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## Bifunctional coordination polymers as efficient catalysts for carbon-dioxide conversion

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**Abstract:** The multidentate ligand H<sub>2</sub>L upon complexation with Zn(II) and Cd(II) provide a one-dimensional polymeric networks. These coordination polymers (CPs) **CP-1** and **CP-2** containing Zn(II) and Cd(II) metals respectively are well characterized. The single crystal structural analysis confirms the formation of one-dimensional coordination polymer with *zigzag* fashion in **CP-1** and ladder chain **CP-2**. Both the CPs are applied as catalysts to synthesize various cyclic carbonates from epoxides and carbon-dioxide. The catalysts are giving better conversion under solvent-free and additive-free condition using 10 bar CO<sub>2</sub> and 100 °C as optimized pressure and temperature. The detailed kinetic experiments suggesting the first order kinetics, the energy of activation (E<sub>a</sub>) is calculated for this catalytic conversion.

**Keywords:** Coordination polymers, CO<sub>2</sub> utilization, Cyclic carbonates, Reaction Kinetics, Activation energy.

### Introduction

The alarmingly increasing carbon-dioxide level in the atmosphere by industrial and other pollutants leads to drastic climate change globally.<sup>[1]</sup> This freely available C-1 source in the atmosphere on one side causing serious health hazardous, it can also be effectively converted into useful value-added products<sup>[2-4]</sup> for mankind. To this purpose, the inert and thermodynamically stable CO<sub>2</sub> might be made reactive by some judicious choice of catalysts.<sup>[5]</sup> In this regard researchers worldwide are attempting to convert CO<sub>2</sub> into many value-added products<sup>[6]</sup> such as carboxylic acids (acetic acid<sup>[7]</sup>, formic acid<sup>[8]</sup>), alcohols<sup>[9]</sup> (methanol, ethanol), organic carbonates<sup>[10-11]</sup> (diethyl carbonate, dimethyl carbonate) and hydrocarbons<sup>[12]</sup> *etc.* Among the various products, the catalytic conversion of CO<sub>2</sub> to cyclic carbonate or polycarbonates from epoxide or diol<sup>[13]</sup> is considered potential. Most of the homogenous catalytic systems thus reported are found to be salen and salphen complexes with a wide variety of metal ions.<sup>[14-16]</sup> In this series, the Zn-salphen catalyst in combination with tetrabutylammonium iodide(TBAI) as co-catalyst, reported by A. W. Kleij and co-workers give maximum conversion of 94% at 45 °C in 18 h at 10 bar CO<sub>2</sub>.<sup>[17]</sup> The same group has reported a modified Zn-salphen catalyst with 80% conversion adapting the same reaction time, but at reduced temperature 25 °C, and pressure of 2 bar CO<sub>2</sub>.<sup>[18]</sup> Similarly the Zn-clusters reported by K. Mashima, with almost similar ambient condition (25 °C, 1 atm) gives 94-99% conversion with reaction time ranging 6-20 h.<sup>[19]</sup> In the same trend, the Al-salen chiral complex by M. North although works at ambient conditions, the use of chiral moiety and long reaction time are remain unaddressed.<sup>[20-22]</sup>

Similarly, the Al – triphenolate based catalyst by A.W. Kleij and co-workers giving 96% conversion with 960 TOF<sup>[23]</sup>; an addition of trace amount of TBAI as a co-catalyst was reported to enhance its TOF to

36000 h<sup>-1</sup> and suggests it is highly efficient.<sup>[23]</sup> Thus the simple metal complexes with Al, and Zn mentioned above are working as catalysts under ambient conditions,<sup>[24]</sup> the metal complexes with various supramolecular assemblies such as MOF,<sup>[25]</sup> coordination polymers<sup>[26-30]</sup> are considered important for such catalytic applications,<sup>[31]</sup> since they are composed with multi-metallic active sites. With this in mind, we in the present report describe the synthesise of two important one-dimensional coordination polymers (CPs) of Zn(II) and Cd(II) complex with multidentate ligand H<sub>2</sub>L and their application as catalyst in converting CO<sub>2</sub> to cyclic carbonate through cycloaddition reaction. More strikingly both these catalysts working efficiently without any co-catalyst provides 87-99% of terminal cyclic carbonate with highest selectivity gains significance in view of CO<sub>2</sub> utilization.

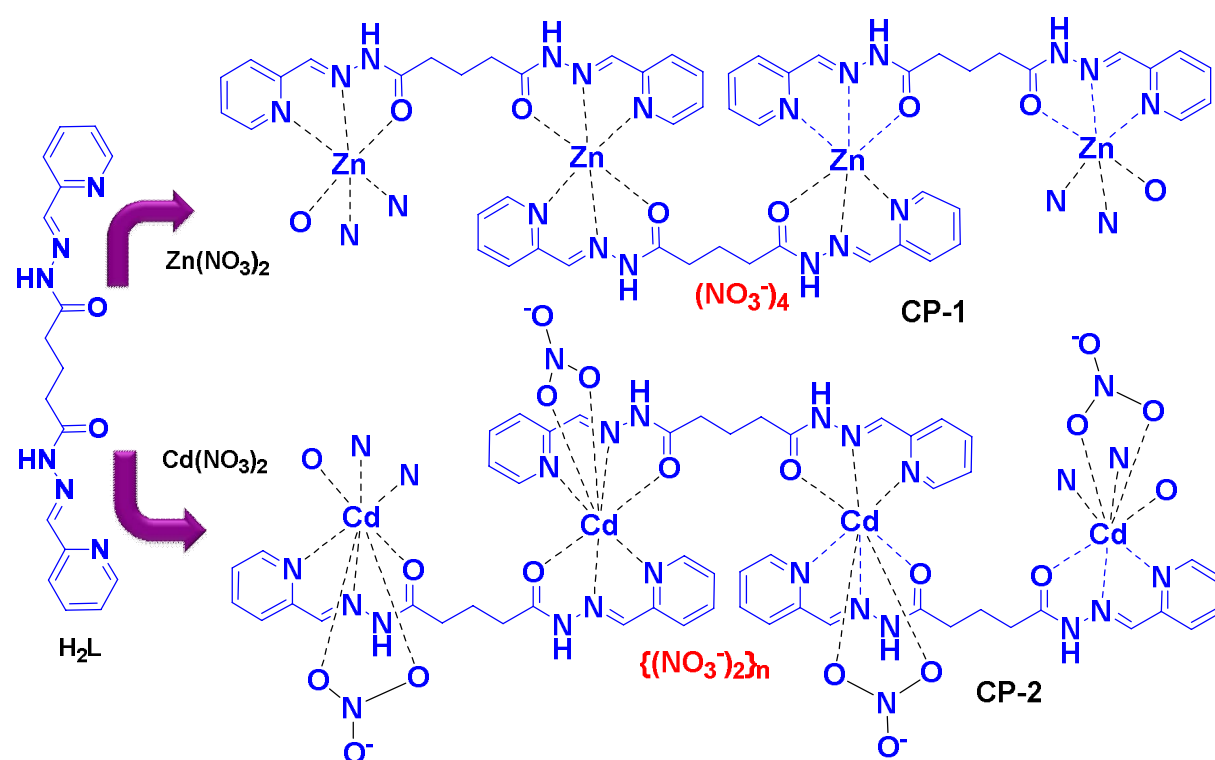
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## Results and Discussion

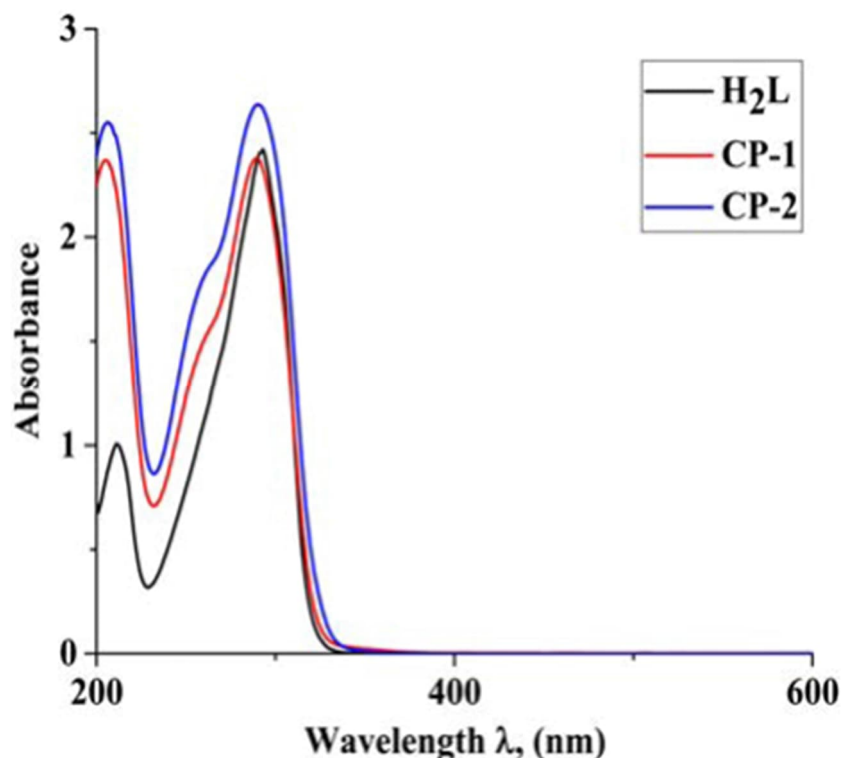
The multidentate ligand H<sub>2</sub>L with glutarate-di-aza spacer was synthesized following our recent reports.<sup>[32]</sup> The ligand H<sub>2</sub>L upon complexation with Zn(NO<sub>3</sub>)<sub>2</sub> and Cd(NO<sub>3</sub>)<sub>2</sub> in 1:1 metal-ligand ratio leads to the formation of a one dimensional coordination polymers, **CP-1** and **CP-2** respectively (Scheme 1).



**Scheme 1.** Synthesis (i) {[Zn<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>(NO<sub>3</sub>)<sub>4</sub>]<sub>n</sub> (**CP-1**) (ii) {[Cd<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>]<sub>n</sub> (**CP-2**).

The ESI-MS spectra of the CPs provide an intense peak correspond to the monomeric unit. The intense peak at m/z = 803.71 (calc. 803.13) for **CP-1**, is attributed to [Zn<sub>2</sub>L<sub>2</sub>]<sup>+</sup>H<sup>+</sup> and the m/z = 899.90 (calc. 899.08) for CP-2 is attributed to [Cd<sub>2</sub>L<sub>2</sub>]<sup>+</sup>H<sup>+</sup> (S1-S2). This mono positive ions obtained by successive de-protonation

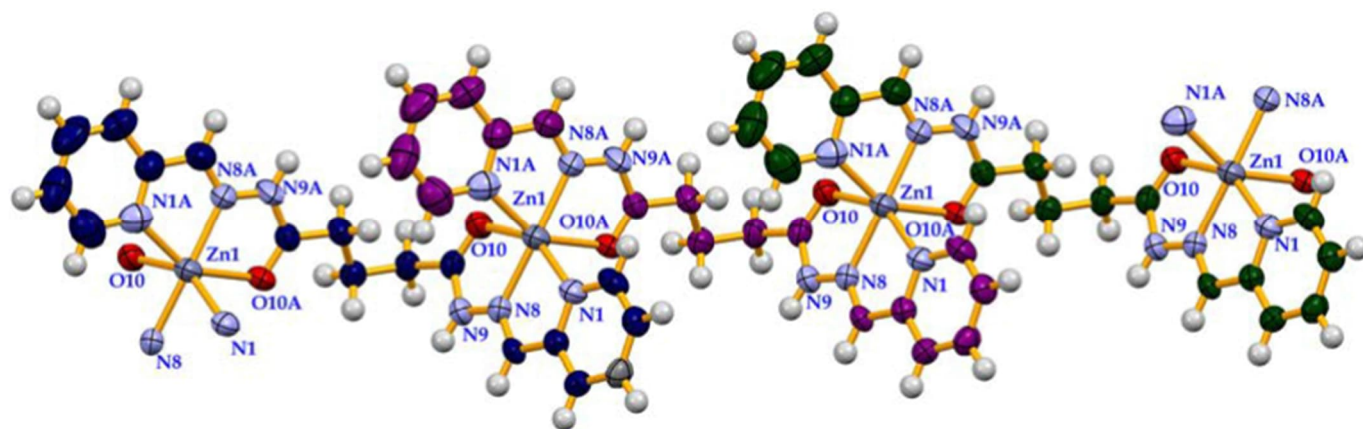
of the labile  $\text{-NHs}$  of ligand  $\text{H}_2\text{L}$  indicate a monomeric units of the polymers. The elemental analysis establishes that the polymeric units **CP-1** and **CP-2** exists with two and six water molecules respectively. The absorption spectra of **CP-1** and **CP-2**, show an absorption maxima at 290 nm correspond to ligand centered transitions along with a weak shoulder at 265nm, attributable to LMCT transitions (Figure 1).



**Figure 1.** UV-Vis spectra for  $\text{H}_2\text{L}$ , **CP-1** and **CP-2** in water ( $3 \times 10^{-5}$  M)

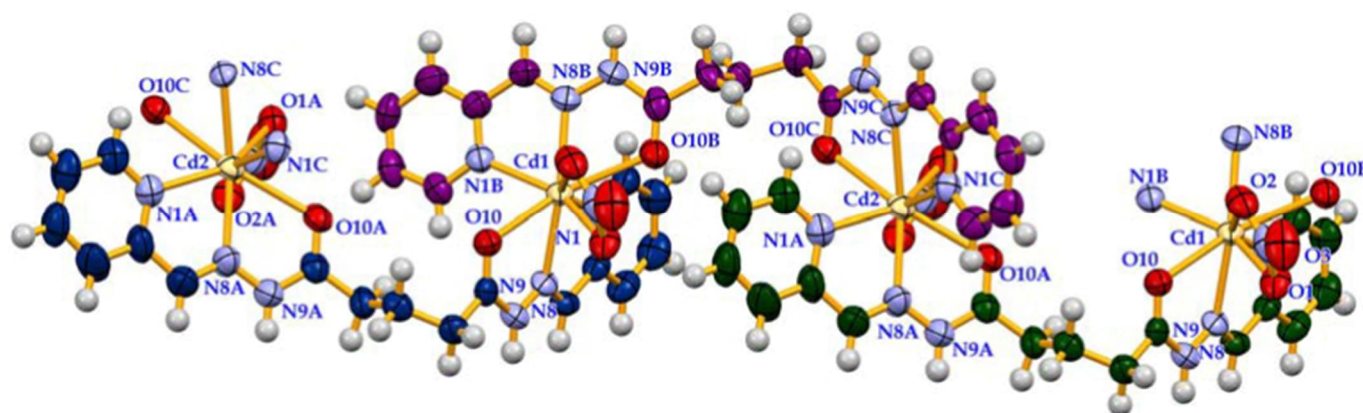
### Structural description by single crystal XRD

The suitable crystals of **CP-1** were obtained by diffusion of acetonitrile into its aqueous solution. The monoclinic crystal structure showed six-coordination and established a distorted octahedral geometry around  $\text{Zn(II)}$  ion as shown in Figure 2. The two  $\text{N}_2\text{O}$  cleft from  $\text{H}_2\text{L}$  coordinated to the metal centre are almost orthogonal to each other showing an angle value between  $\text{N}_2\text{O-Zn}$  coordination planes of about  $83^\circ$ . In the complex each ligand is oriented in the polymeric form along  $\text{M-M}$  and the motif is extended along the  $x$ -axis. The crystallographic structure establishes that the complex is composed of a tetracationic monomeric unit and are extended in a polymer chain. Each tetracationic  $[\text{Zn}_2(\text{H}_2\text{L})_2]^{4+}$  dimeric unit is counterbalanced by four nitrate ions in the crystal lattice. Along the polymer the metal ions are separated by  $8.802(2)$  Å.



**Figure 2.** Crystal structure of **CP-1**  $[\text{Zn}_2(\text{H}_2\text{L})_2]_n$  with 50% probability factors for thermal ellipsoid. The anions and hydrogen are omitted for clarity.

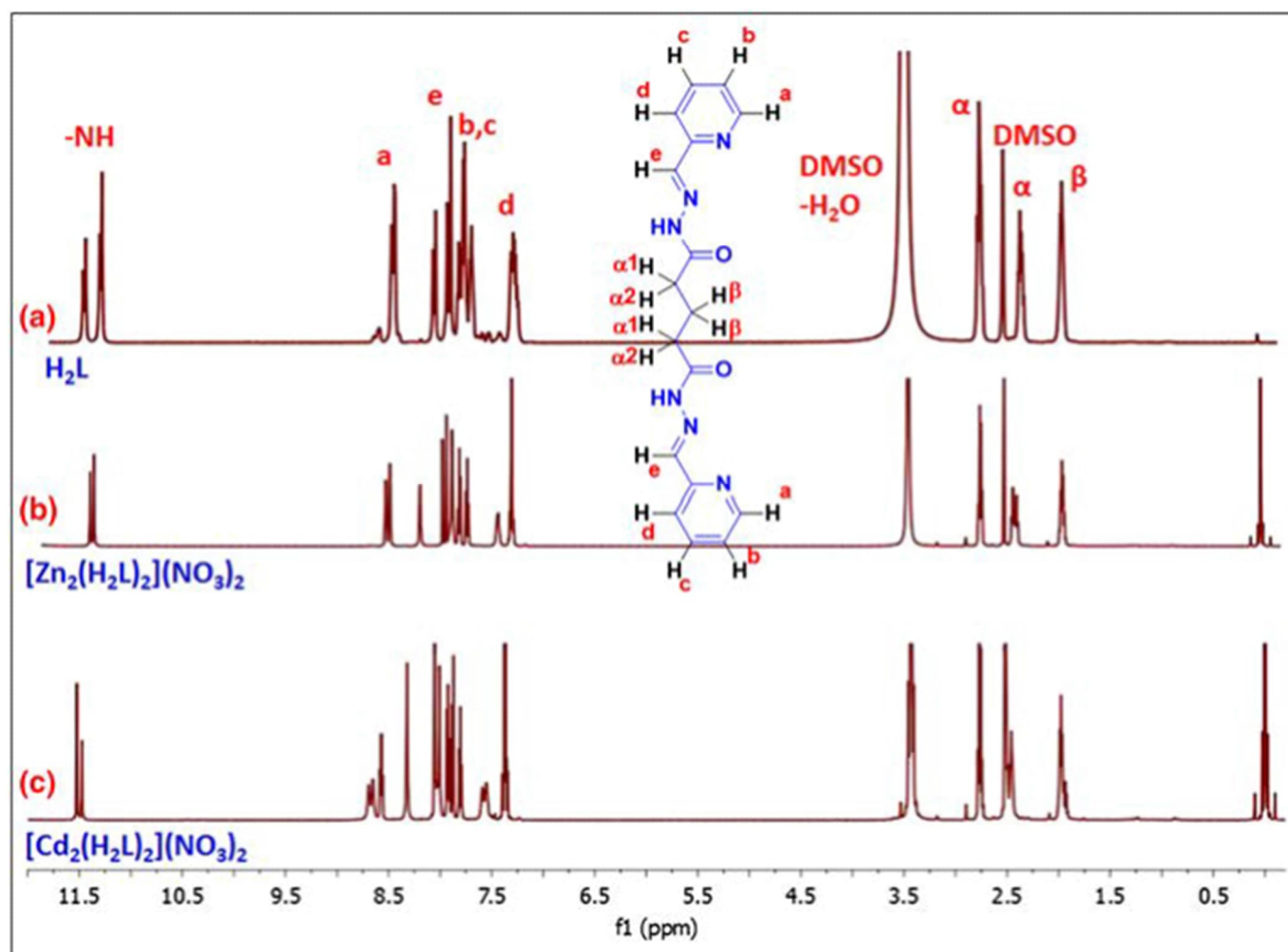
Colourless crystals of complex **CP-2**,  $\{[\text{Cd}_2(\text{H}_2\text{L})_2(\text{NO}_3)_2](\text{NO}_3)_2\}_n$ , were obtained by diffusion of isopropyl alcohol into its aqueous solution. Low symmetry structure revealed eight-coordination around both two Cd(II) centers. The Cd coordination spheres consist half units of two different **H<sub>2</sub>L** ligands and one bidentate nitrate anion. The structure show approximately  $72^\circ$  angular separation in  $\text{N}_2\text{O}$ -Cd coordination planes of ligands and  $\text{N}_2\text{O}$ -Cd to  $\text{O}_2$ -Cd angles of about  $67$  and  $64^\circ$  for the first coordination sphere, respectively. For the second sphere the angular separation of the ligands is identical, but the coordination angles to the nitrate show slightly deviating values of about  $71$  and  $63^\circ$ . The bond distances and angles around the two independent Cd(II) centers are almost the same and the overall geometry around both Cd(II) centers resembles triangular dodecahedron (S7). The **H<sub>2</sub>L** ligands are assembled in a side-by-side orientation with metal axis possessing intermetallic Cd–Cd distances of  $8.3753(7)$  and  $8.5267(7)$  Å (Figure 3). One half of the ligand moiety coordinating on one Cd center, the other half of the ligand coordinated to the next Cd center in the polymeric chain through their  $\text{N}_2\text{O}$  clefts. Thus two such ligands forming ladder type coordination with alternative metal center assemble a one dimensional polymeric chain in z-axis. In addition to two coordinated nitrates the remaining positive charges are counterbalanced by two nitrates in the crystal lattice. Further details of crystallographic analysis of **CP-1** and **CP-2** are shown in Supplementary Material (S3-S7).



**Figure 3.** Crystal structure of **CP-2**  $[\text{Cd}_2(\text{H}_2\text{L})_2(\text{NO}_3)_2]_n$  with 50% probability factors for thermal ellipsoid. The anions and hydrogen are omitted for clarity.

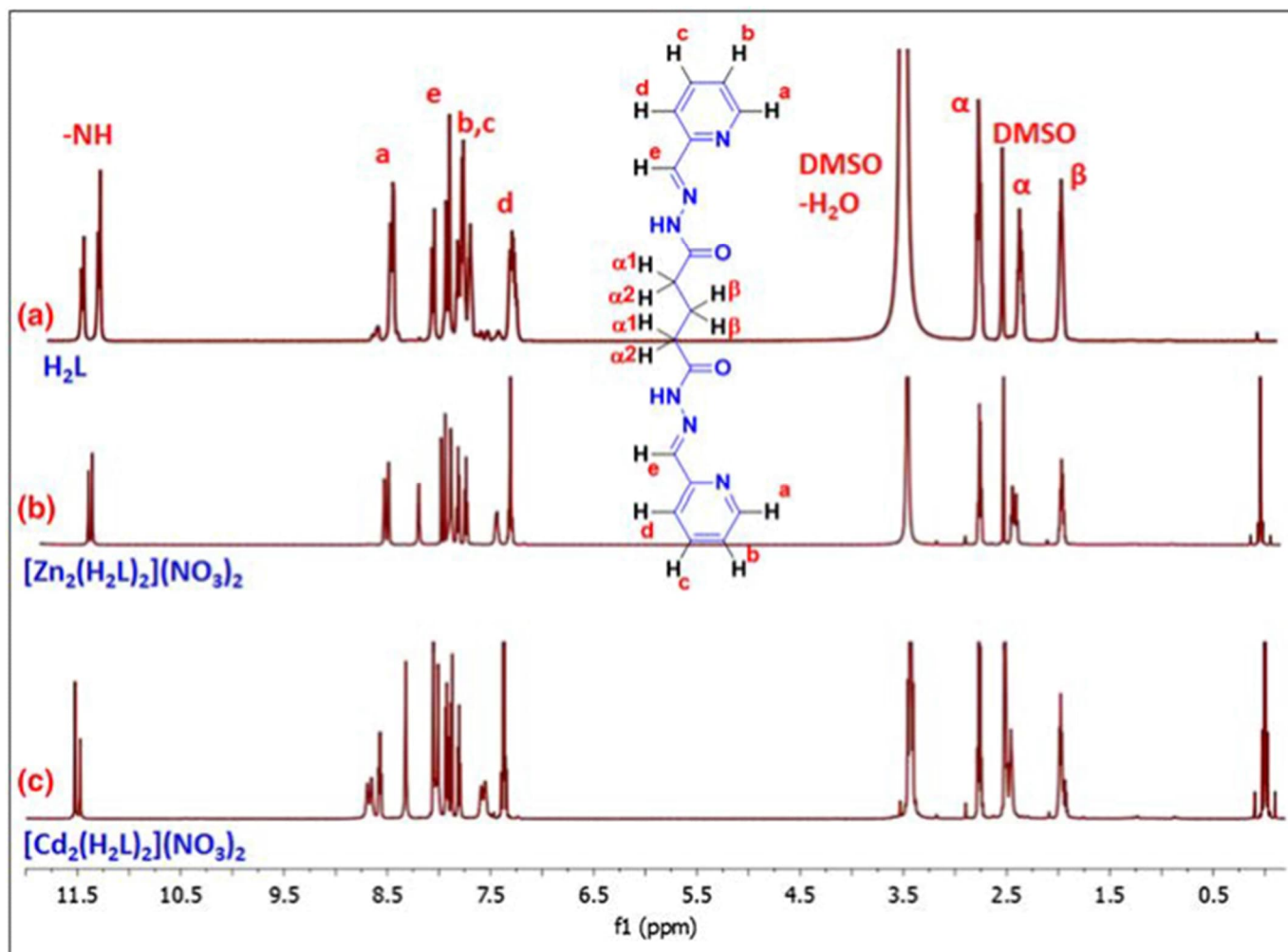
## $^1\text{H}$ NMR for coordination polymers

In the  $^1\text{H}$  NMR spectra (Figure 4), the ligand ( $\text{H}_2\text{L}$ ) and their coordination polymers **CP-1** and **CP-2** (S9-S10), show the signals in the range of 8.6 to 7.3  $\delta$  are correspond to the pyridyl and azomethine hydrogen of the ligand. The distinctive singlets at 11.5  $\delta$  attributed to  $-\text{NH}$ s are confirmed by  $\text{D}_2\text{O}$  exchange. The methylene groups ( $-\alpha^1, \alpha^2\text{CH}_2-\beta\text{CH}_2-\alpha^1, \alpha^2\text{CH}_2-$ ) in the spacer of the ligands  $\text{H}_2\text{L}$  depicting three well-resolved resonances at 2.77, 2.36 and 1.94  $\delta$  respectively, the integral ratio of all of them are equivalent to two hydrogens (Figure 4). Although the  $^1\text{H}$  NMR of ligand and its CPs, showing no difference in the aliphatic region correspond to  $\text{CH}_2$  spacers, a systematic variable temperature study performed in the range 20-70  $^\circ\text{C}$  on these complexes derives interesting information about the conformation of the ligand strands (Figure 5).



**Figure 4.**  $^1\text{H}$  NMR for a) ligand, b) **CP-1** c) **CP-2** in  $\text{DMSO-d}_6$

The resonance at 1.94  $\delta$  in the up-field appeared for middle  $\text{CH}_2$  group in both **CP-1** and **CP-2** shows no change in the chemical shift as well as a spectral pattern with respect to the effect of varying temperature indicate that they are from the metal centers. However upon increasing the temperature the peaks at 2.77, 2.36  $\delta$  attributable to terminal  $\text{CH}_2$ s are showing a very distinct change from its narrow pattern to broad pattern indicate their close proximity with the metal center (Figure 5).



**Figure 5.** VT  $^1\text{H-NMR}$  (DMSO- $d_6$ ) for (a) **CP-1** and (b) **CP-2** (aliphatic region)

### Cycloaddition of carbon-dioxide into cyclic carbonate

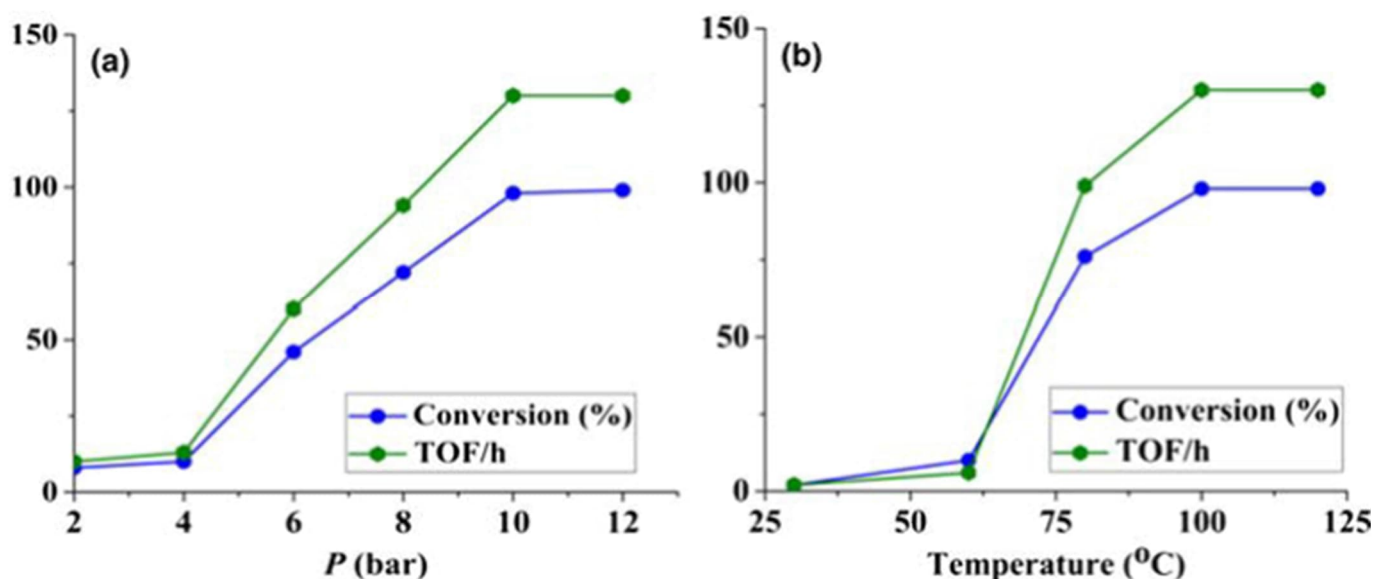
As stated above both the CPs possessing multimetallic active sites, similar to that of MOFs we inspired to examine their catalytic activity. Accordingly, both the CPs were applied as catalysts for the synthesis of cyclic carbonates from epoxide. Initially, the **CP-1** and **CP-2** were screened for their catalytic performance using styrene oxide as a substrate under solvent-free condition using 10 bar  $\text{CO}_2$  (S13). A model reaction performed initially in the absence of catalyst showed no conversion of styrene oxide to styrene carbonate (Table 1, Entry 1). But when added tetra butyl ammonium bromide (TBAB), a sudden raise in the yield to 68% (Table-1, Entry 2) was observed. The combination of **CP-1** (0.2 mmol) and TBAB, together raised the conversion to 99% within 4 h (Table-1, Entry 3).

**Table 1.** Screening of catalyst<sup>[a]</sup>

Entry	Catalyst	Yield <sup>[b]</sup> %	TON <sup>[c]</sup>	TOF <sup>[d]</sup> h <sup>-1</sup>
1	<b>Blank</b>	No reaction	---	---
2	<b>TBAB</b>	68	---	---
3	<b>CP-1<sup>[e]</sup></b>	99	493	123
4	<b>CP-1</b>	99	493	123
5	<b>CP-2</b>	87	432	108

<sup>[a]</sup>All reactions were carried out using 100 mmol of styrene oxide, 0.2 mmol of catalyst, 10 bar carbon-dioxide, at 100 °C for 4h under solvent free condition. <sup>[b]</sup> Isolated yield, <sup>[c]</sup> TON = mmol of product formed/mmol of catalyst used, <sup>[d]</sup> TOF = TON/reaction time, <sup>[e]</sup> TBAB used.

Surprisingly in our successive attempt adding **CP-1** (0.2 mol %) without any co-catalysts, the conversion has remained as 99% styrene carbonate (Table-1, Entry 4). Similarly, when applied **CP-2** (0.2 mol%) as catalyst, the conversion was achieved as 87% of cyclic carbonates (Table-1, Entry 5). This minimum amount 0.2 mmol of catalyst **CP-1** and **CP-2** required to catalyse 100 mmol substrate (1:500 ratio of catalyst: substrate) encouraged us to adopt these catalyst in such CO<sub>2</sub> reactions for further investigation. In addition, the reduction in the reaction time, non-requirement of co-catalyst at 100 °C are considered advantages for effective usage of this catalyst in the synthesis of cyclic carbonate from epoxide. Generally, in such CO<sub>2</sub> reactions, there is a possibility for the formation of both cyclic carbonate and polycarbonate. But the present catalyst producing 100% cyclic carbonate, it is noteworthy to mention that this catalyst is highly selective towards cyclic carbonate. Although both the catalysts adapted in solvent-free condition seems to be efficient, based on the yield the **CP-1** giving 99% yield was found better, than the **CP-2**.



**Figure 6.** (a) Pressure optimization, (b) Temperature optimization parameters using 0.2 mmol **CP-1**, 100 mmol styrene oxide for 4h. The conversion was determined from <sup>1</sup>H NMR; TOF = TON/4



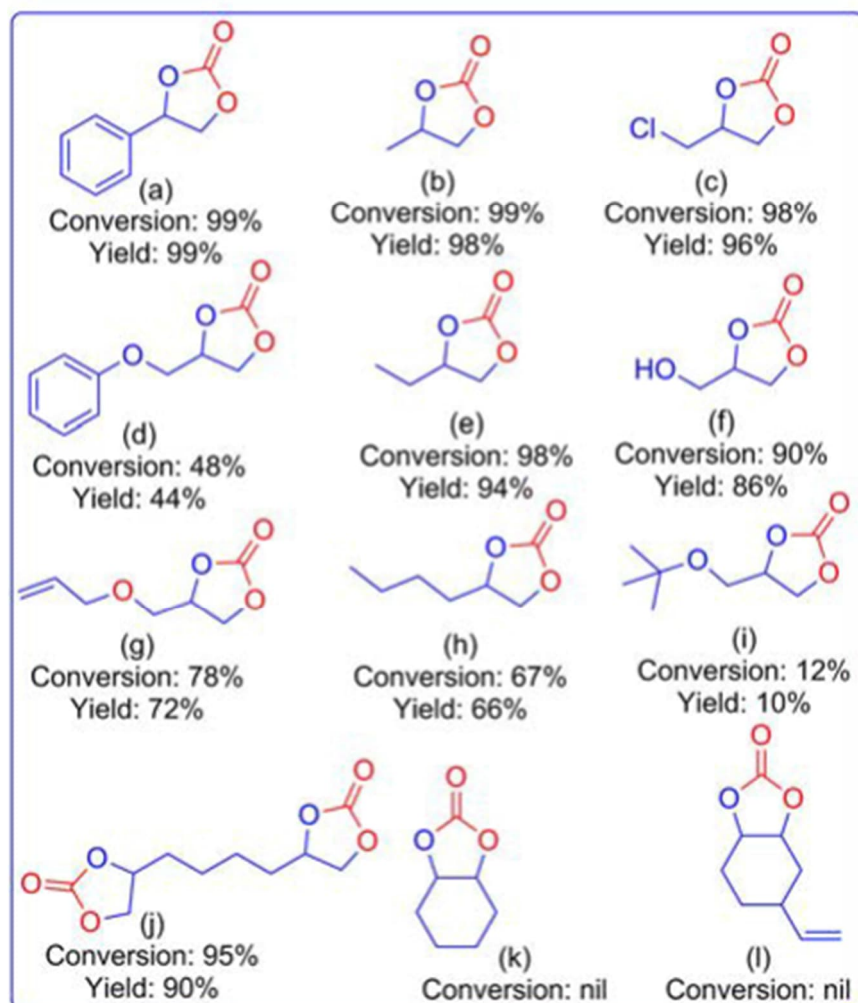
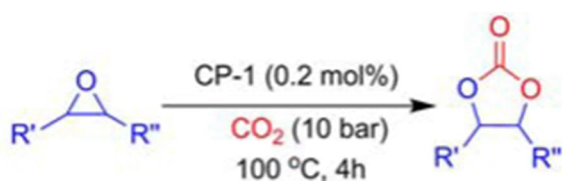
Identifying the **CP-1** as an efficient catalyst, next we attempted to optimize various other parameters such as temperature and pressure. The pressure of the CO<sub>2</sub> was varied from 2-12 bar and their respective conversions and TOF calculated are plotted in figure 6a. During the reaction, the initial and final pressure of the carbon-dioxide were measured, which showed a fall in the pressure of approximately 4 bar indicating consumption of CO<sub>2</sub> during the reaction. So in the initial pressure ranging 2 to 4 bar, the conversion was found very low, but upon increasing the pressure beyond this range the conversion was found increased significantly. As noticed in the above plot, the maximum conversion 98% was achieved at 10 bar CO<sub>2</sub>, and 100 °C.

Keeping the CO<sub>2</sub> pressure constant at 10 bar, the temperature was varied up to 120 °C from 30 °C in view of its optimization (figure 6b). The reactions performed at room temperature (30 °C) and 60 °C giving trace amount of conversion around less than 10%, a raise in the temperature to 80 °C, raised the conversion of styrene epoxide to 76%. A further increase in the temperature to 100 °C provides a further enhancement in the conversion to 99% as shown in figure 6b. So the 10 bar CO<sub>2</sub> at 100 °C giving highest conversion, the optimized reaction temperature is ultimately fixed as 100 °C for **CP-1**.

### Screening of substrates

The efficient conversion of neat styrene epoxide to styrene carbonate shown by **CP-1** inspired us to explore its catalytic role on various substituted terminal and internal epoxides adapting the above-optimized reaction conditions. Except few, most of the aliphatic substituted terminal epoxides used here is giving better conversion and the results are summarized in Chart 1. All these reactions were carried out using 100 mmol of epoxide, 0.2 mmol of **CP-1**, 10 bar carbon-dioxide, at 100 °C for 4h under solvent-free condition. Conversions were determined using <sup>1</sup>H NMR for reaction mixture. Yield here represent the isolated yield after column chromatography.

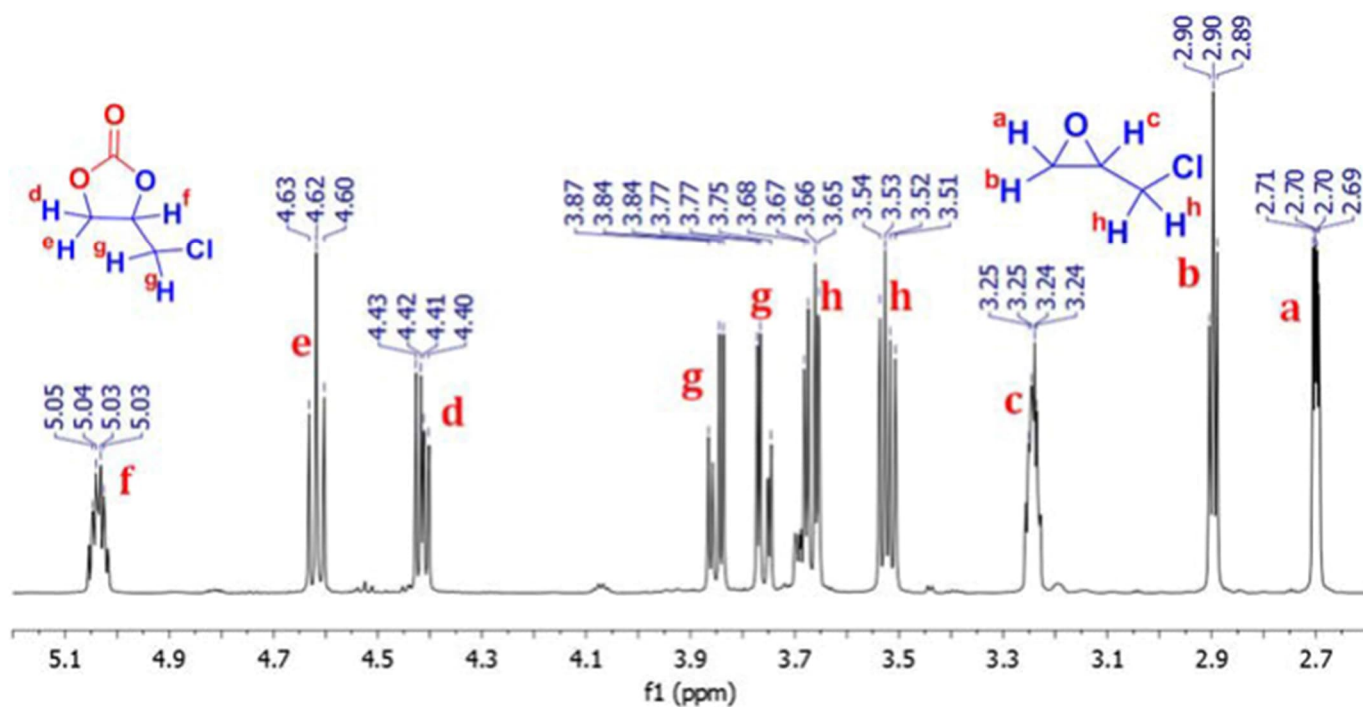
In Chart 1 adapting alkyl substituted epoxides, in the case of propylene oxide, 98% yield was obtained (b); with epoxy butane the yield was 94% (e); with epoxy hexane it was further reduced to 66% (h); and with tertiary butyl epoxide it is found very low, *i.e.*, 10% (i). The decreasing trend of conversion here shows that as the aliphatic substituent's increases, the respective conversions decreases. The maximum TOF was obtained in the conversion of propylene carbonate as 216/h and 192/h for glycidol carbonate and 190/h using epichlorohydrin carbonate. The catalyst is found to give a yield ranging 44 to 99% with 100% selectivity on various substrates without any external co-catalysts. The catalyst is giving 72% yield with allyl glycidyl ether (g), 44% yield in case of phenyl glycidyl ether (d) and 86% yield with glycidol (f). In the case of 1,2,7,8-diepoxy octane, the 90% yield (j) was obtained. Based on the conversion shown in Chart 1, the cyclic epoxides such as cyclohexene oxide (k) and 4-vinyl-1-cyclohexene oxide (l), giving no conversion, the terminal epoxides (a-j) are effectively converted into respective carbonate. Thus the **CP-1** is found effective in catalysing the cycloaddition reaction for terminal epoxides. (S14-S15)



**Chart 1.** Screening of substrates using **CP-1**

### Reaction kinetics

As this catalyst is working efficiently, we aimed to understand the reaction path by studying its kinetics. Accordingly, we performed a series of kinetic experiments<sup>[33-36]</sup> using epichlorohydrin (Epo) as a model substrate, under the solvent-free condition and the conversions were determined using <sup>1</sup>H NMR (Figure 7).



**Figure 7.**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) for the reaction mixture with a mixture of epoxide and a cyclic carbonate

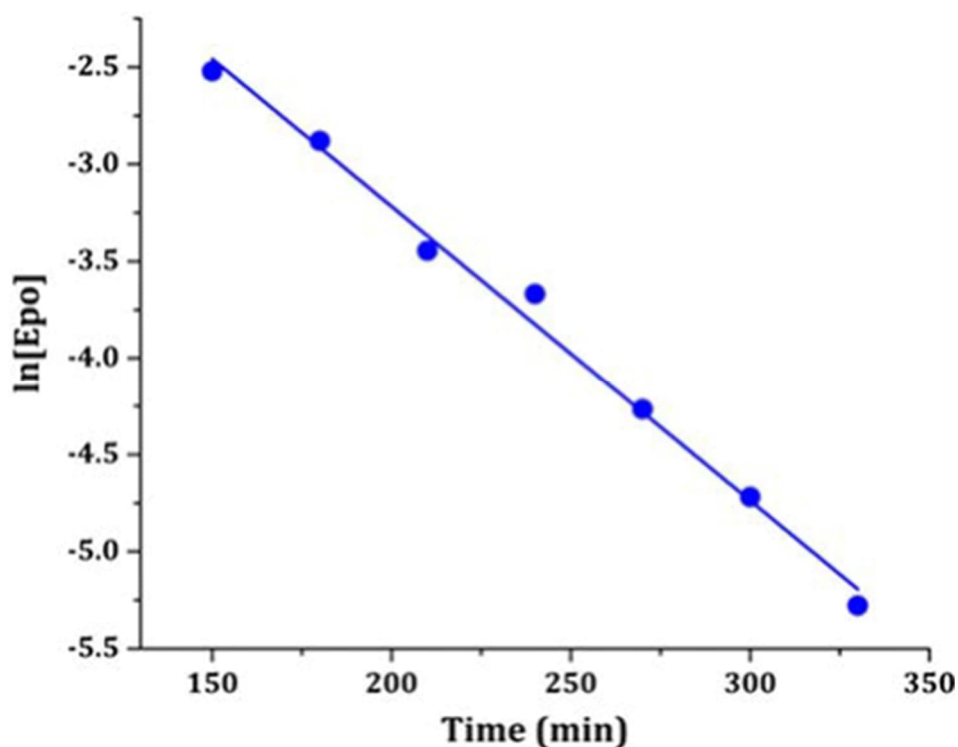
The general equation for determining the rate of a reaction is described as

$$\text{Rate} = k[\text{Epo}]^a[\text{CO}_2]^b[\text{CP-1}]^c \dots \dots \dots (1)$$

Firstly the reaction runs without any co-catalyst or additive, secondly the concentration of  $\text{CO}_2$  and concentration of **CP-1** remains unaltered. Hence the equation-1 can be re-written as

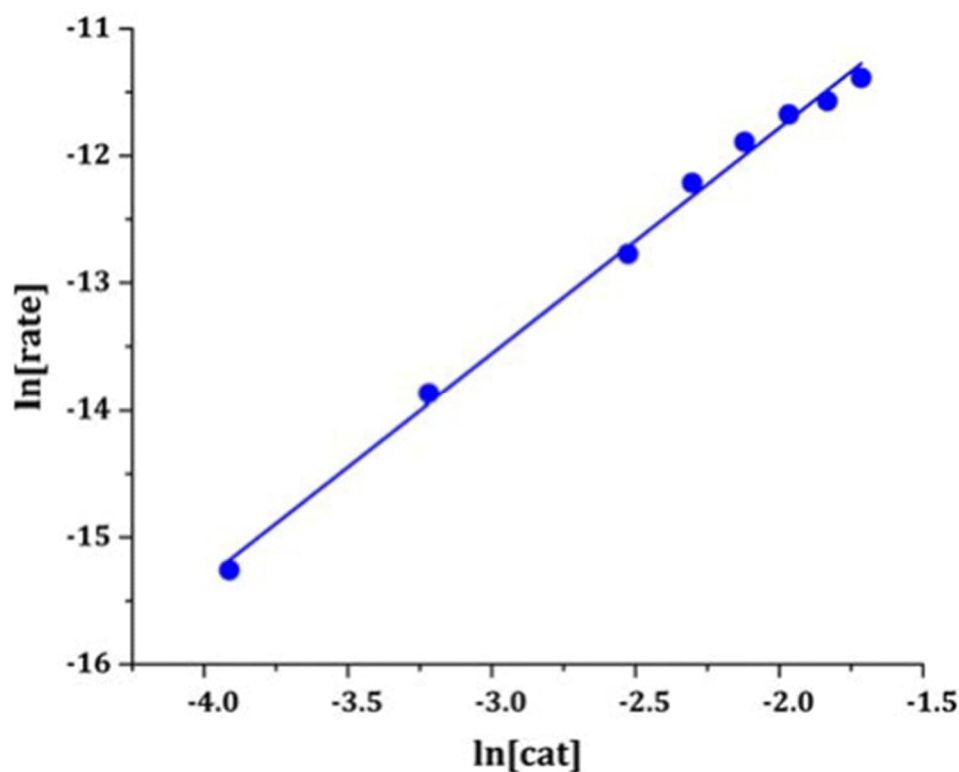
$$\text{Rate} = k_{\text{obs}}[\text{Epo}]^a, \text{ where } k_{\text{obs}} = [\text{CO}_2]^b[\text{CP-1}]^c \dots \dots \dots (2)$$

Where a, b and c represents the order of the reaction with respect to Epo,  $\text{CO}_2$  and **CP-1**. Initially, to determine the order of the reaction, a series of experiments were conducted using 0.06 mmol of catalyst, as a function of reaction time with 30 min interval. The respective conversions of epichlorohydrin to epichlorohydrin carbonate were calculated. The plot derived between  $\ln[\text{Epo}]$  and reaction time providing a straight line indicates that the reaction follows first-order kinetics and, it gives an understanding that the rate of the reaction depends mainly on the concentration of epoxide. When the plot is drawn between  $\ln[\text{Epo}]$  versus reaction time ranging 0 to 330 min at every 30 min interval, this linear least square fit show a significant deviation in its  $R^2$  value. However, in the range 150 to 330 min, the plot drawn versus conversion giving an excellent linear least square fit  $R^2 = 0.99$ , it is convincing to conclude that the reaction follows two step kinetic process. In the initial period ranging 0-150 min, the reaction follows zero-order kinetics (S16). But the best straight line obtained during 150-330 min the reaction obeys first-order kinetic is obvious to understand (Figure 8). This is because, initially the epoxide acts as solvent and substrate, but after forming the cyclic carbonate as the main product, the reaction follows first-order kinetics. It is noteworthy to mention that a similar behavior was observed by M. North's in the case of Al-heteroscorpionate complex.<sup>[37-39]</sup>



**Figure 8.** Kinetic plot for  $\ln[\text{Epo}]$  with time for determining the order of the reaction. (●  $y = -0.015x - 0.177$ ,  $R^2 = 0.99$ )

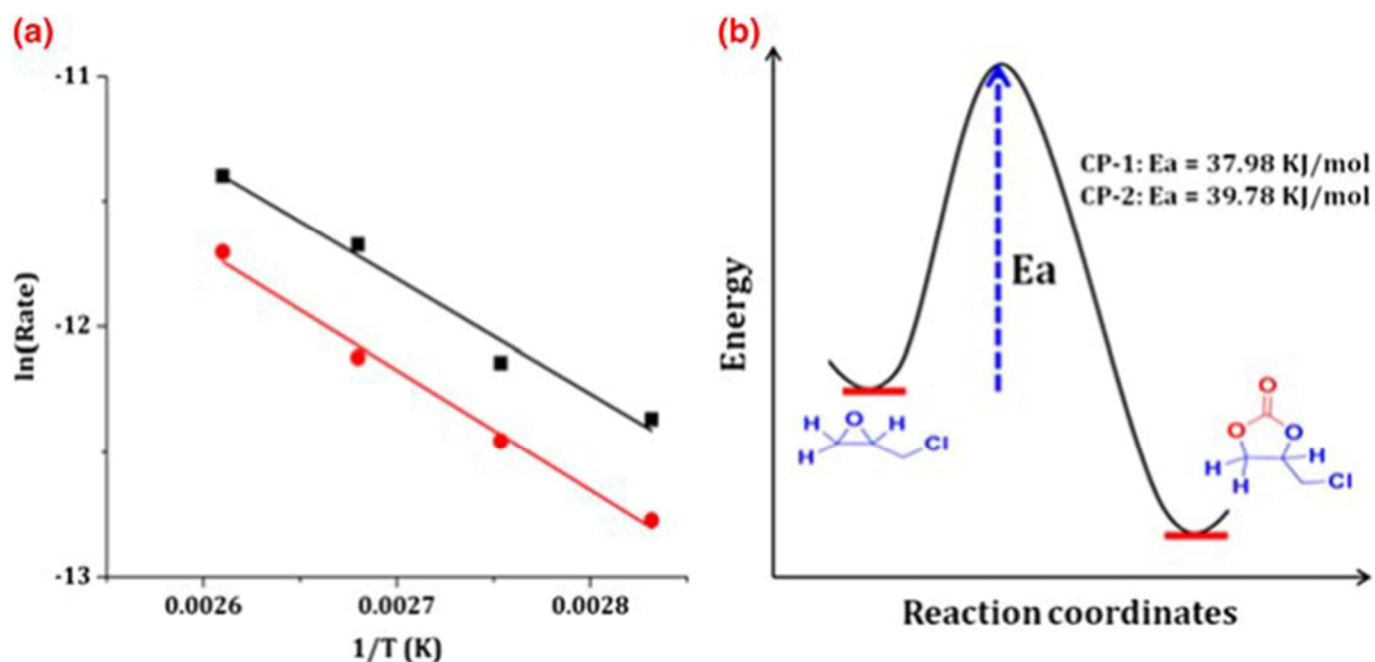
Similarly to evaluate the efficiency of the catalyst, a set of experiments were carried out by varying the catalyst concentration of **CP-1**, from 0.02 mol% to 0.2 mol%. All the reactions were conducted using 10 bar  $\text{CO}_2$ , 100 mmol of epichlorohydrin at  $100^\circ\text{C}$  for 3 h and the respective data are plotted in Figure 9. The kinetic plot in figure 9 indicates that the rate of the reaction increases as the catalyst concentration increases. The plot derived between the concentrations of the catalyst  $\ln[\text{cat}]$  *versus* the rate of the reaction  $\ln[\text{rate}]$  provides an additional information about the efficiency of the catalyst **CP-1**.



**Figure 9.** The kinetic plot as a function of the catalyst using  $\ln[\text{rate}]$  Vs  $\ln[\text{cat}]$  ( $\bullet$   $y = 1.77x - 8.22$ ,  $R^2 = 0.99$ )

### Activation energy

The energy required for the conversion of epoxide to cyclic carbonate *via* transition state is known as activation energy. Accordingly, the activation energy in the conversion of epoxide to cyclic carbonate was established using the Arrhenius equation. The activation energy for the  $\text{CO}_2$  insertion into epichlorohydrin catalyzed by **CP-1** was determined by varying the range of temperature from 60 to 120 °C. The plot drawn between the rate and temperature clearly provide a straight line and obeys the Arrhenius equation as shown in Figure 10. So the slope of the straight line  $[-(E_a/R)]$  is used to derive  $E_a$ . The conversion of epichlorohydrin to epichlorohydrin carbonate, catalyzed by **CP-1** and **CP-2**, (0.06 mmol) at 10 bar  $\text{CO}_2$ , and temperature varied from 80 to 120 °C. The activation energy for **CP-1** is calculated as 37.98 KJ/mol and for **CP-2** is 39.78 KJ/mol (Figure 10).



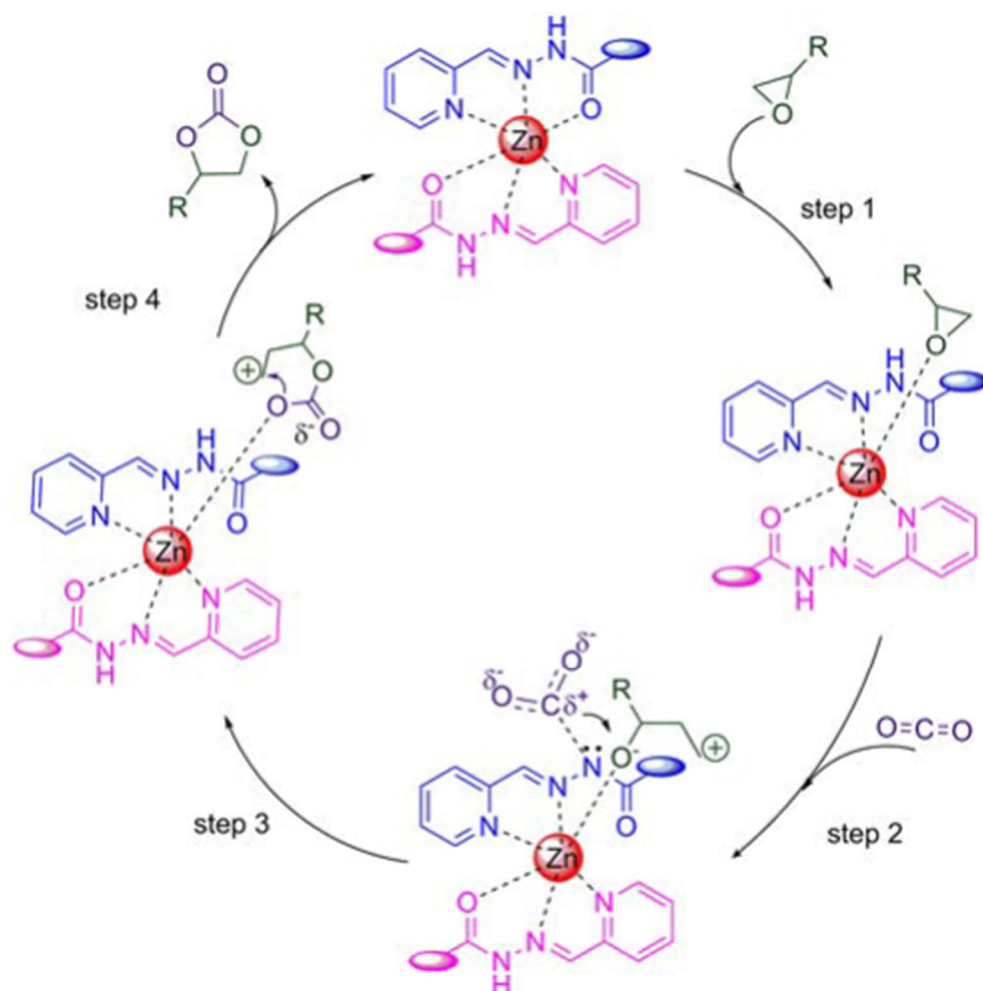
**Figure 10.** Arrhenius plot for determining the activation energy for CP-1 ( $\blacksquare$   $y = -4568.65x + 0.52$ ,  $R^2 = 0.9696$ ;  $E_a = 37.98$  KJ/mol) and CP-2 ( $\bullet$   $y = -4785.10x + 0.74$ ,  $R^2 = 0.9877$ ;  $E_a = 39.78$  KJ/mol)

In view of activation energy of various catalysts used we made a comparative analysis with reported catalysts. In this regard the Aluminium unsymmetrical Schiff base catalyst used for conversion of epoxide to cyclic carbonate reported with 34 KJ/mol of  $E_a$  in the temperature range 80-150°C.<sup>[34]</sup> The same catalyst in combination with TBAB the respective activation energy calculated was 23 KJ/mol which showed a significant reduction. Various catalytic systems reported in the literature are possessing activation energy in the range 35-70 KJ/mol.<sup>[40]</sup> The highest activation energy 98.4 KJ/mol was reported for the iron amino-bis(phenolate) complex catalyst, for the conversion of propylene oxide in combination with TBAB.<sup>[41]</sup> It is understandable that when a catalyst is efficient, that the actual activation energy required for the catalytic conversion needs to be minimum. Keeping this in view the present catalysts **CP-1** and **CP-2** possessing 37.9 and 39.7 KJ/mol respectively calculated for the conversion of epoxide to cyclic carbonates at 80-110 °C gives hope that they are efficient when compared to various catalysts mentioned above.

## Mechanism

The CPs are bifunctional in nature with Lewis acidic sites of the metal center and the basic nature of the ligand. The catalytic mechanism in the reaction is explained in four steps as shown in Scheme 2. The labile NH proton on the ligand leads to enhance the activity of the catalyst without any external additives. Based on the kinetic experiments, the mechanism for the catalytic conversion is described as follows. The epoxide is activated by the metal centers interacting *via* an oxygen atom and leads to the formation of metal-alkoxide in step 1. The epoxide oxygen is electron rich, when compared to ketonic oxygen of the ligand, which favors the metal-alkoxide interaction more feasible. Simultaneously, the nitride ( $N^-$ ) ion of the ligand activates the  $CO_2$ , implying that the carbon atom has a partial positive charge ( $\delta^+$ ) and the oxygen atoms with a partial negative charge ( $\delta^-$ ). Thus each metal center and the labile NH in the ligand are involved in the catalytic reaction. The metal-alkoxide intermediate is quite stable for rapid  $CO_2$  attack, leading to the

CO<sub>2</sub> insertion to form the carbonate intermediate. This nucleophilic attack on the carbonate in step 4 facilitate the ring closure and produce the end product as cyclic carbonate as depicted in Scheme 2.<sup>[42-45]</sup>



**Scheme 2.** A probable mechanism for the cycloaddition reaction

Interestingly a comparative analysis with respect to the present catalysts (**CP-1** and **CP-2**) against reported zinc containing catalysts are considered noteworthy in view of its reaction time, CO<sub>2</sub> pressure and temperature. Among the various zinc catalyst reported in the literature such as ZnBr<sub>2</sub><sup>[46]</sup>, Zn-CMP<sup>[47]</sup> although are found efficient in view of their high conversion and short reaction time (1h), they all require harsh reaction condition such as 17-30 bar CO<sub>2</sub> pressure, and temperature ranging 120-140 °C and additive such as HBGB (Hexa butyl guanidinium bromide), TBAB, *etc.* The Zn –Cluster by Mashima<sup>[19]</sup> and Zn – azatrane complex<sup>[48]</sup> required more than 24h. The Zn-porphyrin complexes by Ema<sup>[49]</sup> although provides yield up to 92% with short reaction time such as 3 h, with 17 bar CO<sub>2</sub> pressure at 120 °C. Thus both **CP-1** and **CP-2** giving excellent conversion up to 99%, the advantage is that these catalysts works without any additive and comparatively moderate conditions such as 4 h reaction time, 100 °C temperature and 10 bar CO<sub>2</sub> pressure (S17).

## Conclusions

The ligand H<sub>2</sub>L upon complexation with Zn(NO<sub>3</sub>)<sub>2</sub> and Cd(NO<sub>3</sub>)<sub>2</sub> has provided two important coordination polymers **CP-1** and **CP-2**. The single crystal X-ray structures of these **CP-1** and **CP-2** clearly indicates the formation of coordination polymers with zinc and cadmium. Both these coordination polymers are applied as a catalyst for cycloaddition of carbon-dioxide to epoxides. Among them, the **CP-1** in solvent-free condition produced better yield when compared to **CP-2** without any external additives. Further, the optimization and substrate screening were carried out using **CP-1**, which gave better conversion with aliphatic substituted terminal epoxides without use of any external additives. The kinetic experiments performed with epichlorohydrin as a substrate with 0.06 mmol of the catalyst, suggests the reaction follows first-order kinetics. From the Arrhenius plot, the activation energy for **CP-1** and **CP-2** is calculated as 37.9 and 39.7 KJ/mol. This detailed study gives an understanding that the **CP-1** needs less energy than **CP-2** for promoting the cyclic carbonate is matches to our experimental results.

## Experimental Section

### Materials and methods

All the chemicals were purchased from Aldrich & Co. IR spectra were recorded using KBr pellets (1% w/w) on a PerkinElmer Spectrum GX FT-IR spectrophotometer. Electronic spectra were recorded on a Shimadzu UV 3101PC spectrophotometer. Electrospray ionization mass spectrometry (ESI MS) measurements were carried out on a Waters QToF-micro instrument for all of these complexes upon dissolving in methanol-water solvents. CHNS analyses were done using a PerkinElmer 2400 CHNS/O analyzer. The X-ray data were collected at 123 K on an Agilent SuperNova single-source diffractometer equipped with an Eos CCD detector using mirror-monochromated Mo-K $\alpha$  ( $\lambda = 0.71073$  Å) radiation. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance II 500 or 600 MHz FT-NMR spectrometer. Chemical shifts for proton resonances are reported in ppm ( $\delta$ ) relative to tetramethylsilane. All the catalytic products were established based on the <sup>1</sup>H NMR spectra.

### Synthesis of coordination polymers

**CP-1.** {[Zn<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>](NO<sub>3</sub>)<sub>4</sub>]<sub>n</sub>: Methanolic solution of ligand H<sub>2</sub>L (1137 mg, 3.36 mmol) and zinc (II) nitrate hexahydrate (1000 mg, 3.36 mmol) were mixed and stirred. The transparent solution of the ligand turns turbid leading to the formation of a precipitate. The reaction mixture was heated at 60 °C for 2h and then allowed to stir at RT for 14 h. The white precipitate obtained was filtered, washed with cold methanol and dried. White solid. Yield. 85% (1810 mg). IR (KBr)  $\nu = 3478$  (-OH), 3134, 2792 (-NH), 1642 (int, C=O), 1554 (int, C=N), 1480, 1397, 1315, 1231, 1194, 1156, 1100, 1036, 1015, 948, 780, 643, 520 cm<sup>-1</sup>. UV-Vis [water,  $\lambda$ , nm, ( $\epsilon$ /M<sup>-1</sup>): 290(79286), 265(53593), 205(78576). Elemental analysis: {[Zn<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>](NO<sub>3</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>} calc. for C<sub>34</sub>H<sub>40</sub>Zn<sub>2</sub>N<sub>16</sub>O<sub>18</sub>. Calc (Expt.). C, 37.41 (37.44), H, 3.69 (3.80), N, 20.53 (20.93)%. ESI<sup>+</sup> m/z = 803.13(calc) 803.71 (found) for [Zn<sub>2</sub>L<sub>2</sub>]H<sup>+</sup>.

**CP-2.** {[Cd<sub>2</sub>(H<sub>2</sub>L)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub>]<sub>n</sub>: Methanolic solution of ligand H<sub>2</sub>L (548 mg, 1.6208 mmol) and cadmium (II) nitrate hexahydrate (500 mg, 1.6208 mmol) were mixed and stirred. The transparent solution of the ligand turns slowly turbid then to precipitate. The reaction mixture is heated at 60 °C for 2h and then allowed to stir at RT for 14 h. The resultant precipitate obtained was filtered, washed with methanol and



dried. Solid, Yield: 73% (770 mg). IR (KBr)  $\nu = 3460$  (-OH), 3154 (-NH), 1668 (-C=O), 1562 (-CH=N), 1340, 1303, 1148, 1037, 938, 778, 627, 513  $\text{cm}^{-1}$ . UV-Vis [water,  $\lambda$ , nm, ( $\epsilon/\text{M}^{-1}$ ): 290(86766), 265(62733), 206(84800). Elemental analysis:  $\{[\text{Cd}_2(\text{H}_2\text{L})_2(\text{NO}_3)_2](\text{NO}_3)_2(\text{H}_2\text{O})_6\}_n$  calc. for  $\text{C}_{34}\text{H}_{48}\text{Cd}_2\text{N}_{16}\text{O}_{22}$ . Calc (Expt.). C, 32.47 (32.52), H, 3.85 (3.71), N, 17.82 (18.33)%. ESI<sup>+</sup>  $m/z = 899.90$  (calc) 899.08 (found) for  $[\text{Cd}_2\text{L}_2]\text{H}^+$ .

## Crystal data

**CP-1.** CCDC-1894863.  $\{[\text{Zn}(\text{H}_2\text{L})](\text{NO}_3)_2\}_n$ :  $\text{C}_{17}\text{H}_{18}\text{N}_8\text{O}_8\text{Zn}$  ( $M = 527.76$  g/mol); monoclinic,  $P2_1/c$  (14),  $a = 8.8025(18)$  Å,  $b = 28.507(6)$  Å,  $c = 8.7358(17)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 100.13(3)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2157.9(8)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calc}} = 1.624$  g/cm<sup>3</sup>,  $\mu = 1.202$  mm<sup>-1</sup>,  $F(000) = 1080$ , 13252 reflections collected, of which 3910 independent,  $R_{\text{int}} = 0.1179$ , 46 restraints, 344 parameters, GOF on  $F^2 = 1.020$ ,  $R_1/wR_2 [I \geq 2\sigma(I)] = 0.0939/0.2442$ ,  $R_1/wR_2$  (all data) = 0.1420/0.2925, largest di. peak/hole (e./Å<sup>3</sup>) = 0.664/-0.715.

**CP-2.** CCDC-1894864.  $\{[\text{Cd}_2(\text{H}_2\text{L})_2(\text{NO}_3)_2](\text{NO}_3)_2\}_n$ :  $\text{C}_{34}\text{H}_{38}\text{Cd}_2\text{N}_{16}\text{O}_{21}$  ( $M = 1231.60$  g/mol); triclinic,  $P-1$  (2),  $a = 12.7507(9)$  Å,  $b = 13.2141(8)$  Å,  $c = 16.7002(9)$  Å,  $\alpha = 90.233(5)^\circ$ ,  $\beta = 108.193(6)^\circ$ ,  $\gamma = 114.077(6)^\circ$ ,  $V = 2412.4(3)$ ,  $Z = 2$ ,  $\rho_{\text{calc}} = 1.696$  g/cm<sup>3</sup>,  $\mu = 0.976$  mm<sup>-1</sup>,  $F(000) = 1236$ , 14629 reflections collected, of which 8692 independent,  $R_{\text{int}} = 0.0270$ , 96 restraints, 757 parameters, GOF on  $F^2 = 1.058$ ,  $R_1/wR_2 [I \geq 2\sigma(I)] = 0.0547/0.1373$ ,  $R_1/wR_2$  (all data) = 0.0730/0.1515, largest di. peak/hole (e./Å<sup>3</sup>) = 3.452/-0.707.

## General procedure for cycloaddition of CO<sub>2</sub> to epoxide

To a 100 mL stainless steel vessel, 0.2 mmol of catalyst and 100 mmol of the substrate were charged. The reactor was purged 2-3 times with carbon-dioxide and 10 bar pressure of carbon-dioxide was maintained. The reaction mixture was heated at 100 °C for 4h. The reactor was cooled and the reaction mixture was passed through a silica column to separate the product. The crude reaction mixture was analysed by <sup>1</sup>H NMR for conversion. Since this is a homogenous catalyst, and the catalyst is soluble in the reaction mixture, recovery of the catalyst becomes difficult.

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