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ONO pincer type ligand complexes of Al(III) as efficient catalyst for chemical fixation of CO_2 to epoxides at atmospheric pressure

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ABSTRACT

Carbon dioxide, the main cause of environmental pollution, its utilization to produce valuable products is of utmost interest. A series ONO pincer hydrazone based most active mono-nuclear Al(III) complexes were successfully synthesized and characterized with the help of NMR, IR, mass spectrometry and only complex **2a** was confirmed by single-crystal analysis. The synthesized Al(III) complexes were then employed as capable catalysts for the solvent-free chemical fixation of CO_2 with epoxides at atmospheric pressure and could be reused five times without loss of any catalytic activity. In addition, the catalytic mechanism was investigated by analyzing intermediates via ^{1}H NMR, ^{13}C NMR, and mass MALDI-TOF. The excellent catalytic performance could be due to simultaneous attack and the opening of the epoxide by metal centers to form an alkoxide ion which activates the CO_2 the same time.

1. Introduction

Worldwide industrialization and rapid urbanization are posing serious threats to our environment due to the large-scale anthropogenic production of CO_2, which is greatly affecting the concept of green chemistry. Global warming and greenhouse effect are mainly originating from the CO_2 emission[1]. Nevertheless, the scientific community is taking a great and ever-increasing interest in the CO_2 transformation into valuable chemical products. Because of its abundance, ready availability, non-toxic and reusable nature, CO_2 is a valuable one-carbon (C1) building block in organic transformations [1–3]. As a well-known fact, CO_2 has a high thermodynamic stability and kinetic inertness due to the carbon is in its highest oxidation state hence making it a challenge to activate and valorise CO_2 to valuable products. Among the various approaches employed for CO_2 utilization, synthesis of cyclic carbonates and polycarbonates from the chemical fixation of CO_2 to epoxides, are extensively studied and even well commercialized [2,4,5]. Environment-friendly and 100% atom efficient, the redox neutral fixation of CO_2 to epoxides to form cyclic carbonates with no appreciable toxicity [6–9] is specifically investigated in recent years because of its numerous uses as solvents, electrolytes, synthetic building blocks, fine chemicals, industrial lubricants and as monomers for polymers [10–14]. Over the past two decades, huge progress has been made in the chemical fixation of CO_2 to epoxides which can be clearly observed from the increase in the number of publications since 2000 [15]. Various metal complexes based on zinc [16–19], chromium [20–22], iron [23–26], cobalt [27–33], magnesium [17,34], vanadium [35–37], tin [38] etc. have been reported as catalyst for the CO_2 cycloaddition to epoxides. Among the metal complexes, aluminium has been extensively studied for the CO_2/epoxides cycloaddition. This due to its environment-friendly nature, earth abundance, nontoxicity, and high Lewis acidity making aluminium the ideal choice for the ring-opening of epoxides [39]. Various research groups reported the CO_2/epoxides cycloaddition with salen and related ligand-based monometallic [27,40–44] and bimetallic [39,45–50] aluminium complexes. Amongst the aluminium complexes, bimetallic aluminium(salen) complexes [51,52] reported by North and other groups [50] are

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0021-9517/

efficient catalysts for the CO_2 cycloaddition at ambient pressure. The most active catalyst amongst the mononuclear Al complexes is the hexachlorinated aluminium(III)–aminetriphenolate complex, reported by Kleij et al., in combination with tetrabutylammonium iodide as co-catalyst demonstrating the highest TOF of 24,000 h^{-1} for the cycloaddition of CO_2 to 1,2-epoxy-hexane. This high TOF was obtained at 90 °C under a high pressure of 10 bar along with a high catalyst to co-catalyst ratio [39]. Similarly, the highest ratio of cat/co-cat (1:120) was reported by Qin et al. using the porphyrin ligand-based aluminium complex for synthesis of cyclic carbonates at a relatively high pressure of 10 bar [53]. Unfortunately, the synthesis of the porphyrin ligand requires a very long and tedious synthetic procedure. Till today, the reported literature suggests that most of the aluminium complexes studied for cycloaddition of CO_2 to epoxides are based on salen, salophen and phenolate scaffolds. Keeping these factors in minds, we hereby report a novel, highly active monometallic aluminium complexes supported by an ONO pincer type hydrazone moiety for the chemical fixation of CO_2 at atmospheric pressure. Furthermore, NMR and MALDI-TOF analyses were used to investigate the mechanistic insight of the CO_2/epoxides coupling reaction catalyzed by these Al complexes.

2. Results and discussion

A family of hydrazone-based ligands **1**–**4** and their respective aluminum complexes **1a–4a** were obtained in good yield by the reaction of the respective ligand with the metal salt in methanol as solvent, following the published procedure (Scheme 1) [54]. These complexes were characterized further by nuclear magnetic resonance (NMRs) (ESI S1-S16), infrared spectroscopy (ESI S17-S24), High-resolution mass spectrometry (HR-MS) (ESI S25-S31) and elemental analysis. Complex **2a** was successfully analyzed by single-crystal X-ray analysis (see Fig. 1). For all complexes, the ^{1}H NMR spectroscopic analysis revealed the disappearance of the OH proton of the ligand due to the binding with the Al ion. In addition, the position of the NH proton was slightly shifted and the downfield shifting of the azomethine C=N proton clearly confirmed the successful coordination of the ligand to the metal ion. The formation of these complexes was further supported by FT-IR, which shows the disappearance of the hydroxyl band. Furthermore, the appearance of a new band for the C—O vibration and the shift of the azomethine C=N stretch vibration towards a lower wavenumber was observed as well. Moreover, the obtained results of HR-MS analysis of these complexes exactly matched with the calculated results. Finally, the exact coordination of the different ligands to the Al ion was confirmed by single-crystal X-ray analysis. The single-crystal analysis revealed that the complex **2a**

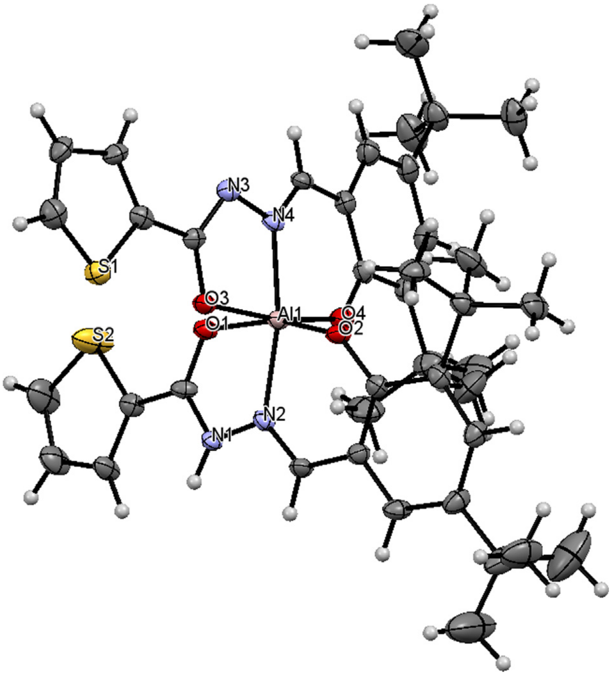
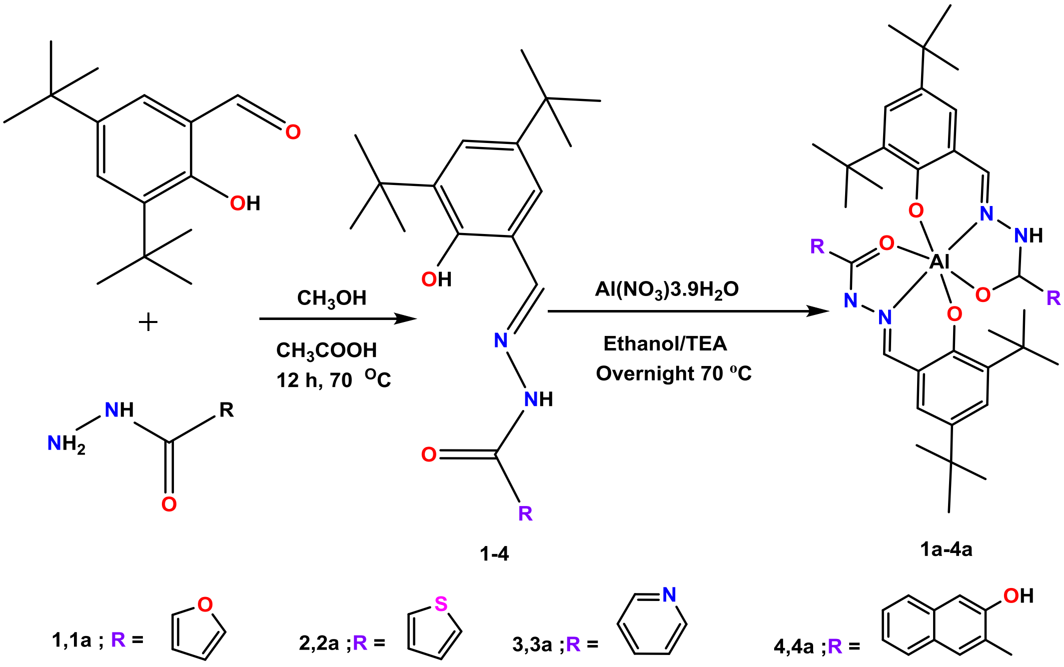


Fig. 1. ORTEP diagram of complex **2a** (Labelling of carbon and hydrogen atoms is omitted for clarity).



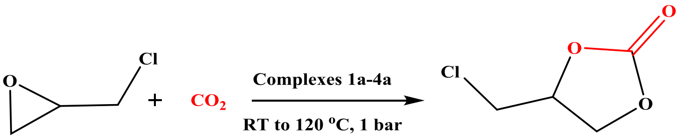
Scheme 1. General synthetic procedure of the hydrazone ligands **1**–**4** and their respective complexes **1a–4a.**

crystalizes in a triclinic system having a space group P-1. The detailed crystallographic data has been depicted in supporting information (ESI Table 1). A distorted octahedral coordination of the Al(III) is obtained by two ONO tridentate ligands having the different protonation states. The two axial positions are occupied by two imino nitrogen atoms (Al1-N2 2.002 A) and (Al1-N4 1.949 A), while four oxygen atoms construct the equatorial plane of the distorted octahedron. The distortion is further supported by comparing trans bond angles around the Al center of the octahedron. The trans bond angles between O1—Al—O2, O3—Al—O4, and N2—Al—N4 are 164.98 (13), 168.64 (14) and 168.78 (14) while cis bond angles between the O2—Al—O3 and O1—Al—O4 are 91.92 (12) and 89.14 (12) respectively. Similarly, the bond distances within the coordination sphere also exhibit distortion i.e. the bond length between the Al—O (phenolate) in the complex for Al—O2 and Al—O4 are 1.819(3) and 1.811(3), which are shorter than the Al—O (hydrazonato) bond lengths for Al—O1 2.015(3) and Al—O3 1.940(3) respectively.

3. Catalysis

After successful synthesis and characterization of these novel monometallic Al(III) complexes, these complexes (**1a–4a**) were employed as excellent catalysts along with co-catalyst for the chemical fixation of CO_2 under non-solvent conditions. Epichlorohydrin (ECH) was used as a model substrate for the optimization of the reaction conditions. No cyclic carbonate formation was achieved by using precursors like metal salts and ligands individually. This reveals the cooperative effect of the metal and their ligand scaffold in the complexes to precede the cycloaddition of CO_2 to epoxides. Afterwards, all Al-complexes were screened for the optimization of the reaction parameters. Initially, the reaction was performed at room temperature for 24 h and only traces of cyclic carbonate were observed at room temperature (Table 1 entry 1). A steady increase in the cyclic carbonate synthesis was monitored by increasing the temperature up to 120 °C (Table 1 entry 2–5) reflecting an enhancement in the product at an elevated temperature whereby the highest yield was observed at 120 °C and was chosen as the optimum temperature for further reactions in this study. Another very important parameter in the chemical fixation of CO_2 to epoxides is the carbon dioxide pressure. Most of the catalytic systems, except a few, are working at high pressure. Fortunately, the catalyst along with the co-catalyst has shown a satisfactory catalytic performance at ambient pressure. In order to confirm the further co-operative effect of catalyst and co-catalysts (DMAP, TBAB, TBAC, and TBAI), control experiments under the same reaction conditions were performed. However, these control experiments revealed a low conversion of the substrate (Table 1 entries 6–13). Thereafter, the effect of these four co-catalysts (DMAP, TBAB, TBAC, and TBAI) on these Al-complexes was employed to enhance the formation of cyclic carbonates and diminish the time duration (Table 1 entries 5, 7–21)

Table 1
Optimization of reaction conditions for the cycloaddition of CO_2 to epichlorohydrin as model substrate by complexes (**1a–4a**).



Entry	Catalyst	Co-catalyst	Temp (°C)	Time (Hr)	$^{\sigma}$Conversion%
1^{a}	**2a**	DMAP	RT	24	–
2^{a}	**2a**	DMAP	50	24	3
3^{a}	**2a**	DMAP	75	24	10
4^{a}	**2a**	DMAP	100	6	50
5^{a}	**2a**	DMAP	120	2	>99
6^{a}	**1a**	–	120	2	50
7^{a}	**2a**	–	120	2	65
8^{a}	**3a**	–	120	2	40
9^{a}	**4a**	–	120	2	35
10^{a}	–	DMAP	120	2	20
11^{a}	–	TBAB	120	2	17
12^{a}	–	TBAC	120	2	15
13^{a}	–	TBAI	120	2	10
14^{a}	**2a**	TBAB	120	2	70
15^{a}	**2a**	TBAC	120	2	85
16^{a}	**2a**	TBAI	120	2	50
17^{a}	**1a**	DMAP	120	2	85
18^{a}	**1a**	TBAB	120	2	75
19^{a}	**1a**	TBAC	120	2	80
20^{a}	**1a**	TBAI	120	2	60
21^{a}	**3a**	DMAP	120	2	87
22^{a}	**3a**	TBAB	120	2	65
23^{a}	**3a**	TBAC	120	2	85
24^{a}	**3a**	TBAI	120	2	75
25^{a}	**4a**	DMAP	120	2	91
26^{a}	**4a**	TBAB	120	2	80
27^{a}	**4a**	TBAC	120	2	78
28^{a}	**4a**	TBAI	120	2	70
29^{b}	**2a**	DMAP	120	2	30
30^{c}	**2a**	DMAP	120	2	10

Reaction conditions: Pressure 1 bar, temperature 120 °C, catalyst/substrate ratio (mol%/mol%); **a**; 0.1 mol%, **b**; 0.01 mol%, **c**; 0.002 mol%. $^{\sigma}$Conversion is based on ^{1}H NMR. Selectivity >99. DMAP: 4-dimethylaminopyridine; TBAB: tetrabutylammonium bromide; TBAC: tetrabutylammonium chloride; TBAI: tetrabutylammonium iodide.

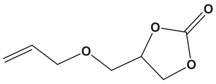
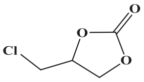
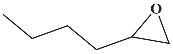
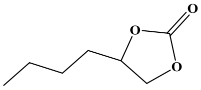
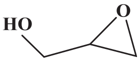
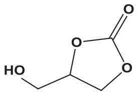
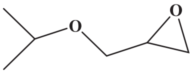
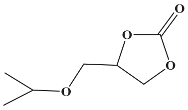
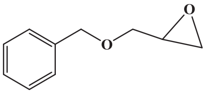
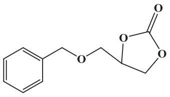
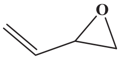
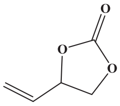
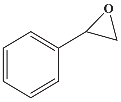
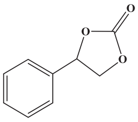
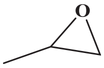
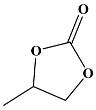
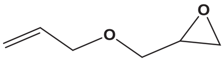
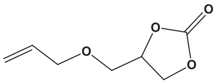
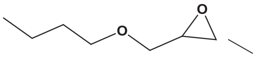
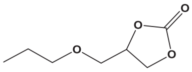
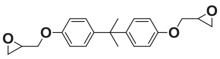
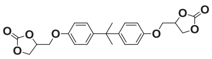
[55]. After the optimization and comparison of all the results summarized in (Table 1) complex **2a** along with co-catalyst DMAP (Table 1 entry 5) exhibit a superior activity compared to the other combinations of catalyst/co-catatalyst Interestingly, the co-catalyst DMAP in combination with all four complexes demonstrated the highest activity (Table 1 entries 5, 10, 14 and 18). In addition, the catalyst loading was investigated to obtain the optimum catalyst amount by employing catalyst and substrate ratio in ranging from 0.01 mol% to 0.002 mol%. A decrease in the yield of the cyclic carbonate was observed with a lowering of the catalyst loading (Table 1 entries 22, 23). It was found that the catalytic systems having an aromatic ring like pyridine or naphthalene moiety in the side chain of complex **3a** and **4a** were found to be the least reactive compared to **1a** and **2a** having a furan and thiophene in the side chain, respectively. This could be explained based on the low basicity of pyridine and naphthalene due to delocalization effect.

Finally, applying the optimized reaction conditions to monitor the flexibility of the complex **2a** for the CO_2 fixation, different substrates were screened. Excellent conversions and selectivities (>99%) (see ESI S32 for ^{1}H and ^{13}C spectra of all products) were recorded under ambient pressure for nearly all tested epoxides using complex **2a** (Table 2). Natural epoxy resin like DGEBA was also explored to observe the effect and conversion towards natural epoxides (Table 2 entry 11).

As evidenced from Table 2, epichlorohydrin was found to be the most reactive substrate because of the presence of an electron-withdrawing group like Cl [38]. The presence of the electron-withdrawing group in the epoxide will increase the electrophilicity of the secondary carbon, facilitating the ring-opening step and hence, increase the reaction rate. In contrast, the presence of an electron-donating group reduced the electrophilicity resulting in a decline in reactivity which is demonstrated by the relatively long reaction time, i.e. 20 h for some substrates like PO and SO.

Most importantly, the investigated complex **2a** was highly reactive among reported monometallic aluminum complexes, based on pressure (Table 3), and comparable to bimetallic aluminum complexes that belong to the extensively studied salen, salphen, porphyrin, etc. ligated system.

Table 2
Cycloaddition of CO_2 to tested epoxides by complex **2a**.

Entry	Substrate	Product	Time (h)	[≠]Conversion	[π]Yield(%)	[¶]TOF	[#]TON
1			2	>99	98	500	1000
2			6	>99	97	166	1000
3			16	>99	95	58	930
4			6	>99	97	166	1000
5			6	>99	97	166	1000
6			8	>99	97	125	1000
7			20	>99	97	50	1000
8			20	>99	90	50	1000
9			8	>99	96	125	1000
10			8	>99	97	125	1000
11			12	20	15	16	195

Reaction conditions: Pressure 1 bar, temperature 120 °C, catalyst **2a** 0.1 mol%, DMAP 0.1 mol%, 13.48 mmoles substrate.

[≠] Conversion is based on ^{1}H NMR. Selectivity >99.

[π] Isolated yield.

[#] TON = number of mmol of product/number of mmol of catalyst.

[¶] TOF = TON/time. Standard deviation ±1% for obtained conversions.

Table 3
Comparison of monometallic complex **2a** with reported Al complexes.

S/NO	Cat (mol%)	Co-Cat (mol%)	Sub (mmol)	Temp (°C)	Press (bar)	Time (h^{-1})	Yield (%)	Ref.
Monometallic complexes								
1a	(0.1)	DMAP (0.1)	ECH (13.48)	120	1	2	>99	This work
1b	(0.1)	DMAP (0.1)	SO (13.48)	120	1	20	>99	This work
2	(0.125)	TBAI (0.125)	PO (192)	25	6	8	62	[56]
3	(0.004)	TBAB (0.008)	PO (100)	120	25	8	99	[41]
4	(0.05)	TBAB (0.25)	PO (42.9)	80	10	0.5	23	[42]
5	(1.0)	TBAB (1.0)	SO (2)	110	1	48	90	[43]
6	(0.5)	–	AGE	100	10	2.5	95	[57]
7	(0.05)	TBAI (0.25)	EH (10)	90	10	2	96	[39]
Bimetallic Al complexes								
8	(2.5)	TBAB (2.5)	SO (2)	25	1	24	98	[45]
9	(2.5)	–	SO (1.66)	26	1	6	89	[58]
10	(2.5)	–	SO (1.66)	26	1	24	86	[59]
11	(1.5)	TBAB (1.5)	SO (1.66)	25	1	24	83	[60]
12	(0.25)	TBAB (0.5)	SO (1.66)	50	1	24	85	[61]
13	(2.5)	TBAB (2.5)	SO (1.66)	26	1	24	93	[47]
14	(0.5)	–	PO	50	5	24	50	[60]
15	(0.3)	TBAB (0.9)	SO (16.63)	85	1	24	91	[50]

Substrate used: ECH = Epichlorohydrin; PO = Propylene oxide; EH = 1,2 epoxy hexane; AGE = Allyl glycidyl ether; SO = Styrene oxide.

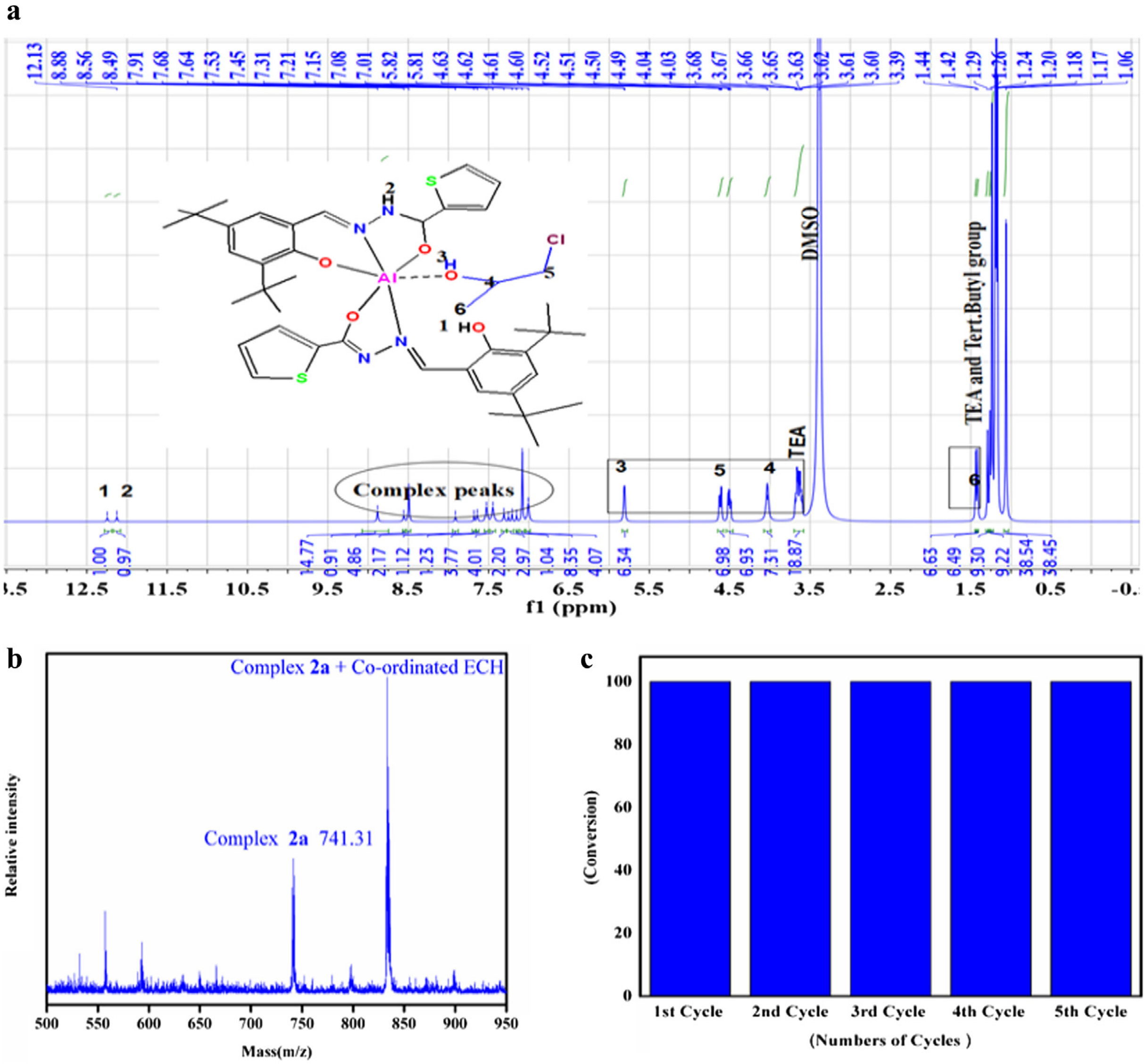


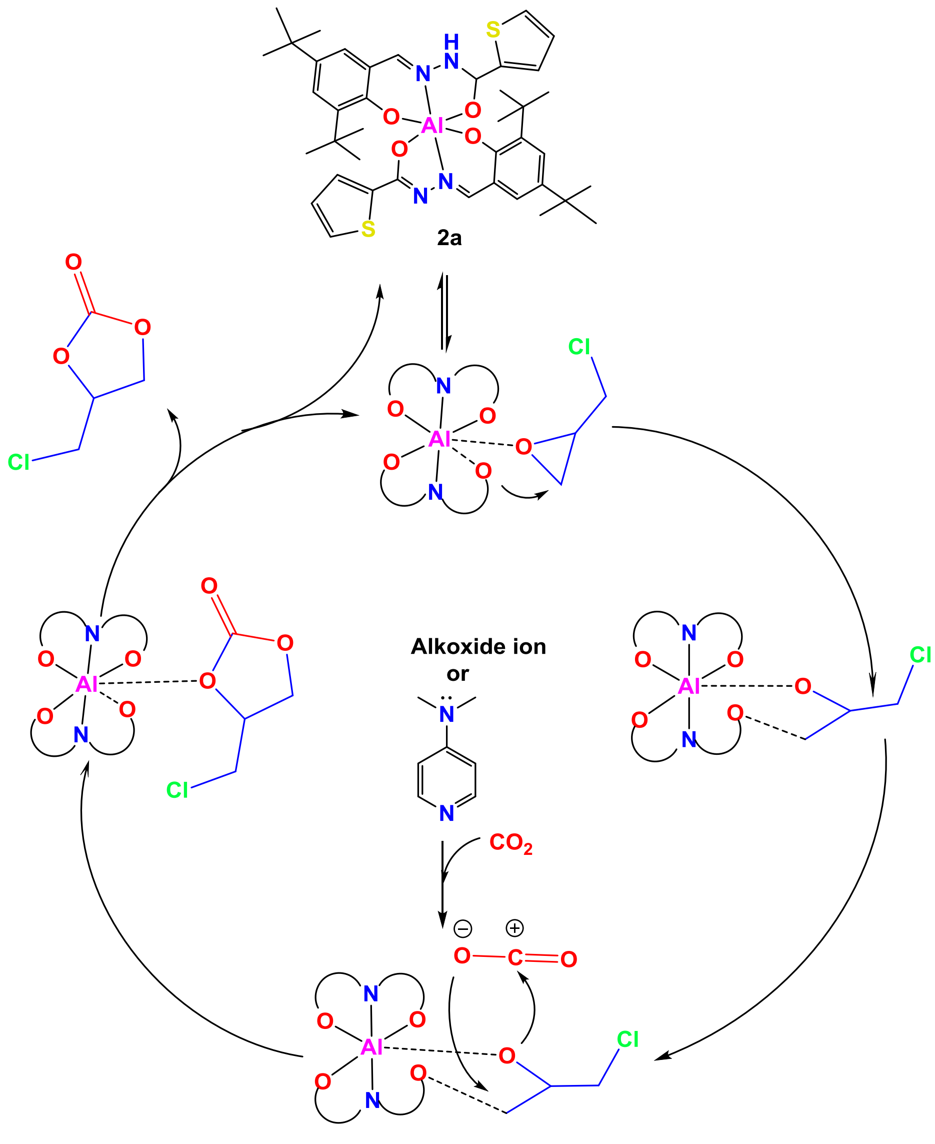
Fig. 2. **(a)** ^{1}H NMR spectrum of intermediate formed by mixing of complex **2a** and epichlorohydrin (1:10 ratio) **(b)** Maldi-TOF MS spectrum of the intermediate obtained by mixing complex **2a** and epichlorohydrin (1:10 ratio). **(c)** Recycling of catalyst up to 5 cycles.

The tendency of any catalytic system possessing a high tolerance towards the reaction conditions during the course of catalysis is very convenient. There was no decline in the catalytic performance of catalyst **2a** until five runs (Fig. 2c). After obtaining the cyclic carbonates using column chromatography with an eluent mixture of ethyl acetate and n-hexane (1:3), the catalyst **2a** was recovered using methanol as eluent.

4. Mechanistic approach

Based on the experimental findings, a cooperative Lewis acid and Lewis base mechanism is proposed for the novel mononuclear Al(III)-complexes. The ONO tridentate hydrazone Al(III)-complexes act as an electrophile and the alkoxide ion or co-catalyst (when used) as a nucleophile. We consider that the ring-opening of epoxides occurs by electrophilic interaction of Al(III) to epoxides as reported by Lu [40]. ^{1}H NMR and MALDI TOF analysis of the reaction mixture (Fig. 2a and b) further supports the coordination of Al (III) to epoxides. In the first step, the aluminum complex (**2a**) activates the epoxide by coordinating to the 'O' of the epoxides forming an intermediate (confirmed by ^{1}H NMR (Fig. 2a) and ^{13}C NMR (ESI Fig. S33 and MALDI TOF (Fig. 2b)). The shifting along with the appearance of new peaks in the ^{1}H NMR and ^{13}C NMR spectrum of the mixture of **2a** and epichlorohydrin (1:10 ratio) clearly indicates the coordination of metal to epoxides generating an intermediate prior to the cleavage of an Al—O bond of the complex (alkoxide formation). Secondly, the cleavages of one Al—O bond results in the generation of an alkoxide ion, which acts as an internal base and activates the CO_2 molecule.

In the presence of a co-catalyst, the co-catalyst will also activate the CO_2. The high catalytic activity of the complex without any co-catalyst further supports these steps. After mixing the catalyst and epoxide (1:10 ratio) under argon for one hour at 70 °C, the intermediate could be characterized using MALDI-TOF MS and ^{1}H NMR and ^{13}C NMR. A molecular ion peak at m/z 741.31 and m/z 833.31 in the MALDI-TOF spectrum (Fig. 2b) corresponds to the unreacted complex and the complex coordinated to epichlorohydrin respectively. ^{1}H NMR and ^{13}C NMR further reveal new peaks (ESI Fig. S33) that differ from those of ECH and the reaction product. This clearly confirms the coordination, which is followed by the ring-opening of the ECH by the aluminum complex. This assumption of ring-opening of ECH to form a new species was fur-



Scheme 2. Proposed mechanism for the CO_2/epoxides coupling reaction by complex **2a**.

ther supported by the matching of the peaks in the ^{1}H NMR (Fig. 2a) and ^{13}C NMR (ESI Fig. 33) spectra of this intermediate with the reported product [62]. Based on the experimental observation, a plausible mechanism could be demonstrated as shown in Scheme 2. The metal complex (**2a**) initiates the coupling reaction by coordinating to the epoxide followed by ring-opening of the epichlorohydrin and the cleavage of an Al—O bond of the complex resulting in a metal-alkoxide. The resulting alkoxide-ion (or added co-catalyst (DMAP)) activates the CO_2 to form a metal–alkoxide carboxylate that liberates the cyclic carbonates *via* a backbiting pathway. The highest catalytic activity could be attributed to the instant coordination and activation of both epoxide and CO_2 simultaneously by the complex and their alkoxide ion respectively.

5. Experimental

5.1. Materials and facilities

All chemicals including epoxides were purchased from Aladdin and Sigma Aldrich and used without any further purification unless otherwise stated. NMR spectra were recorded Bruker 500 MHz spectrometer using $CDCl_3$ and DMSO d_6 as a solvent. Fourier Transform Infrared (FTIR) spectra were recorded on Perkin-Elmer spectrometer. MS spectra for ligand and complexes were determined using a Trace MS 2000 organic mass spectrometry, and the signals were given in *m*/*z*. MALDI-TOF measurements for intermediate studies were performed with a Voyager-DE STR Bio spectrometry workstation mass spectrometer, employing a 19 kV accelerating voltage with pulsed ion extraction (PIE).

5.2. Synthesis of ligands

Ligands were synthesized by reacting 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde with 2-furoic hydrazide (**1**), 2 thiophenecarboxylic acid hydrazide **(2)**, (reported ligand) nicotinic hydrazide [63] **(3)** and 3-hydroxy-2-naphthoic acid hydrazide **(4)** in methanol as a solvent in the presence of few drops of acetic acid. After refluxing overnight at 70 °C for 12 h, the reaction mixtures were allowed to cool at room temperature. White precipitates were obtained, filtered and washed with cold methanol. Recrystallization in ethanol afforded needle-shaped crystals after slow evaporation of the solvent.

1: Elemental analysis: calcd for $C_{20}H_{26}N_2O_3$: C, 70.15; H, 7.65; N, 8.18; O, 14.02 Found: C, 70.44; H, 7.29; N, 8.19; O, 14.06. *m*/*z* calcd: 342.1943; found, 342.35. Selected IR bands (ν_{max}/cm^{-1}): 3209 (N—H); 3044 (Ar—C—H) 2958 (aliphatic C—H); 1600 (C═N); 1655 (C(O)N); 1290 (phenolic C—OH); 1184 (C—O), 1015 (N═N); δH (500 MHz; DMSO d_6; Me_4Si): 12.24 (1H, s, OH); 12.16 (1H, s, NH); 8.59 (1H, s, CH(O)—N); 7.99–6.73 (5H, 3s, 1d, Ar–H), 1.41–1.29 (18H, 2s aliphatic H). ^{13}C NMR (DMSO d_6): 155.14, 154.35, 151.94, 146.61, 140.93, 136.16, 126, 21,126.10, 117.47, 115.97, 112.72, 100.00, 31.75, 29.77.

2: Elemental analysis: calcd for $C_{20}H_{26}N_2O_2S$: C, 67.01; H, 7.31; N, 7.81; O, 8.93; S, 8.94. Found C, 67.39; H, 7.37; N, 7.77; O, 11.16; S, 8.64; S, 8.64. *m*/*z* calcd: 358.17; found, 358.30. Selected IR bands: (ν_{max}/cm^{-1}): 3447 phenolic, OH); 3209 (N—H); 3087 (Ar—C—H) 2959 (aliphatic C—H); 1529 (C═N); 1656 (C(O)N); 1319 (phenolic C—OH); 1200 (C—O), 1072 (N═N); ^{1}H NMR (500 MHz; DMSO d_6; Me_4Si): 12.23 (1H, s, OH); 12.13 (1H, s, NH); 8.56 (1H, s, CH(O)N); 7.93–7.24 (5H, 3s, 1d, Ar–H), 1.42–1.30 (18H, 2s aliphatic H) ^{13}C NMR (DMSO d_6):157.95, 155.12, 151.59, 140.96, 137.76, 136.16, 132.77, 129.86, 128.72, 126.27, 126.10, 117.47, 31.77, 29.78

3: Elemental analysis: calcd for $C_{21}H_{27}N_3O_2$: C, 71.36; H, 7.70; N, 11.89; O, 9.05 Found: C, 70.97; H, 8.10; N, 12.00; O, 10.27. Selected IR bands (ν_{max}/cm^{-1}): 3268 (N—H); 3183 (Ar—C—H) 2964 (aliphatic C—H); 1594 (C═N); 1654 (C(O)—N); 1298 (phenolic C—OH); 1162 (C—O), 1036 (N═N) ^{1}H NMR (500 MHz; DMSO d_6; Me4Si): 12.38 (1H, s, OH); 12.20 (1H, s, NH) 11.24; 9.10 (1H, s, CH(O)N); 8.80–7.26 (6H, Ar—H), 1.43–1.30 (18H, 2s aliphatic H). ^{13}C NMR (DMSO d_6): 161.89, 155.25, 153.04, 152.37, 140.98, 136.37, 136.18, 135.97, 128.98, 126.39, 126.28, 124.18, 120.68, 117.33, 35.15, 34.38, 31.77, 29.77.

4: Elemental analysis: calcd for $C_{26}H_{30}N_2O_3$: C, 74.61; H, 7.22; N, 6.69; O, 11.47. Found: C, 74.31; H, 6.86; N, 6.81; O, 12.01. *m*/*z* calcd 418.22; found, 418.40. Selected IR bands (ν_{max}/cm^{-1}): 3255 (N—H); 3067 (Ar—C—H) 2961 (aliphatic C—H); 1575 (C═N); 1651 (C(O)—N); 1290 (phenolic C—OH); 1200 (C—O), 1052 (N═N).^{1}H NMR (500 MHz; DMSO d_6; Me_4Si): 12.24 (1H, s, OH); 12.21 (1H, s, OH) 11.24 (1H, s, NH); 8.65 (1H, s, CH (O) N); 8.47–7.27 (8H, 2s, 4 d, 2 t Ar—H), 1.44–1.30 (18H, 2s aliphatic H).^{13}C NMR (DMSO d_6): 163.59, 155.25, 154.19, 152.37, 140.94, 136.37, 136.18, 131.04, 129.16, 128.78, 127.28, 126.38, 126.34, 124.34, 120.68, 117.43, 111.07, 31.77, 29.78.

5.3. Synthesis of complexes

Four novel Al (III) complexes **1a–4a** were synthesized by reaction of the respective ligand **1**, **2**, **3**, and **4** with $Al(NO_3)_3{\cdot}9H_2O$ using a 2:1 ratio of metal salt and ligand. The reaction mixtures were refluxed overnight using ethanol as solvent in the presence of few drops of trimethylamine as base. A dark yellow solution was formed which was cooled to room temperature for crystallization.

5.3.1. 1a

Dark yellowish solid was obtained after removing solvent from the reaction mixture by a rotary evaporator. Unfortunately, several trials to obtain single crystals failed. Elemental calcd: for $C_{40}H_{50}AlN_4O_6$: C, 67.68; H, 7.10; 3.80; N, 7.89; O, 13.52. Found; C, 67.46; H, 6.69; N, 8.24; O, 13.91. *m*/*z* calcd: 707.34; found, 707.33 Selected IR bands (ν_{max}/cm^{-1}): 3442 (O—H); 3212 (N—H); 2959 (aliphatic C—H); 1529 (C═N); 1655 (C(O)—N); 1172; 1130 (C—O), 1010 (N═N);. ^{1}H NMR (500 MHz; DMSO d_6; Me_4Si): 10.70 (2H CH (O)—N); 8.47 (1H, s, NH); 7.82–6.61 (5H, 3s, 1 d, Ar—H), 1.43–1.26 (18H, 2s aliphatic H). ^{13}C NMR (DMSO d_6): 162.55, 160.78, 155.75, 148.59, 145.44, 138.70, 137.03, 127.90, 127.61, 118.71, 113.61, 112.22, 35.34, 34.11, 31.87, 30.03.

5.3.2. 2a

After slow evaporation of the solvent from the reaction mixture, single crystals suitable for analysis were obtained. *m*/*z* calcd:741.31; found, 741.31. Elemental analysis: calcd for $C_{40}H_{50}AlN_4O_4S_2$: C, 64.75; H, 6.79; N, 7.55; O, 8.63; S, 8.64, Found: 64.38; H, 7.10; N, 7.15; O, 9.02; S, 8.46. Selected IR bands (ν_{max}/cm^{-1}): 3427 (O—H), 3229 (N—H); 2962 (aliphatic C—H); 1600 (C═N); 1616–1172 (C—O), 1010 (N═N); ^{1}H NMR (500 MHz; DMSO d_6; Me4Si): 8.59 (1H, s, NH); 7.75 (1H, s, CH(O)N); 7.38–6.90 (5H, 3s, 1 d, Ar—H), 1.22–1.07 (18H, 2s aliphatic H). ^{13}C NMR (DMSO d_6): 162.08, 156.66, 139.52, 136.02, 130.12, 128.69, 127.73, 126.28, 117.05, 34.85, 33.79, 31.45, 29.11.

5.3.3. 3a

A dark yellow solution was obtained, which was kept at room temperature to obtain single crystals but unfortunately unsuccessful. After evaporation of the solvent, a yellow solid was obtained. Elemental analysis calcd for $C_{42}H_{52}AlN_6O_4$: C, 68.93; H, 7.16; N, 11.48; O, 8.74. Found: C, 69.31.15; H, 6.83; N, 11.77, O, 9.11. *m*/*z* calcd: 731.39; found: 731.38. Selected IR bands (ν_{max}/cm^{-1}): 3432 (N-H); 3054 (Ar—C—H) 2950 (aliphatic C—H); 1531 (C═N); 1635 (C(O)—N); 1290 (phenolic C—OH); 1173 (C—O), 1036 (N═N); ^{1}H NMR (500 MHz; DMSO d_6; Me_4Si): 9.15 (1H, s, NH) 8.68 (1H, s, CH (O)—N); 8.58–6.99 (6H, Ar—H), 1.25–1.10 (18H, 2s Aliphatic H). ^{13}C NMR (DMSO d_6): 165.58, 162.24, 157.59, 151.30, 149.19, 139.63, 136.02, 135.84, 128.79, 126.42, 123.17, 116.97, 34.89, 33.84, 31.47, 29.12.

5.3.4. 4a

A dark yellow solid was obtained after the removal of the solvent. Unfortunately, several trials to obtain single crystals failed. Elemental analysis, calcd for $C_{52}H_{58}AlN_4O_6$: C, 72.45; H, 6.78; N, 6.50; O, 11.14 Found: C, 72.81; H, 6.39; N, 6.19, O, 11.47. *m/z* calcd 861.42; found, 861.41. Selected IR bands (ν_{max}/cm^{-1}): 3442 (O—H); 3048 (Ar—C—H) 2962 (aliphatic C—H); 1538 (C═N); 1632 (C(O)—N); 1174 (C—O), 1028 (N═N); ^{1}H NMR (500 MHz; DMSO d_6; Me_4Si): 13.6 (2H, s, OH);8.78 (1H, s, NH); 8.27 (1H, s, CH(O)—N); 7.86–7.13 (8H Ar—H), 1.25 (Is Aliphatic -H 9)-1.07 (9H, 1s Aliphatic 9H). ^{13}C NMR (DMSO d_6): 168.44, 162.06, 156.39, 148.67, 138.65, 136.10, 134.93, 129.76, 129.09, 127.75, 127.04, 125.97, 123.20, 119.74, 117.65, 117.43, 110.33, 34.98, 34.02, 31.96, 29.54.

5.4. Carbon dioxide fixation

The chemical fixation of CO_2 was conducted by using a 30 mL stainless steel autoclave containing a magnetic stir and dipped into an oil bath. The calculated amount of Al catalyst /co-catalyst along with the respective epoxide was charged into the autoclave, flushed three times with CO_2 at room temperature. The reactor was heated to 120 °C in the oil bath and then pressurized to 1 bar of CO_2. The reaction mixture was stirred continuously under 1 bar CO_2 pressure for the desired period for reaction time. After completion, the reactor was allowed to cool to room temperature slowly. In this manner, pressure changes are avoided. ^{1}H NMR analysis of the crude product was performed by taking small samples from the reaction mixtures. The isolated yield of the cyclic organic carbonates was obtained by column chromatography using a mixture of ethyl acetate and n-hexane (1:3) as eluents. The complex **2a** was recovered from the reaction mixture by passing methanol as eluent through the column and was used for 5 times for the next run without any loss of catalytic activity. TON was calculated as moles of product produced per mole of catalyst and TOF as TON per hour.

6. Conclusion

A family of four ONO pincer type hydrazone ligands, as well as the four corresponding mononuclear Al(III) complexes, were successfully synthesized and fully characterized. These new Al(III) complexes were applied as a catalyst for the cycloaddition of CO_2 to epoxides at mild pressure along with co-catalyst. Of those four new Al-compounds, **2a** exhibited the best catalytic performance then reported monometallic reported aluminium complexes under optimized reaction conditions. In addition, the catalyst can be recycled for five catalytic cycles without dropping the catalytic activity. The mechanistic study has been investigated via NMR and MALDI-TOF analysis.

Declaration of Competing Interest

There are no conflicts to declare.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcat.2019.07.033.

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