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

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Abstract

The catalytic activities of several Cu and Mn aza complexes for cyclic carbonate synthesis from CO_2 and epoxides are reported. The various factors affecting activation of CO_2 by metal complexes and its utilization in cyclic carbonate synthesis have been investigated. FT-IR, UV–vis and EPR spectroscopic investigations reveal that CO_2 coordinates to Cu in η^1–C mode of coordination. Nature of the ligand and substitution influence the lability of metal–CO_2 bonding. The differences in the catalytic activities are correlated with the mode and strength of CO_2 binding.

Keywords: Carbon dioxide; Cyclic carbonates; Polycarbonates; CO_2 fixation; CO_2 activation; CO_2 utilization; Catalysis by Cu and Mn complexes; Benign synthesis; Spectroscopy

1. Introduction

Utilization of CO_2 as C_1-feedstock in chemicals and fuels synthesis is of great interest [1–4]. The coupling of CO_2 with epoxides yielding cyclic and polycarbonates (Scheme 1) is one of the most efficient ways of CO_2 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 complexes 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/co-catalysts [13–15]. We report here the application of cyclen complexes (Fig. 1) in this reaction.

Activation of CO_2 is the key step for its further participation in the cycloaddition reaction. CO_2 coordinates to metal ions in different coordination modes. The strength and lability of metal–CO_2 bond and the mode of coordination control the reactivity in different CO_2 fixation reactions. Peraza macrocycles have been known for CO_2 activation [16]. The Cu complex of *N*,*N*',*N*″-triallyl-1,4,7-triazacyclononane reductively couples two CO_2 molecules yielding the oxalate anion ($C_2O_4^{2-}$) [17]. Ni-cyclam was an efficient and selective catalyst for electroreduction of CO_2 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-

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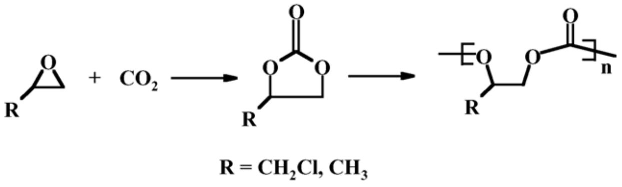

Scheme 1.

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

$Cu(NO_3)_2·2.5H_2O$, $Cu(CH_3COO)_2·H_2O$ 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], $Cu(H_2O)(phenanthroline)_2(NO_3)_2$ (Cu(phen)) [23], $Cu(NO_3)(bipyridine)_2(H_2O)(NO_3)$ (Cu(bipy)) [23], $[Cu(cyclen)(NO_2)]ClO_4$ (Cu(cyclen)) [24] and $[Cu(Me_4cyclen)(CH_3CN)](ClO_4)_2$ (($Cu(Me_4cyclen)$) [24] were prepared by the known procedures. The analogous Mn(cyclen) and $Mn(Me_4cyclen)$ 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)

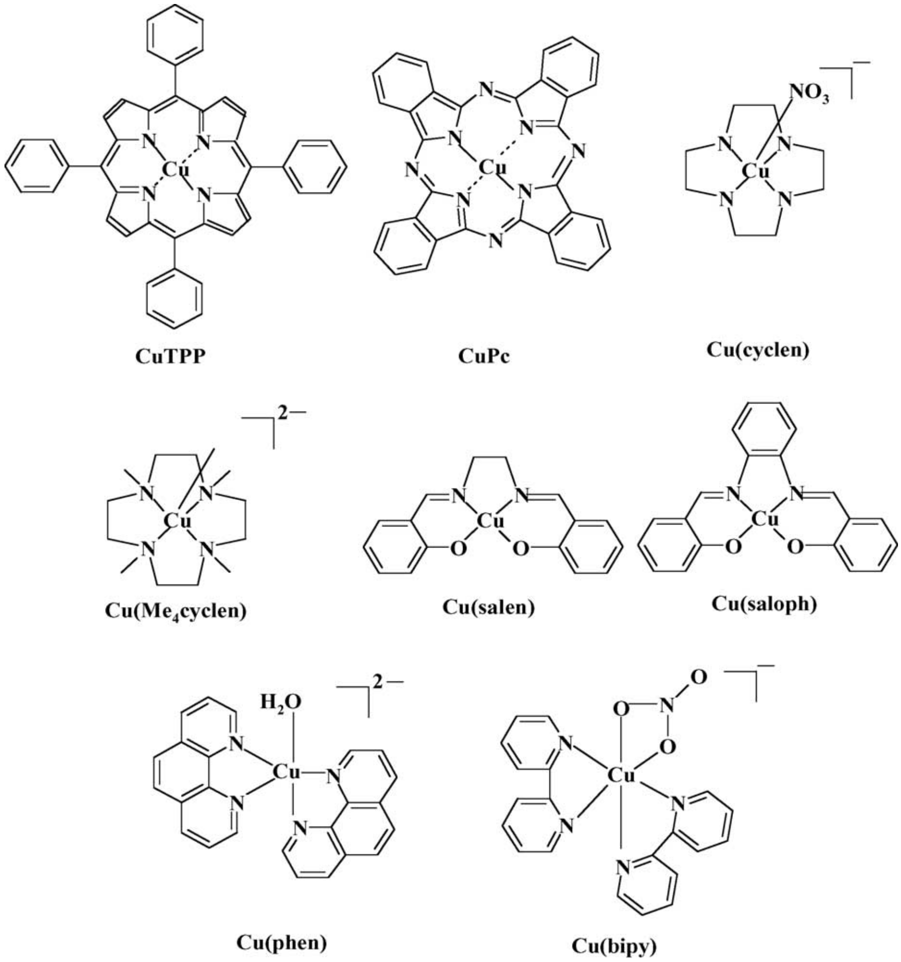

Fig. 1. Structures of metal complexes investigated in the present study.