An eight-connected metal organic framework based on Cu₅ clusters: Synthesis, structure, magnetic and catalytic properties

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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, [Cu₅(µ₃-OH)(H₂O)₆][(NO₂)-C₆H₃-(COO)₂]₄].5H₂O, (1). The compound contains Cu₅ pentameric cluster units connected by 5-nitro isophthalate (NIPA) moieties forming a CdCl₂-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 Cu₅ 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.¹ The necessary feature for most of the above applications is to have sufficiently large and permanent porosity available within the framework.² These compounds also presents unique possibilities of combining the well developed chemistry of the organic and the inorganic.³ The inorganic part has been explored for the development of multidimensional molecular based magnets and more recently, the “porous magnets”.⁴ 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.⁵

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).⁶ 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.⁷

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, [Cu₅(µ₃-OH)(H₂O)₆][(NO₂)-C₆H₃-(COO)₂]₄].5H₂O, (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(CH₃COO)₂.H₂O [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 Cu(CH₃COO)₂·H₂O (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 (I) (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 absorption correction was applied using the SADABS program.

**XRD and single-crystal structure studies**

Powder X-ray diffraction (XRD) patterns were recorded on well ground samples in the 2θ range 5-50º using Cu-Kα 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-Kα (λ = 0.71073 Å) radiation. Data were collected with ω scan width of 0.3º. A total of 606 frames were collected in three different setting of φ (0, 90, 180º) keeping the sample-to-detector distance fixed at 6.03 cm and the detector position (2θ) fixed at -25º. The data were reduced using SAINTPLUS⁸ and an empirical absorption correction was applied using the SADABS program.⁹ The structure was solved and refined using SHELXL97¹⁰ present in the WinGx suit of programs (ver. 1.63.04a).¹¹ The hydrogen position of the μ₃-OH groups and the water molecules in compound (I) 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 μ₃-OH group.¹² 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 \( I^2 \) was carried out using the WinGx package of programs.¹¹ 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-benzilidene aniline and trimethylsilyl...
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 N₂ 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 [(NO₂)₂-C₅H₇-(COO)₂]₄.5H₂O, (I)

The asymmetric unit of Cu₅(μ₃-OH)₂(H₂O)₆{(NO₂)₆-C₅H₇-(COO)₂}₄.5H₂O, (I) consists of 40 non-hydrogen atoms, of which three Cu²⁺ ions are crystallographically independent along with two 5-nitroisophthalate (NIPA), one μ³-hydroxyl groups, three coordinated water molecule and three lattice water molecules (Supplementary Data, Fig. S3). One of the Cu²⁺ 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 (I) forms a pentamer cluster (Fig. 1). The Cu₅ clusters are formed by the connectivity involving two μ₃ hydroxyl groups. The central copper, Cu(1), is also connected with the other copper atom, Cu(2), through a μ₂-H₂O 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 μ₂-H₂O 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 Cu²⁺ ions through three 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 Cu²⁺ 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 Schlaffi symbol of (4°)₃(4°.6°.8°). This net connectivity resembles the bonding observed in the CdCl₂ 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 CdCl₂–like layer connected through the NIPA(1) unit giving rise to the three–dimensional structure.

CdCl₂–like layers pillared by the carboxylate units have been observed earlier.¹³ In the lanthanum compound,

![Image](image_url)
\[ [M_2(\text{H}_2\text{O})_4]\{[C_5\text{H}_3\text{N(COO)}_2]\}_2[C_6\text{H}_4(\text{COO})_2]\}, \ M = \text{La, Pr, and Nd}, \]

the layers are formed by the connectivity between \( M_2(\text{H}_2\text{O})_4 \) dimers and the pyridine–2,3–dicarboxylate units. This layer is pillared (cross-linked) by the terephthalate unit forming the three–dimensional structure. In (I), the connectivity between the Cu\(_5\) units and one of the NIPA acids forms the CdCl\(_2\)–like layers. The second NIPA acid connects the Cu\(_5\) pentameric units of the adjacent layer similar to the terephthalate units in \([M_2(\text{H}_2\text{O})_4]\{[C_5\text{H}_3\text{N(COO)}_2]\}_2[C_6\text{H}_4(\text{COO})_2]\] (Fig. 5).

The presence of the water molecules, coordinated and lattice water gives rise to O–H···O type hydrogen bond interactions. The important observed O–H···O interactions with O···O contact distances are in the range of 2.652(3) – 2.852(7) and the O–H···O bond angles are in the range of 146 – 172. This suggests that the hydrogen bond interactions are relatively strong.\(^{14}\) 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\(^5\)4\(^4\)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 (I)
Fig. 5 – (a) The CdCl$_2$ layer. (b) The CdCl$_2$-like layer observed in [M$_2$(H$_2$O)$_4$][(C$_5$H$_3$N(COO)$_2$)$_2$][C$_6$H$_4$-(COO)$_2$]], M=La, Pr, and Nd. (c) The CdCl$_2$-like layer observed in (I). The layers are cross-linked by terephthalate units in [M$_2$(H$_2$O)$_4$][(C$_5$H$_3$N(COO)$_2$)$_2$][C$_6$H$_4$-(COO)$_2$]] and NIPA(1) in (I) (see text).

Fig. 6 – (a) The eight-connected net formed by the connectivity between the Cu$_5$ units. The connectivity involving NIPA(1) and NIPA(2) are shaded differently. (b) The eight-connected net based on the connectivity between Cu$_5$ and NIPA(1) and NIPA(2) units.

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

<table>
<thead>
<tr>
<th>D – H … A</th>
<th>D – H (Å)</th>
<th>H … A (Å)</th>
<th>D … A (Å)</th>
<th>D – H … A (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(3)-H(31)···O(11)</td>
<td>0.95(3)</td>
<td>1.82(3)</td>
<td>2.652(3)</td>
<td>146(5)</td>
</tr>
<tr>
<td>O(3)-H(32)···O(16)</td>
<td>0.95(4)</td>
<td>1.74(4)</td>
<td>2.678(5)</td>
<td>169(4)</td>
</tr>
<tr>
<td>O(9)-H(91)···C(15)</td>
<td>0.95(9)</td>
<td>2.00(8)</td>
<td>2.852(7)</td>
<td>148(8)</td>
</tr>
<tr>
<td>O(9)-H(92)···O(300)</td>
<td>0.95(2)</td>
<td>1.82(2)</td>
<td>2.759(5)</td>
<td>172(7)</td>
</tr>
<tr>
<td>O(10)-H(101)···O(5)</td>
<td>0.95(3)</td>
<td>1.78(3)</td>
<td>2.697(4)</td>
<td>164(4)</td>
</tr>
</tbody>
</table>
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 (I) 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 (I) 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–rehydation 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 (I). The powder XRD pattern of the fully dehydrated phase of (I) (heated at 125 °C for 1 h) indicates a new phase. The single crystalline nature of the compound was lost during the dehydration of (I), 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 (I) 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 (I). In addition, we have exchanged the water molecules with D₂O molecules and investigated the changes by IR spectroscopy. The IR band for water appeared in the region ~3215 – 3615 cm⁻¹ and the D₂O exchanged sample exhibited two additional bands at ~2455 and ~2425 cm⁻¹ (Supplementary Data, Fig. S8). The additional bands correspond to the coordinated and lattice D₂O stretching vibrations. This study indicates that the water molecules in (I) can be replaced by the D₂O molecule. This also establishes the reversibility of the adsorption of the water molecules (I).

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 (I) 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 (I) with two triangles connected through the center could

![Fig. 7 – The reversible water uptake in (I). 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.](image)
give interesting magnetic behavior. The temperature dependent magnetic susceptibility studies were performed on the powdered sample using a SQUID magnetometer (Quantum Design Inc., USA). At room temperature, the $\chi_MT$ value of (1) is 1.78 emu mol$^{-1}$ K for five Cu$^{2+}$ ions ($\chi_M T = 0.375$ emu mol$^{-1}$ K for a $S = \frac{1}{2}$ system, single Cu$^{2+}$ ions), which is somewhat lower than the value expected for five non–coupled Cu$^{2+}$ ions. The molar magnetic susceptibility, $\chi_M$, value of (1) increases slowly from 0.0059 emu mol$^{-1}$ at room temperature to a maximum value of 0.0834 at 5 K (Fig. 8). The field-cooled (FC) and zero-field-cooled (ZFC) measurements did not exhibit any appreciable differences in the magnetic susceptibility behavior up to 5 K (Supplementary Data, Fig. S10). A fit of the $1/\chi_M$ vs $T$ data in the temperature range 50 – 300 K for the Curie-Weiss behavior gave a value for $C$ 2.39 emu/mol and $\theta_P$ -96.94 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 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 g of (1), 0.1 mmol) was suspended in freshly distilled CH$_2$Cl$_2$ solution (10 mL) of imine (A, 0.09 g, 0.5 mmol). Trimethylsilyl cyanide (0.075 g, 0.75 mmol) was added at 0 °C, and the reaction mixture was stirred for 6 h (Scheme 1).

The product, aminonitrile (B), was isolated and analyzed by 1H 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, Cu(CH$_3$COO)$_2$.H$_2$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 (I) was examined after the catalytic studies using PXRD, which did not exhibit observable differences. This suggests that (I) 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 (I) is stable and can be used recyclably.

Conclusions

The synthesis, structure and characterization of a new three dimensional MOF, \([\text{Cu}_6(\mu_3-\text{OH})_2(\text{H}_2\text{O})_6\{(\text{NO}_2)\text{C}_6\text{H}_4\text{-(COO)}_2\}_4\text{H}_2\text{O}](\text{I})\), was achieved. The observation of CdCl₂-like layers, formed by the connectivity between Cu₅ 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 (I). These data can be obtained free of charge from The Cambridge Crystallographic Data Center (CCDC) via 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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