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REVIEW ARTICLE

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Fixation and sequestration of carbon dioxide by copper(II) complexes

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Abstract. The fixation of carbon dioxide (CO_2) is an important global challenge. A significant increase of the atmospheric CO_2 due to the industrial emissions and a steady increase in combustion of fossil fuels is a widespread environmental concern. This article is a short literature review on the recent developments in the field of CO_2 activation and fixation by bioinspired copper(II) catalysts. In our laboratory, copper(II) complexes of bidentate ligands have been reported as catalysts for the fixation of CO_2. The molecular structure of one of the complexes has shown unusual trigonal bipyramid geometry (τ, 0.936) by the coordination of two ligand units and a water molecule. All the complexes exhibited a well-defined Cu(II)/Cu(I) redox potentials around 0.352 to 0.401 V in acetonitrile. The rhombic EPR spectra of the complexes indicate the existence of a geometrical equilibrium between trigonal bipyramidal and square pyramidal at 70 K. The d-d transitions around 750–800 and 930–955 nm further supports five coordination geometry in solution. These copper(II) complexes have successfully fixed atmospheric CO_2 as CO_3^{2-} by using Et_3N as sacrificial reducing agent and afforded $[Cu(L)CO_3(H_2O)]$. The CO_3^{2-} bound complex has shown a distorted square pyramidal geometry (τ, 0.369) around copper(II) center *via* the coordination of only one ligand unit, a carbonate, and water molecules. The catalysts are active enough to fix CO_2 for eight repeating cycles without any change in the efficiency. The fixation of CO_2 possibly proceeds *via* the formation of Cu(I)-species. This is supported by X-ray structure, which reveals distorted tetrahedral geometry by the coordination of two units of ligand.

Keywords. Carbon dioxide fixation; sequestration; copper(II)complexes; catalysis – reaction mechanism.

1. Introduction

Carbon dioxide (CO_2) is one of the main greenhouse gases causing global warming and climate change. The atmospheric CO_2 concentration is steadily increasing due to industrial emissions and prodigious usage of fossil fuels.[1–3] These result in the continuous rise of the global average temperature. In recent years, capture of CO_2 and carbon recycling have gained great attention as they could help in carbon recycling, thereby mimicking Nature that makes thousands of compounds from atmospheric CO_2.[4,5] Alternatively, great efforts are made to develop techniques for carbon capture and storage (CCS) to fix atmospheric CO_2 and store in a supercritical state.[6] Another rational approach is to utilize CO_2 as C1-building block for synthesizing valuable organic compounds due to the low cost and nontoxicity of CO_2.[1–3,7–9] However, the utilization of carbon dioxide is challenging, as it is a non-polar linear molecule containing carbon in higher oxidation state. It is thermodynamically stable with a short C=O bond distance 1.16 Å.[10] So far, four major methods such as chemical,[1,3,7–9] photochemical,[11] electrochemical[11–13] and enzymatic methods[7–9,14] are exploited to catalyze the CO_2 fixation/conversion. In the first three methods, the low selectivity is often reported due to the stable form of the carbon in the CO_2 molecule and it is energetically challenging to acquire high catalytic performances.[1,3,7–14] The enzymatic method provides an eco-friendly and promising way for efficient CO_2 fixation/conversion through superior stereo-specificity and regio/chemo-selectivity.[13,15–18] The metalloenzyme carbon monoxide
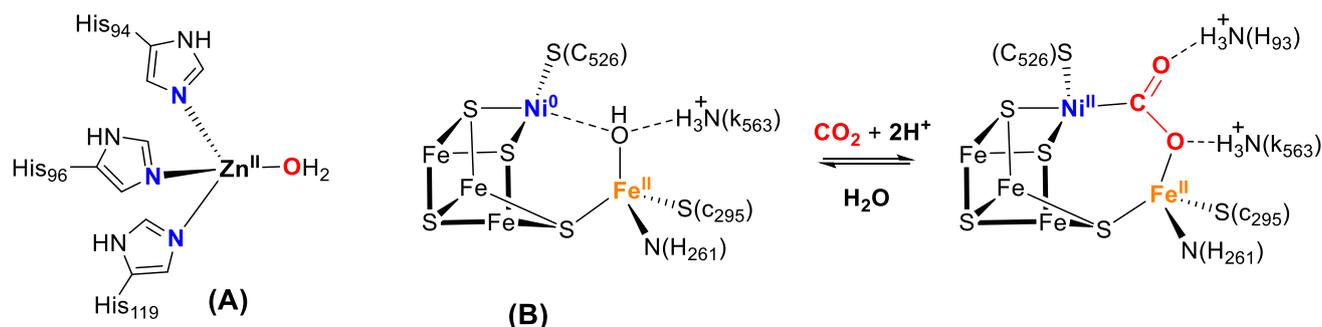
Scheme 1.   The active site of carbonic anhydrase enzyme (A) and carbon monoxide dehydrogenase (B).

dehydrogenase (CODH) is capable of performing both CO_2 to CO reduction and CO to CO_2 oxidation. The [Ni-4Fe-4S] core adopted by CODH active site to handle this redox-mediated interconversion.[19] The zinc(II) containing carbonic anhydrase enzyme catalyzes CO_2 to CO_3^{2-} conversion *via* non-redox pathway at pH of 7.0 and D-ribulose-1,5-bisphosphate carboxylase/oxygenase in the photosystem II is known to play crucial roles in the fixation and activation of CO_2 (Scheme 1).[20–27]

The current state of the work in this field has been well summarized in a few reviews giving wider perspective.[28–32] Kitajima and co-workers reported the hydroxo complexes of a divalent metal (Mn, Fe, Co, Ni, Cu, and Zn) using hindered tris(pyrazoly1)borate ligand (hydrotris(3,5-diisopropyl-1-pyrazolyl)-borate). The reactivities of the hydroxo complexes towards CO_2 fixation are reported in the order of Zn^{2+} > Cu^{2+} > Ni^{2+} = Co^{2+} > Mn^{2+} > Fe^{2+}.[33] But only a few attempts have been made for CO_2 activation and fixation using ecologically viable copper catalysts. In the present review, we briefly discussed the salient features of previous reports and our very recent findings[34] in CO_2 fixation by using copper catalysts. In our work, we have isolated mononuclear copper(II) complexes of simple bidentate ligands. The steric and electronic influence of the ligand nitrogen donor set on the spectral and redox behavior and CO_2 fixation reactions have been probed. The X-ray crystal structures of one of the complexes, a key Cu(I) intermediate, and product-bound complexes have been determined.[34]
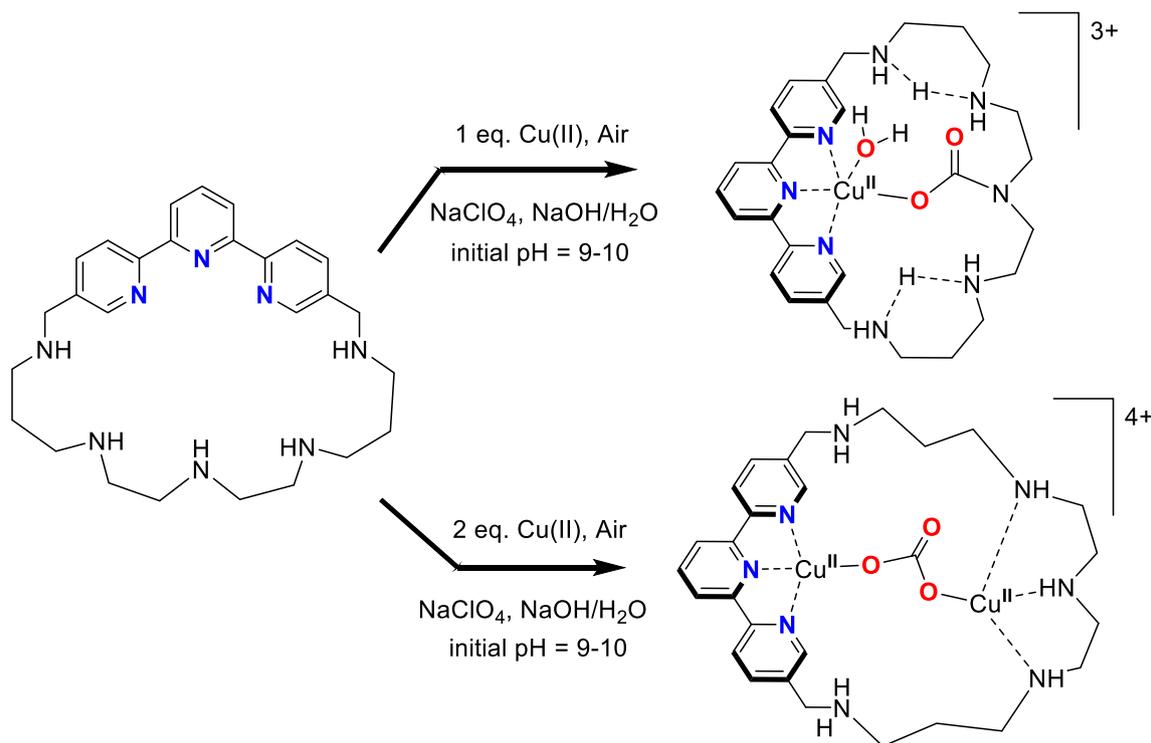
2.   Fixation of CO_2 to CO_3^{2-}

In 2004, Garcıa-Espanaa and co-workers showed the fixation of CO_2 into carbonate by using copper(II) complexes of a terpyridinophane aza receptor at pH, 9–10.[35] The *in situ* generated mononuclear copper(II) complex afforded carbamate-bound complexes. On the other hand, *in situ*

generated dinuclear complex catalyzed the formation of carbonate-bound complexes (Scheme 2).[35] The carbamate and bicarbonate are coordinated to copper center as bridging ligands within the hydrophobic macrocyclic cavity. However, the copper(II) complexes of ligands containing the same polyamine bridge but pyridine or phenanthroline spacers fail to show fixation of CO_2 under identical conditions.

Comba and coworkers have reported the dicopper(II) complexes of pseudo-octapeptides, synthetic analogs of ascidiacyclamide and the patellamide ligands as the copper-containing carbonic anhydrase models.[36] The ascidiacyclamide and the patellamides are found in ascidians of the Pacific and Indian Oceans. These complexes are projected as an efficient model for carbonic anhydrase with k_{cat} up to 7.3×10^3 s^{-1} and a turnover number (TON) of at least 1700, which is closer to the enzyme-catalyzed reaction (k_{cat}, 2×10^5– 1.4×10^6 s^{-1}). The k_{cat} depends on the configuration of the isopropyl side chains of the pseudo-octapeptide scaffold, and the naturally observed R*,S*,R*,S* geometry is revealed as more efficient than the S*,S*,S*,S* catalyst isomers. The heterocyclic donor groups of the pseudo-octapeptides vary the catalytic efficiency of the complexes. The dicopper(II) complex of the ligand with four imidazole groups is a more efficient catalyst than that of the close analog of ascidiacyclamide with two thiazole and two oxazoline rings. The conversion of CO_2 into CO_3^{2-} proceeded via nucleophilic attack of a Cu(II)-coordinated hydroxide as similar to Zn(II) containing carbonic anhydrase enzymes. They observed that the formation of the catalyst-CO_2 adduct and release of carbonate/bicarbonate are relatively fast processes (Scheme 3).[36]

Mautner and co-workers have synthesized two carbanato-bridged copper(II) complexes [Cu$_3$(dmMePEA)$_3$(μ_3-CO$_3$) (ClO$_4$)$_3$]ClO$_4$ and Cu$_2$(iptren)$_2$(μ_3-CO$_3$)](ClO$_4$)$_2$·H$_2$O from Cu(ClO$_4$)$_2$ and a polydentate amine ligand, dmMePEA = N-((4-methoxy-3,5-dimethylpyridin-2-yl)methyl)-N-methyl-2-(pyridin-2-yl)ethan-1-amine and iptren = N$'$-isopropyl-N$''$, N$''$-bis(2-(isopropylamino)ethyl)-ethane-1,2-diamine. The CO_3^{2-} is formed from the atmospheric CO_2 under slightly basic methanol solution. The various coordination modes of CO_3^{2-} ion and magnetic properties were reported.[37] However, these reports fail to explain the mechanism of CO_2 fixation and employed alkaline pH.

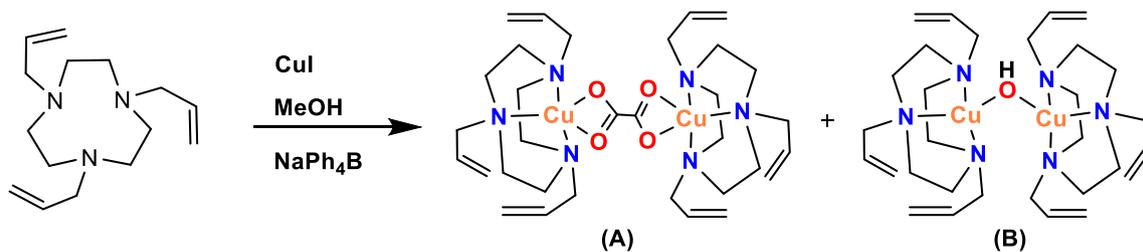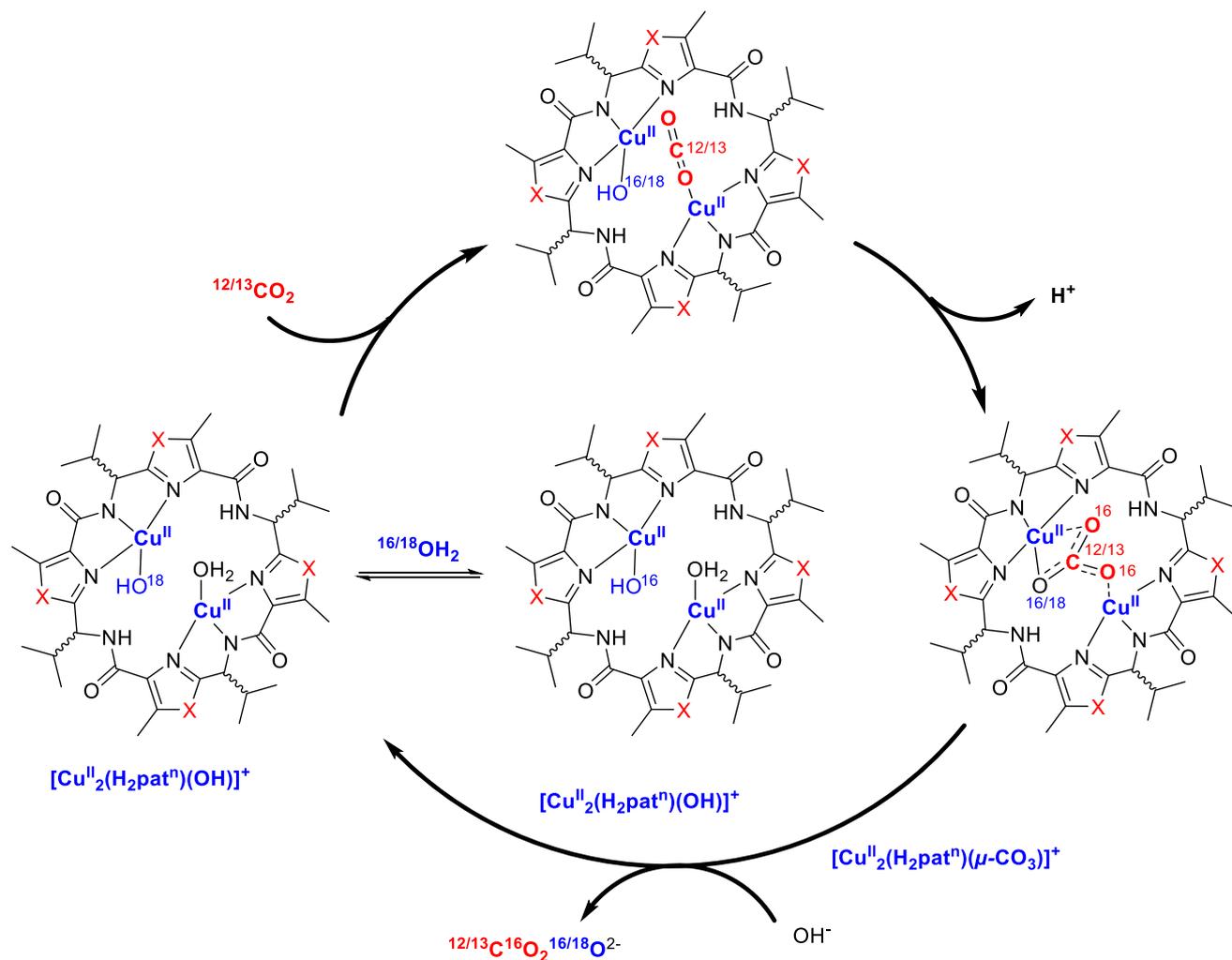**Scheme 2.** Fixation of CO_2 as carbomate and carbonate.

3. Fixation of CO_2 to $C_2O_4^{2-}$

In 2001, Peacock and co-workers reported the first example of CO_2 reduction into oxalate catalyzed by copper(II) complex of N, N', N''-triallyl-1,4,7-triazacyclononane and isolated $[LCu(\mu\text{-}C_2O_4)CuL][Ph_4B]_2$ as a byproduct while synthesizing $[LCu(\mu\text{-}OH)CuL]$ $(BPh_4)_2$ by aerial oxidation.[38] The structure of $[LCu(\mu\text{-}C_2O_4)CuL][Ph_4B]_2$ and its formation are further established using $CsHCO_3$. The oxalate formation is proposed to proceeds *via* the intermediate $[LCu^{II}(HCO_3^{\bullet-})]^+$ triggered by internal electron transfer (Scheme 4). Later in 2010, Bouwman and co-workers have impressively shown the electrocatalytic conversion of CO_2 into oxalate. It is catalyzed by a pre-organized dinuclear copper complex of disulfide ligand of [N-(2-mercaptopropyl)-N, N-bis(2-pyridylmethyl)amine.[39]

The reduction of the binuclear Cu(II) complex and subsequent activation of CO_2 resulted in the formation of bis(oxalate)-bound tetranuclear Cu(II) complex. The oxalate ligands are coordinated to copper(II) centers *via* head-to-head bridging. The coordinated oxalate is electrocatalytically released as insoluble $Li_2C_2O_4$ by the reaction of supporting electrolyte used ($LiClO_4$) and regenerated the original copper(II) complexes in acetonitrile (Scheme 5). The catalytic turnover has been achieved by applying the potential of -0.03 V vs NHE which facilitates the reduction of Cu(II) to

Cu(I) followed by CO_2 fixation. This potential is almost 2 V less negative than that required for the outer-sphere reduction of CO_2 to CO but closer to that for oxalate (0.39 V). The Cu(I) complex is selectively oxidized by CO_2 rather than O_2 as it offers a low-energy pathway to the formation of the metal bound CO_2 radical anion and then dimerized to generate the thermodynamically-favored oxalate bound complex. Maverick and co-workers reported macrocyclic complexes $[Cu_2(m\text{-}xpt)_2X_2](PF_6)_2$ (X = Cl^-, NO_3^-) that facilitated a CO_2 reduction in presence of sodium ascorbate in dimethylformamide (DMF).[40] The m-xylene spacer is used to connect two pyridyltriazole chelating units of ligand. A single complex molecule has used for reductive coupling of CO_2 instead of two molecules of binuclear Cu(I) complex used in Bouwman's studies. The binuclear complex $[Cu_2(m\text{-}xpt)_2X_2](PF_6)_2$ selectively captures CO_2 from the air and reduces it to generate oxalate and coordinated as an oxalate-bridge (Scheme 6A).[40]

The oxalic acid is released by treating with dilute mineral acid, which regenerates the original copper complex. Fujisawa and co-workers have reported the conversion of CO_2 into oxalate by using copper(II) complexes of hydrotris(3,5-diisopropyl-1-pyrazolyl)borate anion and non-innocent ligand α-keto acid.[41] The α-ketocarboxylato copper(II) complex $[\{Cu(L)\}\{O_2CC(O)CH(CH_3)_2\}]$ is spontaneously converted into the

Scheme 3. CO_2 fixation by the copper(II) complexes of patellamides ligands.

Scheme 4. The fixation CO_2 as oxalate bridged copper(II) complex [LCu(μ-C_2O_4)CuL][Ph$_4$B]$_2$ (A) and [LCu(μ-OH)CuL](BPh$_4$)$_2$ (B).

binuclear oxalato copper(II) complex [{Cu(L)}$_2$(μ-C_2O_4)] upon exposure to O_2/CO_2 gas (Scheme 6B).[41] Additionally, the bicarbonato copper(I) complex and the α-ketocarboxylato copper(I) complex of the same ligand were spontaneously converted into the oxalato complex [{Cu(L1)}$_2$(μ-C_2O_4)] in Ar atmosphere and O_2 atmosphere, respectively. Alkaline workup of the oxalato copper(II) complex released sodium oxalate from the copper coordination sphere. The formation of the oxalate ion is promoted by decomposition of

the α-ketocarboxylate ligands presumably to a $CO_2^{\bullet-}$ radical anion that remained bound for coupling and *via* a side-on-coordinated oxalate ion. The conversion of copper(I) bicarbonate complex into oxalate is similar to that of Peacock's report.

4. Copper(II) complexes of bidentate ligands

We have an ongoing interest to develop copper complexes for CO_2 fixation and study its mechanism.
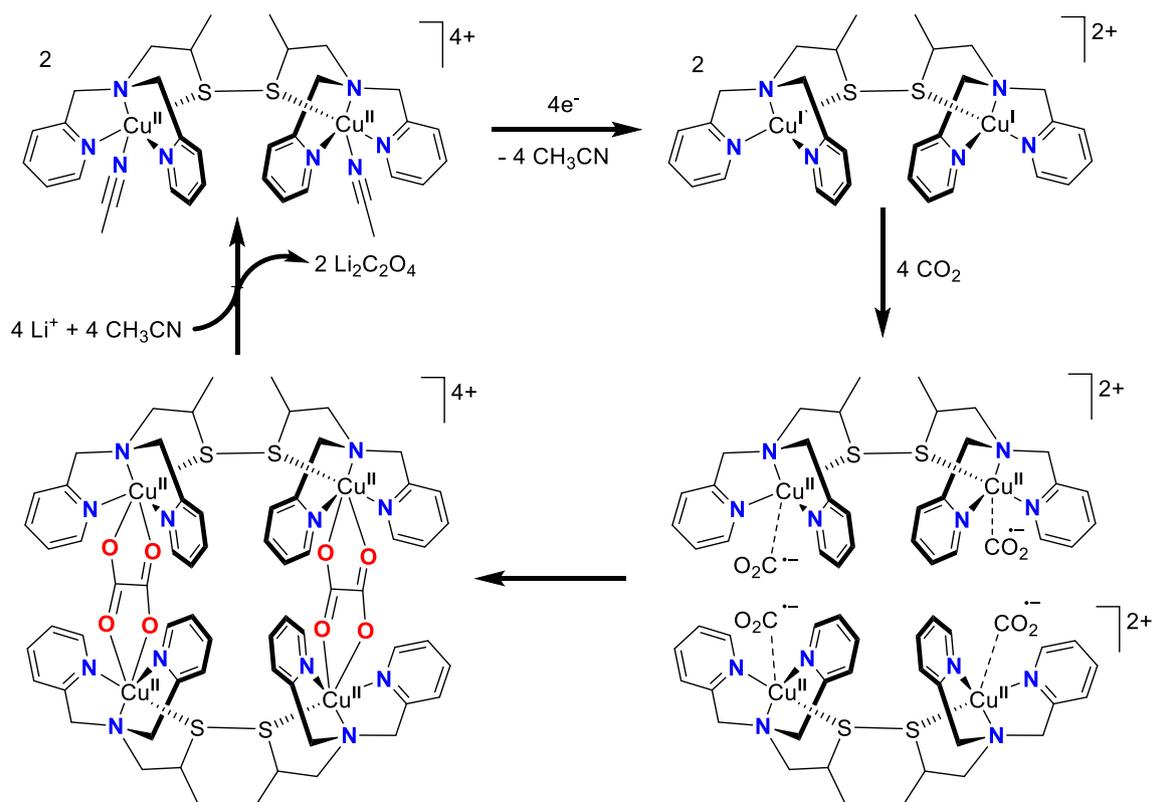
Scheme 5. Electrocatalytic reduction of CO_2 into oxalate by Cu(I) complex.
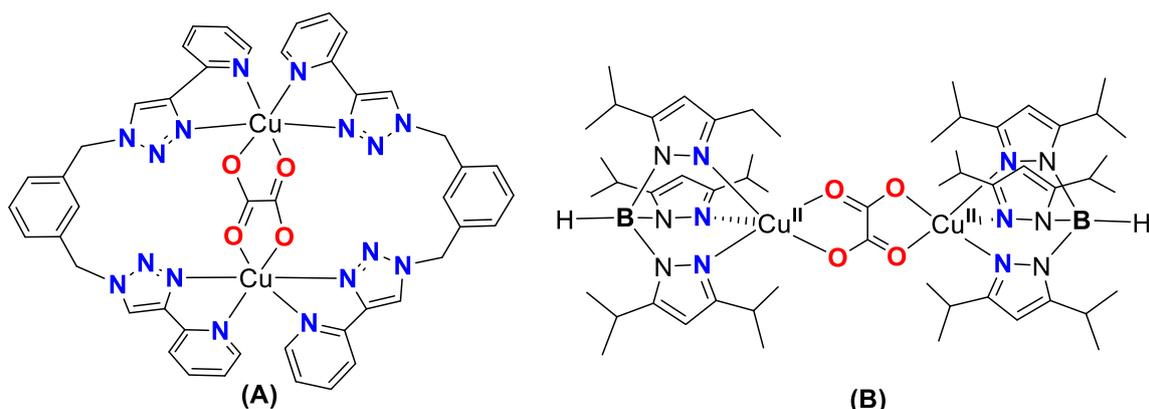
Scheme 6. Structure of oxalato copper(II) complexes of $m-$xpt ligands (A) and hydrotris(3,5-diisopropyl-1-pyrazolyl)borate (B).

Recently, we have reported simple copper(II) complexes $[Cu(L)_2(H_2O)](ClO_4)_2$, **1–5** (Scheme 7) of bidentate ligands (L1-L2). They were used as the catalyst for fixation of atmospheric CO_2 under mild conditions (Scheme 7).[34] The molecular structure of one of the complexes, complex bridged with CO_3^{2-} (originated from atmospheric CO_2) and key copper(I)-intermediate have been successfully characterized by single crystal X-ray study (Figure 1). The structure of **2** exhibits a trigonal bipyramid coordination geometry around copper(II) center, which is coordinated to nitrogens of two ligand units and one equatorially coordinated water molecule. The d-d bands around 750–800 nm ($d_{xz} \approx d_{yz} \rightarrow d_z^2$) and 930–955 nm ($d_{xy} \approx d_{x^2-y^2} \rightarrow d_z^2$) confirm the existence of five-coordinate geometry in acetonitrile solution, similar to solid state. The rhombic EPR splitting of g-values in x, y and z-axis indicate that the geometry is in between the trigonal bipyramidal and square pyramidal geometries with the ground state raised from a linear combination of $d_{x^2-y^2}$ and d_z^2 orbitals. All the complexes exhibited a well-defined Cu(II)/Cu(I) redox potentials around 0.352 to
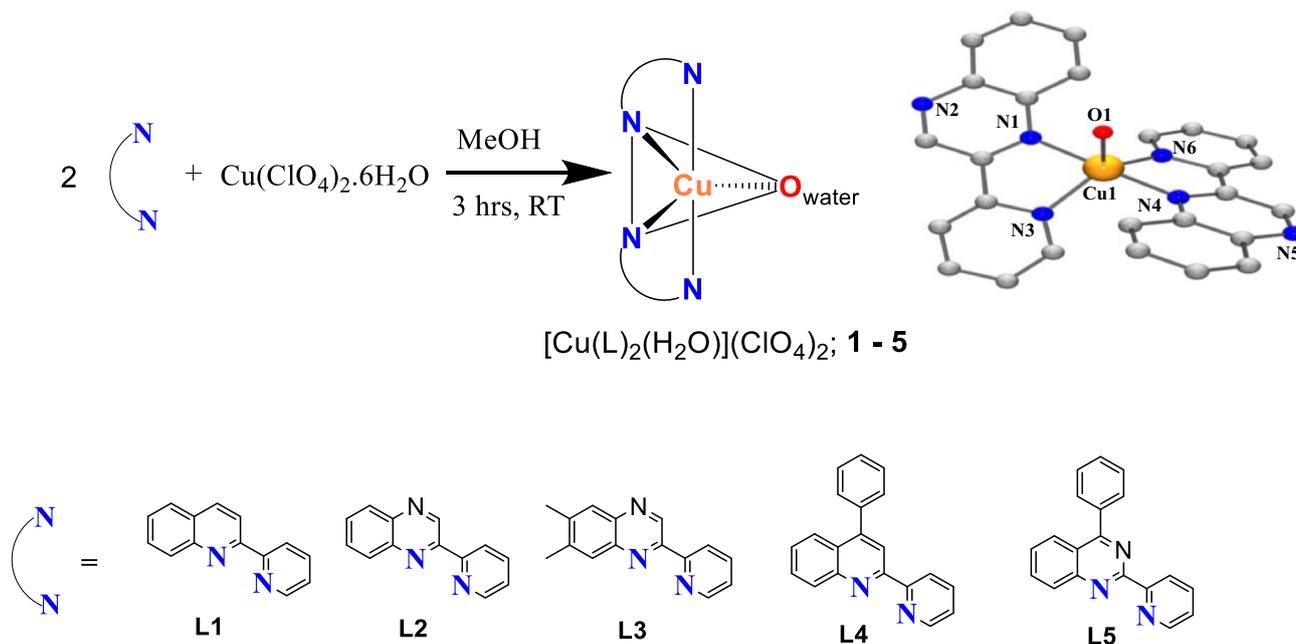
Scheme 7. Synthesis of Cu(II) complexes of bidentate ligands and the molecular structure of $[Cu(L2)_2(H_2O)](ClO_4)_2$ **2.**

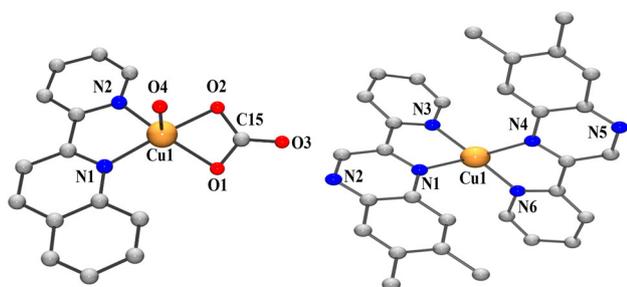**Figure 1.** The molecular structures of $[Cu(L1)(CO_3)(H_2O)]$ **1a** and Cu(I)-species $[Cu(L3)_2]ClO_4$ **3b**.

0.401 V Vs Ag/Ag$^+$. The fixation and kinetic studies have shown that atmospheric CO_2 fixation is simultaneous and selective over other atmospheric gases. Our ligand architecture, donor properties of the heterocyclic nitrogen donors provide important differences to other related previously reported catalysts. Further, our ligands are able to adopt preferable tetrahedral coordination geometry for key copper(I) intermediate to fix carbon dioxide (cf. below). To the best of our knowledge, our report is the novel example of copper(II) complexes based on bidentate ligands for simultaneous fixation and sequestration of atmospheric carbon dioxide under mild conditions.

4.1 *Carbon dioxide fixation and kinetic studies*

The CO_2 fixation reaction was catalyzed by **1–5** in acetonitrile at room temperature and Et$_3$N used as sacrificial reducing agent.[42,43] The complex **1** catalyzed fixation of atmospheric CO_2 and afforded a complex of blue color, $[Cu(L1)(CO_3)(H_2O)]$ (**1a**) with a yield of 29% in presence of one equivalent Et$_3$N. The efficiency of CO_2 fixation was enhanced and shown a yield of 74% while purging pure CO_2 gas under the identical conditions. **1a** has shown a new electronic absorption band at 614 nm (ε, 362 M^{-1} cm^{-1}) and IR stretching frequency at 1647 cm^{-1} for bound CO_3^{2-}. This CO_3^{2-} bound complex was successfully crystallized from the reaction mixture and its molecular structure shows distorted square pyramidal geometry (τ, 0.369) around copper(II) center *via* the coordination of only one ligand unit, a carbonate, and water molecules. One of the ligand units in the parent complex is replaced by more basic CO_3^{2-} ion (pK_a, 10.2), which is originated from CO_2. The addition of one equivalent of H$^+$ (HCl) to **1a** liberates HCO_3^- and regenerates **1**. This regeneration of **1** is well supported by the appearance of mass values m/z, 475.08 in ESI-MS and d-d transition band around 776 and 943 nm is similar to the spectral signatures of **1**. Further, **1a** exhibited less positive Cu(II)/Cu(I) redox potential (0.090 V) than that of **1** (0.390 V). This is possibly due to the coordination of better electron donor CO_3^{2-} anion, which increases the electron density around copper center as compared to the ligand L1. Similarly, the fixation of atmospheric CO_2 by using **2** with Et$_3$N yielded a blue color solid $[Cu(L2)(CO_3)(H_2O)]$ (**2a**) and the yield is almost identical (26%) to **1a** and increased to 73% on purging pure CO_2 gas under identical condition. The complex **3** afforded the highest amount of CO_2 fixation and yielded
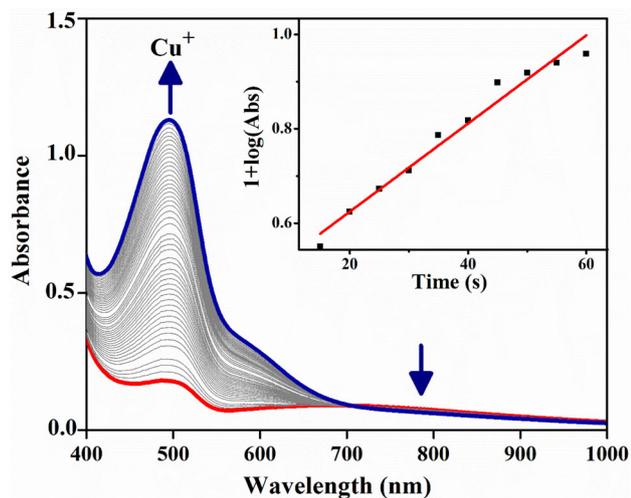
Figure 2. The kinetics of Cu(I)-species formation by the reaction of **1** (1×10^{-3} M) with one equivalent of Et$_3$N in acetonitrile at 25 °C. Inset: plot of $[1 + \log(\text{abs})]$ vs time.

$[\text{Cu(L3)(CO}_3)(\text{H}_2\text{O})]$ (**3a**) of 32% and 81% using atmosphere and pure CO_2, respectively. The complex **3** with electron donating methyl group offers more nucleophilic nature on the metal center and facilitates efficient CO_2 fixation. On the other hand, the phenyl substituted complexes **4** and **5** exhibited only decreased amounts of CO_3^{2-} bound complexes $[\text{Cu(L4)(CO}_3)(\text{H}_2\text{O})]$ (**4a**) and $[\text{Cu(L5)(CO}_3)(\text{H}_2\text{O})]$ (**5a**), respectively, from the atmosphere ($\sim$20%) and pure CO_2($\sim$66%) under identical conditions. The lower yield of **4a** and **5a** is possibly due to electron withdrawing nature of phenyl groups and that invariably decrease the nucleophilicity on metal center leads to less CO_2 fixation. Similar to **1a**, the Cu(II)/Cu(I) redox potential of **2a**–**5a** are less positive than those of their respective parent complexes. The IR stretching frequency for copper-bound CO_3^{2-} appeared almost in the same region at 1649 cm^{-1} for **3a**–**5a**, identical to **1a**.

The CO_2 fixation mechanism is possibly operating *via* copper(I) species followed by deprotonation of the coordinated water molecule. Then, CO_2 is activated through the nucleophilic attack as similar to the carbonic anhydrase enzyme.[21–24] The formation of copper(I) species is spectroscopically monitored by the absorption band around 450–500 nm. The complex **1** shows formation of copper(I) species with the rate (k_{obs}) of 9.35×10^{-3} s^{-1} (Figure 2) and this rate for **1** is almost identical to that of **2** (8.72×10^{-3} s^{-1}) and **3** (10.31×10^{-3} s^{-1}). A slight decrease in the rate of formation is observed for **4** (5.41×10^{-3} s^{-1}) and **5** (5.57×10^{-3} s^{-1}) due to steric hindrance offered by phenyl groups. Interestingly, the copper(I) species $[\text{Cu(L3)}_2]\text{ClO}_4$ (**3b**) of **3** has been crystallized from the reaction mixture. It adopted a distorted tetrahedral geometry by the coordination of two units of ligand L3 (Figure 1) and a

perchlorate anion in the outer coordination sphere. The reduced copper(I) species is nucleophilic in nature and subsequently reacts with CO_2 molecule and then finally yielded the corresponding CO_3^{2-} bound complex of type $[\text{Cu(L)(CO}_3)\text{H}_2\text{O}]$.

A completely distinct CO_3^{2-} to Cu(II) LMCT transition around 614–673 nm was observed for CO_3^{2-} bound complexes along with the disappearance of original d-d transitions. The treatment of CO_3^{2-} bound complexes with one equivalent of H$^+$ (HCl) resulted in regeneration of the respective parent copper(II) complexes by aerial oxidation[42,43] or possibly facilitated by H$^+$. The purging of CO_2 into this solution results in the formation of CO_3^{2-} bound complexes again. The catalysts were active up to eight consecutive cycles and a thereafter a slight decrease in efficiency was noted in every subsequent step. The blank reaction without catalyst showed no fixation of atmospheric or pure CO_2 under identical conditions. Also, no CO_2 fixation was observed while using copper(II) complexes without sacrificial reducing agent Et$_3$N. The Et$_3$N facilitates the one electron reduction of Cu(II) into Cu(I)-species[44,45] and subsequently CO_2 fixation. The involvement of Cu(I)-species in CO_2 fixation has been reported by Bouwman and co-workers[39] and Maverick co-workers.[40] However, interestingly, Comba and co-workers have reported the involvement of Cu(II)-species using patellamides ligands.[36] The analogs copper(II) complexes of 2,2′-bipyridine and 1,10-phenanthroline showed no concomitant CO_2 fixation from the atmosphere or pure CO_2 under identical conditions. Also, well-explored copper(II) complexes $[\text{Cu(BPMN)}](\text{ClO}_4)_2$ (BPMN = N, N'-bis(2-pyridylmethyl)-N, N'-dimethylethane-1,2-diamine), $[\text{Cu(}iso\text{-bpmen)}](\text{ClO}_4)_2$ (iso-bpmen = N, N-bis (2-pyridylmethyl)-N',N''-dimethylethane-1,2-diamine) exhibited no fixation of CO_2 under similar reaction conditions.

The CO_2 fixation mechanism possibly proceeds through the geometrical conversion from trigonal bipyramidal to flattened tetrahedral geometry during the reduction of copper(II) to copper(I) and then to square pyramidal geometry at the product formation stage (Scheme 8). These processes are accomplished with the loss of the water molecule and with slight changes in Cu-N bond distances and followed by the displacement of one of the ligand units by CO_3^{2-} ion. The ligand architecture, donor properties of the heterocyclic nitrogen donors and the enforced structures provide important differences to other catalysts reported. The ligands L1–L5 have the unique ability to provide a preferable tetrahedral coordination geometry for stabilization of key copper(I) intermediate and subsequent carbon dioxide fixation. The analogs copper(II) complexes
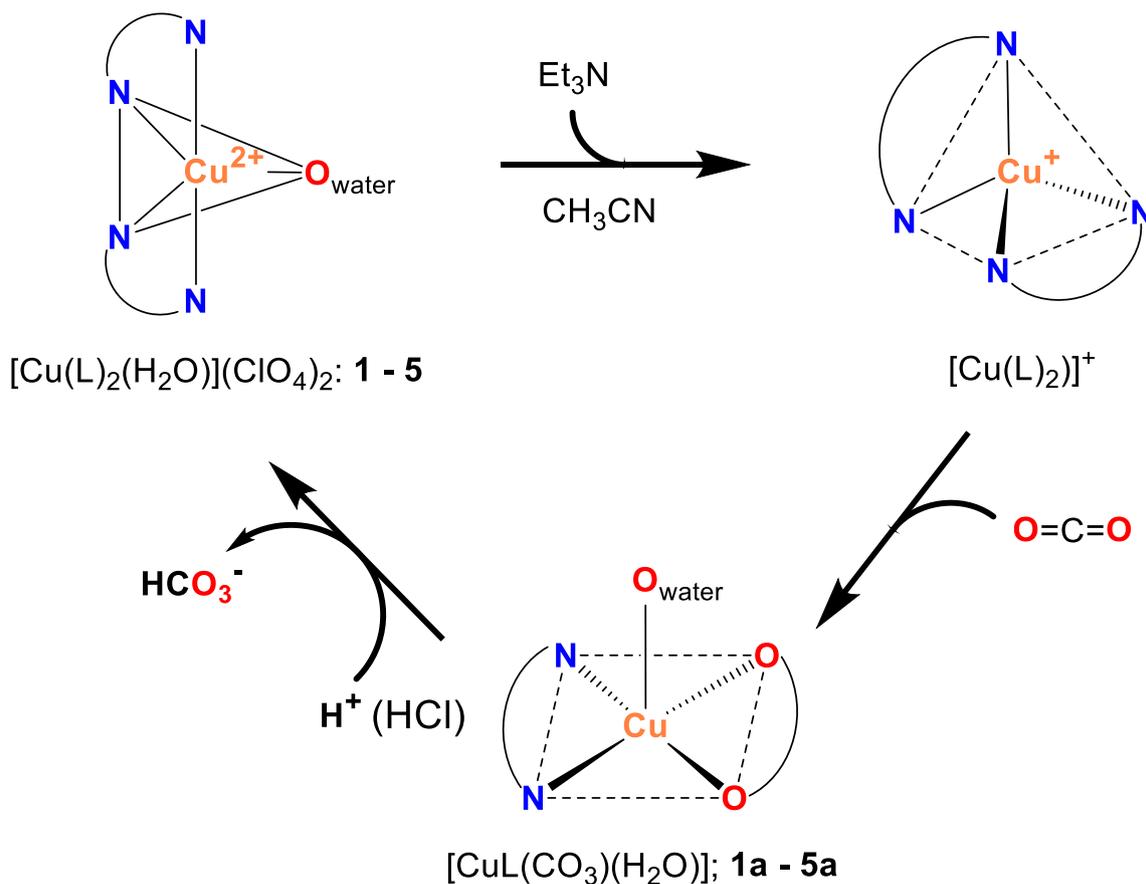
Scheme 8. Fixation of CO_2 by **1–5** and their catalytic cycle.

of 2,2′-bipyridine, 1,10-phenanthroline and relevant linear tetradentate N4 ligands were unable to stabilize copper(I)-species for carbon dioxide fixation from the atmosphere and commercial source under identical conditions.

5. Summary

In summary, previously reported copper(II) complexes mostly utilized polydentate macrocyclic and tripodal ligands, which facilitated the conversion of CO_2 into carbonate and oxalate *via* nucleophilic attack of a Cu-coordinated hydroxide and $CO_2^{\bullet-}$ radical anion, respectively. Our copper(II) complexes used only simple bidentate ligands and they catalyzed selective fixation of CO_2 from the atmosphere. The single crystal X-ray structure of one of the complexes showed an unusual trigonal bipyramid geometry around copper(II) center, coordinated to two ligand units and a water molecule. The complexes exhibited a well-defined Cu(II)/Cu(I) reduction potentials around 0.352 to 0.401 V, which are more positive than CO_2 reduction potential. The d-d transitions and unusual rhombic EPR spectra of the complexes reveal a geometry in between the trigonal bipyramidal and square pyramidal. Atmospheric CO_2 has been fixed as CO_3^{2-} selectively using Et_3N as a sacrificial reducing agent. One of the CO_3^{2-} bound complexes shows distorted square pyramidal geometry around copper(II) center *via* the coordination of only one ligand unit, a carbonate and water molecules. The fixation of CO_2 possibly proceeds via the copper(I) species, which is accomplished by the geometrical interconversions. One of the key copper(I) intermediate has been crystallized in distorted tetrahedral geometry by the coordination of two units of ligand. The bound carbonate was liberated as HCO_3^- by addition of H^+ and regenerated the parent complexes under N_2 atmosphere. The regenerated catalysts were active up to eight consecutive cycles. The catalytic and kinetic studies have shown that fixation of atmospheric CO_2 by the present complexes is selective and simultaneous over other atmospheric gases under mild conditions.

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