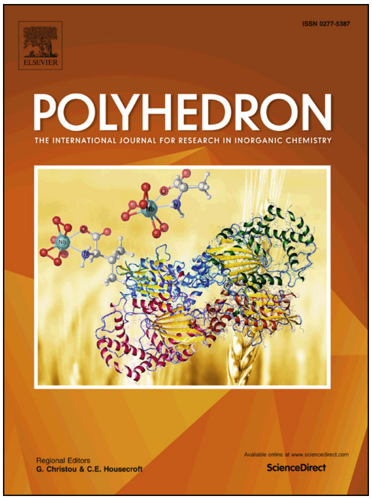

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PII: S0277-5387(18)30107-4
DOI: https://doi.org/10.1016/j.poly.2018.02.023
Reference: POLY 13058

To appear in: *Polyhedron*

Received Date: 10 January 2018
Accepted Date: 23 February 2018

Please cite this article as: D. Saha, S. Gayen, S. Koner, Cu(II)/Cu(II)-Mg(II) Containing Pyridine-2,5-dicarboxylate Frameworks: Synthesis, Structural Diversity, Inter-conversion and Heterogeneous Catalytic Epoxidation, *Polyhedron* (2018), doi: https://doi.org/10.1016/j.poly.2018.02.023

Cu(II)/Cu(II)-Mg(II) Containing Pyridine-2,5-dicarboxylate Frameworks: Synthesis, Structural Diversity, Inter-conversion and Heterogeneous Catalytic Epoxidation

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Abstract

Ligand concentration dependent structural diversity and inter-conversion of hydrothermally synthesized metal carboxylate compounds, $\{[Mg(H_2O)_6][Cu(pdc)_2]\cdot 2H_2O\}_n$ (**1**), $\{[CuMg(pdc)_2(H_2O)_4]\cdot 2H_2O\}_n$ (**2**), $\{2(Him)\cdot[Cu(pdc)_2]\}_n$ (**3**), and $\{[Cu(pdc)(im)_2]\cdot 2H_2O\}_n$ (**4**) (H_2Pdc = pyridine-2,5-dicarboxylic acid and im = imidazole), have been thoroughly investigated. Formation of compounds **1**-**4** depends on the concentration of imidazole. Structure of all four compounds has been verified by single crystal X-ray diffraction and other physicochemical studies. Compound **3** catalyzes olefin epoxidation reaction in heterogeneous condition.

1. Introduction

Metal organic framework (MOF) is nothing but a symmetric arrangement of metal ions which are connected through organic linkers and extended into 1, 2 and 3-dimensional networks via coordination bonding and other weak bonding interactions [1]. MOF has wide range of application potential in various fields, including gas adsorption, gas storage, gas separation or gas purification, membranes and coating, sensing, luminescence, drug delivery, artificial nucleases for the hydrolytic cleavage of DNA and RNA, magnetic, catalysis etc. [2-11]. Designing of metal organic framework has now reached at higher level of sophistication, however, challenges still remain to control over the structure of the material that deals with supramolecular chemistry and crystal engineering [12-13]. There are various synthesis methods to design metal organic frameworks (MOFs) such as diffusion based crystallization and hydro-, solvo- and ionothermal synthesis etc. Hydrothermal method is one of the most popular methods utilized in the preparation of MOFs [14]. However, the control of products in hydrothermal reactions pose great challenge to chemists, since there are many factors influence the crystallization of MOFs and the structural motifs that acquire by the prepared compound. This includes the solvent and reaction temperature, pH of the media, molar ratio of raw materials, reaction time, and so on [15-19]. Therefore, investigations to get deeper insight into the interplay between the structure of compounds and various stimuli are still important.

A variety of reactions have been studied using MOF as catalyst [20]. C=C bond functionalization reaction is one of the important reactions in organic chemistry that can lead to a diverse array of derivatives. Epoxidation is one of these types of reactions, and epoxides are active intermediates for industrial applications as feedstock for value added products [21]. Olefin epoxidation catalyzed by transition metal complexes has been a subject of great interest in the past few decades [22]. In this context several copper catalyzed epoxidation reaction have been reported [23]. Usually epoxidation is carried out in the presence of an oxidant such as hydrogen peroxide, TBHP or peracids.

Hydroperoxides in combination with suitable catalysts constitute an adequate system from the viewpoint of green chemistry.

In this study, we report our research over the structural inter-conversion amongst four metal carboxylate framework compounds, $\{[Mg(H_2O)_6][Cu(pdc)_2]\cdot 2H_2O\}_n$ (H_2Pdc = pyridine-2,5-dicarboxylic acid) (**1**), $\{[CuMg(pdc)_2(H_2O)_4]\cdot 2H_2O\}_n$ (**2**), $\{2(Him)\cdot[Cu(pdc)_2]\}_n$ (im = imidazole) (**3**), and $\{[Cu(pdc)(im)_2]\cdot 2H_2O\}_n$ (**4**). Synthesis, X-ray crystal structure and catalytic efficacy of the new compound **3** in olefin epoxidation reaction are also described here. Synthesis, characterization and catalytic efficacy of others compounds were reported elsewhere [24].

2. Experimental section

2.1. Materials

Pyridine-2,5-dicarboxylic acid, magnesium nitrate hexahydrate, copper nitrate trihydrate, imidazole and alkenes were purchased either from Sigma–Aldrich or Merck (India) and were used as received. Ethanol was purchased from Merck (India) and was distilled and dried before use.

2.2. Physical measurements

Elemental analysis was performed on a Vario-Micro V2.0.11 elemental (CHNSO) analyzer. Fourier-transformed infrared spectra of KBr pellets were measured using a Perkin Elmer RX I FT-IR spectrometer. PXRD was recorded on a Bruker D8 Advance X-ray powder diffractometer (PXRD) equipped with Cu-Kα radiation (λ = 1.54 Å). In situ temperature-resolved PXRD patterns were performed using a similar device equipped with a high-temperature chamber (Anton Paar HTK 16N) and TCU 2000N temperature control unit using Cu-Kα radiation. The sample was loaded on a Pt plate and heated at a rate of 5 °C min^{-1} under nitrogen. TG-DT analysis was made using a PerkinElmer (SINGAPORE) Pyris Diamond TG/DTA unit. The heating rate was programmed at 5°C min^{-1} with a protecting stream of N_2 flowing at a rate of 150 mL min^{-1}. The metal content of the sample was estimated on a Varian Techtron AA-ABQ atomic absorption spectrometer. The products of the catalytic reactions were identified and quantified by a Varian CP-3800 Gas Chromatograph using a CP-Sil 8 CB capillary column.

2.3. Synthesis of the compounds

All compounds were prepared from same reaction mixture. Pyridine-2,5-dicarboxylic acid (0.167 g, 1 mmol) and imidazole first added in 10 ml of milli-Q water and the mixture was stirred for 0.5 h, to this mixture magnesium nitrate hexahydrate (0.128 g, 0.5 mmol) and copper nitrate trihydrate (0.120 g, 0.5 mmol) were added and the final mixture was stirred for 0.25 h. Compounds were obtained in crystalline form in a 20 ml capacity Teflon-lined acid digestion bomb, at 175 °C for 3 days followed by slow cooling at a rate of 5 °C h^{-1} to room temperature. Compounds **1**, **2**, **3** and **4** were obtained respectively from 1, 2, 3 and 4 mmol of imidazole. For characterization of the bulk compound, PXRD study (Fig. S1), elemental analysis and IR spectroscopic study were undertaken. Blue block crystals of compound **3** suitable for X-ray analysis were obtained in about 62% yield based on Copper. Anal. Calc. for $\{2(\text{Him})\cdot[\text{Cu(pdc)}_2]\}_n$ **3**: C, 45.16%; H, 3.03%; N, 15.80%. Found: C, 45.22%; H, 3.05%; N, 15.73%. Selected IR peaks (KBr disk, ν, cm^{-1}): 1616, 1555 [υ_{as} (CO_2^-)], 1396 [υ_s (CO_2^-)], 1336, 1274 [υ_s (C-O)], 3112-3160 [υ_s (N-H)], and 3457 s.br [υ (O-H)].

PXRD patterns (Figs. S2, S3 and S4), elemental analysis data and IR spectroscopic data of other compounds were given in supporting information.

2.4. X-ray crystallography

X-ray diffraction data for **3** was collected at 293K on a Bruker SMART APEX CCD X-ray diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073Å). Determination of integrated intensities and cell refinement were performed with the SAINT software package using a narrow-frame integration algorithm [25]. An empirical absorption correction (SADABS) was applied [26]. The structure was solved by direct methods and refined using full-matrix least-squares technique against F^2 with anisotropic displacement parameters for non-hydrogen atoms with the programs SHELXS97 [27] and SHELXL2014/7 [28]. The C-bound Hydrogen atoms were freely refined. In the final difference Fourier maps there were no remarkable peaks except the ghost peaks surrounding the metal centers. A summary of crystal data and relevant refinement parameters for compound **3** is given in Table S1. X-ray diffraction data for compound **1**, **2**, and **4** were also collected in the same manner as of compound **3** as described above to determine the cell parameters (Table S1) and matched with the corresponding data of previously reported $\{[Mg(H_2O)_6][Cu(pdc)_2]\cdot 2H_2O\}_n$ (**1**), $\{[CuMg(pdc)_2(H_2O)_4]\cdot 2H_2O\}_n$ (**2**), and $\{[Cu(pdc)(im)_2]\cdot 2H_2O\}_n$ (**4**) [24].

2.5. Catalytic reaction

The catalytic reactions were carried out in a glass batch reactor according to the following procedure. Substrate (10 mmol), ethanol (10 ml) and catalysts (2 mg) were first mixed. The mixture was then equilibrated to desired temperature in an oil bath. After addition of hydrogen peroxide (14.4 mmol, 1.5 equiv.) the reaction mixture was stirred continuously. Reactions were performed in open air. The products of the reactions were collected at different time intervals and were identified and quantified by gas chromatography.

3. Results and discussion

3.1. Imidazole dependent structural diversity and inter-conversion

Compound **1**, **2**, **3** and **4** were synthesized from an identical reaction mixture with different imidazole concentration (Fig. 1). All compounds except **4** crystallized in triclinic space group *P-1* with *Z* = 1. Increase of the imidazole concentration led to the formation of compounds **1** to **4**. Basic structure of **1**, **2** and **3** are same. They are 1-D coordination polymer contains copper(II) ions connected by pdc dianions forming $\{[Cu(pdc)_2]^{2-}\}_n$ ribbon like chains. Coordination geometry of copper(II) in **1**, **2** and **3** is distorted octahedron where two nitrogen atoms and two oxygen atoms from two chelating pdc dianions formed the basal plane of the octahedron while axial positions are occupied by two oxygen atoms from two different pdc dianions. When 1 mmol of imidazole is used, compound **1** is formed where negative charge of $\{[Cu(pdc)_2]^{2-}\}_n$ is satisfied by the $[Mg(H_2O)_6]^{2+}$ ions and ultimately forming a hydrogen bonded 2D network through hydrogen of coordinated water molecule and free carboxylato oxygen atom. Upon increasing the amount of imidazole to 2 mmol, hydrothermal treatment of the reaction mixture afforded compound **2** where $\{[Cu(pdc)_2]^{2-}\}_n$ chains are linked with Mg(II) ions through carboxylate oxygen atoms and a 2D network was formed. In compound **2**, free carboxylate oxygen atoms present in compound **1** involve in bonding with Mg(II) ions and replace two coordinated water molecules of Mg(II) ions present in **1**. Upon adjusting the amount of imidazole to 3 mmol, magnesium ions were replaced by the imidazolium ions and compound **3** was thus formed. Structure of compound **3** is close resembles with compound **1** but only difference is that the place of hexa-aqua Mg(II) ions are occupied by uncoordinated imidazolium ions. When amount of the imidazole was adjusted to 4 mmol, imidazole coordinates to the Cu(II) ion and compound **4** was formed. In compound **4,** each Cu(II) ion is coordinated by two nitrogen atoms from two imidazole molecules, one carboxylato oxygen atom and one nitrogen atom from a pdc dianions and forms a chelate, and one carboxylato oxygen atom from another pdc^{2-} ligand. Here, pdc^{2-} ligand connects two copper(II) ions in a similar fashion as in other compounds forming 1D chain of distorted square pyramidal Cu(II) coordination geometry. Another difference is that instead of four connecting pdc^{2-} ligands with one Cu(II) center, here involve only two.

Structural inter-conversions are shown in Fig. 1. Upon increasing imidazole concentration **1** was converted to **2, 3** and **4** through hydrothermal treatment. Similarly **3** was converted to **4**. But our attempts in converting **2** to **3** and **2** to **4** were not successful. It is pertinent to mention that in presence of excess magnesium nitrate, compound **3** converted to **1** upon hydrothermal treatment.

3.2. X-ray structure of $\{2(Him)\cdot[Cu(pdc)_2]\}_n$ (**3**)

Compound **3** crystallizes in the triclinic space group *P-1* with *Z* = 1 and possesses a polymeric ribbon like 1D chain structure consist of copper(II) ion and carboxylate linker. The chain propagates parallel to the crystallographic *a* axis (Fig. 2). Chain is anionic in nature and the overall charge is balanced by uncoordinated imidazolium cations. Crystallographically unique $[Cu(pdc)_2]^{2-}$ units construct the ribbon, where each

Cu^{2+} adopts tetragonally distorted octahedron geometry (Fig. 3). An ORTEP diagram with atom-numbering scheme is shown in the Fig. S5. Selected bond distances and the bond angles are collated in Table S2. Four donor atoms (N1, O3 and ^{c}N1, ^{c}O3; c = $-x$, $-y$, $-z$) from two chelating pdc^{2-} ligands occupy the equatorial positions where N1 and O3 of pdc^{2-} ligand form chelate with metal center and axial positions are occupied by two carboxylato oxygen atoms (^{a}O1 and ^{d}O1; a = $-1+x$, y, z; d = $1-x$, $-y$, $-z$) from two different pdc^{2-} ligands. The pdc^{2-} ligand shows μ_3 connectivity mode. In one site it form a chelate with copper center through one heterocyclic nitrogen atom (N1) and one carboxylato oxygen (O3) atom adjacent to ring nitrogen and in another site it links with another copper center through oxygen (O1) of different carboxylate group. Among the four carboxylato oxygen atoms of pdc^{2-} ligand, two (O2 and O4) remain uncoordinated. Those 1-D chains are connected through imidazolium ions by intermolecular H-bonding between hydrogen bonded with the ring nitrogen of imidazolium ion and free carboxylato oxygen atom of pdc^{2-} ligand resulting a 2D supramoleculer structure (Table S3 and Fig. 2).

*3.3. Thermal analysis of compound **3***

TG measurement confirms that the compound **3** was thermally stable up to around 325 °C (Fig. S6). Compound **3** shows a single stage mass loss. A sharp mass loss at around 325 °C indicates the decomposition of the compound **3**. The corresponding DTA curve of compound **3** shows an endothermic peak centered at 353 °C. The final solid product of thermal decomposition was identified as CuO (Fig. S7) with total mass loss of 88.57 % (calcd. 88.05 %). Being a 1D chain structure, the high thermal stability of this MOF can be explained in terms of the salt like nature, rigidity of the linkers, strong bonds between the metal ions and the organic linkers, absence of solvent molecules, etc. Thermal stability of compound **3** also verified by variable temperature PXRD study. Major experimental PXRD peaks of compound **3** are well matched with the simulated one up to *ca.* 300 °C (Fig. 4).

*3.4. Catalytic activities of compound **3***

Catalytic epoxidation of alkenes using compound **3** was carried out at 60 °C in heterogeneous conditions. We examined the epoxidation of 1-hexene and cyclooctene in six different solvents to find the optimal solvent. The best conversion and selectivity were found in ethanol. Although acetonitrile acts as very good solvent, but selectivity is less in case of styrene and cyclohexene epoxidation. The conversion increases in the order $CH_2Cl_2<CHCl_3<MeOH<CH_3COCH_3<EtOH<CH_3CN$ (Fig. S8). But the selectivity increases in the order $CH_2Cl_2<CHCl_3<CH_3COCH_3<CH_3CN<MeOH<EtOH$ for styrene and cyclohexene (Fig. S9). To monitor the temperature effect, we tuned the reaction temperature from 30–78 °C for the epoxidation of cyclooctene and 1-hexene, a good yield with good product selectivity was obtained at a moderate temperature of 60 °C (Fig. S10) in ethanol. At higher temperatures the conversion decreases, as H_2O_2 starts to degrade at higher temperatures. The epoxidation of alkenes were studied here goes smoothly, showing an excellent conversion (80% to 100%) to form epoxides as the major product. Results of the catalytic epoxidation of different substrates are given in Table 1. Oxidation of cyclohexene proceeded smoothly, showing 100% conversion after 8 h of reaction to form epoxycyclohexane with ca. 72% selectivity and some amount of alkenes were converted to 2-cyclohexene-1-ol and 2-cyclohexene-1-one. Cyclooctene was effectively converted to epoxycyclooctane with ca. 100% selectivity and conversion. In

case of linear alkenes, 1-hexene shows almost complete conversion and producing epoxide as the sole product, but in case of 1-octene the conversion was not complete; the conversion only limited to 80% after 8 h of reaction. It suggests that the catalytic activity decreases along with chain length of alkene. This may due to the larger hexyl group of 1-octene connected to double bond sterically hinders it in approaching to the active site with respect to 1-hexene in which its double bond carries a smaller butyl group. Consequently, the conversion was lowered in catalytic reaction. To study conjugated olefins, styrene, 4-methylstyrene and *trans*-stilbene were used. Styrene and 4-methylstyrene were converted with 100% efficiency, and the product selectivity remained around 78 and 70%, respectively, with benzaldehyde as the usual corresponding bi-product. The epoxidation of *trans*-stilbene with H_2O_2 gives stilbene oxide in 82% conversion but 100% selectivity. A different substrate, limonene, was also subjected to oxidation reaction; 100% conversion with a product selectivity of 86% and along with some unidentified products. A graphical representation of relative efficacy of **3** for the epoxidation of various alkenes in ethanol with time is given in Fig. S11. Compound **1** catalyses the same reaction but in homogeneous condition [24a]. Therefore, it can be said that counter ion in compound **3** and also the nature of supramolecular interactions play crucial role to maintain heterogeneity of the reaction. To ascertain the heterogeneous nature of catalyst, a hot filtration test was performed. The liquid phase of the reaction mixture was collected by filtration after ca. 36% of the reaction was completed for epoxycyclooctane. The supernatant solution was then kept in the reaction conditions for another 24 h. Almost no progress of the reaction was observed during this period, which excludes the presence of active species in the solution. Besides, Atomic absorption spectrometric analysis (sensitivity up to 0.001 ppm) of the supernatant solution of reaction mixture thus collected by filtration confirms the absence of copper ions in the liquid phase. For the recycling study, catalyst was recovered by centrifugation, washed thoroughly with ethanol, then activated at 140 °C under vacuum for 3 h, and reused five times using cyclooctene. All repeated reactions gave almost identical conversion (Fig. 5). The IR spectra and PXRD patterns of a fresh and a used sample of the catalyst did not show any significant differences which convincingly demonstrated that its structural integrity is well maintained after several cycles of reactions (Figs. S12, S13).

4. Conclusion

In essence, we have investigated structural inter-conversion of four metal carboxylate compounds, $\{[Mg(H_2O)_6][Cu(pdc)_2]\cdot 2H_2O\}_n$ (**1**), $\{[CuMg(pdc)_2(H_2O)_4]\cdot 2H_2O\}_n$ (**2**), $\{2(Him)\cdot[Cu(pdc)_2]\}_n$ (**3**), and $\{[Cu(pdc)(im)_2]\cdot 2H_2O\}_n$ (**4**) (H_2Pdc = pyridine-2,5-dicarboxylic acid and im = imidazole). All are synthesized through hydrothermal route. All of them except compound **4** crystallized in same space group and there is a close similarity of some of the basic structural features among them. Compound **3** catalyzes olefin epoxidation reaction in heterogeneous condition where H_2O_2 acts as oxidizing agent.

Acknowledgements

D. Saha acknowledges University Grants Commission, New Delhi, India for financial assistance (Minor Research Project No. F. PSW-188/15-16 (ERO)). S. Gayen is thankful to the University Grants Commission (UGC), New Delhi, (Award letter No.

22/12/2013(ii)EU-V) through National eligibility test (NET) Fellowship. Funding received from UGC in a major project (to SK) is also gratefully acknowledged.

Supplementary data

CCDC 1586363 contains the supplementary crystallographic data for compound **3**. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://xxxxxxxxxxxxxxxxxxxx.

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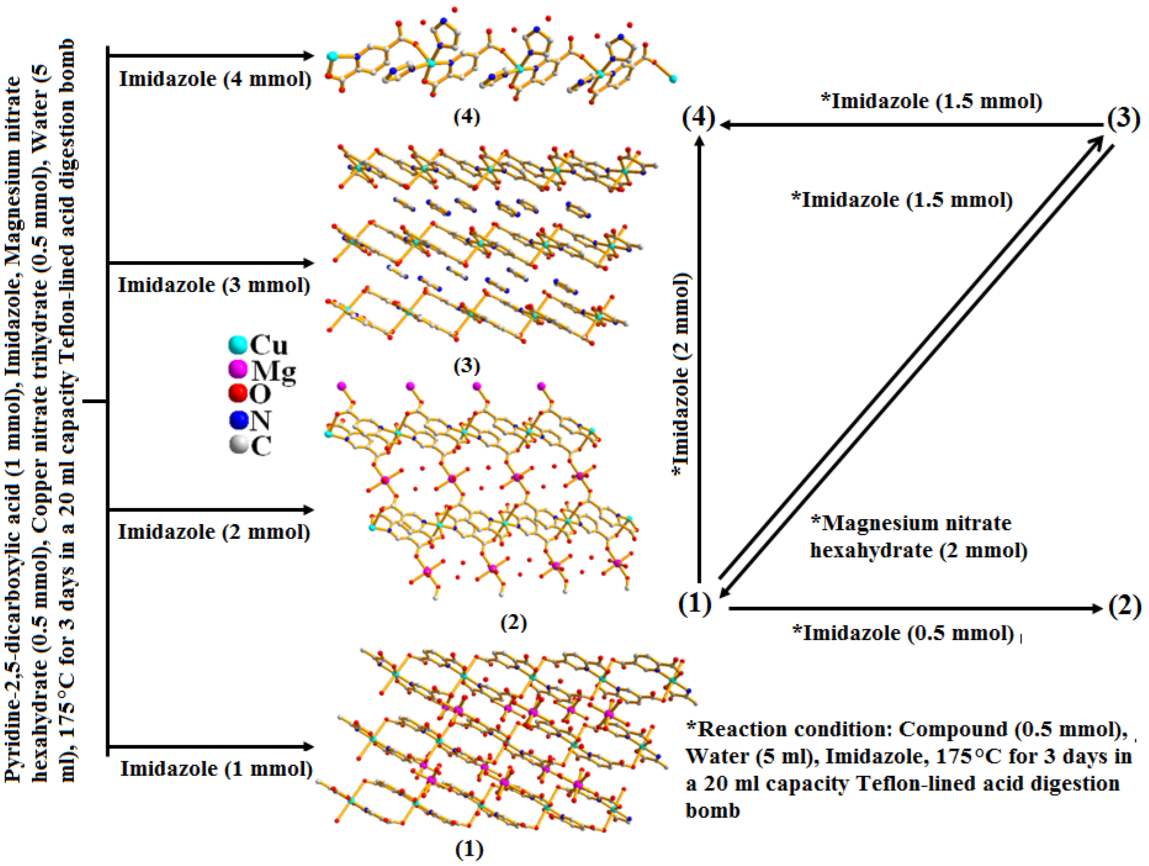


Fig. 1. Imidazole dependent structural variation and transformation

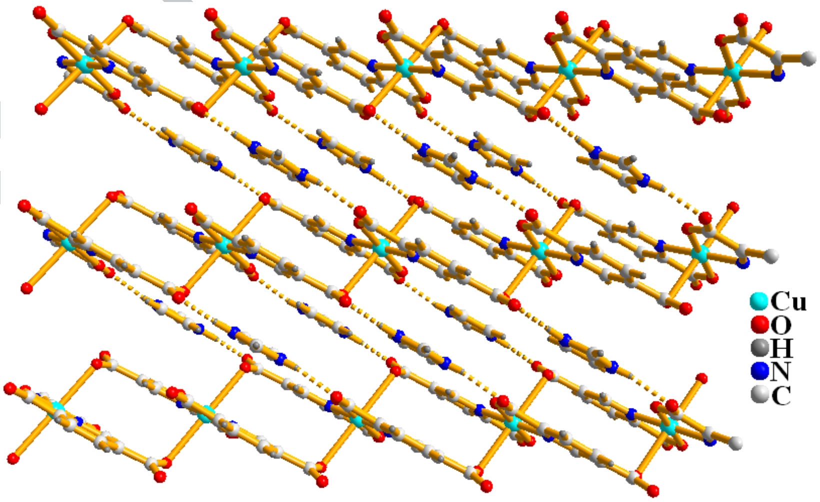


Fig. 2. 1D Chain of compound **3**. Dotted lines are showing hydrogen bonded 2D net.

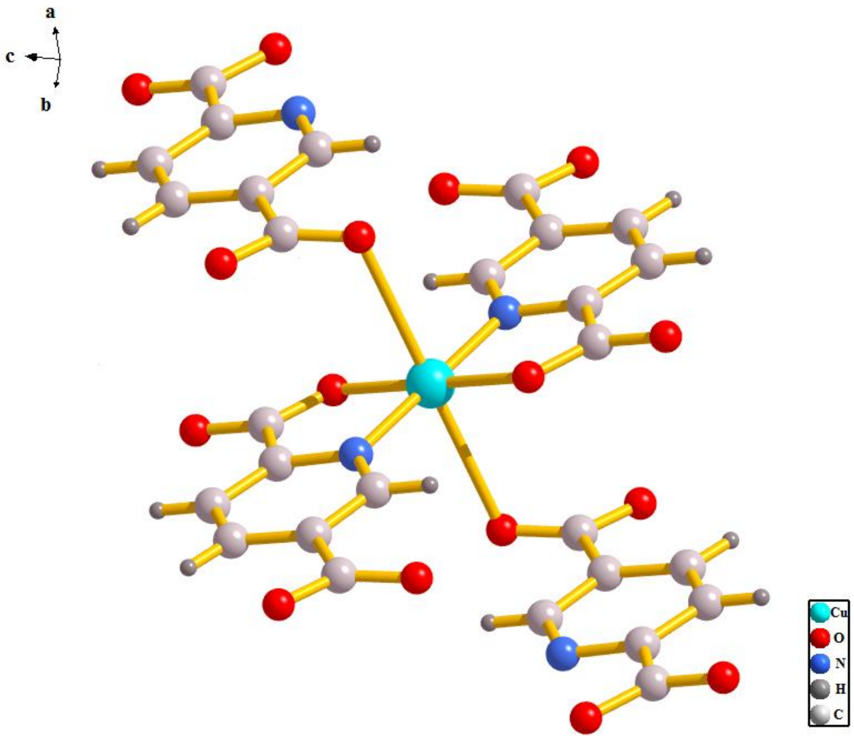


Fig. 3. Metal-ligand coordination of compound **3**

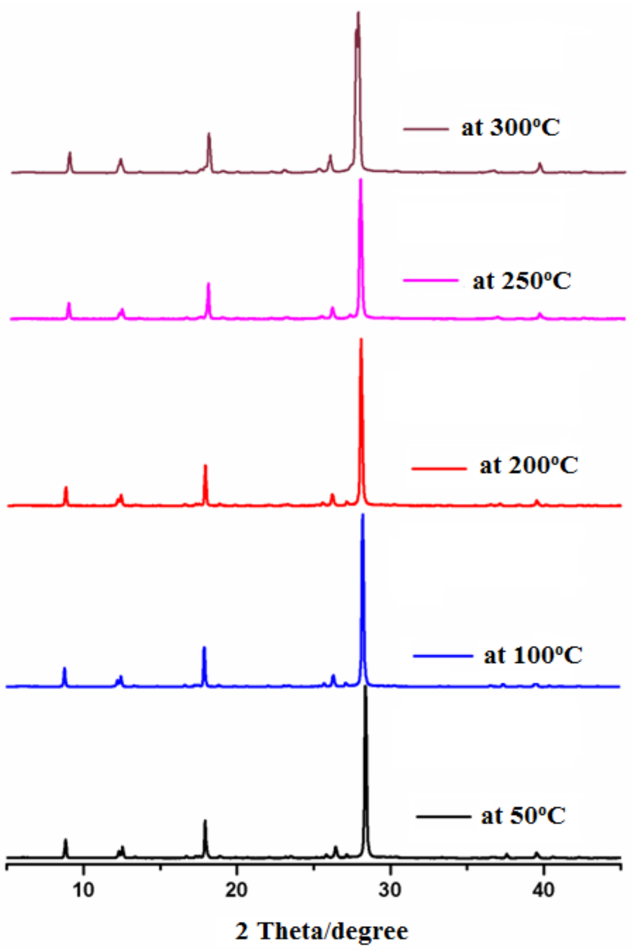


Fig. 4. Variable temperature PXRD pattern of compound **3**

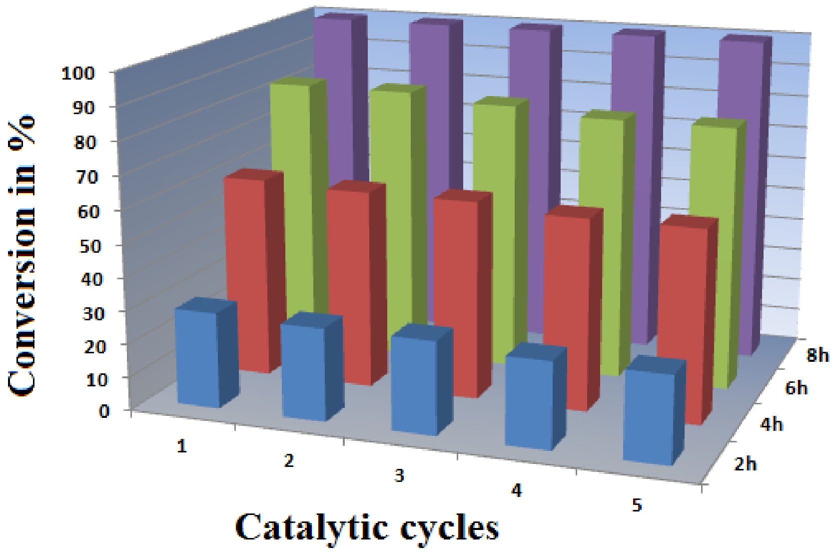
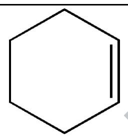
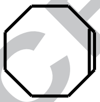
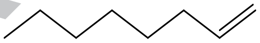
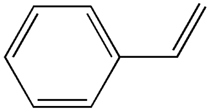
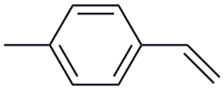
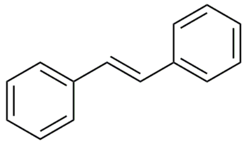
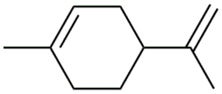


Fig. 5. Catalytic activity of **3** in different catalytic cycles for cyclooctene oxidation. Reaction conditions are the same as given in the footnote of Table 1.

Table 1. Oxidation of selected olefins by H_2O_2 with catalyst **3**[a]

Substrate	Conversion (wt %)	% yield of product		TOF[b] (h^{-1})
		Epoxide	Others	
	100	72	28[c]	332
	100	100	-	332
	92	92	-	305
	80	80	-	265
	100	78	22[d]	332
	100	70	30[e]	332

	82	100	-	271
	100	86[f]	14[g]	332

[a] Reaction condition: Substrate (10 mmol), ethanol (10 ml) and catalysts (2 mg); hydrogen peroxide (1.5 equiv.); temperature: 60 °C; reaction time: 8 h; The products of the reactions were collected at different time intervals and were identified and quantified by Varian CP-3800 gas chromatograph equipped with an FID detector and a CP-Sil 8 CB capillary column. [b] Turn over frequency (TOF) = moles converted per moles of active site per hour. [c] 2-cyclohexen-1-ol and 2-cyclohexene-1-one. [d] Benzaldehyde. Benzoicacid. [e] 4-Methylbenzaldehyde. [f] Limonene oxide. [g] Unidentified product.

Cu(II)/Cu(II)-Mg(II) Containing Pyridine-2,5-dicarboxylate Frameworks: Synthesis, Structural Diversity, Inter-conversion and Heterogeneous Catalytic Epoxidation

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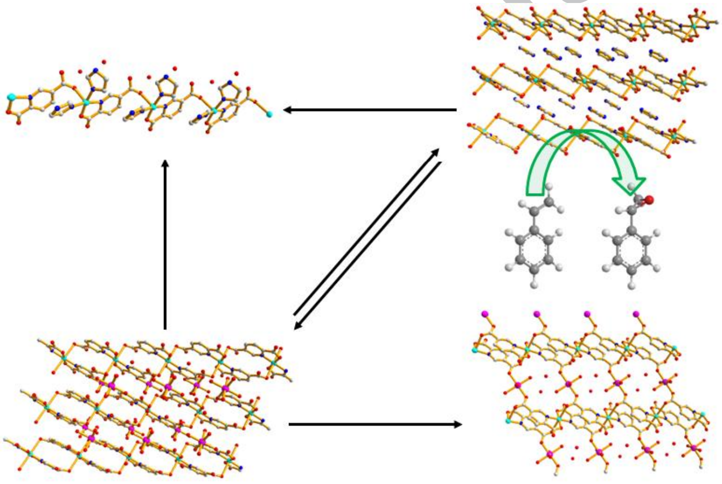
Graphical abstract for pictogram



Graphical Abstract

Structural conversion of four metal carboxylate compounds, $\{[Mg(H_2O)_6][Cu(pdc)_2]\cdot2H_2O\}_n$ (**1**), $\{[CuMg(pdc)_2(H_2O)_4]\cdot2H_2O\}_n$ (**2**), $\{2(Him)\cdot[Cu(pdc)_2]\}_n$ (**3**), and $\{[Cu(pdc)(im)_2]\cdot2H_2O\}_n$ (**4**) (H_2Pdc = pyridine-2,5-dicarboxylic acid and im = imidazole) have been investigate through hydrothermal reaction. The new compound, **3**, has been characterized by single crystal X-ray diffraction and other physicochemical studies. High thermal stability of compound **3** was established by variable temperature PXRD study. Compound **3** catalyzes olefin epoxidation reaction in heterogeneous condition where H_2O_2 acts as oxidizing agent. Catalytic activities were tested in different temperature and solvent medium.