

# A copper metal-organic hydrogel as a catalyst for SO<sub>2</sub> and CO<sub>2</sub> fixation under ambient condition

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**Abstract:** A copper metal-organic hydrogel (MOG) has been synthesised using an amino acid-based ligand, Na<sub>2</sub>HL {H<sub>3</sub>L = 2-{(3,5-di-tert-butyl-2-hydroxybenzyl)amino succinic acid} as a gelator. The metallohydrogel exhibits pH-responsive nature as well as chemical responsiveness. Besides, it shows rapid thixotropic behavior when external mechanical forces are applied. The metal – organic hydrogel can be used as a heterogeneous catalyst for the reaction of SO<sub>2</sub> and CO<sub>2</sub> with epoxides to produce cyclic 1,3,2-dioxathiolane-2-oxides and carbonates, respectively. The conversions were found to be dependent on the size and type of the side chain of the epoxides.

### Introduction

In recent years, metal-organic gels (MOGs) have attracted a great deal of attention due to their potential application in sensing,<sup>1-4</sup> molecular recognition,<sup>5</sup> catalysis,<sup>6</sup> drug delivery,<sup>7-9</sup> and dye adsorption.<sup>10,11</sup> Low molecular weight MOGs are formed<sup>12</sup> due to various non-covalent interactions<sup>13</sup> which are responsible for the rapid self-assembly process of the discrete metal complexes and formation of the microstructures where a significant amount of solvent molecules are entrapped inside the network. These weak non-covalent interactions, as well as the microstructure, can be easily deformed through the external stimuli<sup>14,15</sup> and material can undergo the gel to sol transition or vice-versa. The easy synthetic procedure and heterogenous nature<sup>16,17</sup> of the MOGs attracted the researchers' attention in the field of catalysis. With the appropriate choice of the transition metals, the desired catalytic properties of the MOGs can be achieved successfully.

Sulfur dioxide is a major environmental pollutant and causes acid rain. Thus, the conversion of SO<sub>2</sub> to value-added products is desirable. 1,3,2-Dioxathiolane-2-oxides<sup>18</sup> are important electrophilic synthons in the field of organic chemistry due to their high reactivity towards nucleophiles and are more reactive than epoxides. The sulfites are used as an additive in the electrolyte of the lithium-ion batteries.<sup>19</sup> Although the chemistry of the 1,3,2-dioxathiolane-2-oxides is known since 1932, an efficient method for the synthesis of 1,3,2-dioxathiolane-2-oxides remains a challenge. The cycloaddition of epoxides and the SO<sub>2</sub> is one of the best routes to the cyclic sulfite.<sup>20</sup> Conventionally 1,3,2-dioxathiolane-2-oxides are synthesized using thionyl chloride and 1,2-diols, where chloride containing by-products are generated.<sup>21,22</sup> Metal-catalyzed cycloaddition of epoxides and

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Homepage: http://www.iitkgp.ac.in/department/CY/faculty/cy-mxb the SO<sub>2</sub> is the most atom-economical and efficient method for the synthesis of 1,3,2-dioxathiolane-2-oxides. There are only a few report<sup>23</sup> on such cycloaddition. There is only one report on the diastereoselective synthesis of cyclic sulfites using SO<sub>2</sub> and epoxides under comparatively milder condition.<sup>23</sup> Till date, there is no report on the MOG or MOF catalyzed fixation of SO<sub>2</sub>.

Carbon dioxide, one of the major greenhouse gases in the atmosphere, is the most abundant and cheapest source of C1 building unit.<sup>24-26</sup> Therefore, the capture and chemical conversion of the CO<sub>2</sub> as a renewable C1 building unit is essential. But the selection of the suitable catalyst is crucial for the activation and the successful fixation of carbon dioxide. The transition metal containing MOFs<sup>27-33</sup> and MOGs<sup>34,35</sup> have the potential as heterogeneous catalysts for the fixation of CO<sub>2</sub>. MOGs have more advantages over the MOFs, as syntheses of MOGs are much more straightforward. However, very few MOGs are reported for the CO<sub>2</sub> fixation reaction.

Moreover, the heterogeneous nature of these catalysts makes them suitable for the easy recovery and reusability for the next catalytic cycle. Depending upon the reaction conditions and the Lewis acidity of the metal center, the linear carbonates transform into either cyclic carbonates<sup>36</sup> or polycarbonates.<sup>37</sup> It has been shown that MOFs<sup>27,28,38,39</sup> exhibit substrate size dependent selectivity for the chemical conversion of CO<sub>2</sub>. Recently we have reported the synthesis of a metal-organic hydrogel using a low molecular weight gelator, which was found to be an efficient catalyst for the fixation of CO<sub>2</sub>.<sup>35</sup>

Herein, we report the synthesis of copper(II) containing multiresponsive metallohydrogel using Na<sub>2</sub>HL {H<sub>3</sub>L = 2-{(3,5-ditert-butyl-2-hydroxybenzyl)amino succinic acid},<sup>40</sup> and its catalytic activity towards fixation of SO<sub>2</sub> and CO<sub>2</sub> with epoxides.

## **Results and Discussion**

The ligand, Na<sub>2</sub>HL was prepared following the procedure reported from this laboratory.<sup>40</sup> The aqueous solution of the ligand (0.03 mmol in 0.5 mL) and copper chloride (0.03 mmol in 0.5 mL) were mixed in a glass vial at room temperature, and instantly a dark green MOG was formed (Figure 1).



Figure 1 Formation of the metal-organic hydrogel

Supporting information for this article is given via a link at the end of the document.

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The formation of the hydrogel was confirmed by an inverted vial test. The minimum gelation concentration (MGC) for MOG was found to be 2.28% (w/v) in water having effective gelation ratio for metal and gelator 1:1 (Figure S1, Supplementary Information). No gel formation was observed in common organic solvents. In the earlier report from this laboratory,<sup>40</sup> it was shown that the ligand, H<sub>3</sub>L on reaction with FeCl<sub>3</sub> affords the complex anion [Fe(HL)2], where one of the carboxylic groups in each ligand is not bonded with the metal center, and they are involved in intramolecular hydrogen bonding. Based on the observation, we theorized that reaction of copper chloride with the disodium salt of the ligand in water would afford a copper complex with free carboxylate groups and the hydrogen bonding interactions of these carboxylate groups with solvent water will afford the hydrogel. Thus we propose that the ligand forms a 1:1 complex with Cu2+ ion and due to the extensive hydrogen-bonding interactions with the solvent water the hydrogel is formed.

The hydrogel is stable at room temperature and does not show any deformation or gel-sol transformation in a sealed vial for months. Due to multiple cooperative non-covalent interactions, the MOG shows a quick thixotropic behavior when the external mechanical force is applied. On shaking, the MOG transforms into a viscous solution, and on standing for a few minutes at room temperature, the sol converts into to gel due to the shear thinning property of the MOG (Figure 2).



Figure 2 Multi-stimuli responsive and pH responsive nature of the MOG

The MOG was also found to be pH sensitive in nature and stable between the pH 4 to 9. The MOG is chemoresponsive (Figure 2) in nature. When a few drops of dilute aqueous  $NH_3$  is added to the MOG the gel brakes immediately, and a dark green solution is formed due to the formation of a metal-amine complex. The addition of dilute trifluoroacetic acid dropwise to this solution, the gel is formed.

The MOG turns into a hazy pale green solution when hydrochloric acid (pH below 4) is added dropwise, and upon addition of an equivalent amount of dilute aqueous NaOH solution to the hazy solution, the gel is reformed. However, above pH 9, the gel brakes again and it turns into a dark green solution. The reversible sol-gel transformation takes place due to the breaking and reformation of the bonds as well as weak noncovalent interactions between the metal and the gelator molecules.

The morphology of the MOG was investigated by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), and optical microscopy (OM) (Figure 3). The FESEM image shows the entangled network with foam like structures. The OM image of the MOG reveals the dendritic growth of the metallogel. The TEM image reveals the formation of a highly entangled network sponge-like structure containing cavities inside it. This entangled structure entrapped solvent molecules and is responsible for the gel formation. The AFM image confirms that the MOG consists of a spongy structure with a rough surface.



Figure 3 Different type of microscopic images of Cu-MOG; (a) FESEM, (b) TEM, (c) AFM and (d) OM image



**Figure 4** Plot of storage modulus (G') and loss modulus (G'') with (a) shear stress at 1 rad sec<sup>-1</sup>; with (b) frequency at 0.5% strain and with (c) time for step strain experiment for Cu-MOG

The mechanical strength of the metallohydrogel was measured by amplitude sweep (Figure 4a). The yield stress of the MOG at the crossover point was found to be 1.3 Pa. In the frequency sweep experiment, the G' and G'' were plotted against angular frequency ( $\omega$ ) over a region 1 to 100 rad sec<sup>-1</sup> (Figure 4b). The G' was found to be larger than G'' over the entire region of frequency, and the frequency-invariant characteristic confirms the viscoelastic nature of the metallogel. The shear strain during frequency sweep was found to be 0.5%. To confirm the thixotropic behavior, we performed the step strain experiment9 (Figure 4c) at 25°C. At first, a constant strain of 0.5% was applied to the gel, and then the strain was increased to 50% and

was kept for a few minutes. Then the strain was decreased to 0.5% and kept for few minutes. It was observed that when the applied strain was 50%, the loss modulus (G') was higher than the storage modulus (G'') indicating the sol-like nature of MOG. Immediately after decreasing the strain from 50% to 0.5%, the MOG recovered to the initial state. After every cycle of gel-to-sol transformation and vice versa during the experiment, the recovery of the MOG was almost 100%.

From the MALDI-TOF spectrum of the MOG, we found a peak at m/z 414 which corresponds to the 1:1 complex of copper and the ligand (Figure S2 and S3, Supplementary Information).

The xerogel was further characterized by IR spectroscopy and Thermogravimetric analysis (TGA). The IR spectrum (Figure S4, Supplementary Information) Cu-MOG shows metal coordinated carboxylate stretching  $v_{as}$  (COO<sup>-</sup>) stretch at 1558 and  $v_s$  (COO<sup>-</sup>) 1406 cm<sup>-1</sup>.

From the thermogravimetric analysis (TGA), it was found that the Cu-MOG is stable up to 190 °C (Figure S5, Supplementary Information). After 190 °C the material starts degrading and near to 800 °C only metal oxide exists.

From the observed morphology we expected that the xerogel might exhibit some porosity and we conducted reversible N<sub>2</sub> sorption measurements at 77K (Figure 5). The BET surface area for Cu-MOG was measured to be 50.64 m<sup>2</sup> g<sup>-1</sup> and it exhibits a saturated sorption amount of N<sub>2</sub> of 27 cm<sup>3</sup> g<sup>-1</sup>. The desorption curve is lower than the adsorption curve. This may be due to the weak interaction between the surface of the Cu-MOG and the N<sub>2</sub> molecules which lead to the faster desorption. After the N<sub>2</sub> sorption experiment, we have carried out CO<sub>2</sub> sorption measurement at 273 K (Figure 6) and we can see that Cu-MOG can uptake 6.5 cm<sup>3</sup> g<sup>-1</sup> amount of CO<sub>2</sub> gas.



Various Lewis bases, as well as alkali metals, have been used as homogeneous catalysts for the reaction of SO<sub>2</sub> with epoxides.<sup>19</sup> There is only one report on the amine functionalized silica as a heterogeneous catalyst for the reaction of SO<sub>2</sub> with epoxides.<sup>19</sup> However, the reactions were carried out at 100 °C, and the diastereoselectivity was found to be very poor. To the best of our knowledge, there is no report on the fixation of SO<sub>2</sub> using MOGs or MOFs. The reaction of SO<sub>2</sub> and epoxides using the xerogel as a catalyst produced a mixture of cyclic sulfites and poly sulfites.

For the optimization of the reaction, 1,2-epoxybutane was chosen as a substrate. In a typical solvent-free condition, 1,2-epoxybutane (10 mmol) was carried out with sulfur dioxide purged through bladder in the presence of 0.02 mmol of the MOG xerogel as a catalyst along with 5 mol% TBAB as a cocatalyst at room temperature. After 8 hours, the conversion of the starting epoxides was found to be good. But the yield of the cyclic sulfite was low. The <sup>1</sup>H NMR spectrum of the product is the same as that of the mixture of the products. The yield of the cyclic sulfite was found to be 21% (Table 1, entry 2). The conversions in the cases of propylene oxide (30%), 1,2-epoxy-3-phenoxy propane (16%) were found to be low. Interestingly the diastereomeric ratios (dr) were found to be excellent, from 70:30 to 90:10. It may be noted that there are very few reports on the diastereoselective synthesis of 1,3,2-dioxathiolane-2-oxides.<sup>20</sup>



Figure 6 CO<sub>2</sub> adsorption isotherm for Cu-MOG

Table 1 Cycloaddition of various epoxides with SO2<sup>a</sup> MOG, TBAB RT Entry Substrate Conversion<sup>b, c</sup> (%) dr<sup>d</sup> 1 30 80:20 2 21 70:30 3 20 70:30 4 21 60:40 5 16 90:10

We then proceeded to test the efficacy of the xerogel as a catalyst for the reaction of SO<sub>2</sub> and CO<sub>2</sub> with epoxides for their chemical fixation. In recent years, copper-containing MOFs have been shown to catalyze the chemical fixation of CO<sub>2</sub>.<sup>41,42</sup> However, it is worth mentioning that the synthesis of MOGs is

<sup>a</sup>Reaction conditions: epoxide (10 mmol), catalyst (0.02 mmol), TBAB (0.16 g, 5 mol%) under SO<sub>2</sub> (1 bar), 300 K and 8 h. <sup>b</sup>From <sup>1</sup>H NMR. <sup>c</sup>Average of three reactions. <sup>d</sup>Diastereomeric ratio from <sup>1</sup>H NMR of the isolated products. <sup>e</sup>Mixture of the products stirred at 60 °C in the presence of the MOG for 8 hrs.

57

6<sup>e</sup>

90.10

Takenaka et al. reported that in the reaction of propylene oxide in the initial stage poly(propylene sulfite) was formed in more amount and cyclic sulfite was formed in low amount and with time the yield of the cyclic sulfite increased.<sup>19</sup> Accordingly, after 8 hours we removed the SO<sub>2</sub> source, and stirred the mixture of the products of the reaction of SO<sub>2</sub> with 1,2- epoxybutane in the presence of the MOG for 60 hours at room temperature, and the yield of 4-ethyl-dioxathiolane-2-oxide increased from 21% to 51%. We then proceeded to examine the conversion of the polymeric product to the cyclic sulfite under the heating condition. The mixture of the products obtained from the reaction of 1,2epoxybutane with SO<sub>2</sub> was stirred at 60 °C in the presence of the MOG for 8 hours, and the yield of the cyclic product was found to be 57% (Table 1, entry 6). However, in the absence of the MOG, we could not detect any increase in the conversion of the polymeric sulfite to the cyclic product. It may be noted that a reaction of 1,2-epoxybutane with SO<sub>2</sub> carried out only in the presence of TBAB afforded only 1% of the mixture of products. We could not detect any product formation in the absence of the MOG as well as TBAB.

All the products have been characterized by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy. Also, one of the major diastereomers of 4-phenoxy-1,3,2-dioxathiolane-2-oxide has been structurally characterized by single crystal X-ray crystallography (Figure 7).

Figure 7 ORTEP view of 4-phenoxy dioxathiolane-2-oxide. Hydrogen atoms omitted for clarity

The cycloaddition of the propylene oxide (10 mmol) was carried out with carbon dioxide purged at 1 atm pressure using 0.02 mmol of the MOG xerogel as a catalyst along with 5 mol% tetrabutylammonium bromide (TBAB) as a co-catalyst at room temperature. After 48 hours, the yield of the product was found to be 78% (Table 2, entry 1). After the optimization of the reaction condition, we have carried the reaction using various types of epoxides containing short to long side chain aliphatic and aromatic group. For the straight chain substrate, we found a good to moderate conversion. With increasing bulk of the substituent, the conversion of the epoxide to the carbonate decreases sharply as the approach of the epoxy oxygen to the metal center becomes unfavorable. Due to this, low conversions to carbonate were observed in the cases of tert-butyl glycidyl ether and styrene oxide. Since the reactions were carried out under a solvent-free condition, the lipophilicity or solubility of the epoxide does not play an essential role in the observed trend in the conversion. Thus the decrease in the conversion with the increase in bulk of the side chain may be explained by the steric effect of the epoxide side chain. The critical step in the reaction of epoxide with CO<sub>2</sub> is the activation of the epoxide ring by the metal center.32 With the increase in the bulk of the epoxide, the coordination of the epoxide oxygen to the copper center is more difficult, and thus the conversion to cyclic carbonate decreases with the increase in the size of the epoxide side chain. The control reaction of 1,2-epoxybutane with  $CO_2$  in the presence of TBAB and in the absence of MOG afforded the cyclic carbonate in 3% yield. The control experiment in the absence of the MOG as well as TBAB was carried out and we could not detect any product formation.

Table 2 Cycloaddition of various epoxides with CO2<sup>4</sup>



<sup>a</sup>Reaction conditions: epoxide (10 mmol), catalyst (0.02 mmol), TBAB (0.16 g, 5 mol%) under CO<sub>2</sub> (1 bar), 300 K and 48 h. <sup>b</sup>From <sup>1</sup>H NMR <sup>c</sup>Average of three reactions

In the cases of the reaction of SO<sub>2</sub> and CO<sub>2</sub>, the xerogel was recollected by centrifugation and washed with acetone (2 × 3 mL). After drying the material in an oven at 60 °C for 1 hour, we have tested the recyclability of the xerogel using propylene oxide as a model substrate for CO<sub>2</sub> and 1,2-epoxybutane for SO<sub>2</sub> fixation.



Figure 8 Recyclability study of the Cu-MOG

In the case of the reaction of  $SO_2$ , after the first cycle, the activity drops (Figure 8) because of the decomposition of the xerogel by the acid generated from the reaction of  $SO_2$  with moister. So in

the reaction of SO<sub>2</sub>, the catalyst is not recyclable. However, in the case of CO<sub>2</sub> fixation, up to five cycles the efficiency of the material was found to be very good (Figure 8). The powder X-ray diffraction analysis of the used xerogel shows that the integrity of the material remains intact (Figure S6, Supplimentary Information).

#### Conclusions

In conclusion, a new copper containing metal-organic hydrogel has been synthesised using the disodium salt of the ligand, 2-{(3,5-di-tert-butyl-2-hydroxybenzyl)amino succinic acid}, Na<sub>2</sub>HL. The xerogel of the Cu-MOG can be used as a catalyst for the chemical conversion of SO<sub>2</sub> to cyclic 1,3,2-dioxathiolane-2-oxides with high diastereoselectivity and the conversion of CO<sub>2</sub> to carbonates on reaction with the epoxides at room temperature and under one atmospheric pressure.

### **Experimental Section**

All the chemicals, L-aspartic acid was bought from SRL chemicals, 2,4di-tert-butyl phenol was bought from Sigma-Aldrich and zinc acetate, sodium hydroxide was commercially available. Analytical reagent grade solvents were used without further distillation. Propylene oxide, 1,2epoxybutane, 1,2-epoxyhexane, tert-butyl glycidyl ether, 1,2-epoxy-3phenoxypropane were bought from Sigma-Aldrich and styrene oxide was bought from Merck. The CO<sub>2</sub> gas used for the catalysis was 99.9% pure. The SO<sub>2</sub> gas used for the catalysis was prepared in the laboratory. The ligand, Na<sub>2</sub>HL was synthesized by the procedure reported from our laboratory.<sup>36</sup>

The morphology of the xerogel was characterised using a field emission scanning electron microscope (Zeiss EVO 60 with Oxford EDS detector) operating at 5–10 KV. The sample was prepared by dropping the diluted solution of MOG on the thin aluminium sheets and then dried in air. To minimise the sample charging a thin layer of Au was coated on the sample before the experiment.

The gel sample was characterised by an analytical TEM (FEI. TECNAIG220S-TWIN) instrument operated at 120 kV. The sample was prepared by dropping the much-diluted solution of gels on the carbon-coated copper grids, and the samples were allowed to dry for overnight.

The morphology of the MOG was analysed by atomic force microscope (Agilent 5500). AFM sample was prepared by dropping the very dilute solution of MOG on a small piece of the glass slide and allowed to dry overnight before imaging.

The gel sample was characterised by an optical image analyser (Leica DMLM) instrument. The sample was prepared by dropping the very dilute solution of the MOG on the glass slide.

For the MOG, rheological measurements were carried out on an MCR 102 (Anton Paar) modular compact rheometer using a 25 mm diameter parallel plate with a constant tool gap of 1 mm. The MOG was placed on the lower plate, and a stress amplitude sweep experiment was carried out at a constant angular frequency of 1 rad sec<sup>-1</sup> at 298K to obtain storage or elastic modulus, G', and loss or viscous modulus, G''. The frequency sweep measurement was carried out in the linear viscoelastic range at constant stress.

The MALDI-TOF spectrum of the MOG was recorded using 2,5dihydroxybenzoic acid as the matrix in the Bruker Daltonics, model: Ultraflextreme instrument.

#### X-ray crystallography

Single-crystal X-ray data of the 4-phenoxy dioxathiolane-2-oxide were collected on Bruker Smart APEX II CCD system that uses graphite monochromated Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). The structure was solved by the direct method and refined by the least square method on F2 employing WinGX<sup>43</sup> package, and the relevant programs {SHELX-97<sup>44</sup> and ORTEP-3<sup>45</sup>} implemented therein. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms on C-atoms were fixed at calculated positions and refinement of complexes are summarized in Table S1. CCDC 1860491 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data\_request/cif.

#### Synthesis of the Metal - Organic Gel

Ten different glass vials were taken and in each of the vials the disodium salt of the ligand, Na<sub>2</sub>HL (0.012 g. 0.03 mmol) dissolved in water (0.5 mL) was placed. To the vials aqueous solution (0.5 mL) of CuCl<sub>2</sub>·2H<sub>2</sub>O (0.1 to 1.0 equivalent) was added and on standing at room temperature for five minutes the gel formation was tested by inverted vial technique.

#### General Procedure for the cycloaddition of SO<sub>2</sub> to epoxides

The epoxide (10 mmol) was taken in a Schlenk tube to this was added the MOG (0.116 g; 0.2 mol% based on the MOG complex) and tetrabutylammonium bromide (TBAB, 5 mol%). Sulfur dioxide was purged through a bladder for 8 hours at room temperature. The conversion of the epoxide was calculated using the <sup>1</sup>H NMR spectra of the crude product using calculated amount of mesitylene as an internal standard.

#### General Procedure for the cycloaddition of $\text{CO}_2$ to epoxides

The reaction of the epoxide with  $CO_2$  was carried out in an analogues manner as described above for the reaction of  $SO_2$ , only difference being instead of 8 hours of stirring, the reaction was carried out for 48 hours. The conversion of epoxide into cyclic carbonate was calculated from the <sup>1</sup>H NMR spectra of the crude product using calculated amount of mesitylene as an internal standard.

The reaction mixture was centrifuged to recover the catalyst for reusing the catalyst. Then the clear solution was decanted, and the xerogel material was washed thoroughly with acetone and dried in an oven. Then the reaction was done under the same condition as previously described using propylene oxide as a substrate.

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A copper(II) hydrogel has been synthesized and characterized. The xerogel can be used as heterogeneous and recyclable catalyst for the conversion of  $SO_2$  1,3,2dioxathiolane-2-oxides with high diastereoselectivity. The xerogel can also be used for the chemical fixation of  $CO_2$ .



#### **Copper Hydrogel Catalysis**

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