

Factors affecting activation and utilization of carbon dioxide in cyclic carbonates synthesis over Cu and Mn peraza macrocyclic complexes

R. Srivastava, T.H. Bennur, D. Srinivas*

Catalysis Division, National Chemical Laboratory, Pashan road, Pune 411008, India

Received 14 September 2004; received in revised form 20 October 2004; accepted 21 October 2004

Available online 2 December 2004

Abstract

The catalytic activities of several Cu and Mn aza complexes for cyclic carbonate synthesis from CO₂ and epoxides are reported. The various factors affecting activation of CO₂ by metal complexes and its utilization in cyclic carbonate synthesis have been investigated. FT-IR, UV–vis and EPR spectroscopic investigations reveal that CO₂ coordinates to Cu in η^1 -C mode of coordination. Nature of the ligand and substitution influence the lability of metal–CO₂ bonding. The differences in the catalytic activities are correlated with the mode and strength of CO₂ binding.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Carbon dioxide; Cyclic carbonates; Polycarbonates; CO₂ fixation; CO₂ activation; CO₂ utilization; Catalysis by Cu and Mn complexes; Benign synthesis; Spectroscopy

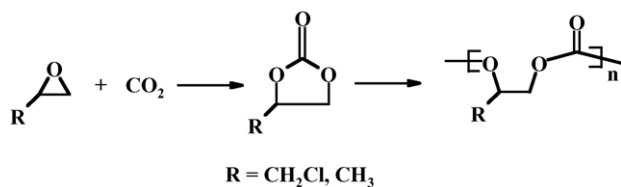
1. Introduction

Utilization of CO₂ as C₁-feedstock in chemicals and fuels synthesis is of great interest [1–4]. The coupling of CO₂ with epoxides yielding cyclic and polycarbonates (Scheme 1) is one of the most efficient ways of CO₂ utilization [5–7]. Inoue et al. [8] reported this alternative, phosgene-free, eco-friendly approach for cyclic and polycarbonates, for the first time, in 1969. Since then significant progress has been made toward developing more efficient catalysts for this reaction [9–11]. BASF (Ludwigshafen, Germany) [12] and Chimie-Asahi corporation (Taiwan) [6] produce cyclic carbonates in large capacities (several ten thousands of tons annually) using inexpensive catalysts. The reactions in the commercial process, however, have to be conducted at high temperatures (453–473 K) and high pressures (50–80 bar). Porphyrin, phthalocyanine and Schiff base com-

plexes catalyze this cycloaddition reaction, at mild conditions (393 K, 6.9 bar), in the presence of nucleophiles such as *N,N*-dimethylaminopyridine (DMAP), quaternary ammonium and phosphonium salts or imidazoles as promoters/cocatalysts [13–15]. We report here the application of cyclen complexes (Fig. 1) in this reaction.

Activation of CO₂ is the key step for its further participation in the cycloaddition reaction. CO₂ coordinates to metal ions in different coordination modes. The strength and lability of metal–CO₂ bond and the mode of coordination control the reactivity in different CO₂ fixation reactions. Peraza macrocycles have been known for CO₂ activation [16]. The Cu complex of *N,N',N''*-triallyl-1,4,7-triazacyclononane reductively couples two CO₂ molecules yielding the oxalate anion (C₂O₄²⁻) [17]. Ni-cyclam was an efficient and selective catalyst for electroreduction of CO₂ on Hg electrode in water [18]. The application of Cu and Mn–cyclen complexes (Fig. 1) in cyclic carbonate synthesis is reported here, for the first time. The catalytic activities of the Cu and Mn–cyclen complexes (12-membered saturated ring system) are com-

* Corresponding author. Tel.: +91 20 2589 3761; fax: +91 20 2589 3761.
E-mail address: srinivas@cata.ncl.res.in (D. Srinivas).



Scheme 1.

pared with those of phthalocyanine and tetraphenylporphyrin complexes (16-membered unsaturated ring systems; Fig. 1) as well as Schiff base (salen and saloph), bipyridine (bipy) and phenanthroline (phen) complexes (acyclic systems). The influence of the macrocyclic ring, central metal ion and peripheral substitution on the catalytic activity is investigated. The activation and mode of CO_2 coordination and cyclic carbonate formation over the Cu complexes are explored using in situ FT-IR, UV-vis and EPR spectroscopic techniques. There have been some theoretical studies on Cu^{1+} - CO_2 coordinations [19]. We report here a spectroscopic evidence for the activated Cu^{2+} - CO_2 complexes.

2. Experimental

2.1. Synthesis and physical measurements

$\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$, $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$ and Cu-phthalocyanine (CuPc) were procured from Aldrich. All the other reagents and solvents were obtained from Merck India Ltd. The copper complexes CuTPP [20], Cu(salen) [21], Cu(saloph) [22], $\text{Cu}(\text{H}_2\text{O})(\text{phenanthroline})_2(\text{NO}_3)_2$ (Cu(phen)) [23], $\text{Cu}(\text{NO}_3)(\text{bipyridine})_2(\text{H}_2\text{O})(\text{NO}_3)$ (Cu(bipy)) [23], $[\text{Cu}(\text{cyclen})(\text{NO}_2)]\text{ClO}_4$ (Cu(cyclen)) [24] and $[\text{Cu}(\text{Me}_4\text{cyclen})(\text{CH}_3\text{CN})](\text{ClO}_4)_2$ ((Cu(Me₄cyclen))) [24] were prepared by the known procedures. The analogous Mn(cyclen) and Mn(Me₄cyclen) complexes were also prepared in a similar manner.

Physicochemical characterization by elemental analysis, FT-IR, UV-vis and EPR spectroscopy confirmed the formation and purity of the complexes. The results agreed well with the earlier reports [20–24]. FT-IR spectra were recorded on a Shimadzu 8201 PC spectrophotometer. UV-vis spectra were measured on a Shimadzu UV-2550 spectrometer in the range 200–800 nm. Electron paramagnetic resonance (EPR)

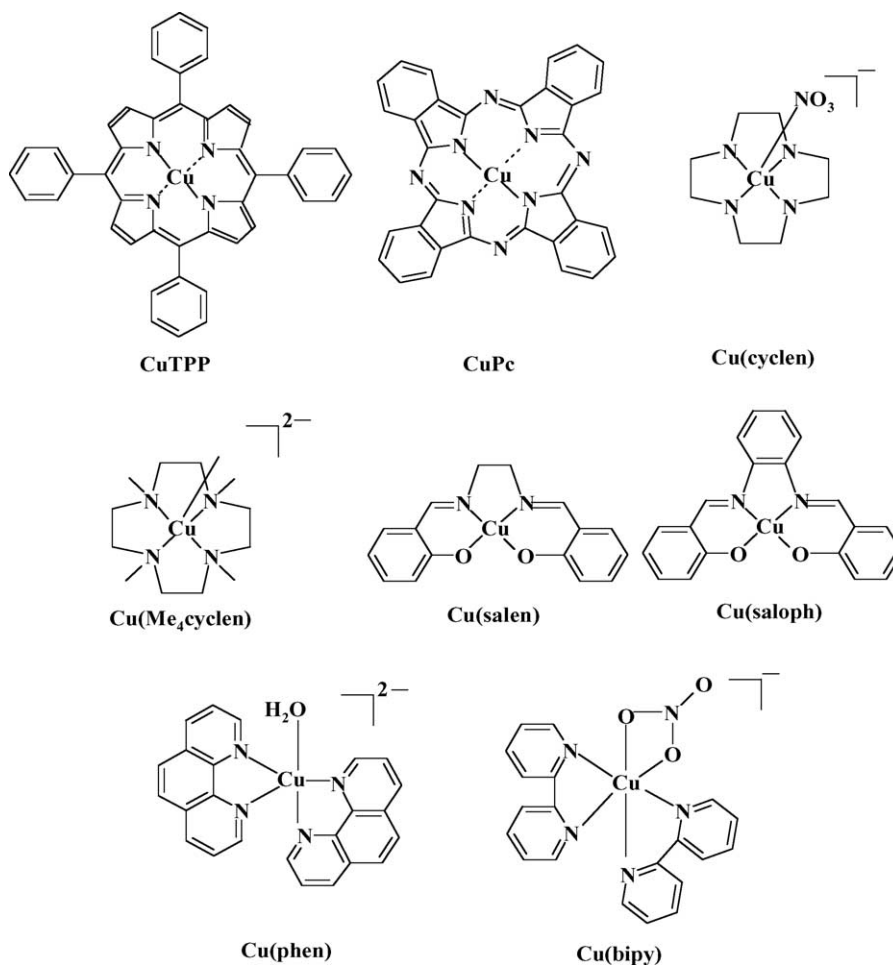


Fig. 1. Structures of metal complexes investigated in the present study.

measurements were made on a Bruker EMX spectrometer at X-band frequency with 100 kHz field modulation.

2.2. Cyclic carbonate synthesis: reaction procedure

In a typical cycloaddition reaction, epoxide (18 mmol), catalyst, *N,N*-dimethylaminopyridine (DMAP, co-catalyst; 0.0072 mmol) and solvent (20 ml) were taken in a 300 ml stainless steel PARR pressure reactor. The reactor was pressurized with CO₂ (6.9 bar), temperature was raised to 393 K and the reaction was conducted for 4 h. The reactor was then cooled to 298 K and unreacted CO₂ was vented out. The products were isolated and analyzed quantitatively by gas chromatography (Varian 3400; CP-SIL8CB column; with a 30 m-long, and 0.53 mm-i.d.). The products were identified by GC-MS (Shimadzu QP-5000; with a 30 m-long, 0.25 mm-i.d., and 0.25 μm-thick capillary column DB-1), GC-IR (Perkin Elmer 2000; BP-1 column; with a 25 m-long, and 0.32 mm-i.d.) and ¹H NMR (Bruker AC 200).

Spectral characteristics of the products: chloropropylene carbonate—IR(cm⁻¹): ν_{C=O}, 1800, ν_{C-O}, 1133, 1080; ¹H NMR (CDCl₃), δ(ppm): 5.03–4.94 (1H, m), 4.61–4.52 (1H, q), 4.44–4.35 (1H, q), 3.84–3.74 (2H, m); propylene carbonate—IR (cm⁻¹): ν_{C=O}, 1793, ν_{C-O}, 1121, 1078; ¹H NMR (CDCl₃), δ(ppm): 4.88–4.77 (1H, m), 4.55–4.49 (1H, t), 4.01–3.96 (1H, t), 1.45 (3H, d).

3. Results and discussion

3.1. Catalytic activity

The reaction of epoxide (ECH, epichlorohydrin and PO, propylene oxide) and CO₂ yielded the corresponding cyclic carbonate as the selective product (>92%); diols and ethers formed in minor amounts. Table 1 presents the catalytic

activity of different Cu and Mn-peraza complexes. Ligand structure has a marked effect on the catalytic activity. With different ligands the catalytic activity (turnover frequency per hour (TOF)) in chloropropylene carbonate synthesis decreased (from 502 to 400; Table 1) in the order: phthalocyanine (Pc) > tetraphenyl porphyrin (TPP) > phenanthroline (phen) > saloph > salen > cyclen > bipyridine (bipy). In propylene carbonate synthesis the catalytic activity decreased (from 286 to 191; Table 1) in the order: cyclen > phen > saloph > bipy > salen. Among the cyclic systems the unsaturated ligand systems (Pc and TPP) are more efficient than the saturated ligand system (cyclen). The metal complexes of cyclic aza ligands exhibited higher activity than the acyclic systems (bipy and phen). Electron donating substituents (methyl, Me) decreased the catalytic activity (compare entry nos. 3 and 8). On the other hand, a remarkable increase in TOF (from 258 to 449) was observed when Cu²⁺ replaced by Mn³⁺. Electron withdrawing substituents on epoxide facilitated the cycloaddition. The reaction with epichlorohydrin is more facile than with propylene oxide (Table 1). The differences in catalytic activity are due to differences in the mode of CO₂ binding. The following section dealing with spectral studies reveals the differences in the type of CO₂ coordination to Cu complexes.

3.2. Spectroscopic studies

The activation of CO₂ and formation of cyclic carbonate (from CO₂ and epichlorohydrin) over Cu(cyclen)–DMAP–CH₃CN system were monitored by FT-IR, UV–vis and EPR spectroscopies. The reactions were conducted as described in the experimental section under pressure conditions (6.9 bar, 398 K, 4 h) and the reaction mixtures were subjected to spectral analysis. The reaction of CO₂ with the catalyst system generated two new IR peaks at 1716 and 1225 cm⁻¹

Table 1
Catalytic activity of Cu and Mn complexes for cyclic carbonate synthesis from CO₂ and epoxide

Catalyst (mmol)	Epoxide	Epoxide conversion (wt%)	TOF	Cyclic carbonate selectivity (%)
CuPc (0.0072)	ECH	80.3	502	97.2
CuTPP (0.0072)	ECH	78.2	489	96.4
[Cu(cyclen)(NO ₃)]ClO ₄ (0.0078)	ECH	71.4	412	95.2
Cu(saloph) (0.0072)	ECH	71.8	449	98.2
Cu(phen) ₂ (NO ₃) ₂ (H ₂ O) (0.0069)	ECH	69.6	454	97.2
Cu(salen) (0.0072)	ECH	66.1	413	95.8
Cu(bipy) ₂ (NO ₃) ₂ (H ₂ O) (0.0069)	ECH	61.4	400	96.7
[Cu(Me ₄ cyclen)(CH ₃ CN)](ClO ₄) ₂ (0.0066)	ECH	37.8	258	96.8
[Mn(Me ₄ cyclen)(NO ₃)](ClO ₄) ₂ (0.0064)	ECH	63.8	449	97.2
[Cu(cyclen)(NO ₃)]ClO ₄ (0.0078)	PO	49.6	286	91.3
Cu(saloph) (0.0072)	PO	34.2	214	97.5
Cu(phen) ₂ (NO ₃) ₂ (H ₂ O) (0.0069)	PO	38.0	248	98.4
Cu(salen) (0.0072)	PO	30.6	191	100
Cu(bipy) ₂ (NO ₃) ₂ (H ₂ O) (0.0069)	PO	29.6	193	97.9
[Mn(Me ₄ cyclen)(NO ₃)](ClO ₄) ₂ (0.0064)	PO	30.2	206	91.8

Reaction conditions: epoxide (18 mmol), catalyst (0.0064–0.0078 mmol), DMAP (0.0072 mmol), CH₂Cl₂ (20 ml), CO₂ (6.9 bar), temperature (393 K), reaction time (4 h). Turnover frequency (TOF), moles of epoxide converted per mole of metal per hour; ECH, epichlorohydrin; PO, propylene carbonate.

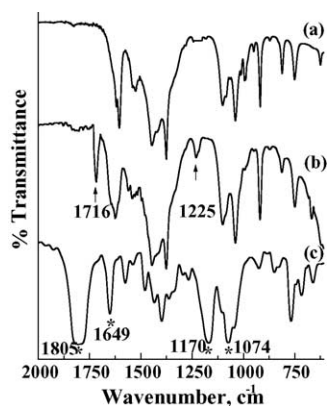


Fig. 2. FT-IR spectra in CH_3CN : (a) $\text{Cu}(\text{cyclen})+\text{DMAP}$, (b) $\text{Cu}(\text{cyclen})+\text{DMAP}+\text{CO}_2$, (c) $\text{Cu}(\text{cyclen})+\text{DMAP}+\text{CO}_2+\text{ECH}$. Asterisk indicates the characteristic IR peaks for cyclic carbonate.

(Fig. 2) attributable to the formation of an activated CO_2 complex [25]. When both CO_2 and ECH were reacted (in CH_3CN) additional peaks (denoted by asterisk; Fig. 2) appeared at 1805, 1649, 1170 and 1074 cm^{-1} . These additional peaks compared well with the IR spectrum of a commercial cyclic carbonate sample. The peaks due to the CO_2 -complex (at 1716 and 1225 cm^{-1}) could not be discerned from the spectra of CO_2+ECH reaction solutions due to overlap of highly intense peaks of cyclic carbonate.

$\text{Cu}(\text{cyclen})\text{-DMAP-CH}_3\text{CN}$ showed a weak d–d band at around 660 nm (Fig. 3). The CO_2 -reacted solution showed new bands at 415 nm consistent with the formation of an activated CO_2 complex. These bands could be attributed to metal-to-ligand charge transfer transitions (Cu (d orbitals) \rightarrow CO_2 (π^* orbitals)) [26]. When both ECH and CO_2 were reacted the d–d band shifted to higher energy side and a new resolved feature appeared at 524 nm (Fig. 3). These spectral variations indicate a change in the molecular structure of the Cu complex due to formation of cyclic carbonate and adduct complexes. Similar conclusions are drawn also from the EPR spectra (vide infra). When the reactions were con-

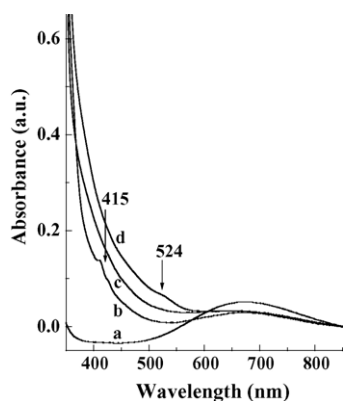


Fig. 3. UV-vis spectra in CH_3CN : (a) $\text{Cu}(\text{cyclen})+\text{DMAP}$, (b) $\text{Cu}(\text{cyclen})+\text{DMAP}+\text{CO}_2$, (c) $\text{Cu}(\text{cyclen})+\text{DMAP}+\text{ECH}$, (d) $\text{Cu}(\text{cyclen})+\text{DMAP}+\text{CO}_2+\text{ECH}$.

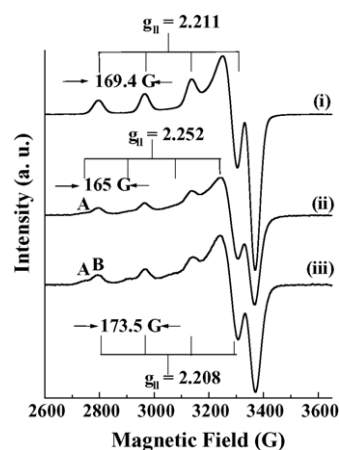


Fig. 4. EPR spectra in CH_3CN at 100 K: (i) $\text{Cu}(\text{cyclen})+\text{DMAP}$, (ii) $\text{Cu}(\text{cyclen})+\text{DMAP}+\text{CO}_2$, (iii) $\text{Cu}(\text{cyclen})+\text{DMAP}+\text{CO}_2+\text{ECH}$.

ducted over $\text{Cu}(\text{phen})$ and $\text{Cu}(\text{bipy})$ complexes (spectra not shown here), the position of the charge transfer band of the activated CO_2 complex shifted from 415 nm (originally observed for $\text{Cu}(\text{cyclen})$ complexes) to 409 nm. This shift in the charge transfer band position can be corresponded to a change in the mode of CO_2 coordination and Cu-CO_2 bond strength.

$\text{Cu}(\text{cyclen})+\text{DMAP}$ in CH_3CN showed an axial EPR spectrum with spin Hamiltonian parameters being $g_{\parallel}=2.211$, $g_{\perp}=2.054$ and $A_{\parallel}^{\text{Cu}}=169.4\text{ G}$ (Fig. 4). Upon reaction with CO_2 new signals (denoted as A in Fig. 4; resolved mainly in the parallel region) appeared at $g_{\parallel}=2.252$ and $A_{\parallel}^{\text{Cu}}=165.0\text{ G}$ in addition to the signals characteristic of $\text{Cu}(\text{cyclen})\text{-DMAP}$ complex. These new EPR signals, in agreement with the FT-IR and UV-vis results, could be attributed to the activated CO_2 complex. The higher g value ($g_{\parallel}=2.252$) compared to that of $\text{Cu}(\text{cyclen})\text{-DMAP}$ complex indicates stronger pentacoordinated Cu^{2+} species [27]. The axial spectrum indicates a symmetric coordination of CO_2 to Cu . Upon reaction with CO_2+ECH , significant changes in the spectral parameters were observed (Fig. 4). Two types of Cu^{2+} with the following spin Hamiltonian parameters were observed. Species A with $g_{\parallel}=2.258$ and $A_{\parallel}^{\text{Cu}}=155.0\text{ G}$ is the activated CO_2 -complex and species B with $g_{\parallel}=2.208$, $g_{\perp}=2.056$ and $A_{\parallel}^{\text{Cu}}=173.5\text{ G}$ is the cyclic carbonate adduct. The origin of species B was confirmed by recording the spectra of $\text{Cu}(\text{cyclen})\text{-DMAP}+\text{propylene carbonate}$.

CO_2 in gaseous state is a linear $\text{D}_{\infty\text{h}}$ triatomic molecule with three fundamental modes of vibration. (ν_1 : 1285, 1388 cm^{-1} ; ν_2 : 667 cm^{-1} ; ν_3 : 2349 cm^{-1}) [28]. By convention ν_1 and ν_3 are referred to as the symmetric and asymmetric C–O stretching modes whereas ν_2 is the degenerate C–O deformational mode. The centro-symmetrical nature of the free CO_2 molecule imposes mutual exclusion restrictions on the vibrational activities and as a result, ν_1 is Raman active while ν_2 and ν_3 are IR active. Apart from the weak bands due to natural abundance $^{13}\text{CO}_2$ and overtone-

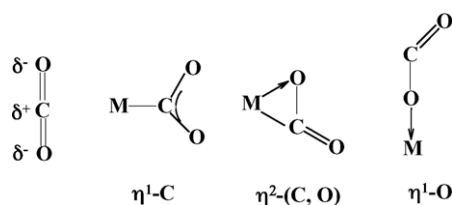


Fig. 5. Modes of CO₂ coordination at metal center in 1:1 metal–CO₂ complexes.

combination bands, a classic Fermi-resonance between ν_1 and $2\nu_2$ at 1285/1388 cm^{-1} is observed in the Raman spectrum. A chemisorbed or complexed CO₂ molecule shows asymmetric and symmetric C–O stretching vibration bands at 1750–1500 and 1350–1150 cm^{-1} , respectively [29]. The positions and numbers of absorption bands indicate a marked decrease in both the C–O bond order and the symmetry of the triatomic species upon complexation.

Carbon dioxide binds to metal ions in different coordination modes [30]. The coordination modes for a monomeric 1:1 complex are shown in (Fig. 5). The position of the C–O stretching band is sensitive to the coordination mode. For η^1 -C coordination the symmetric stretching band occurs in the range 1600–1750 cm^{-1} and for η^2 -coordination this band is observed below 1600 cm^{-1} [25,31]. The difference between ($\nu_3 - \nu_1$) for η^1 -C coordination is $\leq 400 \text{ cm}^{-1}$. While in case of η^2 -(C, O) coordination this difference is $>500 \text{ cm}^{-1}$. Further, for pentacoordinated complexes ($\nu_3 - \nu_1$) is little greater than 400 cm^{-1} while for the hexacoordinated complexes this difference is $\leq 300 \text{ cm}^{-1}$.

Based on this, we may conclude that Cu–cyclen complexes (showing ν_3 and ν_1 IR bands at 1716 and 1225 cm^{-1} , respectively) form a pentacoordinated structure and η^1 -C type CO₂ coordination. It may be noted that Co-tetraaza macrocycles [25] and Schiff bases [32] form similar η^1 -CO₂ complexes and show IR bands at around 1702 and 1217 cm^{-1} .

CO₂ has two sets of π molecular orbitals which are orthogonal [29]. For η^1 and η^2 bonding involving carbon and a metal, these are in two sets: (a) the π , $n\pi$ and π^* molecular orbitals which lie in the plane of metal and CO₂ (parallel), and (b) an equivalent set which is in a plane perpendicular to the first set (perpendicular). The parallel molecular orbitals are the most important in bonding to transition metal. In qualitative terms, for the η^1 -C mode of CO₂ coordination the charge transfer interaction between a filled d_{z^2} metal orbital and the empty π^* orbital of CO₂ is strong. In contrast, for η^2 coordination, the charge transfer transition is not that strong. This coordination has a σ bonding involving the π orbital of CO₂ and an empty d_{z^2} metal orbital together with π -bonding involving a filled d_{xz} metal orbital and the empty π^* orbital of CO₂. Cu²⁺ species having a filled d_{z^2} orbital would form the former type of CO₂ coordination and exhibit distinct charge transfer band in the UV–vis spectrum. The metal to ligand charge transfer transition observed at 415 nm confirms the η^1 coordination for CO₂ in Cu–cyclen complexes in agreement with the FT-IR results. The shift in the charge transfer band position from 415 to 409 nm in Cu–phen and Cu–bipy complexes is perhaps due to weaker CO₂ coordination. It may be noted that Ag(CO₂) system shows charge transfer bands at around 400 nm [26].

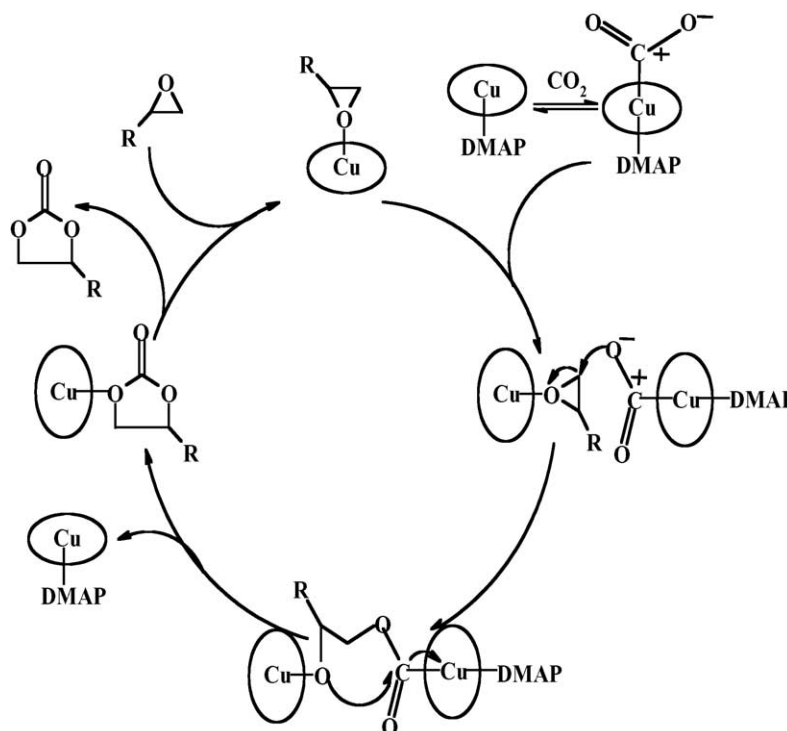


Fig. 6. Possible reaction mechanism for cyclic carbonate synthesis.

The EPR studies suggest that CO₂ coordination influences the geometry as well as ligand field strength at the site of Cu. The higher *g*-value (*g*|| = 2.252) is consistent with a penta-coordinated geometry of Cu. Lower Cu hyperfine constant (*A*||^{Cu} = 155–165 G) indicates more delocalization of the electron density onto the ligand/CO₂ orbitals. These results from EPR agree well with those of FT-IR and UV–vis studies. By and large, the spectral investigations have provided evidence for the formation of Cu²⁺–CO₂ complexes, an activated intermediate in the cyclic carbonate synthesis.

The complexes under study are also known to activate epoxide and facilitate ring opening [33]. Based on these experimental evidences a tentative mechanism is proposed in Fig. 6 which is similar to that reported for Cr(III) salen complexes [15a]. Accordingly, the Cu complex activates the epoxides and the Cu–DMAP system activates CO₂. The activated CO₂ complex then attacks the activated epoxide at the less hindered carbon leading to formation of a dimeric intermediate species which eventually yields the cyclic carbonate. The differences in catalytic activity of Cu complexes (Table 1) can be explained based on the mode of CO₂ coordination. As discussed above, activation of reactants is a crucial step in CO₂ fixation. The metal–substrate bonding should be optimal. Metal complexes with unsaturated aza ligands (PC and TPP) provide optimal bonding and enable higher yields of cyclic carbonate. In contrast, the complexes with acyclic ligands (phen and bipy) form weaker metal–CO₂ bonds and result in lower catalytic activity. Methyl substitution on cyclen results in more stable metal–CO₂ complexes which are less reactive giving lower yields of product carbonate. In other words, the metal–CO₂/epoxide bonding should neither be too strong nor too weak. By a suitable fine-tuning of the ligand system it is possible to develop a highly active catalyst.

4. Conclusions

The catalytic activities of several Cu and Mn complexes with cyclic and acyclic ligands for cyclic carbonate synthesis from CO₂ and epoxides have been reported. The nature of the ligand system, substituents, central metal ion and coordination geometry influence the catalytic activity. Cu complexes with macrocyclic unsaturated ligands were found to be more active than those with acyclic ligands. Activation of CO₂ by metal complexes has been investigated by FT-IR, UV–vis and EPR spectroscopies. Copper forms activated complexes with η¹-type coordination for CO₂. The differences in catalytic activity of metal complexes are correlated with the differences in the mode of CO₂ coordination.

Acknowledgements

D.S. thanks Department of Science and Technology (DST) and Council of Scientific and Industrial Research (CSIR),

New Delhi for financial support. R.S. acknowledges CSIR, New Delhi for the award of senior research fellowship.

References

- [1] A. Arakawa, M. Aresta, J.N. Armor, M.A. Barteau, E.A. Beckman, A.T. Bell, J.E. Bercaw, C. Creutz, E. Dinjus, D.A. Dixon, K. Domen, D.L. Dubois, J. Eckert, E. Fujita, D.H. Gibson, W.A. Goddard, D.W. Goodman, J. Keller, G.J. Kubas, H.H. Kung, J.E. Lyons, L.E. Manzer, T.J. Marks, K. Morokuma, K.M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielsen, W.M.H. Sachtler, L.D. Schmidt, A. Sen, G.A. Somorjai, P.C. Stair, B.R. Stults, W. Tumas, *Chem. Rev.* 101 (2001) 953.
- [2] P.T. Anastas, T.C. Williamson (Eds.), *Green Chemistry: Frontiers in Benign Chemical Syntheses and Processes*, Oxford University Press, New York, 1998.
- [3] A. Behr, *Carbon dioxide Activation by Metal Complexes*, VCH, Weinheim, 1988.
- [4] W.N. Ayers, *Catalytic activation of carbon dioxide*, ACS symposium series 363, American Chemical Society, Washington DC, 1988.
- [5] D.J. Darensbourg, R.M. Mackiewicz, A.L. Phelps, D.R. Billodeaux, *Acc. Chem. Res.* (2004), doi:10.1021/ar030240u.
- [6] S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa, S. Konno, *Green Chem.* 5 (2003) 497.
- [7] E.J. Beckman, *Science* 283 (1999) 946.
- [8] S. Inoue, H. Koinuma, T. Tsuruta, *Polym. Lett.* 7 (1969) 287.
- [9] M.S. Super, E.J. Beckman, *Trends Polym. Sci.* 5 (1997) 236.
- [10] D.J. Darensbourg, M.W. Holtcamp, *Coord. Chem. Rev.* 153 (1996) 155.
- [11] (a) R. Srivastava, D. Srinivas, P. Ratnasamy, *Catal. Lett.* 89 (2003) 81;
(b) R. Srivastava, D. Srinivas, P. Ratnasamy, *Catal. Lett.* 91 (2003) 133;
(c) R. Srivastava, D. Srinivas, P. Ratnasamy, Recent advances in the science and technology of zeolites and related materials, in: E.W.J. van Steen, L.H. Callanan, M. Claeys, C.T. O'Connor (Eds.), *Proceeding of the 14th International Zeolite Conference*, Cape Town, South Africa, 24–30 April 2004, Elsevier, Amsterdam, The Netherlands, 2004, pp. 2703–2710.
- [12] *Filtration Industry Analyst*, June 1999 (issue No. 27), p. 2.
- [13] (a) T. Aida, M. Ishikawa, S. Inoue, *Macromolecules* 19 (1986) 8;
(b) T. Aida, S. Inoue, *J. Am. Chem. Soc.* 105 (1983) 1304;
(c) S. Mang, A.I. Cooper, M.E. Colclough, N. Chauhan, A.B. Holmes, *Macromolecules* 33 (2000) 303;
(d) L.M. Stamp, S.A. Mang, A.B. Holmes, K.A. Knights, Y.R. de Miguel, I.F. McConvey, *Chem. Commun.* (2001) 2502;
(e) W.J. Kruper, D.V. Dellar, *J. Org. Chem.* 60 (1995) 725;
(f) R.L. Paddock, Y. Hiyama, J.M. McKay, S.T. Nguyen, *Tetrahedron Lett.* 9 (2004) 2023;
(g) J. Qin, C.M. Thomas, S. Lee, G.W. Coates, *Angew. Chem. Int. Ed. Engl.* 42 (2003) 5484.
- [14] (a) X.-B. Lu, H. Wang, R. He, *J. Mol. Catal. A: Chem.* 186 (2002) 33;
(b) D. Ji, X. Lu, R. He, *Appl. Catal. A: General* 203 (2000) 329;
(c) K. Kasuga, T. Kato, N. Kabata, M. Handa, *Bull. Chem. Soc. Jpn.* 69 (1996) 2885.
- [15] (a) R.L. Paddock, S.T. Nguyen, *J. Am. Chem. Soc.* 123 (2001) 11498;
(b) D.J. Darensbourg, J.C. Yarbrough, *J. Am. Chem. Soc.* 124 (2002) 6335;
(c) X.-B. Lu, Y. Wang, *Angew. Chem. Int. Ed. Engl.* 43 (2004) 3574.
- [16] J. Costamagna, G. Ferraudi, J. Canales, J. Vargas, *Cood. Chem. Rev.* 148 (1996) 221.

- [17] L.J. Farrugia, S. Lopinski, P.A. Lovatt, R.D. Peacock, *Inorg. Chem.* 40 (2001) 558.
- [18] (a) M. Belley, J.P. Collin, R. Ruppert, J.P. Sauvage, *J. Chem. Soc. Chem. Commun.* (1984) 1315;
(b) M. Belley, J.P. Collin, R. Ruppert, J.P. Sauvage, *J. Am. Chem. Soc.* 108 (1986) 7461.
- [19] H. Masuda, N. Fukushima, H. Einaga, *Bull. Chem. Soc. Jpn.* 66 (1993) 3643.
- [20] A.D. Adler, F.R. Long, F. Kampas, J. Kim, *J. Inorg. Nucl. Chem.* 32 (1970) 2443.
- [21] M.M. Bhadbhade, D. Srinivas, *Inorg. Chem.* 32 (1993) 5458.
- [22] E. Suresh, M.M. Bhadbhade, D. Srinivas, *Polyhedron* 15 (1996) 4133.
- [23] K.J. Catalan, S. Jackson, J.D. Zubkowske, D.L. Perry, E.J. Valente, L.A. Feliu, A. Polanco, *Polyhedron* 14 (1995) 2165.
- [24] T.H. Bennur, D. Srinivas, S. Sivasanker, *J. Mol. Catal. A: Chem.* 207 (2004) 163.
- [25] E. Fujita, C. Creutz, N. Sutin, B.S. Brunshwig, *Inorg. Chem.* 32 (1993) 2657.
- [26] G.A. Ozin, H. Huber, D. McIntosh, *Inorg. Chem.* 17 (1978) 1472.
- [27] B.J. Hathaway, in: G. Wilkinson, R.D. Gillard, J.A. McCleverty (Eds.), *Comprehensive Coordination Chemistry*, 5, Pergamon press, Oxford, 1987, p. 558, Chapter 53.
- [28] K. Nakamoto, *Infrared and Raman Spectra*, 4th ed., Wiley, New York, 1986, p. 230.
- [29] (a) W. Leitner, *Coord. Chem. Rev.* 153 (1996) 257;
(b) D.H. Gibson, *Coord. Chem. Rev.* 185/186 (1999) 335.
- [30] X. Yin, J.R. Moss, *Coord. Chem. Rev.* 181 (1999) 27.
- [31] (a) C. Jegat, M. Fouassier, J. Mascetti, *Inorg. Chem.* 30 (1991) 1521;
(b) C. Jegat, M. Fouassier, M. Tranquille, J. Mascetti, *Inorg. Chem.* 30 (1991) 1529.
- [32] S. Gambarotta, F. Arena, C. Floriani, P.F. Zanazzi, *J. Am. Chem. Soc.* 104 (1982) 5082.
- [33] K.B. Hansen, J.L. Leighton, E.N. Jacobsen, *J. Am. Chem. Soc.* 118 (1996) 10924.