Catalytic Conversion of Carbon Dioxide Using Binuclear Double-Stranded Helicates: Cyclic Carbonate from Epoxides and Diol

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Cite This: ACS Omega 2020, 5, 14890–14899

ABSTRACT: The construction of sophisticated molecular architectures from chemical subunits requires careful selection of the spacers, precise synthetic strategies, and substantial efforts. Here, we report a series of binuclear double-stranded helicates synthesized from different combinations of pyridyl hydrazone-based multidentate ligands (H₃1, H₂2, H₂3) by increasing the methylene spacer and transition metals (Co, Ni, and Zn). The ligands H₃1 (N′1,N′3-bis((E)-pyridin-2-ylmethylene)-malonohydrazide), H₂2 (N′1,N′4-bis((E)-pyridin-2-ylmethylene)-succinohydrazide), and H₂3 (N′1,N′3-bis((E)-pyridin-2-ylmethylene)glutarohydrazide) and their respective complexes with Co, Ni, and Zn were obtained. Single-crystal X-ray diffraction studies of these binuclear metallohelicates confirm the double-stranded helical structure of the complexes derived from H₂2. The set of helicates Co-1, Co-2, and Co-3; Ni-1, Ni-2, and Ni-3; and Zn-1, Zn-2, and Zn-3 were investigated for its catalytic activity in the cyclic carbonate formation reaction. Intriguingly, among the synthesized catalyst, Co-1 was found to be better in terms of conversions with the calculated TOF (turnover frequency) of 128/h. The catalytic performance was significantly improved by adding 0.2 mmol of tetrabutylammonium bromide by achieving 76% conversion in 30 min, with the observed TOF of 15,934 h⁻¹/molecule and 7967 h⁻¹/Co center. The results obtained herein show that the double-stranded helicates are effective catalysts for converting both terminal and non-terminal epoxides into their corresponding cyclic carbonates. The striking feature of this catalytic protocol lies in demonstrating the catalytic activity for the conversion of diol to cyclic carbonate, and the detailed kinetic experiments tempted us to propose a tentative reaction mechanism for this conversion.

INTRODUCTION

The utilization of carbon dioxide is of scientific and societal interest due to its direct implications on economic and environmental aspects.¹⁻⁴ Though CO₂ is deemed to be a major contributor to climate change, on the contrary, it also serves as an advantageous and inexpensive C₁ source for a diverse array of chemical synthesis.⁵⁻⁶ However, CO₂ being a fully oxidized molecule, its inherent thermodynamic stability necessitates the need for a catalyst to activate and explore its potential applications.⁷ From the viewpoint of atom economy and low energy requirements, utilization of CO₂ for the synthesis of cyclic carbonate has attracted great attention from industry and academics.

Among the pioneering studies that utilize CO₂, the formation of cyclic carbonates has received growing interest due to its wide spectrum of applications ranging from electrolytes for lithium-ion batteries to synthetic targets for versatile materials. The reaction is 100% atom economical and deserves a wide variety of industrial applications.⁸ Attempts have been made to identify a suitable catalytic system, including homogeneous and heterogeneous catalysts⁹⁻¹¹ such as ammonium salts,¹² metal complexes,¹² functional polymers,¹³ supported nanoparticles,¹⁴ metal organic frameworks,¹⁵ and ion exchange resins. Considering the reaction mechanism involved in the reaction of CO₂ and epoxide, it requires a bifunctional catalyst for higher cyclic carbonate yields.

On the other hand, mimicking the unparalleled efficiency of multiple metal-centered enzyme catalysis has motivated chemists to design and develop artificial helical architectures for its potential applications.¹⁶ Helicates, the fascinating structural motif, are well-explored for its application in biological systems due to its structural resemblance with DNA.¹⁷⁻¹⁹ Interestingly, these interesting tunable chemical strands are rarely deployed as catalysts for organic transformations.²⁰ Among the best known catalytic systems,²¹ aluminum–triphenolate²² with...
a TOF up to 36,000/h and magnesium–porphyrin that showed TOF = 46,000/h are reported to be the highest with excellent conversion. These reports identified and dictated that the catalyst with suitable Lewis acidic sites (Al/Mg) are in a multinuclear form and responsible for the efficient catalytic activity. Helicates being known for its multimetallic center and our long-standing interest in helicate chemistry, together prompted us to consider that this strategy would be amenable to achieve cyclic carbonate with high yield and selectivity. Herein, we demonstrate the catalytic activity of binuclear helicates with different Lewis acidic centers for the synthesis of cyclic carbonate. Recently, biodegradable diols are identified as an alternative to epoxide for the synthesis of cyclic carbonate. However, the formation of the water molecule during the progress of the reaction promoting reverse reaction makes it highly challenging. The less-reactive hydroxyl group may be activated by adapting a harsh reaction condition.

With this understanding, the present manuscript demonstrates the catalytic activity of a series of binuclear double-stranded helicates for two important reactions: (i) epoxide and CO₂ to cyclic carbonate and (ii) in single-phase conversion of diol to glutaconate with one, two, and three –CH₂ groups, respectively, as shown above. In addition to the Co(III) recently shown to have TOF = 46,000/h are reported to be the highest with magnesium and Zn.

**RESULTS AND DISCUSSION**

**X-ray Structures for Ligand and Helicates.** The ligand H₂N is crystallized by slow evaporation of its methanolic solution at room temperature. The crystal structure was resolved in the monoclinic system of the P2₁/c space group with four molecules in the unit cell. The ligand possesses “S” conformation, showing the twist angle of the alkyl –CH₂ group ∠ C9C8C7 = 108.10° (Figure S10). The single-crystal analyses for both Co-2 and Co-3 are existing in meso conformation and with two anions in the lattice. In addition, all the labile NH₃⁺ are in a deprotonated form, and the Co²⁺ adopted is oxidized to Co³⁺, similar to our earlier observation.

The suitable crystals for Ni-2 are obtained by diffusing the THF into the aqueous solution of the sample (Figure 3). The molecule is found to be discrete ionic [Ni₂(H₂)₂Cl₄] with four chloride anions in the lattice and all the NH moieties.

**Figure 1.** (a) Structure of multidentate ligands (H₁-H₂-H₃). (b) Structure of binuclear double-stranded metallohelicates with Co, Ni, and Zn.

multidentate ligands (H₁-H₂-H₃) and their cobalt helicate formation are already well-established, whereas the helicate formation nickel and zinc and their catalytic application are included in this manuscript.

Pyridylhydrazone-based multidentate ligands H₁–H₃ (Figure 1a) and their respective binuclear double-stranded Co(III), Ni(II), and Zn(II) helicates were synthesized (Figure 1b) as per our earlier-reported procedure and are found matching with the analytical data reported therein. The multidentate ligands H₁, H₂, and H₃ are obtained by varying malonate, succinate, and glutarate spacers with one, two, and three –CH₂ groups, respectively, as shown above. In addition to the Co(III) recently reported by us, we have extended the synthesis to Ni(II) and Zn(II) helicates adopting a similar synthetic protocol (Figures S1-S9). Meanwhile, in the cases of helicates Co-1, Co-2, and Co-3 complexes, the cobalt metal were found to exist in the +3 state, whereas in the nickel and zinc complexes, the respective metal are found to be in the +2 oxidation state.

In the absorption spectra (Figure 2), the three well-resolved metal-centered transitions for Ni-1, Ni-2, Ni-3 at 1364, 1423, and 1390 and 1130, 1140, and 1154 nm, respectively, correspond to 3A₂g → 3T₂g and the third electronic transitions at 872, 872, and 868 nm correspond to 3A₂g → 3T₁g. These transitions match the distorted octahedral geometry of related Ni(II) complexes. The absorption spectra for the corresponding Zn(II) helicates show a similar pattern; the ligand-centered transitions occurred at 290 nm. The transition at 365 nm represents σ → π*, corresponding to ketonic oxygen to metal, while the metal-centered region is flat.
the mesocate form, while in the latter, the neutral ligands are assembled in helicate conformation.28

**Solution-State Spectral Analysis of Metallohelicates.**
The $^1$H NMR recorded in DMSO for cobalt helicate showed a narrow spectral resonance in the diamagnetic range, which confirms the existence of Co(III).24 The $^1$H NMR spectra for Zn-1 showed unresolved peaks with slight broad features indicating their coordination (Figure S11). The signals at 8.52–7.65 ppm correspond to aromatic and azomethine protons, and the peak at 3.80–3.78 ppm is attributed to the methylene proton. In the case of Zn-2, the aromatic and aliphatic region shows well-resolved signals (Figures S12–S13). The ligand H$_2$ in DMSO gives two unresolved triplets at 2.95–2.97 ppm and 2.56–2.53 ppm, which correspond to two methylene protons (Figure 5a). The same methylene group in complex Zn-2, showing four well-resolved signals 3.00–2.98 (t, 1H), 2.94 (s, 1H), 2.63 (s, 1H), 2.61–2.58 (t, 1H) (Figure 5b), suggests that the methylene protons become diastereotopic upon coordination to metal ions.28 It is also observed that the molecule is behaving highly dynamic in the solution state; two singlets found at $\delta = 2.94$ and 2.63 ppm correspond to the mesocate structure, and the triplets at $\delta = 3.00$ and 2.61 ppm strongly supports the helicate structure (Figure 5b). Interestingly, upon deuterium exchange, the intensity of one set of signals is greatly reduced (Figure 5c). However, upon recording the $^1$H NMR solely in D$_2$O solvent, all those signals attributed to –CH$_2$– protons get merged into a single peak at $\delta = 2.85$ ppm (Figure 5d). This apparent change in the spectral pattern suggests that the conformational changes occurred around the –CH$_2$– group and thus led to the transformation of nonsymmetric to highly symmetric ligand strands. These spectral observations suggest the existence of a solely mesocate structure in water.29 However, in the case of Zn-3, there are no significant changes in ligands, and helicate patterns in $^1$H NMR other than minor resonance shift indicates that the ligand upon coordination does not exhibit reasonable structural modification (Figures S14–S15).

**Cyclic Carbonate from Epoxide.** Addition of CO$_2$ to epoxide permits the synthesis of cyclic carbonate or polycarbonate in the presence of an appropriate catalyst. Driven by the tunable nature of metallohelicates, we attempted here to study its catalytic activity for the synthesis of cyclic carbonate. In this regard, we screened the metallohelicates as catalyst for the reaction of styrene oxide and CO$_2$ under solvent-free condition at 100 °C and 1 MPa for 4 h. Beforehand, we examined the
reaction in blank condition (without catalyst) using just ligands H2 to H2 (without metal) for the conversion of styrene oxide and observed no product and a trace amount of conversion, respectively (Table 1, entries 1–4). These results indicate the importance of catalyst and metal centers for this reaction. Subsequently, the screening of metallohelicates as catalysts and the respective yields of cyclic carbonates are included in Table 1 (Table 1, entries 8–13). Intriguingly, the cobalt-based catalysts demonstrate excellent catalytic activity and resulted in the desired cyclic carbonate with high yields of 90–98% (Table 1, entries 5–7). The change of the metal center to Ni and Zn resulted in slightly decreased yields ranging from 82 to 95% (Table 1, entries 8–10) and from 76 to 94% (Table 1, entries 11–13), respectively. This observation matches well with the literature precedents that the cobalt centers in the +3 oxidation state are found to be the most active catalyst for this reaction.30

Figure 4. X-ray structure of cationic \([\text{Zn}_2(\text{H}_2)_2]^{-}\) (nitrate counter ions are omitted for clarity).

Figure 5. $^1$H NMR spectra for Zn-2 with the aliphatic region showing a diastereotopic peak pattern. (a) Ligand H2 in DMSO. (b) \([\text{Zn}(\text{H}_2)_2]^{4+}\) in DMSO. (c) D$_2$O exchange for \([\text{Zn}(\text{H}_2)_2]^{4+}\). (d) NMR recorded in D$_2$O for \([\text{Zn}(\text{H}_2)_2]^{4+}\).
Among the catalysts screened, Co-1 has produced the maximum yield of styrene carbonate (98%) with TOF of 128/h (Table 1, entry 5), while the other helicate systems resulted in the desired product in the range of 76−94% yield with a TOF range of 100−128/h (Table 1, Entries 6−13). Thus, the metallohelicate Co-1 has been selected as a suitable catalyst for further optimization.

Table 1. Catalyst Screening for the Reaction of CO₂ to Epoxide

| entry | catalyst | yield (%) | TON | TOF (h⁻¹) |
|-------|----------|-----------|-----|-----------|
| 1     | blank    | trace     |     |           |
| 2     | H₂₁      | trace     |     |           |
| 3     | H₂₂      | trace     |     |           |
| 4     | H₂₃      | trace     |     |           |
| 5     | Co-1     | 98        | 513 | 128       |
| 6     | Co-2     | 94        | 492 | 123       |
| 7     | Co-3     | 90        | 472 | 118       |
| 8     | Ni-1     | 82        | 430 | 108       |
| 9     | Ni-2     | 93        | 487 | 122       |
| 10    | Ni-3     | 95        | 488 | 122       |
| 11    | Zn-1     | 76        | 398 | 100       |
| 12    | Zn-2     | 76        | 398 | 100       |
| 13    | Zn-3     | 94        | 492 | 123       |

All reactions were carried out using 100 mmol of styrene oxide, 0.2 mmol of catalyst, and 1 MPa CO₂ at 100 °C for 4 h under solvent-free condition. "Isolated yield. "TON = mmol of product formed/mmol of catalyst used, "TOF (TON/reaction time) calculated after the completion of the reaction time. All the catalysts are selectively giving cyclic carbonate as per ¹H NMR spectral data.

Optimization of Reaction Conditions. With the identified choice of catalyst, the reaction parameters such as CO₂ pressure, temperature, catalyst loading, and effect of tetrabutylammonium bromide (TBAB) in the reaction of styrene oxide and CO₂ were studied to achieve the best catalytic activity. Figure 6 represents the optimization of temperature and pressure with respect to the TOF number for the formation of styrene carbonate. The reaction with varying CO₂ pressures ranging from 0.2 to 1.2 MPa at 100 °C, were performed, and the results are summarized in Figure 6a. The maximum conversion was obtained at 1 MPa CO₂ with a TOF value of 128/h (per molecule), and 64/h (per Co centre) is found to be the optimized pressure. Then, reaction at different temperatures ranging from 30 to 120 °C revealed that the catalytic activity increases relative to the rise in temperature (Figure 6b).

Then, we studied the effect of catalyst loading keeping the other parameters constant and observed a maximum conversion with 0.2 mmol of catalyst (Table 2). Surprisingly, by decreasing the catalyst loading to 0.1 mmol, a slight increase in TOF to 136/h was observed (Table 2, entry 3); however, with further decrease, it showed a detrimental effect on both conversion and TOF (Table 2, entries 4−7). Here, 0.2 mmol of catalyst is fixed as the optimized catalyst load.

Furthermore, to improve the TOF, attempts were made by using TBAB (0.2 mmol) as an additive, and to our delight, it has a pronounced positive effect and resulted in an excellent conversion and TOF. With varied reaction times, we could observe a significant change in TOF, which motivated us to have a further improvisation on TOF.

Interestingly, even with a decreased catalyst loading of 0.01 and 0.2 mmol of TBAB at 0.5

Table 2. Optimization of Catalyst Loading and Effect of TBAB

| entry | catalyst (mmol) | TBAB (mmol) | time (h) | conversion (%) | TON | TOF (h⁻¹) |
|-------|-----------------|-------------|----------|---------------|-----|-----------|
| 1     | 0.2             |             | 4        | 98            | 513 | 128       |
| 2     | 0.15            |             | 4        | 75            | 524 | 131       |
| 3     | 0.1             |             | 4        | 52            | 545 | 136       |
| 4     | 0.08            |             | 4        | 14            | 183 | 46        |
| 5     | 0.06            |             | 4        | 3             | 52  | 13        |
| 6     | 0.04            |             | 4        | 2             | 52  | 13        |
| 7     | 0.02            |             | 4        | 2             | 105 | 26        |
| 8     | 0.02            | 0.2         | 3        | 99            | 5189| 1730      |
| 9     | 0.02            | 0.2         | 2        | 99            | 5189| 2595      |
| 10    | 0.02            | 0.2         | 1        | 98            | 5150| 5150      |
| 11    | 0.02            | 0.2         | 0.5      | 88            | 4612| 9225      |
| 12    | 0.01            | 0.2         | 1        | 80            | 8386| 8386      |
| 13    | 0.01            | 0.2         | 0.5      | 76            | 7967| 15,934    |
| 14    | blank           | 0.2         | 1        | 5             |     |           |

Reactions were carried out using 100 mmol of styrene oxide, 0.2−0.01 mmol of Co-1, 0.2 mmol of TBAB, and 10 bar CO₂ at 100 °C for 30 min to 4 h under solvent-free condition. Conversion determined by ¹H-NMR; the selective cyclic carbonate formation is also observed. TON = mmol of product formed/mmol of catalyst used, TOF = TON/reaction time. TOF is calculated per molecule of the catalyst.

Figure 6. (a) Pressure versus conversion and TOF plot. (b) Temperature versus conversion and TOF plot for the catalytic synthesis of cyclic carbonates using 0.2 mmol catalysts and 100 mmol of the styrene oxide for 4 h. The conversion was determined by ¹H NMR, and TOF = TON/4.
h, 76% of styrene carbonate with 15,934/h of TOF (7967 h⁻¹/Co center) was achieved (Table 2, entry 13). The obtained TOF is comparable and/or higher than those of most active catalytic systems. These results suggest that the cooperative effect of the metallohelicate catalyst and TBAB reflects a reduction in the reaction time with better catalytic activity. It is imperative to mention here that the plain catalyst (only helical complexes under additive-free condition) is proven to give better conversion; the addition of additive increased the efficiency of the catalytic activity to a remarkable raise in the TOF value.

With the optimized reaction conditions, we examined the substrate scope with various alkyl- or aromatic-substituted terminal epoxides (a–j) and non-terminal epoxides (k,l), and the reactions were performed without additives (see Supporting Information for details). As shown in Chart 1, the Co-1 has also attempted for a substrate containing bis-epoxides (1,2,7,8-diepoxo octane) and observed a good yield of 94% (j) with a TOF of 98/h (Figure S16).

**Cyclic Carbonate from Diol.** The catalytic activity found above for Co-1 prompted us further to study its catalytic performance using biodegradable 1,2-diols as an alternative precursor to epoxide for the synthesis of cyclic carbonate with CO₂. By considering the significance and challenges involved in this reaction, we attempted with the same catalytic system in converting diol to cyclic carbonate. Ethylene glycol was chosen as a model substrate and acetonitrile as a solvent using 2.5 MPa CO₂. Initially, the blank reaction was carried out and monitored up to 8 h, which showed no conversion of cyclic carbonate (Table 3, entry 1). Among the cobalt-based metallohelicates, Co-1 was found to be better in terms of conversion (34%), whereas others resulted in trace conversion (Table 3, entries 2–5).

**Table 3. Synthesis of 5-Membered Cyclic Carbonate from Ethylene Glycol and Carbon Dioxide**

| entry | catalyst | dehydrating agents | carboxylation reaction (%) | hydration reaction (%) |
|-------|----------|--------------------|----------------------------|------------------------|
| 1     | blank    | MeCN               | no reaction                |                        |
| 2     | Co-1     | MeCN               | 34                         |                        |
| 3     | Co-2     | MeCN               | trace                      |                        |
| 4     | Co-3     | MeCN               | trace                      |                        |
| 5     | Co-1     | 2-CNPy             | 15                         | 15                     |
| 6     | Co-2     | 2-CNPy             | 19                         | 42                     |
| 7     | Co-3     | 2-CNPy             | 65                         | 46                     |
| 8     | Ni-1     | 2-CNPy             | 16                         | 20                     |
| 9     | Ni-2     | 2-CNPy             | 34                         | 29                     |
| 10    | Ni-3     | 2-CNPy             | 19                         | 24                     |
| 11    | Zn-1     | 2-CNPy             | 34                         | 30                     |
| 12    | Zn-2     | 2-CNPy             | 21                         | 28                     |
| 13    | Zn-3     | 2-CNPy             | 27                         | 25                     |

*All reactions were carried out using 0.25 mmol of catalyst, 32 mmol of ethylene glycol, 96 mmol of 2-pyridine carboxylate, at 2.5 MPa CO₂, 100 °C for 8 h. *conversion was calculated using ¹H-NMR.

The challenge involved in the reaction is the formation of water as a by-product, which in turn maintains equilibrium and reduces the conversion of the desired product. This problem with the interference of water molecules can be by-passed by using a suitable dehydrating agent. With the literature knowledge, we replaced acetonitrile with 2-cyanopyridine as a dehydrating agent. For this conversion, Co-3 worked well with the combination of 2-cyanopyridine and enhanced the conversion of diols to cyclic carbonate (65%), and the results are summarized in Table 3. The formed by-product water is also subsequently been used for the effective conversion of 2-cyanopyridine to 2-picolinamide. Thus, Co-3 helicate can simultaneously catalyze both the reaction in the same reactor vessels (Figure S17).

**Reaction Kinetics.** In order to determine the path of the reaction, kinetic experiments were performed with styrene oxide as a model substrate under optimized reaction conditions.
As an attempt to understand the rate of the reaction, rate eq 1 was simplified to eq 2, considering the excess use of CO2 and the concentration of catalyst remains constant during the reaction. The natural logarithm of the rate law (eq 2) results in eq 3, which is possible to afford the order “c” of the reaction with respect to the catalyst concentration by examination of a double logarithmic plot.

$$\text{rate} = k \cdot [\text{CO}_2]^c \cdot [\text{epoxide}]^d \cdot [\text{cat}]^f$$

(1)

Since [epoxide] is a variable, [CO2] and [cat] are constant, the rate can be expressed as equation 2.

$$\text{rate} = k_{\text{obs}} \cdot [\text{epoxide}]^d$$

with $k_{\text{obs}} = [\text{CO}_2]^c \cdot [\text{cat}]^f$

(2)

By taking natural logarithmic on both sides of eq 2,

$$\ln(\text{rate}) = \ln(k_{\text{obs}}) + b \ln[\text{epoxide}]$$

(3)

To investigate the mechanism of the reaction, the co-catalyst free reaction was studied to understand the order of the reaction using Co-1 as a catalyst, and the conversion was recorded in the interval of 30 min. The linear fit plot drawn against ln[Epoxide] versus time (Figure 7a) confirms that the reaction follows first-order kinetics.

In addition, to evaluate the catalytic function of the helicate Co-1, the kinetic experiments were carried out by varying the catalyst concentration from 0.02 to 0.2 mmol. All the reactions were carried out using 1 MPa CO2, 100 mmol of styrene oxide at 100 °C for 4 h. The plot shown in Figure 7b drawn against ln[Cat] versus ln[rate] suggests that as the concentration of the catalyst increases, the rate of the reaction also increases (Figure 7b).

The activation energy in the conversion of epoxide to cyclic carbonate was established by using the Arrhenius equation.

$$k = A e^{-E_a/(RT)}$$

where $E_a$ is the activation energy (kJ.mol$^{-1}$), $R$ is the universal gas constant (8.314 Jmol$^{-1}$K$^{-1}$), and temperature $T$ is the absolute temperature. The activation energy for the CO2 insertion into styrene oxide catalyzed by Co-1 was determined from the range of 30 – 120 °C. The plot between the rates with respect to temperature fitted in a straight line and obeyed the Arrhenius equation (Figure 7c). So, the slope of the straight line is related to the activation energy.
Mechanism. The catalytic mechanism in the reaction is explained in four steps as shown in Figure 7d. The labile NH proton on the ligand leads to the enhanced 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 to be more feasible. Simultaneously, the nitride (N⁻) ion of the ligand activates the CO₂, implying that the carbon atom has a partial positive charge (δ⁺) and the oxygen atoms have a partial negative charge (δ⁻). 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 a rapid CO₂ attack, leading to the CO₂ insertion to form the carbonate intermediate. This nucleophilic attack on the carbonate in step 4 facilitates the ring closure and produces the end product as cyclic carbonate as depicted in Figure 7d.35

■ CONCLUSIONS

In summary, a series of Co-, Ni-, and Zn-based binuclear double-stranded helicates of pyridylhydroxy-based ligands were synthesized. The d–d transitions in the UV–vis spectra indicate an octahedral geometry at the metal center. The X-ray structure of the molecules confirms the formation of a helical type of molecule. Ni-2 and Zn-2 end-up with helicate formation in the solid state, and all the helicates are applied as a catalyst for the preparation of cyclic carbonates. The catalyst converts epoxide to cyclic carbonate selectively, giving better conversion with most of the aliphatic epoxides, under solvent-free conditions.

The use of 0.2 mmol TABAB significantly improved the conversion of 76% (in 30 min reaction time) and TOF 15934 h⁻¹/molecule, and 7967 h⁻¹/Co center was achieved, which is comparable to most of the reported active metal catalysts. Based on the kinetic studies, a probable mechanism is proposed. The catalyst was also found to be active to convert biodegradable 1,2-diols to corresponding cyclic carbonate using 2-cyanopyridine as a dehydrating agent.

■ EXPERIMENTAL SECTION

Materials and General Methods. All the chemicals were purchased from Aldrich & Co. IR spectra were recorded using KBr pellets (1% w/w) on a Perkin-Elmer Spectrum GX FT-IR spectrophotometer. Electronic spectra were recorded on a Shimadzu UV 3101PC spectrophotometer. Mass analyses were performed using the positive and negative ion spray ionization technique on a Waters Q-Tof-micro mass spectrometer for all these complexes upon dissolving in methanol–water solvents. CHNS analyses were done using a Perkin-Elmer 2400 CHNS/O analyzer. Single crystal structures were determined using a BRUKER SMART APEX (CCD) diffractometer. 1H and 13C NMR spectra were recorded on a Bruker Avance II 500 MHz or Jeol 600 MHz FT-NMR spectrometer. Chemical shifts for proton resonances are reported in ppm (δ) relative to tetramethylsilane, and 13C spectra are calibrated with reference to DMSO-d₆. All the catalytic products were established based on 1H NMR spectra. The 100 MHz high-pressure catalytic reactor was from AMAR equipment.

Synthesis of Nickel and Zinc Metallohelicates. Ni-1. [Ni₂(H₂1)₂Cl₂(H₂O)]: To a methanolic solution of ligand H₂1 (652 mg, 2.10 mmol), nickel chloride hexahydrate (500 mg, 2.10 mmol) in methanol was added dropwise. The colorless solution of the ligand turns into pale green and then dark green. The reaction mixture is heated to 60 °C for 2 h and then allowed to stir at RT for 14 h. The solution was evaporated under reduced pressure to yield a greenish black solid. Yield: 52%. IR (KBr): ν = 3404, 3076, 2900, 1612, 1530, 1468, 1230, 1170, 983, 772 cm⁻¹. UV–vis [water, λmax (ε/M⁻¹)] = 1422(1357), 1139(1693), 870(1693). Elemental analysis: calcld for C₃₂H₄₀Cl₄Ni₂N₁₂O₁₁: C, 39.22; H, 4.11; N, 17.15%. Found: C, 37.21; H, 4.42; N, 17.05. ESI(+)–MS: m/z calcld for [Ni₂⁺]H⁺ 733.08, expit 733.46.

Ni-2. [Ni₂(H₂2)₂Cl₂(H₂O)]: A similar procedure adapting H₂2 (1364 mg, 4.20 mmol) and nickel chloride hexahydrate (1000 mg, 4.20 mmol) and evaporated to obtained pale green powder. Yield: 52%. IR (KBr): ν = 3395, 3023, 2936, 1625, 1534, 1355, 1153, 935, 778 cm⁻¹. UV–vis [water, λmax (ε/M⁻¹)] = 1386(1986), 1153(847), 865(515), 318(1003), 255(33165). Elemental analysis: calcld for C₃₄H₄₄Cl₄Ni₂N₁₂O₈: C, 39.22; H, 4.45; N, 16.16%. Found: C, 39.59; H, 5.04; N, 16.16. ESI(+)–MS: m/z calcld for [Ni₂⁺]H⁺ 789.14, expit 789.13.

Zn-1. [Zn₂(H₂1)₂Cl₂(H₂O)]: A similar procedure adapting H₂1 (720 mg, 2.10 mmol) and nickel chloride hexahydrate (500 mg, 2.10 mmol) to yield green solid. Yield: 55%. IR (KBr): ν = 3395, 3023, 2936, 1625, 1534, 1355, 1153, 935, 778 cm⁻¹. UV–vis [water, λmax (ε/M⁻¹)] = 1386(1986), 1153(847), 865(515), 318(1003), 255(33165). Elemental analysis: calcld for C₃₂H₄₀Cl₄Ni₂N₁₂O₁₁: C, 40.42; H, 4.65; N, 16.16%. Found: C, 40.59; H, 5.00; N, 16.16. ESI(+)–MS: m/z calcld for [Ni₂⁺]H⁺ 789.14, expit 789.13.

Zn-2. [Zn₂(H₂2)₂Cl₂(H₂O)]: A similar procedure adapting H₂2 (753 mg, 2.32 mmol) and zinc chloride dihydrate (400 mg, 2.32 mmol), and a yellow solid is obtained. 1H NMR (D₂O, TMS, 600 MHz): δ = 8.52 (s, 1H), 8.46 (s, 1H), 8.18–8.15 (t, 2H), 8.09 (s, 2H), 7.70–7.68 (d, 2H), 7.65 (s, 2H), 3.80–3.78 (t, 2H) ppm. IR (KBr): ν = 3413, 3192, 2936, 2852, 2345, 1607, 1560, 1440, 1384, 1305, 1230, 1155, 1100, 1018, 776, 638 cm⁻¹. UV–vis [water, λmax (ε/M⁻¹)] = 367, 3076, 2900, 1612, 1230 cm⁻¹. Elemental analysis: calcld for C₃₂H₄₄Cl₄Zn₂N₁₂O₁₂: C, 39.42; H, 4.65; N, 16.16%. Found: C, 39.42; H, 4.65; N, 16.08. ESI(+)–MS: m/z calcld for [Zn₂⁺]K⁺ 783.03, expit 783.70.

Zn-3. [Zn₂(H₂3)₂Cl₂(H₂O)]: A similar procedure adapting H₂3 (786 mg, 2.32 mmol) and zinc chloride dihydrate (400 mg, 2.32 mmol) to yield a colorless solid. 1H NMR (D₂O, TMS, 500 MHz): δ = 11.51–11.47 (d, 1H), 8.61–8.56 (d, 2H), 8.28–8.26 (d, 1H), 8.04–8.01 (d, 1H), 7.99–7.94 (m, 1H), 7.91–7.87 (m, 1H), 7.82–7.77 (m, 1H), 7.56–7.53 (t, 1H).
To a 100 mL stainless steel high-pressure reactor vessel, 0.2 g of catalyst (0.005 mol) was used. The colorless precipitate obtained was filtered, washed with methanol, and dried to yield a colorless solid. Yield: 72%. IR (KBr): ν = 3420, 1636, 1540, 1380, 1233, 1172, 982, 779 cm⁻¹. UV–vis [water, λmax (ε/M⁻¹)]: 292 (81366), 269 (47196), 206 (80093). Elemental analysis: calcd for [Zn₂(H₂)]. Found: C, 35.41; H, 3.59; N, 20.72%. ESI(+)–MS: m/z calcd for [Zn₃₂]H⁺ 775.0981, expt 775.6658.

**General Protocol for Cycloaddition of CO₂ to Epoxide.**

To a 100 mL stainless steel high-pressure reactor vessel, 0.2 mmol of catalyst and 100 mmol of substrate were charged. The reactor was purged with carbon dioxide 2–3 times, and 1 MPa pressure of carbon dioxide was fixed and the reaction mixture was heated at 100 °C for 4 h. The reactor was cooled, and the reaction mixture was passed through a silica column to separate the catalyst and isolate it.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b04241.

Characterization data of all the ligands and the complexes such as ESI-MS, UV–vis, FT-IR, NMR, and crystal data and characterization of catalytic product brief description (PDF)

Crystallographic data of H₂ (CIF)

Crystallographic data of Ni₂(CIF)

Crystallographic data of Zn₂ (CIF)

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# ACKNOWLEDGMENTS

CSMCRI communication number: 157/2019. R.A. and E.C. acknowledge the CSIR for SRF and Indus Magic project no. CSC-0123 for financial assistance. S.S. thanks DST for the INSPIRE Faculty award (DST/INSPIRE/04-I/2017/000003). Dr. S. Kannan is greatly acknowledged for the reactor facilities and discussion to perform this work. P.S. acknowledges DST- SERB New Delhi (project nos. SR/S1/IC-23/2011 & SR/S2/RJN-62-2012) for the financial support. We are thankful to ADCIF for the instrument support.

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