cyanosilylation of the imine using (1).

MOFs. Fujita et al. established the earliest example of a MOF with Lewis acid catalytic activity during the cyanosilylation of carbonyl compounds. It prompted us to carry out a similar study with compound (1) as it contains labile coordinated water molecule. In a typical experiment, activated powdered catalyst ( $0.115 \text{ g}$  of (1),  $0.1 \text{ mmol}$ ) was suspended in freshly distilled  $\text{CH}_2\text{Cl}_2$  solution ( $10 \text{ mL}$ ) of imine (A,  $0.09 \text{ g}$ ,  $0.5 \text{ mmol}$ ). Trimethylsilyl cyanide ( $0.075 \text{ g}$ ,  $0.75 \text{ mmol}$ ) was added at  $0 \text{ }^\circ\text{C}$ , and the reaction mixture was stirred for  $6 \text{ h}$  (Scheme 1).

The product, aminonitrile (B), was isolated and analyzed by  $1\text{H NMR}$  spectra. The control experiment in the absence of copper nitroisophthalate compound has also been carried out to ensure that the reaction proceeds catalytically. In addition, we have also carried out the reaction in the presence of copper acetate,  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ . From the catalytic studies, we observed that compound (1) exhibited a

near quantitative conversion of the imine to the aminonitrile (~95 %), whereas copper acetate has an activity of only 7 %. The mechanism of the catalysis is presented in Fig. 9. The compound (**1**) was examined after the catalytic studies using PXRD, which did not exhibit observable differences. This suggests that (**1**) is stable under the experimental conditions. We have also repeated the cyanosilylation studies on the used catalyst, which also indicated that the heterogeneous catalytic conversion of imines were comparable to the studies performed using the fresh catalyst. This study suggests that the compound (**1**) is stable and can be used recyclably.

### Conclusions

The synthesis, structure and characterization of a new three dimensional MOF,  $[\text{Cu}_5(\mu_3\text{-OH})_2(\text{H}_2\text{O})_6\{(\text{NO}_2)\text{-C}_6\text{H}_3\text{-(COO)}_2\}_4].5\text{H}_2\text{O}$ , (**1**), was achieved. The observation of  $\text{CdCl}_2$ -like layers, formed by the connectivity between  $\text{Cu}_5$  pentamers and the nitroisophthalic acid, is noteworthy. The bonded water molecules are reversibly adsorbed; the process appears to involve a structural as well as a color change. The magnetic studies indicate predominant antiferromagnetic behavior. The catalytic studies suggest that the compound is a good Lewis acid catalyst and it exhibits a near quantitative conversion of the imine to the aminonitrile (~95 %).

### Supplementary Data

CCDC 823464 contains the crystallographic data for compound (**1**). These data can be obtained free of charge from The Cambridge Crystallographic Data Center (CCDC) via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). All other supplementary data associated with this article, viz., Figs S1 – S11 and Tables S1 and S2, may be obtained from the authors on request.

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