New Set of Multicomponent Crystals as Efficient Heterogeneous Catalysts for the Synthesis of Cyclic Carbonates

Arunangshu Kundu,† Swagata Saikia,† Manoj Majumder,§ Oindrila Sengupta,‖ Biswajit Bhattacharya,† Gobinda Chandra De,‡ and Sushobhan Ghosh*†

†Department of Chemistry, Gauhati University, Guwahati 781014, Assam, India
‡Department of Chemistry, Coochbehar Panchanan Barma University, Cooch Behar, West Bengal 736101, India
§Department of Chemistry, Mathabhanga College, Mathabhanga, West Bengal 736146, India
‖Department of Chemistry, Beinstein College of Science, Guwahati 781040, Assam, India
*IISER Kolkata, Mohanpur, West Bengal 741246, India

Supporting Information

ABSTRACT: Three new multicomponent crystals 1a−1c of Zn(II), Mn(II), and Co(II), respectively, were synthesized by the reaction of 2,6-bis(hydroxymethyl)pyridine, the respective metal salts, and sodium benzoate in a 1:1:2 ratio. One component of these multicomponent crystals 1a−1c is the dicationic 2,6-bis(hydroxymethyl)pyridine metal complex and the other component is the dianionic tetranbenzoate complex of the same metal. The complexes were fully characterized by single-crystal X-ray structure determination. The X-ray structure of these compounds 1a−1c reveals the formation of 1D supramolecular chain parallel to the crystallographic b axis via H-bonding interactions between the dicationic and dianionic parts of the respective compound. The Mn(II) (1b) and Co(II) (1c) complexes show antiferromagnetic coupling between the two associated metal centers via the H-bonding interaction pathway. All the three compounds 1a−1c were tested as heterogeneous catalytic systems for the successful conversion of epoxides to cyclic carbonates in solvent-free condition under approximately 10 bar of pressure of CO2 and temperature ranging between 60 and 80 °C along with tetrabutyl ammonium bromide acting as a cocatalyst. All the three compounds 1a−1c were found to have turnover number more than 1000 for the respective epoxides except for the conversion of cyclohexene oxide to cyclohexene carbonate.

INTRODUCTION

The increasing level of carbon dioxide in the atmosphere due to the burning of fossil fuels and other environmental emission sources has caused alarming impacts on earth’s climate. Hence, the conversion of carbon dioxide into valuable chemical feedstock has become an imperative. Several processes are known including the conversion of CO2 into methanol,1−6 urea,7 polycarbonates,8−10 and cyclic carbonates.11−32 Several catalytic systems have been designed for the synthesis of cyclic carbonates involving metal−organic framework materials and discrete metal complexes11−32 under both homogeneous and heterogeneous reaction conditions.16,18 From the mechanistic point of synthesis of cyclic carbonates by different catalytic systems, it is clear that the catalyst should provide a Lewis acidic site for the initial binding of the epoxide molecules.33−35 Looking at the scope of catalysts for the conversion of CO2 into cyclic carbonates, we planned to design supramolecular heterogeneous catalytic systems which can provide green methods for this conversion process. Supramolecular chemistry and self-assemblies have attracted much attention in recent years.36−45 Development of new topologies and utilization of the supramolecular aggregates as functional materials have evolved as major aspects in this research area. It may be noted that noncovalent interactions, namely, strong and weak hydrogen bonds, C−H···π interactions, π/π stacking, halogen−halogen, sulfur−sulfur, gold−gold, and so forth, are being increasingly utilized to generate self-assembled structures.36−43 It is also well known that some crystals may contain more than one chemical species, and these multicomponent crystals are known as cocrystals.44−50 In comparison to the large number of organic cocrystals, there are only a few multicomponent crystals containing only metal complexes as the components.52−60 2,6-Bis(hydroxymethyl)pyridine (dhmp) has been extensively investigated as a ligand in coordination compounds.51−64 A few mononuclear complexes of 2,6-bis(hydroxymethyl)pyridine are reported where the hydrogen atoms corresponding to the hydroxyl groups of the 2,6-bis(hydroxymethyl)pyridine molecule get hydrogen bonded to the respective counterions to form supramolecular aggregation in the resulting crystal lattice,61,62 which shows interesting magnetic properties in the case of cobalt complex.63 In this report, we have synthesized three new set of multicomponent crystals 1a−c, (Scheme 1).

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where the mononuclear 2,6-bis(hydroxymethyl)pyridine complex cations [Co(II)(L)2]2+,[Mn(II)(L)2]2+,[Zn(II)(L)2]2+ cocrystallize with the respective benzoate complex anions [Co(II)(PhCOO)4]2−,[Mn(II)(PhCOO)4]2−,[Zn(II)(PhCOO)4]2− (Scheme 1). The cocrystallization results in the formation of supramolecular 1D chains via the H-bonding interaction between the H-atoms of the respective hydroxymethyl groups of the [M(II)(L)2]2+ cation and the benzoate carboxylate group of the respective [M(II)(PhCOO)4]2− anion. These supramolecular multicomponent crystals showed the antiferromagnetic exchange interaction in the case of 1b and 1c through the intermolecular H-bonding interaction pathway. All of the three complexes are found to catalyze the conversion of epoxide and CO2 to cyclic carbonates under solvent-free heterogeneous conditions. Many heterogeneous catalytic systems are known to the best of our knowledge, this is the first example of multicomponent crystals acting as heterogeneous catalysts for the conversion of CO2 into cyclic carbonates.

## RESULTS AND DISCUSSION

### Syntheses and Characterization.

The complexes 1a−1c (Table 1) were synthesized by refluxing the 2,6-bis(hydroxymethyl)pyridine (L), sodium benzoate, and metal salts (1:1:2) in a methanol–water mixture (Scheme 1). The single crystals suitable for diffraction quality were grown by slow evaporation of the respective solutions over one week.

### Description of the Structure of \[\text{Zn}^{II}\text{L}_2\] \([\text{Zn}^{II}\text{L}_2\text{COO}_4]_2\text{−} \) (1a), \([\text{Mn}^{II}\text{L}_2]\text{[Mn}^{II}\text{L}_2\text{COO}_4]_2\text{−} \) (1b), and \([\text{Co}^{II}\text{L}_2]\text{[Co}^{II}\text{L}_2\text{COO}_4]_2\text{−} \) (1c).

The structures of 1a, 1b, and 1c are shown in Figure 1. In all of the cases, the dipositive metallic 2,6-
bis(hydroxymethyl)pyridine cation \([\text{M}^{II}L_2]\) cocrystallizes with dianionic metal tetrabenzoate \([\text{M}^{II}(\text{PhCOO})_4]\). In the structure of 1a, the coordination environment of dicationic Zn(II) is occupied by four alkoxy oxygen atoms and two pyridyl nitrogen donor atoms. The coordination environment of Zn(II) is pseudo octahedral with the \(\text{N}1-\text{Zn}1-\text{O}2\) and \(\text{N}1-\text{Zn}1-\text{O}1\) angles as 102.32° and 77.4°, respectively. The distance between \(\text{Zn}1-\text{N}1\) is 2.021 Å, whereas the distances between \(\text{Zn}1-\text{O}1\) and \(\text{Zn}1-\text{O}2\) are 2.165 and 2.167 Å, respectively. The coordination environment of the dianionic zinc(II) is occupied by four benzoate anions. The average distance between the carboxylate oxygen and the Zn(II) in zinc carboxylate complexes is between 1.99 and 2.37 Å.65 In the case of 1a, four \(\text{Zn}-\text{O}\) distances lie in the range of 2.09–2.10 Å, whereas the other four \(\text{Zn}-\text{O}\) distances lie in the range of 2.536–2.549 Å which is above the average bond distance between the \(\text{Zn}-\text{O}\) in carboxylate complexes. The bond angles around the Zn(II) are 126.90°, 117.10°, 87.27°, and 126.90° (Table S1). The bond angles between \(\text{Zn}1-\text{N}1\) ranging from 77.13° to 102.78° and \(\text{N}1-\text{Zn}1-\text{O}2\) ranging from 77.42° to 102.68°. The dianionic \([\text{Co}^{II}(\text{PhCOO})_4]\) environment is tetrahedral and occupied by four benzoate anions with all of the four \(\text{Co}-\text{O}\) distances being equal to 2.146 Å and the \(\text{O}-\text{Co}-\text{O}\) angles varying from 84.87° to 127.16° (Table S1). The dicationic \([\text{Co}^{II}L_2]\) interacts with the dianionic \([\text{Co}^{II}(\text{PhCOO})_4]\) with the formation of H-bonding between \(\text{H}2\text{A}-\text{O}3\) and \(\text{H}1\text{A}-\text{O}6\). The H-bonding interaction (Figure S2) produces a 1D chain parallel to crystallographic \(b\) axis (H-bond parameters given in Table 2).

**Magnetic Studies.** Magnetic Study of 1c. Magnetic susceptibility measurements were carried out on crushed single crystals of 1c with an applied magnetic field of 1000 G in the temperature range 1.5–300 K using a quantum designed SQUID magnetometer. The magnetic properties of 1c, in the form of \(\chi_M\) versus \(T\) and \(\chi_M T\) versus \(T\) per two Co(II) ions, are presented in Figure 3. The \(\chi_M T\) value per two Co(II) centers at

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**Figure 1.** Coordination environments of metal ions and ligands in the complexes 1a, 1b, and 1c.

**Figure 2.** Crystal packing diagram of 1a.

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300 K is 5.60 cm$^3$ mol$^{-1}$ K which is much higher than those expected for an isolated spin-only value of 2.24 cm$^3$ mol$^{-1}$ K for two uncoupled Co(II) ions, one high spin Co(II) tetrahedral center with $S = 3/2$ spin, and one low spin Co(II) octahedral with $S = 1/2$. The higher value cannot be explained in terms of orbital contribution which is very common for Co(II) octahedral high spin system, but in our case, Co(II) octahedral state is in low spin state because of the presence of strong field ligand and will not exhibit orbital contribution and also other Co(II) center is high spin tetrahedral which also ruled out the possibility of the presence of orbital contribution. Therefore, the higher value of $\chi_M T$ of Co(II) centers may arise from two possibilities. First, the octahedral Co(II) low spin center may undergo John Teller distortion which can induce some orbital contribution due to further splitting of d-orbitals and second possibility may be due to the presence of crossover region with some spin state equilibrium which is very common for the d$^7$ octahedral system. It may happen that at low temperature, low spin is the ground state but with increase in temperature, high spin state forms because of shifting of spin state equilibrium which in turn can induce some amount of orbital contribution into the system and thus can lead to higher $\chi_M T$ value than the theoretical one. First, it exhibits a monotonic decrease in $\chi_M T$ until it reaches a minimum of 4.91 cm$^3$ mol$^{-1}$ K at 18 K with decreasing temperature which indicates the presence of dominant antiferromagnetic interactions taking place between two Co(II) paramagnetic centers. Then, a sudden increase in the $\chi_M T$ (5.38 cm$^3$ mol$^{-1}$ K) value upon further lowering the temperature was observed at 16 K and finally a rapid decrease to a value of 4.39 cm$^3$ mol$^{-1}$ K at 1.5 K, indicating an intermolecular antiferromagnetic interaction or a system of spin canting followed by the effect of saturation phenomena. The dominant antiferromagnetic coupling is mainly occurring by H-bonding interaction between two Co(II) centers, one octahedral center linked to a strong pyridyl ligand and one tetrahedral Co(II) center coordinated to a weak benzoate ligand. Though there is no direct superexchange pathway between the metal centers as they reside in a cocrystal, but still $\chi_M T$ versus $T$ of complex 1c reveals magnetic interaction which can only be supported by H-bonding interaction between the metal centers. This result can be justified by fitting $\chi_M T$ versus $T$ plot with a Co(II) dimer model (Figure 3) with one correction term used to roughly account the orbital contribution and interdimer interaction that gives the value of the coupling constant $J = -6.08$ cm$^{-1}$ using the Hamiltonian $H = -2JS_1S_2$, where $S_1$ and $S_2$ are spin states of two metal centers. The value of the coupling constant obtained for 1c by theoretical calculation was found to be $-84$ cm$^{-1}$. Moreover, $\chi_M^{-1}$ versus $T$ data obey Curie–Weiss law with the best-fitting parameters $C = 5.65$ cm$^3$ mol$^{-1}$ K and $\theta = -2.77$ K (Figure 3). The negative $\theta$ value also indicates the presence of antiferromagnetic interaction at high temperature. However, abrupt rise in $\chi_M T$ value below 18 K suggests a ferromagnetic transition operating in complex 1c; the observed ferromagnetic-like ordering may be attributed to canted antiferromagnetism where perfect antiparallel alignment of the spins on neighboring metal ions between the antiferromagnetic coupling layer is not achieved, leading to the generation of residual spins.

However, complex 1c does not show any hysteresis loop around 2 K. The origin of spin canting is either (i) magnetic anisotropy or (ii) antisymmetric exchange where the spins are slightly tilted from their original position. As it was observed that at higher temperature, antiferromagnetic coupling was operating between two Co(II) centers through H-bonding which is very uncommon occurring in any system of a cocrystal and as an evidence, we are also getting negative coupling constant and negative $\theta$ value after fitting the magnetization curve. However, at lower temperature due to some alignment of the spins from their normal position may result abrupt rise in magnetization below 18 K.

| compound | D–H–A | D–H (Å) | H–A (Å) | D–A (Å) | D–H–A (deg) | symmetry code |
|----------|--------|---------|--------|--------|-------------|---------------|
| compound 1 (Mn) | O1–H1A–O6 | 0.87(3) | 1.73(3) | 2.592(2) | 170(3) | X, Y, Z |
|          | O2–H2A–O3 | 0.84(3) | 1.76(3) | 2.594(2) | 170(3) | X, Y, Z |
| compound 2 (Co) | O1–H1A–O6 | 0.86(7) | 1.98(5) | 2.640(8) | 133(7) | X, Y, Z |
|          | O2–H2A–O3 | 0.86(5) | 1.90(5) | 2.635(7) | 143(6) | X, Y, Z |
| compound 3 (Zn) | O1–H1A–O6 | 0.99(3) | 1.67(4) | 2.651(3) | 170(4) | X, Y, Z |
|          | O2–H2A–O3 | 0.96(3) | 1.70(3) | 2.653(3) | 174(4) | X, Y, Z |

Figure 3. Plot of $\chi_M$ vs $T$ and $\chi_M T$ vs $T$ (inset) (left) where red line indicates theoretical fitting and plot of $\chi_M^{-1}$ vs $T$ data fitting using Curie–Weiss equation in the range 1.5–300 K (right) for compound 1c.
Magnetic Study of 1b. The dc magnetic susceptibility was measured on a crystalline sample of 1b under an applied field of 1000 G in the temperature range 1.5–300 K using a SQUID magnetometer. The $\chi_M T$ value per two Mn(II) centers was found to be 8.34 cm$^3$ mol$^{-1}$ K at 300 K (Figure 4) which is lower than the spin-only value (8.68 cm$^3$ mol$^{-1}$ K) expected for a magnetically isolated two high spin Mn(II) ions, indicating the occurrence of antiferromagnetic coupling between the Mn(II) centers. On lowering the temperature, $\chi_M T$ value gradually decreases to 5.13 cm$^3$ mol$^{-1}$ K at 33 K. However, on further cooling, there is a sharp fall with a $\chi_M T$ value of 3.71 cm$^3$ mol$^{-1}$ K at 2 K. Here, also similar to complex 1c, the magnetic exchange occurs via H-bonding interaction between two Mn(II) octahedral centers (both in high spin state) as no other superexchange pathway present between metal centers. We try to fit the magnetization data with Mn(II) dimeric equation using the Hamiltonian $H = -2J S_1 S_2$. The best fit parameter thus obtained, $J = -5.88$ cm$^{-1}$ with $g = 2$ with the agreement factor $R = 1.86 \times 10^{-4}$ (Figure 4).

The value of the coupling constant obtained for 1b by theoretical calculation was found to be $-2.3$ cm$^{-1}$. Thus, we can see that both of our complexes show some unusual strong magnetic interaction between two metal centers through only H-bonding as there is no bridging ligand present between the metal centers. At low temperature, the interaction is more prominent. For complex 1c, the magnetic interaction is quite interesting. Here, the orbital contribution may arise either due to structural distortion or may be spin state equilibrium operating in the molecule. The complex 1c also shows some sort of ferromagnetic ordering because of spin canting at low temperature. On the other hand, complex 1b shows antiferromagnetic interaction between two isolated Mn(II) centers through the same H-bonding. Though vast number of examples is dominating in the literature with magnetic interaction through superexchange pathway in the presence of bridging ligands between paramagnetic centers, but magnetic coupling only by the operation of H-bonding is very rare.

Catalytic Cycloaddition of Carbon Dioxide. Complexes 1a–1c which are forming H-bonded supramolecular 1D networks were tested as heterogeneous catalysts for the catalytic cycloaddition of carbon dioxide and the epoxides as shown in Scheme 2 under solvent-free condition.

Scheme 2. Catalytic Cycloaddition of CO$_2$ and Epoxides 2a–2g by the Multicomponent Crystals 1a–1c as Heterogeneous Catalysts and TBAB as a Cocatalyst

The reaction of six terminal epoxides 2a–f and cyclohexene oxide (2g) with carbon dioxide to form the corresponding cyclic carbonates 3a–g was investigated using 0.016 mol % complexes 1a–1c and 0.09 mol % TBAB under solvent-free conditions at 60–80 °C and 10 bar carbon dioxide pressure. Reactions were carried out for 10 h and then analyzed by IR and $^1$H NMR spectroscopy to give a conversion, and the cyclic carbonates were isolated and purified to give the chemical yield. The results are shown in Table 3. In general, good to excellent yields were recorded for carbonates 3a–3f except the cyclohexene carbonate (3g). All cyclic carbonates were characterized by IR, $^1$H NMR, $^{13}$C NMR, and ESI MS analysis (Supporting Information Figures S3–S23). The cyclic carbonate 3b was characterized by single-crystal X-ray diffraction (Figure 5). 3b crystallized in the orthorhombic crystal system (crystal data of 3b given in Table S2) in Pn$a_2$ space group. The cell and data are transformed to be consistent with space group Pn$a_2$. The structure, however, is a 75–25% racemic mixture with its enantiomer. The minor component stays as a pseudo-mirror (parallel to ac-plane intersecting b axis at 1/4) related disorder of the major component.

Mechanistic Investigation of the Catalytic Experiment for the Synthesis of Cyclic Carbonates. In order to investigate the mechanism of the cyclic carbonate synthesis and to know the role of the catalyst, the reaction was monitored via $^1$H NMR spectroscopy. The $^1$H NMR spectra (Figure 6) of the Zn-based catalyst 1a in DMSO-$d_6$ show the peaks between 7.9 and 7.3 ppm corresponding to the aromatic H-atoms of 2,6-bis(hydroxymethyl)pyridine and phenyl rings of benzoate and a peak at 4.6 ppm corresponding to the methylene protons of the 2,6-bis(hydroxymethyl)pyridine. Whereas the $^1$H NMR in DMSO-$d_6$ of the regenerated catalyst obtained by washing the residue from the reaction of CO$_2$, propylene oxide, 1a, and tetrabutyl ammonium bromide several times with dry dichloromethane and diethyl ether show the peaks between 8.1 and 6.7 ppm corresponding to the aromatic H-atoms of 2,6-bis(hydroxymethyl)pyridine and phenyl rings of benzoate and a peak at 4.5 ppm corresponding to the methylene protons of the 2,6-bis(hydroxymethyl)pyridine. The peaks at 5.66, 5.41, 4.67, and 0.98 ppm correspond to the peak for the intermediate 1-bromopropan-2-yl hydrogen carbonate attached to one of the...
Zn-metal center of the catalyst 1a, and those at 4.74, 4.44, 3.92, and 1.05 ppm are of the propylene carbonate itself binding to the Zn-metal center of catalyst 1a. This is supported by the fact that the peaks corresponding to propylene carbonate appear more upfield between 4.9 and 4.0 ppm (Figure S29) in $^1$H NMR as compared to the intermediate 1-bromopropan-2-yl hydrogen carbonate. The UV-vis titration experiment of the catalyst 1a (5 × 10$^{-5}$ M) with gradual addition of 10 μL of propylene oxide (1 × 10$^{-1}$ M) in DMSO (Figure S25) shows the clear binding of the propylene oxide with the catalyst 1a, having isosbestic point at around 280 nm; however, the stoichiometric addition of 1a, propylene oxide, and TBAB in DMSO-d$_6$ gives the $^1$H NMR signal which is devoid of considerable chemical shift for the propylene oxide (Figure S28) which might be due to very weak binding interaction of the epoxide substrate with respective metal center in catalyst 1a. The upfield shift corresponding to the aromatic protons of the regenerated catalyst as compared to the original catalyst may be attributed to the reorientation of the benzoate rings in 1a because of binding of the intermediate 1-bromopropan-2-yl hydrogen carbonate, as shown in Scheme 3.

The density functional theory (DFT) calculation was also carried out with the zinc complex 1a. The optimized structures showed the lowest energy in the case of binding of the substrate propylene oxide with the cationic zinc center (1a$^+$) instead of the binding with anionic zinc center (1a$^-$) (Table 4). Hence, it is the cationic zinc center which can actually bind the substrate epoxide. Ring opening of the substrate epoxide and subsequent insertion of CO$_2$ can give the intermediate 1-bromopropan-2-yl hydrogen carbonate. The geometry optimized structure 1a$^+$ clearly shows the binding interaction of the carbonate anion of intermediate 1-bromopropan-2-yl hydrogen carbonate with the cationic zinc center by replacing one of the hydroxyl methyl substituents of one of the bound 2,6-bis(hydroxymethyl)-pyridine ligand (Table 4). Hence, from DFT studies, we get the idea that the epoxide substrate may bind with the cationic metal center and with subsequent insertion of CO$_2$ may give the respective intermediate 1-bromopropan-2-yl hydrogen carbonate attached to the cationic metal site by displacing one of the hydroxyl methyl group. Taking account the geometry optimized structures and correlating the previous report on the mechanistic study with monometallic complexes, we can finally propose the probable reaction mechanism as in Scheme 3. All of the three complexes 1a–1c are having identical X-ray structures with just different transition-metal ions, hence the catalytic mechanism of cycloaddition of CO$_2$ with epoxide by these complexes is supposed to be remain same which indeed is

| Entry | Catalyst | Substrate | Product | TON | Yield [%] |
|-------|----------|-----------|---------|-----|-----------|
| 1     | NBuBr + L + PhCOONa |  |  | 250 | 8% |
|       | 1a       | 2a        | 3a      | 3196 | 62 |
| 2     | 1a       | 2b        | 3b      | 2954 | 59 |
| 3     | 1a       | 2c        | 3c      | 3045 | 60 |
| 4     | 1a       | 2d        | 3d      | 1696 | 71 |
| 5     | 1a       | 2e        | 3e      | 1616 | 70 |
| 6     | 1a       | 2f        | 3f      | 1650 | 70 |
| 7     | 1a       | 2g        | 3g      | 1910 | 77 |
| 8     | 1a       | 2h        | 3h      | 1885 | 74 |
| | 1b       | 2i        | 3i      | 1901 | 75 |

Table 3. Cycloaddition of CO$_2$ and Epoxides 2a–2g Catalyzed by 1a–1c

Figure 5. Single-crystal X-ray structure of the 1, 2 epoxy 3 phenoxy propane carbonate 3b.
reflected experimentally. The regenerated catalysts 1a−1c isolated from the reaction of cyclo-addition of CO₂ and propylene oxide were tested for recyclability, and all of the three catalysts showed catalytic activity up to at least one cycle with small loss in TON (Figure S27).

**Scheme 3. Mechanism of Cyclic Carbonate Formation Involving Catalyst 1a, CO₂, and NBu₄Br**

**Table 4**

| Compound | Relative Energy (eV) |
|----------|----------------------|
| (1a')    | -2959.8493524 a.u. (taking its energy as zero.) |
|          | 0.0 eV               |
| (1a')    | -2959.8386359        |
|          | 0.3 eV               |
|          | 3161.7294435         |
|          | Absolute energy does not make any sense. |

**CONCLUSIONS**

We have synthesized three new set of multicomponent crystals of complexes 1a−1c which have been fully characterized by X-ray single-crystal structure determination. One component constitutes the dicationic metal complex of 2,6-bis-(hydroxymethyl)pyridine ligand, whereas the other component
is dianionic metal tetrabenzoate of the same metal. Intramolecular H-bonding interaction between the hydroxyl H-atoms of dicaticonic component with the benzoate carboxylate oxygen atoms of the dianionic component gives rise to 1D supramolecular chain in 1a–1c. The manganese (1b) and cobalt complexes (1c) show interesting antiferromagnetic interaction between the paramagnetic metal centers through the H-bonding exchange pathway. Complexes 1a–1c showed heterogeneous catalytic activity for the conversion of epoxides to cyclic carbonates in the presence of CO$_2$ and tetrabutyl ammonium bromide cocatalyst with turnover numbers greater than 1000 except in the case of cyclohexene carbonate where the catalytic turnover is less. The cyclic carbonate 3b was characterized by X-ray single-crystal structure determination. The mechanistic study with catalyst 1a and propylene oxide showed the clear involvement of the catalysts in the reaction with the regenerated catalyst 1a getting bound to the intermediate 1-bromopropan-2-yl hydrogen carbonate as observed via NMR, whereas UV–vis titration studies show the initial binding of the epoxide substrate to the catalyst 1a. DFT calculations revealed the involvement of the cationic zinc center during the catalysis with the intermediate 1-bromopropan-2-yl hydrogen carbonate replacing the hydroxymethyl substituent of one of the 2,6-bis(hydroxymethyl)pyridine ligands. The binding of the intermediate 1-bromopropan-2-yl hydrogen carbonate to the catalyst 1a as observed by the $^1$H NMR studies is a proposed structure of the species isolated, and more investigations are underway in order to confirm its structure. Hence, 1a–1c which are multicomponent crystals play useful roles as heterogeneous catalysts in the conversion of epoxides to cyclic carbonates in the presence of the green house gas CO$_2$.

**EXPERIMENTAL SECTION**

All synthetic procedures were performed under normal atmospheric conditions. $^1$H NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer. $^1$H NMR spectra were referenced internally to residual solvent peaks, and chemical shifts are expressed relative to tetramethylsilane, SiMe$_4$ ($\delta$ = 0 ppm). Fourier transform infrared spectra were recorded with an IRAfinity-1S Shimadzu spectrophotometer. ESI MS was recorded in a high-resolution mass spectrometer, AGILENT QTOF 6520. Microanalyses were carried out with a PerkinElmer 2400 CHN analyzer. Magnetic studies were conducted with a Quantum Design Physical Property Measurement System with model 6000; Magnet14Tesla; temperature range 1.8–400 K. 2,6-Bis(hydroxymethyl)pyridine, tetrabutyl ammonium bromide, and all of the epoxides were purchased from Sigma-Aldrich. Zinc nitrate, manganese acetate, cobalt (hydroxymethyl)pyridine ligands. The binding of the intermediate 1-bromopropan-2-yl hydrogen carbonate replacing the hydroxymethyl hydrogen carbonate to the catalyst 1a as observed by the $^1$H NMR studies is a proposed structure of the species isolated, and more investigations are underway in order to confirm its structure. Hence, 1a–1c which are multicomponent crystals play useful roles as heterogeneous catalysts in the conversion of epoxides to cyclic carbonates in the presence of the green house gas CO$_2$.

**Characterization Data for 1a.** Isolated yield by the precipitation of the product is 85%. $^1$H NMR in DMSO-$d_6$: $\delta$ 7.9 (m, 8H, Ph ring of 2,6 DHMP and benzoate), 7.8 (t, 2H, Ph ring of 2,6 DHMP), 7.4–7.3 (m, 16H, Ph ring of benzoate), 6.0 (br, 4H, OH), 4.6 (s, 8H, CH$_2$ of 2,6 DHMP) ppm. $^{13}$C NMR in DMSO-$d_6$: $\delta$ 171.6, 134.6, 131.2, 129.6, 118.6, 63.3 ppm. IR data: 3450, 2976, 2825, 1637, 1556, 1354, 1168, 1134, 937, 852, 779, 715, 682, 630, 522 cm$^{-1}$. Elemental analysis calculated for C$_{42}$H$_{38}$Mn$_2$N$_2$O$_{12}$: C, 57.81; H, 4.39; N, 3.21. Found: C, 57.50; H, 4.65; N, 3.64.

**Characterization Data for 1b.** Isolated yield from precipitation of product is 80%. IR data: 3446, 2974, 2937, 1645, 1558, 1463, 1417, 1371, 1340, 1298, 1078, 881, 815, 715, 624, 511 cm$^{-1}$. Elemental analysis calculated for C$_{42}$H$_{38}$N$_2$O$_{12}$Zn$_2$: C, 56.46; H, 4.39; N, 3.21. Found: C, 56.50; H, 4.65; N, 3.64.

**Characterization Data for 1c.** Isolated yield from precipitation of product is 78%. IR data: 3446, 3062, 2974, 2827, 1610, 1558, 1440, 1386, 1305, 1168, 1136, 1068, 1028, 937, 854, 779, 715, 682, 630, 528 cm$^{-1}$. Elemental analysis calculated for C$_{42}$H$_{38}$Co$_2$N$_2$O$_{12}$: C, 57.28; H, 4.35; N, 3.18. Found: C, 57.62; H, 4.52; N, 3.43.

**Crystallographic Methods.** Single-crystal X-ray diffraction data were collected on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromator and a Mo Kα fine-focus sealed tube ($\lambda$ = 0.71073 Å). Data integration was done using SAINT. Intensities for absorption were corrected using SADABS. Structure solution and refinement were carried out using Bruker SHELXTL.$^{71,72}$ The hydrogen atoms were refined isotropically, and all of the other atoms were refined anisotropically. N–H and O–H hydrogens were located from difference electron density maps, and C–H hydrogens were fixed using the HFIX command in SHELXTL. Molecular graphics were prepared using X-SEED68 and Mercury licensed version 3.9.69.

**COMPUTATIONAL DETAILS OF MAGNETIC STUDIES**

Heisenberg–Dirac–van Vleck spin Hamiltonian has been found to be effective for the description of magnetic properties of dinuclear transition-metal complexes. The exchange interaction between two magnetic centers is derived from the spin coupling Hamiltonian given in eq 1, where $J_{12}$ is the spin coupling constant and $S_1$ and $S_2$ are spin operators for the two respective metal centers.$^{73}$

$$H = 2J_{12}S_1S_2$$

(1)

Here, we have used the broken-symmetry (BS) approach of eq 2 for the DFT-based calculation of the exchange coupling constants given by Yamaguchi.$^{74}$

$$J_{12} = \frac{E^{BS} - E^{HS}}{(S)^{2}_{HS} - (S)^{2}_{BS}}$$

(2)

where $E^{BS}$, $E^{HS}$, $(S)^{2}_{BS}$, $(S)^{2}_{HS}$ are energy and average spin square values for the BS and high-spin (HS) determinants, respectively. Positive and negative values of $J$ correspond to ferromagnetic and antiferromagnetic coupling, respectively.

All of the calculations have been carried out in Gaussian 09 program with hybrid functional (B3LYP) in combination with Ahlrichs’ split valence and triple-$\zeta$ TZVP basis set. In both the systems (Co and Mn), the BS systems are found to be more stable than the HS state, indicating antiferromagnetic coupling.
The J values for the two systems (Co and Mn) are −84 and −2.3 cm⁻¹, respectively. For the geometry optimization of the studied complexes, we have employed DFT-based methodology with the B3LYP functional in conjunction with Hay and Wadt’s double-zeta effective core potential (LANL2DZ) as a basis set. These sets of functional and basis set work well for the transition-metal complexes. All of the optimization computations have been performed in Gaussian 09 suite of program.

General Procedure for Catalyst Screening at 70 °C and 10 bar Pressure. An epoxide (2 gm, 34.45 mmol), catalyst 1a (5 mg, 0.0056 mmol), and Bu₄NBr (10 mg, 0.0311 mmol) were placed in a stainless steel autoclave fitted with a magnetic stirrer bar, and the reactor was heated to 70 °C after being charged with 10 bar pressure of carbon dioxide. The reaction mixture was stirred for 1 hr at this temperature and pressure. The conversion of epoxide to cyclic carbonate was determined by analysis of a sample by ¹H NMR spectroscopy. Cyclic carbonates 3a–3g are all characterized by ¹H NMR and ¹³C NMR as well as ESI MS and IR spectroscopy (figures in Supporting Information file).

Propylene Carbonate (3a). Purified by flash chromatography with hexane/EtOAc (8:2) gave a colorless liquid. ¹H NMR (300 MHz, CDCl₃): δ 4.79 (m, 1H, OCH₂), 4.42 (m, 1H, CH₂), 1.52–1.50 (m, 2H, CH₂), 1.38–1.36 (m, 2H, CH₂), 0.86 (m, 3H, CH₃) ppm. ¹³C NMR (300 MHz, CDCl₃): δ 73.49 (OCH), 70.44 (OCH₂), 64.20 (OCH₂) ppm. IR (KBr) wave number: 2983, 2937, 1789, 1635, 1554 cm⁻¹.

Epoxy Hexane Carbonate (3f). ¹H NMR (300 MHz, CDCl₃): δ 4.67 (m, 1H, O−CH₂), 4.50 (m, 1H, OCH₂), 4.02 (m, 1H, OCH₂), 1.70 (m, 2H, CH₂), 1.33 (m, 4H, CH₂−CH₂), 0.87 (m, 2H, CH₂) ppm. ¹³C NMR (300 MHz, CDCl₃): δ 155.08 (C═O), 77 (OCH), 69.27 (OCH₂), 33.24 (CH₂), 26.18 (CH₂), 22 (CH₂), 13.57 (CH₂) ppm. IR (KBr): 2951, 2868, 1784, 1637, 1552 cm⁻¹. HRMS (ESI⁺): calcd for C₇H₁₀O₃ [M + H⁺], 143.15; found, 143.17. Epoxy Hexane Carbonate (3g). ¹H NMR (300 MHz, CDCl₃): δ 4.67 (s, 2H, OCH₂), 1.86–1.85 (dd, J = 3 Hz, 4H, CH₂), 1.59–1.53 (m, 3J = 6 Hz, 2H, CH₂), 1.44–1.39 (m, J = 6 Hz, 2H, CH₂) ppm. ¹³C NMR (300 MHz, CDCl₃): δ 155.41 (C═O), 75.72 (OCH₂), 26.75 (CH₃), 18.97 (CH₂) ppm. IR (KBr) wave number: 2943, 2868, 1784, 1637, 1552 cm⁻¹. HRMS (ESI⁺): calcd for C₇H₁₀O₃ [M + H⁺], 143.15; found, 143.07.

# ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00101.

Crystallographic data of 1a (CIF)
Crystallographic data of 1b (CIF)
Crystallographic data of 1c (CIF)
Crystallographic data of 3b (CIF)
Bond length and bond angle table for the compounds; crystal packing diagram for 1b–1c; crystal data for cyclic carbonate 3b; NMR data for cyclic carbonates 3a–3g; ESI MS data for cyclic carbonates 3a–3g; IR data for the catalyst 1a and regenerated catalyst 1a; UV–vis titration of the zinc complex 1a with the propylene oxide; simulated powder pattern from the X-ray structure of catalyst 1a–1c and the experimental powder pattern for the precipitated compound of 1a–1c from the reaction mixture; the catalyst recycling for the cycloaddition of CO₂ and propylene oxide 1a–1c; ¹H NMR of 1a, propylene oxide, and TAB in stoichiometric ratio in DMSO-d₆; ¹H NMR of propylene carbonate in DMSO-d₆; and ¹H NMR of propylene oxide in DMSO-d₆ (PDF)

# AUTHOR INFORMATION

Corresponding Author
*E-mail: sushobhan.iisc@gmail.com (S.G.).

ORCID
Sushobhan Ghosh: 0000-0002-8440-7494

Notes
The authors declare no competing financial interest.

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