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Highly active dinuclear cobalt complexes for solvent-free cycloaddition of CO₂ to epoxides at ambient pressure†

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Dinuclear Co-based catalysts are used for the coupling reaction of epoxides and CO₂ in the presence of a cocatalyst. The easily recyclable catalysts efficiently complete the coupling of CO₂ with various epoxides into industrially important cyclic carbonates at low catalyst loading and displayed high catalytic activity under relatively low CO₂ pressure and solvent-free conditions. The maximum TON (168 600) and TOF (3333 h⁻¹) obtained in this work are the highest among the reported Co-complexes.

One of the world's primary energy uses is based on fossil fuels. This energy use is the dominant contributor to CO₂ that exists in our atmosphere and other greenhouse gas emissions. Since the pre-industrial era, the level of CO₂ has been continually increasing, being a component of greenhouse gas, primarily responsible for global warming.¹ One of the active goals in chemistry is to harness a part of this CO₂ stream to produce useful chemical products.² The coupling of epoxides with CO₂ into cyclic carbonates is one of the most promising as well as an eco-friendly method used for the chemical fixation of CO₂.³ This reaction is one of the few known commercially important reactions that utilize CO₂ as a chemical feedstock and has the potential to provide a sustainable basis for the future chemical industry. Even though the coupling reaction of epoxides and

CO₂ is highly exothermic, due to the kinetic and thermodynamic stability of carbon dioxide this coupling does not occur spontaneously because of the high activation energy requirement.⁴ To lower the energy of activation of this coupling reaction, various types of metal free⁵ and metal-based catalysts have been developed including alkali metal salts,⁶ main-group⁷ and transition metal complexes,⁸ metal-organic frameworks (MOFs)⁹ and metal oxides¹⁰ *etc.*

In catalyst designing, the choice of an appropriate ligand in addition to the metal centre is very important and critical for fine-tuning the catalytic activities of metal complexes. For these coupling reactions, the most frequently investigated complexes are that of cobalt,¹¹ iron,¹² chromium,¹³ and zinc¹⁴ metals. Most of the catalytic work based on cobalt complexes is related to porphyrin,¹⁵ salen,¹⁶ bis(phenoxyiminato),¹⁷ and amine-bis(phenolato)¹⁸ ligands. To the best of our knowledge, the highest TON obtained using cobalt complexes is 2930 by Jing and co-workers,¹⁵ using a high pressure of 20 bar at 120 °C, while the highest value of TOF is 662 h⁻¹ obtained by Ghosh and co-workers¹⁹ using a high pressure of 20.68 bar at 130 °C.

Literature studies show that in CO₂ cycloaddition to epoxides, hydrogen bond donor groups on the catalyst facilitate the activation of the epoxides and enhance the progress of the reaction.²⁰ Thus, diols were found to be more efficient to promote the reaction than monohydroxyl alcohols. Furthermore, diols in which the two hydroxyl groups exist on two adjacent carbons (vicinal carbons) are more active than other diols.

Also, it is reported that multinuclear complexes are more efficient towards CO₂ fixation than mononuclear complexes.^{7b,21} Due to the facile synthesis and wide-ranging flexibility in the choice and design of Schiff base ligands, polyhydroxy Schiff base ligands were selected aiming at their dinuclear cobalt complexes. These rich hydrogen-bond donor complexes exhibited exceptional activity towards the solvent-free cycloaddition of CO₂ to epoxides at ambient pressure with and without a cocatalyst. To the best of our knowledge, this is the most active catalytic system based on cobalt complexes with the highest TON and TOF being reported for CO₂ coupling with epoxides.

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Scheme 1 Synthesis of Schiff base ligands (H_4L^1 – H_4L^3) and their corresponding dinuclear cobalt complexes (**1**–**3**).

The Schiff base ligands were firstly synthesized *via* a condensation reaction of various aldehydes with 2-amino-2-hydroxymethyl-propane-1,3-diol, and then their corresponding cobalt complexes were synthesized from the reaction of these ligands with $CoCl_2 \cdot 6H_2O$ in the presence of triethylamine (TEA) as shown in Scheme 1. The obtained products were fully characterized using NMR (1H - and ^{13}C -NMR), FT-IR, ESI-MS, and elemental analysis. The mass spectra of the complexes are in agreement with the formulae $[Co(H_2L^1)]_2$, $[Co(H_2L^2)]_2$, and $[Co(H_2L^3)]_2$. The mass spectrum of the complex **1** shows a base peak at a mass-to-charge ratio (m/z) of 597.9928, corresponding to the dinuclear formula of $[Co_2(H_2L^1)_2H]^-$ (calculated m/z 597.9969). While, complexes **2** and **3** show base peaks at a mass-to-charge ratio (m/z) of 658.0127 and 698.0222 corresponding to formulae of $[Co_2(H_2L^2)_2H]^-$ (calculated m/z 658.0180) and $[Co_2(H_2L^3)_2H]^-$ (calculated m/z 698.0282), respectively (Fig. S10–S12, ESI†).

In the FT-IR spectra, the coordination of the Schiff base ligand to the cobalt metal centre *via* the N-atom is expected to decrease the electron density in the azomethine linkage and hence lower the absorption frequency of $\nu(C=N)$ stretching vibrations.²² Strong and sharp absorption bands appearing in the range of 1635–1638 cm^{-1} in the free ligands are shifted to lower wavenumbers (1626–1633 cm^{-1}) after complexation suggesting the participation of the azomethine group of the ligands in binding to the cobalt metal centre²³ (Fig. S7–S9, ESI†). The powder XRD of complex **2** is in close agreement with the simulated powder XRD pattern of the reported complex (see Fig. S7 in ESI†).

In order to evaluate the catalytic potential of the synthesized dinuclear cobalt complexes (**1**–**3**) for the coupling reactions, epichlorohydrin (substrate) was treated with carbon dioxide starting with 1 bar pressure of CO_2 and 120 °C under solvent-free conditions using 1 mol% (0.05 mmol) of each complex as a catalyst (Table 1, entries 1–3). After 5 hours of reaction time, good conversions were observed for all the catalysts, though catalyst **2** has a relatively high conversion as compared to the other two catalysts, which may be due to the electron donation properties of methoxy groups.

Generally, cocatalysts significantly improve the activity of several catalytic systems towards cyclic carbonate formation from epoxides.²⁴ Therefore, we used the most commonly used cocatalysts, 4-dimethylaminopyridine (DMAP) and tetrabutylammonium bromide (TBAB), along with complex **2** to test

the catalytic activities in the presence of these cocatalysts (Table 1, entries 8 and 9). The catalytic activity of complex **2** was nearly the same with both cocatalysts, though slightly better with TBAB. We then optimized the other reaction conditions, like temperature (°C) and pressure of CO_2 (bar), relative to the molar ratio of catalyst:cocatalyst:substrate, and time (h) for the coupling reaction. For the optimization purpose, epichlorohydrin was used as a substrate. The temperature has a profound effect on the catalytic activity. With the negligible conversion of epichlorohydrin at 75 °C, the conversion increases from 11% (in 24 hours) to 90% (in 5 hours) with increasing the temperature from 75 to 120 °C (Table 1, entries 3–5). However, the catalytic activity is less sensitive to CO_2 pressure increase in comparison to temperature. Thus, increasing the gas pressure from 1 to 10 bar, while keeping other parameters fixed, the conversion of epoxides into cyclic products increases from 58 to 81% in 3 h (Table 1, entries 11–14). Also see Table S1 (ESI†) for the ligands, complexes cocatalysts' conversions.

Based on these observations, 120 °C and 1 bar pressure of CO_2 were adopted as the optimum reaction conditions and TBAB as a cocatalyst for further studies. At catalyst and TBAB loadings of 0.1 mol% each, we were able to achieve the complete conversion of an epichlorohydrin substrate at 120 °C and 1 bar pressure of CO_2 after 6 h (Table 1, entry 10). We then investigated the use of reduced amounts of complex **2** (Table 1, entries 15–23) and observed the TON value of 168 600 (Table 1, entry 23) and the TOF of up to 3333 h^{-1} (Table 1, entry 18), which are the highest values of TON and TOF reported for cobalt-based catalysts (Table S2, ESI†).

Due to the industrial importance of various cyclic carbonates, different epoxide substrates were used for this coupling reaction under the optimized catalytic conditions. Most importantly, the catalyst is effective in the conversion of terminal as well as challenging internal epoxides. The results are summarized in Table 2 (see Fig. S14–S24, ESI† for NMR spectra). It is observed that epichlorohydrin, epibromohydrin, allyl glycidyl ether, butyl glycidyl ether, and glycidyl isopropyl ether are fully converted into the corresponding cyclic carbonates in 6–8 hours (Table 2, entries 1–5). Also, good conversions were obtained in the case of styrene oxide, propylene oxide, and 1,2-epoxyhexane (Table 2, entries 6–8). We also tested the catalyst for internal epoxides. Relatively low conversion was observed at 1 bar. However, at high pressure (10 bar), excellent conversion was observed for all three internal epoxides used (Table 2, entries 9–11).

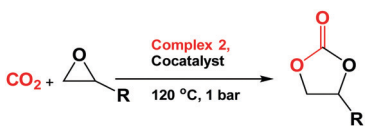
The general mechanism was proposed based on the literature.²⁵ The key feature of the mechanism is the activation of both reaction components, the epoxy ring and carbon dioxide, by the dinuclear complex, and cocatalyst, TBAB. The role of TBAB in the mechanism might be the *in situ* generation of tributylamine, which helps in the activation of CO_2 .^{25,26} The coordination of the epoxide to the metal centre (Lewis acid) is followed by ring opening by bromide from the cocatalyst.²⁶ This intermediate formed is supposed to react with a carbamate salt formed by the decomposition of TBAB to tributylamine and further reacted with CO_2 to afford a complex in which both the epoxide and the CO_2 are activated.²⁶ The displacement of the tributylammonium

Table 1 Optimizing conditions for the solvent-free cycloaddition of CO₂ and epichlorohydrin at 1 bar

								
Entry	Catalyst	Cat. : cocat. : substrate	P (bar)	Temp. (°C)	Time (h)	Conversion (%)	TON	TOF (h ⁻¹)
1	1	1 : 0 : 100	1	120	5	80	80	16
2	2	1 : 0 : 100	1	120	5	90	90	18
3	3	1 : 0 : 100	1	120	5	55	55	11
4	2	1 : 0 : 100	1	100	24	74	74	3
5	2	1 : 0 : 100	1	75	24	11	11	0.5
6	2	1 : 0 : 100	5	75	12	—	—	—
7	2	1 : 0 : 100	5	120	5	80	800	16
8 ^a	2	1 : 1 : 1000	1	120	4	77	770	192
9	2	1 : 1 : 1000	1	120	4	81	810	202
10	2	1 : 1 : 1000	1	120	6	100	1000	167
11	2	1 : 1 : 1000	1	120	3	58	580	193
12	2	1 : 1 : 1000	2	120	3	64	640	213
13	2	1 : 1 : 1000	5	120	3	73	730	243
14	2	1 : 1 : 1000	10	120	3	81	810	270
15	2	1 : 1 : 10 000	1	120	4	46.5	4650	1162
16	2	1 : 1 : 50 000	1	120	12	37.1	18 550	1546
17	2	1 : 1 : 100 000	1	120	24	62.2	62 200	2592
18	2	1 : 1 : 200 000	1	120	3	5	10 000	3333
19	2	1 : 1 : 200 000	1	120	6	10	20 000	3333
20	2	1 : 1 : 200 000	1	120	12	19	38 000	3167
21	2	1 : 1 : 200 000	1	120	24	35	70 000	2917
22	2	1 : 1 : 200 000	1	120	48	66	132 000	2750
23	2	1 : 1 : 200 000	1	120	72	84.3	168 600	2342

TBAB was used as a cocatalyst unless mentioned otherwise.^a DMAP as a cocatalyst. TON and TOF values are calculated per mole of complex.

Table 2 Cycloaddition of CO₂ to different epoxide substrates using complex **2** as a catalyst

				
Entry	Substrate	Conversion (%)	TON	TOF (h ⁻¹)
1 ^a	Epichlorohydrin	100	1000	167
2	Allyl glycidyl ether	100	1000	125
3	Butyl glycidyl ether	100	1000	125
4	Glycidyl iso-propyl ether	100	1000	125
5	Epibromohydrin	100	1000	167
6	Styrene oxide	94	940	118
7	Propylene oxide	81	810	116
8	1,2-Epoxyhexane	77	770	96
9 ^b	3,6-Dioxabicyclo [3,1,0] hexane	56 (100) ^c	560 (1000) ^c	23 (42) ^c
10 ^b	Cyclopentene oxide	45 (100) ^c	450 (1000) ^c	19 (42) ^c
11 ^b	Cyclohexene oxide	20 (84) ^c	200 (840)	8 (35) ^c

Conditions: 0.1 mol% (0.01 mmol) of complex **2**, 0.1 mol% (0.01 mmol) of TBAB. Reaction time is 8 hours unless stated otherwise. TON and TOF values are calculated per mole of complex.^a Reaction time 6 h. ^b Reaction time 24 h and 0.5 mol% of TBAB. ^c 10 bar pressure of CO₂.

group finally affords a metal-coordinated carbonate, which undergoes subsequent ring-closure to form the cyclic carbonate and regenerates the catalyst.²⁶ Therefore, the complex and TBAB take part together to open the epoxy ring and then the subsequent addition of CO₂ to give the corresponding cyclic carbonates in ring opening and re-cyclization processes.

The catalyst is easily recovered from the reaction mixture by centrifugation, washed with acetone and dried under vacuum at 50 °C for 4 hours before starting the next cycle. The conversion after each cycle was determined by ¹H-NMR and the catalyst was characterized by FT-IR. This process was successfully repeated five times without any loss in the catalytic activity, see Fig. 1. The FT-IR spectrum of the recovered catalyst after five cycles closely matches with the fresh catalyst, which indicates that the catalyst retains its identity even after five reaction cycles (Fig. S21, ESI†).

In order to establish the applicability and effectiveness of the catalytic system used in this study, the performance of these catalysts was compared with several examples of molecular catalysts that are based on different transition metals. However, a direct comparison is complex due to different investigated conditions.²⁷ It is difficult to draw a clear comparison with the

**Fig. 1** Recyclability of the complex **2** for the coupling reaction of CO₂ with epichlorohydrin under optimal reaction conditions.

reported catalytic systems, as in most cases the epoxides, cocatalysts and the experimental conditions such as temperature and pressure are not the same. But to give a rough idea of the efficacy of the catalytic system used in this study with the reported complexes, especially with those of Co-complexes, the results are summarized in Table S2 in the ESI.† Though very high TON and TOF values are reported in the case of Al-, Mg-, Fe- and Zn-complexes (Table S2, entries 12–19, ESI†), the TON and TOF values obtained in this study are significantly higher than the highest TON and TOF values reported for cobalt complexes, and also it competes well with other state of the art catalysts (Table S2, entries 1–11, ESI†) with the advantage of working under ambient pressure conditions.

In summary, dinuclear cobalt complexes have been successfully synthesized and used as active catalysts for the synthesis of cyclic carbonates from the coupling reaction of epoxides and carbon dioxide in the presence of TBAB as a cocatalyst. These catalysts efficiently performed the insertion of carbon dioxide into various terminal as well as challenging internal epoxides at low catalyst loading (0.01 mol%) at an ambient gas pressure of CO₂, though high pressure is favourable for internal epoxides, under solvent-free conditions. Notably, the highest values of TON (168 600) and TOF (3333 h⁻¹) are achieved at a low pressure of CO₂ (1 bar) as compared to the other reported cobalt complexes. The reuse of the recycled catalyst for at least five cycles giving the same activity revealed the remarkable stability of these compounds.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 J. F. M. Orr, *Energy Environ. Sci.*, 2009, **2**, 449.
- 2 P. Markewitz, W. Kuckshinrichs, W. Leitner, J. Linssen, P. Zapp, R. Bongartz, A. Schreiber and T. E. Müller, *Energy Environ. Sci.*, 2012, **5**, 7281.
- 3 S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa and S. Konno, *Green Chem.*, 2003, **5**, 497.
- 4 L. Wang, X. Jin, P. Li, J. Zhang, H. He and S. Zhang, *Ind. Eng. Chem. Res.*, 2014, **53**, 8426.
- 5 (a) G. Fiorani, W. Guo and A. W. Kleij, *Green Chem.*, 2015, **17**, 1375; (b) M. Cokoja, M. E. Wilhelm, M. H. Anthofer, W. A. Herrmann and F. E. Kühn, *ChemSusChem*, 2015, **8**, 2436.
- 6 J. W. Comerford, I. D. V. Ingram, M. North and X. Wu, *Green Chem.*, 2015, **17**, 1966.
- 7 (a) C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin and A. W. Kleij, *J. Am. Chem. Soc.*, 2013, **135**, 1228; (b) Z. A. K. Khattak, H. A. Younus, N. Ahmad, B. Yu, H. Ullah, S. Suleman, A. H. Chughtai, B. Moosavi, C. Somboon and F. Verpoort, *J. CO₂ Util.*, 2018, **28**, 313.
- 8 R. R. Shaikh, S. Pornpraprom and V. D'Elia, *ACS Catal.*, 2018, **8**, 419.
- 9 (a) B. Mousavi, S. Chaemchuen, B. Moosavi, Z. Luo, N. Gholampour and F. Verpoort, *New J. Chem.*, 2016, **40**, 5170; (b) A. H. Chughtai, N. Ahmad, H. A. Younus, A. Laypkov and F. Verpoort, *Chem. Soc. Rev.*, 2015, **44**, 6804.
- 10 K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida and K. Kaneda, *J. Am. Chem. Soc.*, 1999, **121**, 4526.
- 11 X.-B. Lu and D. J. Darensbourg, *Chem. Soc. Rev.*, 2012, **41**, 1462.
- 12 (a) C. J. Whiteoak, E. Martin, M. M. Belmonte, J. Benet-Buchholz and A. W. Kleij, *Adv. Synth. Catal.*, 2012, **354**, 469; (b) A. Buonerba, A. De Nisi, A. Grassi, S. Milione, C. Capacchione, S. Vagin and B. Rieger, *Catal. Sci. Technol.*, 2015, **5**, 118; (c) M. Taherimehr, J. P. C. C. Sertà, A. W. Kleij, C. J. Whiteoak and P. P. Pescarmona, *ChemSusChem*, 2015, **8**, 1034; (d) D. Alhashmialameer, J. Collins, K. Hattenhauer and F. M. Kerton, *Catal. Sci. Technol.*, 2016, **6**, 5364; (e) F. Della Monica, S. V. C. Vummaleti, A. Buonerba, A. D. Nisi, M. Monari, S. Milione, A. Grassi, L. Cavallo and C. Capacchione, *Adv. Synth. Catal.*, 2016, **358**, 3231.
- 13 (a) D. Adhikari, S. T. Nguyen and M.-H. Baik, *Chem. Commun.*, 2014, **50**, 2676; (b) Y. Xie, R.-X. Yang, N.-Y. Huang, H.-J. Luo and W.-Q. Deng, *J. Energy Chem.*, 2014, **23**, 22; (c) J. A. Castro-Osma, M. North and X. Wu, *Chem. – Eur. J.*, 2016, **22**, 2100; (d) J. A. Castro-Osma, K. J. Lamb and M. North, *ACS Catal.*, 2016, **6**, 5012.
- 14 (a) Y.-M. Shen, W.-L. Duan and M. Shi, *J. Org. Chem.*, 2003, **68**, 1559; (b) T. Ema, Y. Miyazaki, S. Koyama, Y. Yano and T. Sakai, *Chem. Commun.*, 2012, **48**, 4489; (c) H. Vignesh Babu and K. Muralidharan, *Dalton Trans.*, 2013, **42**, 1238; (d) C. Martin, C. J. Whiteoak, E. Martin, M. Martinez Belmonte, E. C. Escudero-Adán and A. W. Kleij, *Catal. Sci. Technol.*, 2014, **4**, 1615; (e) M. A. Fuchs, C. Altesleben, S. C. Staudt, O. Walter, T. A. Zevaco and E. Dinjus, *Catal. Sci. Technol.*, 2014, **4**, 1658; (f) Y. Ren, J. Chen, C. Qi and H. Jiang, *ChemCatChem*, 2015, **7**, 1535; (g) E. Mercadé, E. Zangrando, C. Claver and C. Godard, *ChemCatChem*, 2016, **8**, 234.
- 15 X. Jiang, F. Gou, F. Chen and H. Jing, *Green Chem.*, 2016, **18**, 3567.
- 16 (a) X.-B. Lu, X.-J. Feng and R. He, *Appl. Catal., A*, 2002, **234**, 25; (b) A. Berkessel and M. Brandenburg, *Org. Lett.*, 2006, **8**, 4401.
- 17 A. Sibauhi, P. Ryan, K. V. Axenov, M. R. Sundberg, M. Leskelä and T. Repo, *J. Mol. Catal. A: Chem.*, 2009, **312**, 87.
- 18 M. Reiter, P. T. Altenbuchner, S. Kissling, E. Herdtweck and B. Rieger, *Eur. J. Inorg. Chem.*, 2015, 1766.
- 19 P. Ramidi, N. Gerasimchuk, Y. Gartia, C. M. Felton and A. Ghosh, *Dalton Trans.*, 2013, **42**, 13151.
- 20 (a) J. Song, Z. Zhang, B. Han, S. Hu, W. Li and Y. Xie, *Green Chem.*, 2008, **10**, 1337; (b) S. Liang, H. Liu, T. Jiang, J. Song, G. Yang and B. Han, *Chem. Commun.*, 2011, **47**, 2131.
- 21 (a) S. He, F. Wang, W.-L. Tong, S.-M. Yiu and M. C. W. Chan, *Chem. Commun.*, 2016, **52**, 1017; (b) M. V. Escárcega-Bobadilla, M. Martínez Belmonte, E. Martin, E. C. Escudero-Adán and A. W. Kleij, *Chem. – Eur. J.*, 2013, **19**, 2641.
- 22 A. Kilic, M. Ulusoy, E. Aytar and M. Durgun, *J. Ind. Eng. Chem.*, 2015, **24**, 98.
- 23 A. Kilic, M. Ulusoy, M. Durgun and E. Aytar, *Inorg. Chim. Acta*, 2014, **411**, 17.
- 24 R. L. Paddock and S. T. Nguyen, *Chem. Commun.*, 2004, 1622.
- 25 W. Clegg, R. W. Harrington, M. North and R. Pasquale, *Chem. – Eur. J.*, 2010, **16**, 6828.
- 26 A. Decortes, A. M. Castilla and A. W. Kleij, *Angew. Chem., Int. Ed.*, 2010, **49**, 9822.
- 27 J. Rintjema and A. W. Kleij, *ChemSusChem*, 2017, **10**, 1274.