**CO₂ Fixation by Dimeric Tb(III) Complexes: Synthesis, Structure, and Magnetism**

Malay Dolai,* Surajit Biswas, Eufemio Moreno-Pineda,* Wolfgang Wernsdorfer, Mahammad Ali,*, Razan A. Alshgari, Saikh Md. Wabaidur, and Ashutosh Ghosh*

**ABSTRACT:** Two dinuclear complexes, [Tb₂(L¹)₂(piv)₂(NO₃)₂]:H₂O (1) and [Tb₂(L²)₂(CF₃COO)₂(H₂O)₄]₂NO₃ (2), have been prepared and characterized by single-crystal X-ray diffraction, where each metal ion is doubly phenoxido-bridged by the two phenolato oxygen atoms of the tetradentate Schiff-base ligand. Previous magnetic studies of 1 show that it is not a single-molecule magnet (SMM), while AC magnetic measurements of 2 show that it relaxes quite fast with μSQUID measurements revealing the presence of an interaction operating between the Tb ions. Through DC, μSQUID, and CASSCF calculations, the strength of the interaction in 2 can be quantified, which is of dipolar origin. Both complexes showed efficient catalytic activity toward the carbon dioxide insertion reaction into epoxides for the formation of organic cyclic carbonates. Catalytic synthesis of organic cyclic carbonates smoothly occurred at 60 °C under 1 bar carbon dioxide pressure and neat conditions. Exocyclic as well as endocyclic epoxides produced a respective cyclic carbonate product with moderate to high yield (43–100%). Moreover, a high turnover number (7300–10000) along with a high turnover frequency (537.5–5000 h⁻¹) are found in this catalytic reaction.

**INTRODUCTION**

Due to the excessive use of fossil fuels, the concentration of atmospheric carbon dioxide (CO₂) has reached values resulting in global warming. Global warming produces various serious environmental threats such as unpredictable climate change, the melting of glaciers, and increments of sea levels. To decrease the constantly increasing CO₂ levels, capture, storage and utilization of CO₂ become more and more essential. Since CO₂ also represents a cheap, abundant, renewable, nonhazardous C1-feedstock,⁴⁻⁶ chemical fixation of carbon dioxide has prospective economical benefits as it produces numerous highly valuable chemicals.⁷⁻⁹ In this context, coupling between carbon dioxide and epoxides for the synthesis of organic cyclic carbonates is the most common CO₂ fixation reaction. This reaction is biocompatible and eco-friendly and represents a 100% atom efficiency.⁹ Moreover, the organic cyclic carbonates have immense applications in diverse fields such as electrolytes of batteries, intermediates of fine chemical/pharmaceuticals, engineering plastic syntheses, polymer production, aprotic green polar solvents, etc.¹⁰⁻¹⁶ There are several catalysts being developed for the preparation of cyclic carbonate from epoxides and carbon dioxide such as transition-metal-based catalysts (like Co,¹⁷,¹⁸ Cr,¹⁹⁻²¹ Fe,²²⁻²⁷ and Zn,²⁸⁻³²), main-group metal complex catalysts (like Li,³³ Al,³⁴⁻³⁷ Mg,³⁸,³⁹ and Ca⁴⁰,⁴¹), and organocatalysts.⁴²⁻⁴⁷ In cycloaddition of CO₂ into epoxides, generally a Lewis acidic site is necessary for the activation of epoxides. Mainly vacant coordination sites of metal nodes fulfill these criteria. The trivalent lanthanide ions (Ln³⁺) can be expedient for this purpose due to their higher Lewis acidic and oxophilic nature.⁴⁸,⁴⁹ The oxophilic nature of lanthanides frequently eases the small solvent molecules’ coordination which can be smoothly disconnected to make vacant coordination sites. Moreover, the strong Ln³⁺–O bond should promote the communication with epoxides to encourage the ring opening and robustness of the molecules upon chemical and thermal exposure. [Ln³⁺(BTB)(H₂O)]₉ [Ln³⁺ = Gd³⁺, Sm³⁺; BTB = 1,3,5-tris (4-carboxy phenyl) benzene])⁵⁰ Gd-pyromellitic dianhydride,⁵¹ [(CH₃)₂NH₂][Ln³⁺(OH)-

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**Image:** Diagram showing the catalytic cycle of CO₂ fixation by the dimeric Tb(III) complexes. The cycle includes the reaction between CO₂ and epoxides, leading to the formation of cyclic carbonates. The diagram highlights the key steps and products of the catalytic process, with labels for CO₂ fixation, solvent-free, green synthesis, and high yield. The complex structure is also depicted, showing coordination bonds and the overall reaction scheme.
(NDC)·(HCOO)]$_2$, and [(CH$_3$)$_2$NH$_2$][Ln$^{III}$]$_2$(OH)-
(BDC)·(HCOO)].[Ln$^{III}$ = Er$^{III}$, Tb$^{III}$; NDC = 1,4-
napthalenedicarboxylate; BDC = 1,4-benzenedicarboxylate].

are a few example of lanthanides acting as catalysts. The
existences of Lewis acidic and basic motifs within the ligand
framework which are design for complexation with lanthanides
also have importance for the enhancement of the catalytic
efficacy for the cyclization reaction, as the presence of a Lewis
acidic center with the close vicinity of a Lewis acidic center
facilitates the fixation of CO$_2$ in the target substrate. Few
previous reports based on the above tactic involve
[Zn$_3$(PDC)$_2$(H$_2$O)$_{10}$], where a lone pair electron in the N
atom of 1,1'-(propene-1,3-diyi)bis(1H-pyrazole-3,5-dicarbox-
ylic acid) (PDC) acts as a Lewis base, and \{[(CH$_3$)$_2$NH$_2$]-
[Zn$^{II}$Tb$^{III}$(TDP)(H$_2$O)]$_2$3DMF·3H$_2$O\}$_n$ where uncoordinated
carboxylate-O atoms functioned as a Lewis base.

Furthermore, in recent years, lanthanide (4f) ion-based
complexes have displayed fascinating properties, leading to
their proposal in several technological applications. 4f complexes
are particularly interesting due to their magnetic properties, such
as the existence of an energy barrier to the reversal of the
magnetization, leading to the so-called single-molecule magnet
(SMM) behavior. Furthermore, multifunctional molecular
materials have attracted attention due to the possibility to
exploit different cooperative physical properties in a single
entity. In this regard, 4f-SMMs have been shown to possess two
or more physical properties allowing even the observation of
cooperative effects.

With this in mind, several strategies have been employed by
synthetic chemists to produce these materials. The choice of a
proper ligand plays a crucial role not only in dinuclear complex
formation but also in promoting exchange interactions between
the spin centers. In order to obtain a high-performance catalyst,
the above strategies were considered, and two multidentate
ligands, N$^\prime$-(2-hydroxy-3-methoxybenzylidene) acetohydrazide
(HL$^1$) and N$^\prime$-(2-hydroxy-3-methoxy-S-bromo benzylidene)
acetohydrazide (HL$^2$), were employed for the synthesis of
\{Tb$_2$(L$^1$)$_2$(piv)$_2$(NO$_3$)$_2$·H$_2$O\} (1) and \{Tb$_2$(L$^2$)$_2$(CF$_3$CO$_2$)$_2$(H$_2$O)$_4$·2NO$_3$\} (2), respectively. In
both cases, the uncoordinated –NH group of each ligand provides a
free lone pair for the transfixation of CO$_2$ molecules.

\{Tb$_2$(L$^1$)$_2$(piv)$_2$(NO$_3$)$_2$·H$_2$O\} (1) and \{Tb$_2$(L$^2$)$_2$(CF$_3$CO$_2$)$_2$(H$_2$O)$_4$·2NO$_3$\} (2) act as efficient catalysts
in cyclodation of carbon dioxide with epoxides at room
temperature under 1 bar CO$_2$ pressure and neat conditions.
Hence, the syntheses, structure, and magnetic and catalytic
properties of 1 and 2 are discussed herein.

RESULTS AND DISCUSSION

Synthesis Procedure. Tetradentate Schiff base ligands
(HL$^1$ and HL$^2$) were prepared according to the reported
procedure. The ligands HL$^1$ and HL$^2$, respectively, were combined with Tb(NO$_3$)$_3$·6H$_2$O and pivalic acid/trifluoro-
acetic acid and triethylamine yielding \{Tb$_2$(L$^1$)$_2$(piv)$_2$(NO$_3$)$_2$·
H$_2$O\} (1) and \{Tb$_2$(L$^2$)$_2$(CF$_3$CO$_2$)$_2$(H$_2$O)$_4$·2NO$_3$\} (2).

Scheme 1. Synthesis of the Ligands (Top) and Syntheses of
Complexes 1 and 2 (Bottom)

The asymmetric unit of complex 2 contains one-half of the
total molecule, that is, \{TbL$^2$(CF$_3$COO-$\eta$)(O1w2w-$\eta$-O)\] for 2 (Figure 1a). The complexes are neutral and possess a
similar structural topology. The side and top views of the
molecular structure of 2 are depicted in Figure 1bc, which
clearly demonstrate that the complex is a dinuclear \{Tb$^{III}$\}$_2$
species where each metal atom is doubly phenoxido-bridged by
the two phenolato oxygen atoms of the ligand. The dinuclear
complex was assembled with the help of two monodeprotonated
ligands. Each ligand binds the metal in its keto form, and four
coordination sites are used for binding the metal centers.
The phenolate oxygen atom behaves as a bridging ligand between
the two terbium(III) centers. Hence, the overall coordination
behavior from each ligand is \(\mu_2\eta^2\eta^2\eta^1\). The phenolato
oxygen bridging results in the formation of a four-membered
Tb$_2$O$_4$ motif (Figure S1a). The Tb–Tb distance within the
four-membered ring is 3.691 Å with a Tb–O–Tb angle of 103.73$^\circ$
for 2. Further, the dinuclear complex is chelated by the coordination
action of two trifluoro-acetate and four water solvents. Thus,
both of the Tb$^{III}$ are nine-coordinated, are surrounded by an
identical coordination environment (O8N), and possess the
distorted monocapped square-antiprism geometry (Figure S1b).
The Tb–O$_{hydrazone}$ bond distances are 2.357 Å which is very
similar to those in other previous work for a keto group involved
in binding. The rest of the Tb–O bond lengths are in the range
2.333–2.631 Å for 2, that is, Tb–O bond lengths for 2 are
greater than for complex 1.

The selected bond lengths and bond angles around metal
centers in 2 are given in Tables S1–S3. Upon inspection of H-
bonding and molecular assemblies on 2, dinuclear units are
interconnected through hydrogen bonding interactions between
the hydrazone H and O of the nitrate counterion (N2–H2N–O8, 2.110 Å)
and between the coordinated water molecules and O of nitrate
(O8–H7b–O7, 2.064 Å; and O6–H6b…O9, 2.127 Å; Figure 1d), simultaneously acting as
templates for an exclusive honeycomb network. The honeycomb
layers of the chelated dinuclear units occupy the vacant space
between successive counteration and dinuclear unit layers
leading to interpenetration of a 3D hydrogen-bonded network
(Figure 1e). However, the displacement of Tb$^{III}$ from the
corresponding least-squares \{O(phenoxido),O(methoxy)\}

\begin{align*}
\text{Complex-1} & \quad \text{Complex-2} \\
\text{Complex-1} & \quad \text{Complex-2}
\end{align*}
Figure 1. (a) Asymmetric unit of 2. (b) Side and (c) top view of the crystal structure of 2. (d) Motif of honeycomb and (e) supramolecular H-bonded 3D network with honeycomb architecture in packing diagram of 2.

Figure 2. (a) $\chi_{M}(T)$ for 2 with $H_{dc} = 1000$ G and in the temperature range from 2.0 to 300.0 K. (b) $M(H)$ curves in the field range of 0 and 7 T at 2 and 3 K. Solid traces in panels a and b are fits employing CF parameters from CASSCF calculations and the Lines model (eq 1). (c) Temperature-dependent $\mu$SQUID loops with a sweep rate of 0.00625 T/s. (d) Sweep-rate dependence of the $\mu$SQUID loops at 30 mK. The inset and dotted lines show the inflection point corresponding to the exchange field between the Tb$^{3+}$ ions.
planes is 0.926 Å for 2, suggesting that the Tb$^{3+}$ ion lies significantly away from the concerned mean plane.

**MAGNETIC CHARACTERIZATION**

The magnetic characteristic of 1 has been previously described, hence, we just provide the magnetic description of 2. Direct current (DC) susceptibility measurements of 2 were carried out in the temperature range from 2 to 300 K in a field of 1000 Oe. The experimental $\chi_M T$ value at room temperature of 23.48 cm$^3$ mol$^{-1}$ K is close to the expected value of 23.63 cm$^3$ mol$^{-1}$ K for two free Tb$^{3+}$ ions (Figure 2a). The $\chi_M T$ values gradually reduce with decreasing temperature and reach a value of 9.76 cm$^3$ mol$^{-1}$ K at 2.0 K. The downturn shown in the $\chi_M T$ behavior of 2 could be a consequence of depopulation of the Stark levels and/or magnetic interaction occurring between the Tb$^{3+}$ ions. The field dependence of the magnetization of 2 ions having parallel spins is an SMM, confirming the fast relaxation characteristics of SMMs, indicating fast relaxation in the system (see Figure S7).

To confirm whether 2 is an SMM, $\mu$SQUID measurements were conducted in a single crystal of the dimeric terbium complex. The hysteresis curves are narrow and do not show the temperature- and sweep-rate-dependent behavior characteristic of SMMs, confirming the fast relaxation characteristics of 2 (Figure 2c,d). Additionally, $\mu$SQUID measurements allow the evaluation of the interaction occurring between the Tb$^{3+}$ centers. A close inspection of the loops at the lowest temperature and different sweep rates shows a small interaction, as revealed by the inflection points between ±0.21 T (Figure 2d). The value of the magnetic field at the crossing at ±0.21 T allows the direct calculation of the exchange coupling $J_{ex}$ between the two Tb$^{3+}$ ions through $H_{ex} = -2J_{ex} m_i g_i \mu_B$, where $m_i = 6, g_i = 3/2, \mu_B$ is the Bohr magneton, and with the two Tb$^{3+}$ ions having parallel easy axes. $J_{ex}$ is found to be $-0.012$ cm$^{-1}$ (18 mK), which corresponds to a purely dipolar interaction.

To rationalize the magnetic properties of 2, CASSCF calculations were performed employing OpenMolcas and the experimental crystal structure of 2 (see Figure 3). The single ion magnetic properties show a highly axial Ising character of the uncoupled ions, with $g_e = g_m = 0$ and $g_e = 18$, with the first excited state lying at $\sim 100$ cm$^{-1}$; however, inspection of the transition matrix elements shows that relaxation is quite effective in 2, indicating that, in this scenario, where no interaction between the Tb$^{3+}$ ions is present, 2 would have behaved as a modest SMM. In contrast, no clear SMM behavior was observed for 2, while DC and $\mu$SQUID studies show that the Tb$^{3+}$ ions interact through dipolar fields. The dipolar interaction effectively couples the magnetic moments of both Tb$^{3+}$ ions, inducing new effective relaxation pathways in 2 and, hence, inducing fast relaxation. Note that relaxation is quite effective for the isolated Tb$^{3+}$ ions; thus, the interaction between the Tb$^{3+}$ ions accelerates the dynamics of the system. Employing the crystal field parameters obtained from CASSCF calculations, and the Lines model, which utilizes an isotropic exchange between the spin component of the angular momenta ($S = S/2$ for Tb$^{3+}$), it is possible to reproduce the $\chi_M T(T)$ and $M(H)$ for 2 (see Figure 2a) with $J_{lines} = -0.042$ cm$^{-1}$ (59 mK) and Hamiltonian of the form:

$$H^i_{Dy} = H^i_{lf} + g_i \mu_B \mu_B^{i} J_{lines} \cdot \mathbf{H}_z$$

where $H^i_{lf} = \sum_{k-k'\neq i} B_{k}B_{k}^{i}O_{k}$ is the ligand field Hamiltonian expressed in Steven’s operator with $O_{k}$ the Stevens factor, $O^i_{k}$ the Stevens operator, and $B_{k}B_{k}^{i}$ the ligand field parameters obtained from CASSCF calculations. Note that although a good agreement for the $\chi_M T(T)$ and $M(H)$ was found, the exchange value obtained from the Lines analysis is not directly comparable to the experimental exchange value obtained from $\mu$SQUID loops.

**CATALYTIC ACTIVITY**

Catalytic activities of synthesized lanthanide complexes (1 and 2) were performed in the addition reaction of carbon dioxide and epoxides for the formation of organic carbonates. Some controlled reactions were carried out in order to optimize the catalytic reaction conditions by taking substrate 2-(chloromethyl) oxirane under 1 atm CO$_2$ pressure at room temperature in the presence of complex 1 or 2 as catalyst. The reaction of 2-(chloromethyl)oxirane (12 mmol) and carbon dioxide under precise conditions in the presence of 1 as catalyst and
tetrabutylammonium bromide (TBAB) as cocatalyst therefore produced 71% of the desired 4-(chloromethyl)-1,3-dioxolan-2-one as product after 2 h (Table 1, entry 1). The same reaction gave 76% of desired carbonate product after 2 h in the presence of catalyst 2 (Table 1, entry 2). When both reactions were executed in the absence of cocatalyst TBAB, then only a trace amount of corresponding product was obtained (Table 1, entries 3 and 4). Again, an identical reaction performed in the presence of TBAB but in the absence of any catalyst yielded 14% of 4-(chloromethyl)-1,3-dioxolan-2-one (Table 1, entry 5). Basically, the metal center Tb of complexes 1 and 2 as the Lewis acidic center only activated the epoxide substrate, but ring opening of activated epoxide occurs through the nucleophilic attack of Br\(^-\) ions (dissociated from TBAB). Thus, the smooth production of organic carbonate by the addition reaction of epoxide and CO\(_2\) is the outcome of the synergistic effect of catalyst and cocatalyst TBAB.\(^{21}\) The cocatalyst screening was further optimized by using various inorganic salts such as sodium chloride (NaCl), potassium iodide (KI), and potassium bromide (KBr) and organic salts like TBAI (tetrabutylammonium iodide) and TBAC (tetrabutylammonium chloride) in this reaction (Table 1, entries 6−10). It was observed that our synthesized lanthanide-based catalysts in conjunction with TBAB have an utmost synergistic effect toward the organic carbonate synthetic reaction. This is because of the higher nucleophilicity of Br\(^-\) than I\(^-\) as well as the improved leaving capability in comparison to Cl\(^-\).\(^{22}\)

The ligands HL\(^1\) and HL\(^2\) were used as catalyst instead of two complexes along with TBAB in two different reaction setups (Table 1, entries 11 and 12). Again, the lanthanide precursor Tb(NO\(_3\))\(_3\)·6H\(_2\)O was also used as catalyst for the same reaction (Table 1, entry 13). In each of these three cases, the obtained results are almost similar with the result when only TBAB was used in the reaction. Thus, it is significant to point out that terbium metal within both HL\(^1\) and HL\(^2\) ligand environments with TBAB efficiently executes the catalytic reaction.

After the selection of cocatalyst for the catalytic reaction, reaction temperature and duration were optimized. From Figure 4a, it is clear that, with the rising reaction temperature, the yield percentage of 4-(chloromethyl)-1,3-dioxolan-2-one also rises, and it reaches a maximum (i.e., 100%) at 60 °C (Figure 4a). An increment in the reaction temperature causes a greater number of collisions between the active sites of catalyst and substrate, and as a result, the yield product is enhanced. The kinetics of this catalytic reaction was monitored, and the results are plotted in Figure 4b. A lower yield of the desired product was found when the catalytic reaction was monitored in the presence of a lower amount of catalyst 1 (0.008 mol %) at 60 °C.

Exocyclic as well as endocyclic epoxides were produced in moderate to high yield for corresponding carbonate products under optimized reaction conditions. 2-(Chloromethyl)oxirane was fully converted into its corresponding carbonates in a very short reaction duration (2 h), whereas other terminal epoxides required relatively more time to produce a high percentage of carbonate product (Table 2, entries 1−8). This is due to the presence of an electron-withdrawing chloro group in 2-(chloromethyl)oxirane making the C=O bond cleavage faster. Further, the side chain of terminal epoxides was increased, and then, the reaction rate was slowed down due to the steric hindrance, causing the production with a relatively lower yield (Table 2, entries 5−8). Styrene oxide and phenyl glycidyl ether produced the respective carbonates in a very good quantity yield (73−81%) after 4−5 h of reaction (Table 2, entries 9−12). Endocyclic epoxide (i.e., cyclohexene oxide) requires a longer

**Table 1. Parameter Optimization for Catalytic 4-(Chloromethyl)-1,3-dioxolan-2-one Synthesis via Addition of CO\(_2\) and 2-(Chloromethyl)oxirane**

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>cocatalyst</th>
<th>time (h)</th>
<th>yield (%)</th>
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<td>TBAB</td>
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<td>71</td>
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<td>2</td>
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<td>trace</td>
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<td>KBr</td>
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<tr>
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<td>TBAB</td>
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<td>18</td>
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<td>Tb(NO(_3))(_3)·6H(_2)O</td>
<td>TBAB</td>
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<td>15</td>
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</table>

\(^{a}\)Reaction conditions: 2-(chloromethyl)oxirane (12 mmol), catalyst (0.01 mol %), cocatalyst (0.8 mol %), carbon dioxide balloon, room temperature. \(^{b}\)Gas chromatography yield.

**Figure 4.** (a) Optimization of reaction temperature [conditions: 2-(chloromethyl) oxirane (12 mmol), 1 (0.01 mol %), TBAB (0.8 mol %), carbon dioxide balloon, 2 h] and (b) kinetics of catalytic reaction [conditions: 2-(chloromethyl) oxirane (12 mmol), 1 (0.01 mol %), TBAB (0.8 mol %), carbon dioxide balloon, 60 °C].
Table 2. Catalytic Addition of CO\textsubscript{2} into Epoxides\textsuperscript{a}

<table>
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<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Epoxides</th>
<th>Product</th>
<th>Time (h)</th>
<th>% GC yield (Selectivity)</th>
<th>TON\textsuperscript{b}</th>
<th>TOF\textsuperscript{c} (h\textsuperscript{-1})</th>
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<td>8</td>
<td>48 (100/45)</td>
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\textsuperscript{a}Reaction conditions: epoxides (12 mmol), catalyst (0.01 mol %), TBAB (0.8 mol %), 60 °C, carbon dioxide balloon, neat conditions. \textsuperscript{b}TON (turnover number): number of moles of product formed per mole of catalyst. \textsuperscript{c}TOF (turnover frequency): number of moles of formed produced per mole of catalyst/time (in h).

Table 3. Comparison of Our Synthesized Catalyst with Previously Reported Lanthanide Metal-Based Catalyst for 4-(Chloromethyl)-1,3-dioxolan-2-one Synthesis via Catalytic Addition Reaction of 2-(Chloromethyl)oxirane and Carbon Dioxide

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Cocatalyst</th>
<th>Reaction Conditions</th>
<th>Yield (%)</th>
<th>TON\textsuperscript{d}/TOF\textsuperscript{e} (h\textsuperscript{-1})</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>[Ln(µ-L)(µ-1,3-bis(4-carboxyphenyl)imidazolium carboxylate(1+), Ln = Yb, X = Br. \textsuperscript{f}La = N\textsubscript{3}N-bis(2-hydroxy-3,5-di-t-butylbenzyl)-2-aminoethanol. \textsuperscript{g}L = Schiff base between S-allyl-2-hydroxy-3-methoxybenzohydrazide and 4-(diethylamino)-2-hydroxybenzaldehyde. \textsuperscript{h}ImBDC = 2-(imidazol-1-yl)terephthalic acid), Ln = Tb. \textsuperscript{i}H\textsubscript{2}abc = 3,3,5,5-azobenzene tetracarboxylic acid. \textsuperscript{j}H\textsubscript{2}L = (S)-2,4-di-tert-butyl-6-[2-(hydroxydiphenylmethyl)-pyrrolidinil]methyl]pheno. \textsuperscript{k}H\textsubscript{2}L = Schiff base between 2-hydroxy-3-(hydroxyethyl)-5-methylbenzaldehyde and isoniazid.</td>
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<td>[Ln\textsubscript{2}(μ-L)(μ-1,3-bis(4-carboxyphenyl)imidazolium carboxylate(1+), Ln = Yb, X = Br. \textsuperscript{f}La = N\textsubscript{3}N-bis(2-hydroxy-3,5-di-t-butylbenzyl)-2-aminoethanol. \textsuperscript{g}L = Schiff base between S-allyl-2-hydroxy-3-methoxybenzohydrazide and 4-(diethylamino)-2-hydroxybenzaldehyde. \textsuperscript{h}ImBDC = 2-(imidazol-1-yl)terephthalic acid), Ln = Tb. \textsuperscript{i}H\textsubscript{2}abc = 3,3,5,5-azobenzene tetracarboxylic acid. \textsuperscript{j}H\textsubscript{2}L = (S)-2,4-di-tert-butyl-6-[2-(hydroxydiphenylmethyl)-pyrrolidinil]methyl]pheno. \textsuperscript{k}H\textsubscript{2}L = Schiff base between 2-hydroxy-3-(hydroxyethyl)-5-methylbenzaldehyde and isoniazid.</td>
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reaction duration (8 h) to produce a moderate yield (43–48%) of carbonate through this catalytic addition reaction (Table 2, entries 13 and 14).

A literature survey for a comparison of 4-(chloromethyl)-1,3-dioxolan-2-one synthesis via catalytic addition reaction of 2-(chloromethyl)oxirane and carbon dioxide in the presence of lanthanide-based metal catalysts is given in Table 3. Three previously published reports \(^{73-80}\) showed that a very high yield of 4-(chloromethyl)-1,3-dioxolan-2-one (94–99%) was produced under neat reaction conditions and high CO\(_2\) pressure (\(\geq 8\) bar). A few other reported methodologies \(^{74,75,77-79}\) produced a high percentage of desired product under 1 bar CO\(_2\) pressure in the presence of cocatalyst after \(\geq 4\) h of reaction. In this report, a high quantity of carbonate product is formed under 1 bar CO\(_2\) pressure in just a 2 h reaction interval. Again, high TON and TOF are observed in this catalytic reaction.

**CATALYTIC REACTION MECHANISM**

The mechanism for the catalytic synthesis of cyclic carbonates by cycloaddition of CO\(_2\) into epoxides in the presence of TBAB is depicted in Figure 5 on the basis of previously published articles. \(^{73-80}\) At first, epoxide is activated by the terbium(III) center of complex 1 or 2 and produces a terbium activated epoxide intermediate. Then, nucleophilic attack of Br\(^-\) of tetrabutylammonium bromide causes the ring-opening of the terbium(III) activated epoxide intermediate in order to form Tb-bonded bromo-alkoxide. Thereafter, nucleophilic attack of the Tb-bonded bromo-alkoxide in carbon dioxide generates a Tb-carbonate intermediate. Finally, ring closure occurs to release cyclic carbonate, catalyst, and bromide for the next catalytic cycle. \(^{75}\) We have framed the mechanism by using the asymmetric unit for clarity. However, we can suppose that the dimeric unit with two metal centers may give a higher yield of the final product as cyclic carbonates.

**CONCLUSION**

Two terbium(III) binuclear complexes based on two tetradentate Schiff-base ligands were synthesized and structurally characterized through single-crystal XRD. The standard magnetic measurements showed that 1 is not an SMM, as reported in a previous article, \(^64\) whereas complex 2 has a fast relaxation with \(\mu\)SQUID measurements and is supported by CASSCF calculations. Besides, complexes 1 and 2 acted as efficient catalysts for the synthesis of organic cyclic carbonates via the addition reaction of carbon dioxide and epoxides. The efficiency of the catalysis of these complexes was compared with previous reports \(^{73-80}\) in tabulated form. Hence, it is observed that the moderate to very good yield of carbonate products with high TON/TOF values is achieved by this catalytic reaction (using complexes 1 and 2 as catalysts) at 60 °C under 1 bar CO\(_2\) pressure and solvent-free conditions from terminal and internal epoxides.

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Notes

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REFERENCES


and styrene oxide into styrene carbonate under mild conversion.


