

Fixation and Sequestration of CO₂ by Ni(II) and Cu(II) Complexes

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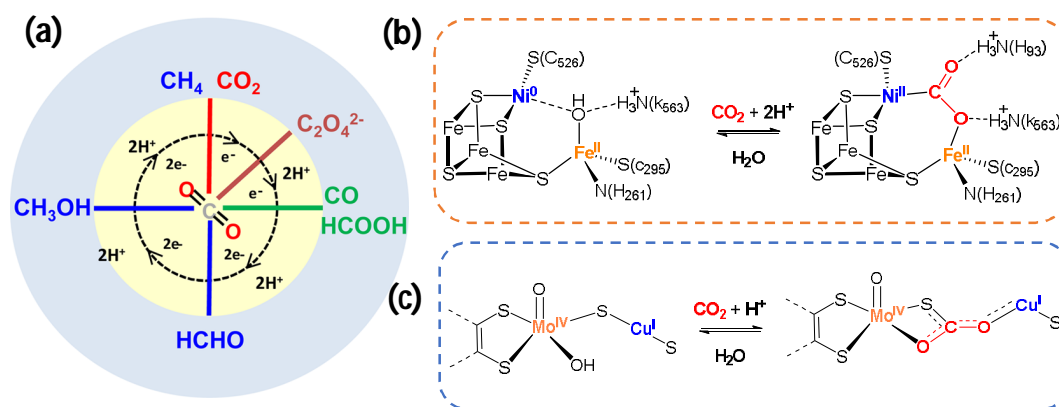
Chapter I. Introduction

Over the past decades, the industrial emission of carbon dioxide (CO₂) has been steadily increasing in the atmosphere.¹⁻⁴ As the CO₂ is an essential component of the greenhouse effect and it contributes substantially to abnormal global climate change. So, the activation/fixation of CO₂ is receiving significant attention around the world and many countries are paying much attention to recycle CO₂ from the atmosphere and industrial emission.¹⁻⁶ The utilization of CO₂ as C1-building block in organic synthesis is evergreen interest.⁷⁻⁹ This transformation involves several multi-electron reductions or C–C bond formation.¹⁰ The coupled two electron-two proton reduction of CO₂ results in the formation of CO, which can then be converted into CH₃OH and CH₄ by four electron-four proton and two electron-two proton reductions respectively. The direct one-electron reduction of CO₂ generates CO₂^{•-}, which can facilitate alternative reaction pathways such as disproportionation of CO₂ into CO and CO₃²⁻ and finally forms formate in the presence of water.^{10c} Also, it can undergo cross-coupling with organic substrates, or C–C coupling to form oxalate. The coupling reactions of CO₂ include cross-coupling with epoxides to generate polycarbonates or cyclic carbonates,¹¹ and coupling with organozinc or other carbanion equivalents to generate carboxylic acids.¹²

So far, four major methods such as chemical, photochemical, electrochemical and enzymatic methods are exploited to catalyze the CO₂ fixation/conversion.¹⁴⁻¹⁷ In the first three methods, the low selectivity has often reported due to the stable form of the carbon in the CO₂ molecule and energetically challenging to acquire high catalytic performances and selectivity. The enzymatic method provides an eco-friendly and promising way for efficient CO₂ fixation/conversion through superior stereo-specificity and regio/chemo-selectivity. In particular, zinc(II) containing metalloenzymes carbonic anhydrase enzyme is known to catalyze CO₂ to CO₃²⁻ conversion via non-redox pathway at pH, 7.0 and *D-ribulose*-1,5-bisphosphate carboxylase/oxygenase in the photosystem II plays crucial roles in the fixation and activation of CO₂.¹⁸ The iron-nickel carbon monoxide dehydrogenase (CODH) is capable of performing both CO₂ to

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CO reduction and CO to CO₂ oxidation. Where nature has adopted [Ni-4Fe-4S] core in CODH active site to handle this redox-mediated interconversion. On the other hand, molybdenum-copper carbon monoxide dehydrogenase ([Mo-Cu]-CODH) catalyzes reversible oxidation of CO ($\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$).¹⁹



Scheme 1. (a) The reduction clock of CO₂ and products formed. (b) The active site structure and CO₂ activation at the Ni, Fe-cluster of carbon monoxide dehydrogenase and (c) CO₂ activation at the [Mo-Cu]-cluster of carbon monoxide dehydrogenase.

In recent years, there is a significant current interest in the design of bioinspired complexes to understand the role metals and cooperative in activation of CO₂/CO and catalysis. This interest originates in recent discoveries of multimetallic sites in nature that catalyze efficiently difficult multielectron transformations. Despite the importance of CO₂ fixation, only very limited experimental and theoretical studies are reported. Particularly, bioinspired copper and nickel complexes are remain poorly investigated for activation of CO₂ and transformation into C1-feedstock. In this context, it is rational approach to design and synthesis bioinspired copper and nickel complexes as catalysts for fixation and conversion CO₂ into valuable added products. The catalytic efficiency of the complexes can be tuned by varying ligand architecture and redox potentials. Thus, in this proposal, we envisioned to develop bioinspired copper(I/II) and nickel(II) complexes as catalysts for selective activation of CO₂ and transformations into useful organic compounds. It is planned to employ these complexes as the catalyst to fix atmospheric CO₂ into valuable C1-feedstock under relatively mild reaction

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conditions. Wherein, the synthesis of industrially valuable chemicals such as cyclic carbonates from epoxide (100% atom economy) and other useful chemicals are planned.

References

- (1) Lindsey, A. S.; Jeskey, H. *Chem. Rev.* **1957**, *57*, 583.
- (2) Diekmann, S.; Weston, J.; Anders, E.; Boland, W.; Schonecker, B.; Hettmann, T.; Langen, J. V.; Erhardt, S.; Mauksch, M.; Brauer, M.; Beckmann, C.; Rost, M.; Sperling, P.; Heinz, E. *Rev. Mol. Biotechnol.* **2002**, *90*, 73.
- (3) Aresta, M.; Dibenedetto, A.; Angelini, A. *Chem. Rev.* **2014**, *114*, 1709.
- (4) Glueck, S. M.; Gumus, S.; Fabian, W. M. F.; Faber, K. *Chem. Soc. Rev.* **2010**, *39*, 313.
- (5) English, N. J.; El-Hendawy, M. M.; Mooney, D. A.; MacElroy, J. M. D. *Coord. Chem. Rev.* **2014**, *269*, 85.
- (6) Mikkelsen, M.; Jorgensena, M.; Krebs, F. C. *Energy Environ. Sci.* **2010**, *3*, 43.
- (7) (a) Lindahl, P. A. *Biochemistry* **2002**, *41*, 2097; (b) Woolley, *Nature* **1975**, *258*, 677; (c) Krishnamurthy, V. M.; Kaufman, G. K.; Urbach, A. R.; Gitlin, I.; Gudiksen, K. L.; Weibel, D. B.; Whitesides, G. M. *Chem. Rev.* **2008**, *108*, 946.
- (8) Lorimer, G. H. *Annu. Rev. Plant Physiol.* **1981**, *32*, 349. (b) Mizioroko, H. M.; Lorimer, G. H. *Annu. Rev. Biochem.* **1983**, *52*, 507.
- (9) J.-H. Jeoung and H. Dobbek, *Science*, **2007**, *318*, 1461.
- (10) Dobbek, H.; Gremer, L.; Kiefersauer, R.; Huber, R.; Meyer, O. *Proc. Natl. Acad. Sci.* **2002**, *99*, 15971.
- (11) Lu, C. C.; Saouma, C. T.; Day, M. W.; Peters, J. C. *J. Am. Chem. Soc.* **2007**, *129*, 4; (b) Saouma, C. T.; Lu, C. C.; Day, M. W.; Peters, J. C. *Chem. Sci.* **2013**, *4*, 4042.
- (12) Arakawa, H.; Aresta, M.; Armor, J. N.; Barteau, M. A.; Beckman, E. J.; Bell, A. T.; Bercaw, J. E.; Creutz, C.; Dinjus, E.; Dixon, D. A.; Domen, K.; DuBois, D. L.; Eckert, J.; Fujita, E.; Gibson, D. H.; Goddard, W. A.; Goodman, D. W.; Keller, J.; Kubas, G. J.; Kung, H. H.; Lyons, J. E.; Manzer, L. E.; Marks, T. J.; Morokuma, K.; Nicholas, K. M.; Periana, R.; Que, L.; Rostrup-Nielson, J.; Sachtler, W. M. H.; Schmidt, L. D.; Sen, A.; Somorjai, G. A.; Stair, P. C.; Stults, B. R.; Tumas, W. *Chem. Rev.* **2001**, *101*, 953.
- (13) Jessop, P. G.; Ikariya, T.; Noyori, R. *Chem. Rev.* **1995**, *95*, 259; (b) Oh, Y.; Hu, X. *Chem. Soc. Rev.* **2013**, *42*, 2253.
- (14) Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; DuBois, D. L.; Dupuis, M.; Ferry, J. G.; Fujita, E.; Hille, R.; Kenis, P. J. A.; Kerfeld, C. A.; Morris, R. H.; Peden, C. H. F.; Portis, A. R.; Ragsdale, S. W.; Rauchfuss, T. B.; Reek, J. N. H.; Seefeldt, L. C.; Thauer, R. K.; Waldrop, G. L. *Chem. Rev.* **2013**, *113*, 6621.
- (15) Kondratenko, E. V.; Mul, G.; Baltrusaitis, J.; Larrazabal, G. O.; Perez-Ramirez, J. *Energy Environ. Sci.* **2013**, *6*, 3112.
- (16) Oh, Y.; Hu, X. *Chem. Soc. Rev.* **2013**, *42*, 2253.
- (17) Aresta, M.; Dibenedetto, A.; Quaranta, E. *Reaction Mechanisms in Carbon Dioxide Conversion*; Springer: Berlin/Heidelberg, Germany, **2015**; pp. 347-371.

- (18) (a) Lindahl, P. A. *Biochemistry* **2002**, *41*, 2097. (b) Woolley, P. *Nature* **1975**, *258*, 677. (c) Krishnamurthy, V. M.; Kaufman, G. K.; Urbach, A. R.; Gitlin, I.; Gudiksen, K. L.; Weibel, D. B.; Whitesides, G. M. *Chem. Rev.* **2008**, *108*, 946.
- (19) (a) Jeoung, J. H.; Dobbek, H. *Science* **2007**, *318*, 1461. (b) Parkin, A.; Seravalli, J.; Vincent, K. A.; Ragsdale, S. W.; Armstrong, F. A. *J. Am. Chem. Soc.* **2007**, *129*, 10328. (c) Dobbek, H.; Gremer, L.; Kiefersauer, R.; Huber, R.; Meyer, O. *Proc. Natl. Acad. Sci.* **2002**, *99*, 15971.

Chapter II. Materials and Methods

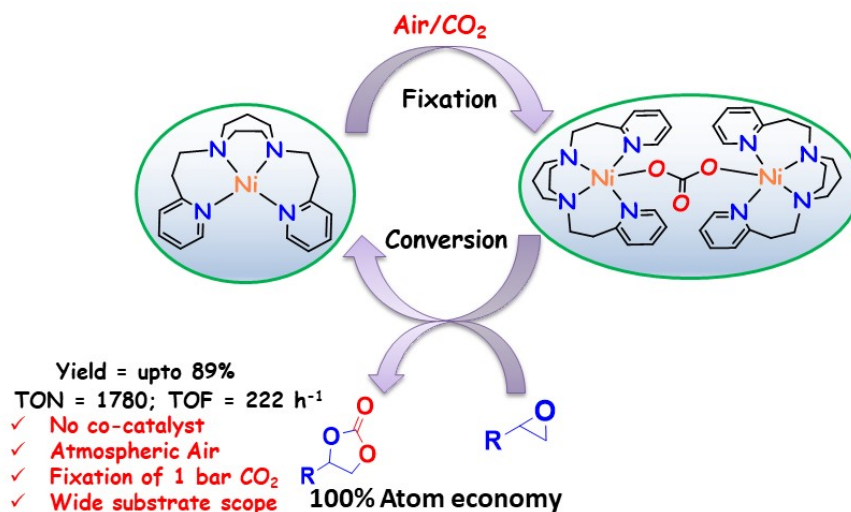
In this chapter, we discuss about synthesis and characterization of ligands and their complexes by using various spectral techniques like NMR, HR-MS, elemental analysis, IR, UV-Vis, EPR, electrochemical techniques and single crystal XRD methods, steric maps calculated by SambVca 2.1 A, and further geometry optimizations were performed by using density functional theory (DFT) methods.

Chapter III. Catalytic Conversion of Atmospheric CO₂ into Organic Carbonates by Nickel(II) Complexes of Diazepane Based N₄-Ligands

Activation of CO₂ and conversion into value-added products is an effective option to mitigate CO₂ emission. The nickel(II) complexes [Ni(L1)](ClO₄)₂ **1**, [Ni(L2)](ClO₄)₂ **2** and [Ni(L3)(CH₃CN)₂](Ph₄B)₂ **3** of diazepane based ligands [1,4-bis[(pyridin-2-yl-methyl)]-1,4-diazepane (L1), 1,4-bis[2-(pyridin-2-yl)ethyl]-1,4-diazepane (L2) and 4-bis[2-(quinoline-2-yl)-methyl]-1,4-diazepane (L3)] have been synthesized and structurally characterized. The complexes were employed as the catalysts for the conversion of atmospheric CO₂ into organic carbonates in the absence of co-catalyst at 1 atmosphere (atm) pressure. The single-crystal X-ray structures of **1** and **2** exhibit distorted square-planar geometry with almost identical Ni-N bond distances (1.891-1.946 Å). The geometry of the complexes rearranged into octahedral in acetonitrile, which was studied by paramagnetic ¹HNMR and electronic spectra. The complexes selectively captured CO₂ from the atmospheric air and readily converted epoxides into cyclic carbonates without any co-catalyst. They showed the maximum yield of 25% (TON, 500) using 1 atm air, which is drastically enhanced up to 89% (TON, 1780) using 1 atm pure CO₂ gas. This is the highest catalytic efficiency reported for CO₂ fixation using nickel-based catalysts to date. The CO₂ fixation reaction without organic substrate showed the formation of carbonate bridged dinuclear nickel(II)

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complexes. They showed characteristic absorption bands around 571 - 612 nm and further confirmed by ESI-MS, IR, and single-crystal X-ray structures. The molecular structure of carbonate-bridged intermediates exhibited two Ni²⁺-centers with distorted square pyramidal geometries for **2a** and **3a** but distorted octahedral and square pyramidal geometries for **1a**. The CO₂ fixation reactions possibly proceeded via the formation of CO₂-bound nickel species. To the best of our knowledge, this report is a first example for the selective fixation of CO₂ from air and its conversion into organic carbonates (up to 25% yield; turnover number (TON), 500 and turnover frequency (TOF) (63 h⁻¹) at 1 atmosphere (atm) air pressure without using any co-catalysts. The usage of 1 atm pure CO₂ showed enhanced yield of cyclic carbonates up to 89%, TON of 1780 and TOF, 222 h⁻¹. It is one of the rare examples of nickel(II) complexes for selective activation and efficient conversion of atmospheric CO₂ into cyclic carbonates without using any co-catalysts under 1 atm pressure.



References

- (1) (a) Palmer, D. A.; van Eldik, R. *Chem Rev.* **1983**, 83, 651. (b) Krogsrud, S.; Komiya, S.; Ito, T.; Albers, J.; Yamamoto, A. *Inorg. Chem.* **1976**, 15, 2798. (c) Gibson, D. H. *Chem. Rev.* **1996**, 96, 2063.
- (2) (a) Eriksson, A. E.; Jones, T. A.; Liljas, A. *Proteins.* **1988**, 4, 274. (b) Schrodtr, A.; Neubrand, A.; Van Eldik, R. *Inorg. Chem.* **1997**, 36, 4579.
- (3) Parkin, A.; Seravalli, J.; Vincent, K. A.; Ragsdale, S. W.; Armstrong, F. A. *J. Am. Chem. Soc.* **2007**, 129, 10328.
- (4) (a) Shaikh, R. R.; Pornpraprom, S.; D'Elia, V. *ACS Catal.* **2018**, 8, 419. (b) Büttner, H.; Longwitz, L.; Steinbauer, J.; Wulf, C.; Werner, T. *Top. Curr. Chem.* **2017**, 375, 50. (c) Comerford, J. W.; Ingram, I. D. V.; North, M.; Wu, X. *Green*

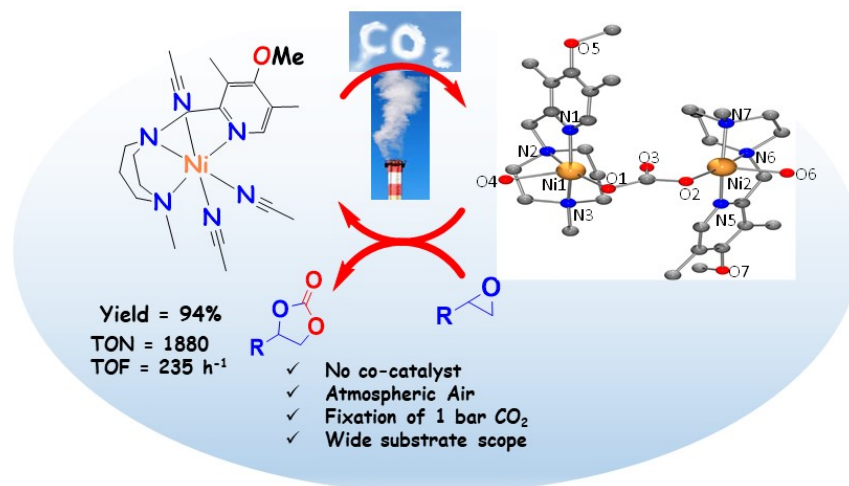
- Chem.* **2015**, *17*, 1966. (d) Martín, C.; Fiorani, G.; Kleij, A. W. *ACS Catal.* **2015**, *5*, 1353. (e) Fiorani, G.; Guo, W.; Kleij, A. W. *Green Chem.* **2015**, *17*, 1375.
- (5) Castro-Osma, J. A.; North, M.; Offermans, W. K.; Leitner, W.; Müller, T. E. *ChemSusChem.* **2016**, *9*, 791. (b) Gaona, M. A.; Cruz-Martínez, F.; Fernández-Baeza, J.; Sánchez-Barba, L. F.; Alonso-Moreno, C.; Rodríguez, A. M.; Rodríguez-Diéguez, A.; Castro-Osma, J. A.; Otero, A.; Lara-Sánchez, A. *Dalton Trans.* **2019**, *48*, 4218.

Chapter IV. Nickel(II) Complexes of N₃-Ligands as Catalysts for Conversion of Atmospheric CO₂ into Cyclic Carbonates

The development of molecular catalysts for the selective activation and conversion of atmospheric carbon dioxide (CO₂) into a value-added product is a great challenge. The nickel(II) complexes [Ni(L)(CH₃CN)₃](BPh₄)₂, **1** - **4** of diazepane based ligands 4-methyl-1-[(pyridin-2-yl-methyl)]-1,4-diazepane (L1), 4-methyl-1-[(2-(pyridine-2-yl)ethyl)]-1,4-diazepane (L2), 4-methyl-1-[(quinoline-2-yl)-methyl]-1,4-diazepane (L3) and 1-(4-methoxy-3,5-dimethyl-pyridin-2-yl)methyl-4-methyl-1,4-diazepane (L4) have been synthesized and characterized as the catalysts for selective activation of atmospheric CO₂. The single-crystal X-ray structure of **1** reveals a distorted octahedral geometry with *cis*-β configuration. Its Ni-N_{py} bond distance (1.986 Å) is shorter than Ni-N_{amine} (2.014, 2.101 Å). The complexes have readily converted epoxides into cyclic carbonates using atmospheric CO₂ at 1 atmosphere (atm) pressure without any cocatalyst. The complex **4** showed the maximum yield of cyclic carbonates up to 31% (TON, 620) using 1 atm air, which was drastically enhanced to 94% (TON, 1880) while using 1 atm pure CO₂ gas. This is the highest catalytic efficiency reported for CO₂ fixation using nickel-based catalysts to date. Furthermore, the complexes converted a wide range of epoxides (eight examples) into corresponding cyclic carbonates with excellent selectivity (>99%) and yields of 59-94% and 11-31% for pure CO₂ and atmospheric air respectively. The CO₂ fixation reaction without epoxide substrates showed the formation of carbonate bridged dinuclear nickel(II) complexes [(LNi^{II})₂CO₃](BPh₄)₂ **1a** - **4a**, which were accompanied by the new absorption bands around 592 - 681 nm. The molecular structure of carbonate-bridged key intermediates found to consist of two Ni²⁺-centers with distorted square pyramidal geometries. They were further confirmed by ESI-MS and IR spectral studies. Thus, the CO₂ fixation reactions likely occurred via CO₂-bound nickel key

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intermediates. The catalytic efficiencies of complexes are strongly influenced by the steric and electronic factors of the complexes, which are tuned by ligand architecture.



References

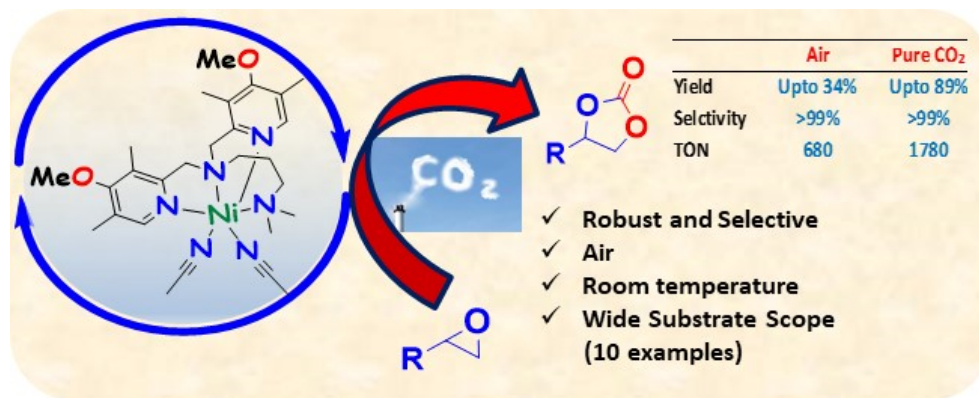
- (1) (a) Glueck, S. M.; Gumus, S.; Fabian, W. M. F.; Faber, K. Biocatalytic Carboxylation. *Chem. Soc. Rev.* **2010**, 39, 313. (b) Sakakura, T. Choi, J. -C and Yasuda, H. *Chem. Rev.* **2007**, 107, 2365. (c) Darensbourg, D. J. *Inorg. Chem.* **2010**, 49, 10765. (d) English, N. J.; El-Hendawy, M. M.; Mooney, D. A.; MacElroy, J. M. D. *Coord. Chem. Rev.* **2014**, 269, 85.
- (2) (a) Castro-Osma, J. A.; Comerford, J. W.; Heath, S.; Jones, O.; Morcillo, M. North, M. *RSC Adv.* **2015**, 5, 3678. (b) Morcillo, M.; North, M.; Villuendas, P. *Synthesis*, **2011**, 1918. (c) Parker, H. L.; Sherwood, J.; Hunt A. J.; Clark, J. H. *ACS Sustain. Chem. Eng.*, **2014**, 2, 1739. (d) Omae, I. *Catal. Today*, **2006**, 115, 33.

Chapter V. Catalytic Fixation of Atmospheric CO₂ into Organic Carbonates Using Nickel(II) Complexes of Tripodal 4N-Ligands Under Mild Condition

Fixation of atmospheric CO₂ into value-added products is an effective option to recycle CO₂. A series of novel nickel(II) complexes of the type [Ni(L)(CH₃CN)₂](BPh₄)₂ **1** – **5**, where L= *N,N*-bis(2-pyridylmethyl)-*N',N'*-dimethylpropane-1,3-diamine (L1), *N,N*-dimethyl-*N'*-(2-(pyridin-2-yl)ethyl)-*N'*-(pyridin-2-ylmethyl) propane-1,3-diamine (L2), *N,N*-bis((4-methoxy-3,5-dimethylpyridin-2-ylmethyl)-*N',N'*-dimethylpropane-1,3-diamine (L3), *N*-(2-(dimethyl amino) benzyl)-*N',N'*-dimethyl-*N*-(pyridin-2-ylmethyl) propane-1,3-diamine (L4) and *N,N*-bis(2-(dimethylamino)benzyl)-*N',N'*-dimethylpropane-1,3-diamine (L5) have been

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synthesized and characterized as the catalysts for the conversion of atmospheric CO₂ into useful organic cyclic carbonates. The single-crystal X-ray structure of **2** exhibited distorted octahedral coordination geometry with *cis-α* configuration. All the complexes are selectively fixed the atmospheric CO₂ from the air on epoxides and are readily converted into five-membered cyclic carbonates under 1 atmospheric (atm) pressure at room temperature. One of the catalysts showed the maximum yield of cyclic carbonates up to 34% (TON, 680) under 1 atm air, which is drastically enhanced to 89% (TON, 1780) while using pure CO₂ gas. The catalytic efficiencies of complexes are strongly influenced by electronic and steric effect, which is fine-tuned by ligand architecture. This is the highest catalytic efficiency reported for CO₂ fixation using nickel-based catalysts to date at room temperature and 1 atm pressure. Furthermore, the catalysts converted a wide range of epoxides (ten examples) into corresponding cyclic carbonate with excellent selectivity (>99%) at room temperature.



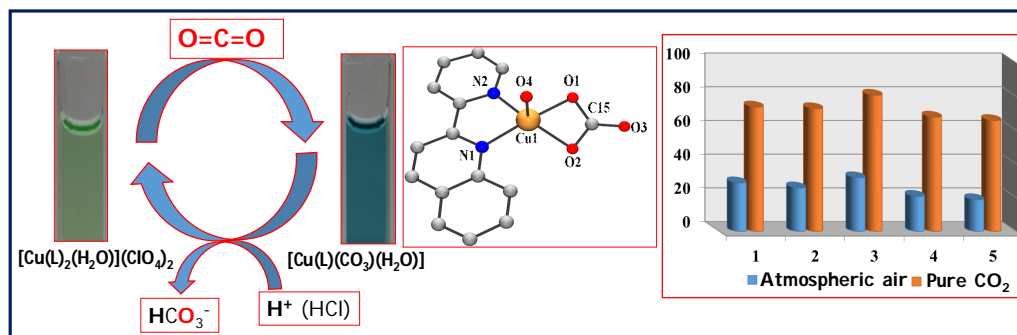
References

- (1) (a) Aresta, M.; Dibenedetto, A.; Angelini, A. *Chem. Rev.* **2014**, *114*, 1709. (b) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 661. (c) Oh, Y.; Hu, X. *Chem. Soc. Rev.* **2013**, *42*, 2253. (d) Krishnamurthy, V. M.; Kaufman, G. K.; Urbach, A. R.; Gitlin, I.; Gudiksen, K. L.; Weibel, D. B.; Whitesides, G. M. *Chem. Rev.* **2008**, *108*, 946.
- (2) (a) Huang, L. -S.; Tsai, C.-Y.; Chuang, H.-J.; Ko, B. -T. *Inorg. Chem.* **2017**, *56*, 6141. (b) Li, C. Y; Su, Y. C; Lin, C. H; Huang, H. Y; Tsai, C. Y; Lee, T. Y; and Ko, B. T. *Dalton Trans.* **2017**, *46*, 15399.

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Chapter VI. Catalytic Fixation of Atmospheric Carbon Dioxide by Copper(II) Complexes of Bidentate Ligands

New copper(II) complexes $[\text{Cu}(\text{L}1)_2(\text{H}_2\text{O})](\text{ClO}_4)_2$, **1** [L1 = 2-pyridin-2-yl-quinoline], $[\text{Cu}(\text{L}2)_2(\text{H}_2\text{O})](\text{ClO}_4)_2$, **2** [L2 = 2-pyridin-2-yl-quinoxaline], $[\text{Cu}(\text{L}3)_2(\text{H}_2\text{O})](\text{ClO}_4)_2$, **3** [L3 = 6,7-dimethyl-2-pyridin-2-yl-quinoxaline], $[\text{Cu}(\text{L}4)_2(\text{H}_2\text{O})](\text{ClO}_4)_2$, **4** [L4 = 4-phenyl-2-pyridin-2-yl-quinoline] and $[\text{Cu}(\text{L}5)_2(\text{H}_2\text{O})](\text{ClO}_4)_2$, **5** [L5 = 4-phenyl-2-pyridin-2-yl-quinazoline] were synthesized and characterized as the catalysts for selective fixation of atmospheric CO_2 . The molecular structure of **2** was determined by single-crystal X-ray studies and showed unusual trigonal bipyramid geometry (τ , 0.936) around copper(II) center by the coordination of two ligand units and a water molecule. The Cu–N_{quin} (2.040, 2.048 Å) bonds are slightly longer than Cu–N_{pyr} (1.987 Å) bonds but shorter than Cu–O_{water} bond (2.117 Å). A well-defined Cu(II)/Cu(I) redox potentials around 0.352 to 0.401 V were observed for **1** - **5** in acetonitrile. The electronic absorption spectra of **1** - **5** showed ligand-based transitions around 208 - 286 nm with a shoulder around 342 - 370 nm. The d-d transitions appeared around 750 - 800 and 930-955 nm in acetonitrile. The rhombic EPR spectra of **1** - **5** have exhibited three different g values g_x , 2.27-2.34; g_y , 2.06 - 2.09; g_z , 1.95 - 1.98 at 70 K. The atmospheric CO_2 has been fixed successfully by **1** - **5** using Et_3N as sacrificial reducing agent and afforded the CO_3^{2-} bound complexes of type $[\text{Cu}(\text{L})\text{CO}_3(\text{H}_2\text{O})]$, which are accomplished by an absorption band around 614 - 673 nm and ν_{st} at 1647 cm^{-1} . This CO_3^{2-} bound complex of **1** has been crystallized from the reaction mixture and it showed distorted square pyramidal geometry (τ , 0.369) around copper(II) center via the coordination of only one ligand unit, a carbonate, and water molecules. Further, the treatment of one equivalent H^+ with carbonate bound Cu(II) complexes have liberated bicarbonate (HCO_3^-) and regenerated the parent complexes under N_2 atmosphere. The regenerated catalysts were active enough to fix the CO_2 for eight repeating cycles without any change in the efficiency. The fixation of CO_2 is possibly proceeds via the formation of Cu(I)-species accomplished by the MLCT band around 450 - 500 nm. The rates of Cu(I)-species formation were determined as k_{obs} , $5.41 - 10.31 \times 10^{-3} \text{ s}^{-1}$ in the presence of Et_3N in acetonitrile at 25 °C. Interestingly, the copper(I)-species of **3** has been successfully crystallized and showed distorted tetrahedral geometry by the coordination of two units of ligand L3.



References

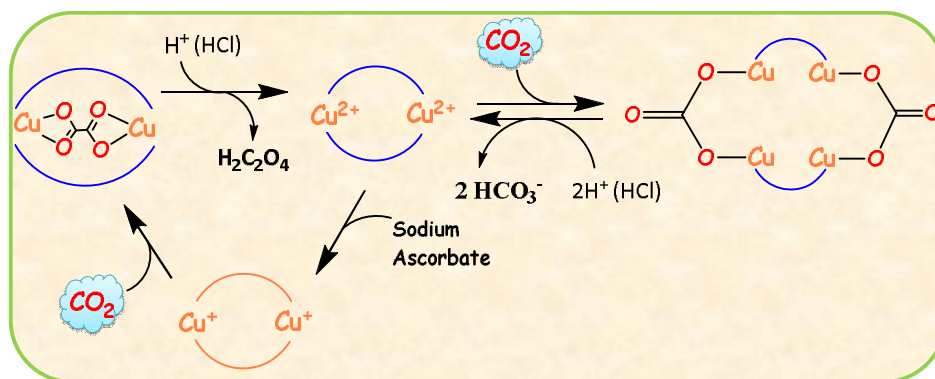
- (1) (a) Kondratenko, E. V.; Mul, G.; Baltrusaitis, J.; Larrazabal, G. O.; Perez-Ramirez, J. *Energy Environ. Sci.* **2013**, *6*, 3112. (b) Appel, A. M.; Bercaw, J. E.; Bocarsly, A. B.; Dobbek, H.; DuBois, D. L.; Dupuis, M.; Ferry, J. G.; Fujita, E.; Hille, R.; Kenis, P. J. A.; Kerfeld, C. A.; Morris, R. H.; Peden, C. H. F.; Portis, A. R.; Ragsdale, S. W.; Rauchfuss, T. B.; Reek, J. N. H.; Seefeldt, L. C.; Thauer, R. K.; Waldrop, G. L. *Chem. Rev.* **2013**, *113*, 6621.
- (2) (a) Li, F.; Xia, C.; Xu, L.; Sun, W.; Chen, G. *Chem Commun.* **2003**, 2042. (b) Li, C. Y.; Su, Y. C.; Lin, C. H.; Huang, H. Y.; Tsai, C. Y.; Lee, T. Y.; and Ko, B. T. *Dalton Trans.* **2017**, *46*, 15399.

Chapter VII. Catalytic Reduction of Carbon Dioxide into Oxalate by Bioinspired Dinuclear Copper(II) Complexes

The technology development for capturing and utilization of CO₂ is evergreen interest in order to restraint the greenhouse gas emissions. The novel dinuclear copper(II) complexes of macrocyclic ligands [LCu₂(CH₃CN)₂]⁴⁺ (L1 = 3,6,9,13,16,19-hexaaza-1,11(1,4)-dibenzena cycloicosaphane), (L2 = 3,7,11,15, 19,23-hexaaza-1,13(1,4)-dibenzenacyclo tetracosaphane), (L3 = 7,19-dimethyl-3,7,11,15,19,23-hexaaza-1,13(1,4)-dibenzen acyclotetraco saphane) and L4 = 5,9,17,21-tetraaza-1,13(1,4)-dipiperazina-7,19(1,4)-dibenzenacyclotetracosaphane have been synthesized and characterized as catalysts for fixation of CO₂ into value-added fine chemicals. A well-defined Cu(II)/Cu(I) redox potentials for **1** (0.385 V), **2** (0.056 V), **3** (0.332 V) and **4** (0.246 V) were observed in acetonitrile. The electronic absorption spectra of **1** - **4** showed ligand-based transitions around 278 - 301 nm and d-d transitions appeared around 570 - 672 nm in acetonitrile. The EPR parameter (g_{\parallel} , 2.246 - 2.265; A_{\parallel} , 157 - 166 × 10⁻⁴ cm⁻¹) suggests that existence of square based geometry around copper

Synopsis

centers. Addition of mild reducing agent sodium ascorbate to dinuclear copper(II) complexes resulted the immediate formation of copper(I) species, which readily activated CO_2 and converted into $\text{C}_2\text{O}_4^{2-}$ and are trapped in the ligand cavity as the bridging ligand between the two copper atoms. One of the $\text{C}_2\text{O}_4^{2-}$ bound complexes has been crystallized from the reaction mixture and it showed distorted trigonal bipyramidal geometry (τ , 0.82, 0.81) around copper(II) center. The formation of oxalate-bridged Cu(II) complexes was further confirmed by ESI-MS and FT-IR. The bound oxalate ion was released as oxalic acid on treatment with mineral acid (HCl), and regenerated the parent dinuclear copper(II) complexes. In contrast, use of Et_3N as a reducing agent the complexes $[\text{Cu}_2(\text{L})]^{4+}$ were readily converted CO_2 into CO_3^{2-} and showed the formation of $[\text{Cu}_4(\text{L}1)_2(\text{CO}_3)_2]^{4+}$. The formation of carbonate-bound complexes was confirmed by ESI-MS, IR, and single crystal XRD studies.



References

- (1) (a) Aresta, M. Carbon dioxide as chemical feedstock (Wiley. com, **2010**). (b) Palmer, D. A.; van Eldik, R. *Chem Rev.* **1983**, 83, 651. (c) Gibson, D. H. *Chem. Rev.* **1996**, 96, 2063.
- (2) (a) Angamuthu, R.; Byers, P.; Lutz, M.; Spek, A. L. *Science*, **2010**, 327, 313. (b) Horn, B.; Limberg, C.; Herwig, C.; Braun, B. *Chem. Commun.* **2013**, 49, 10923. (c) Takisawa, H.; Morishima, Y.; Soma, S.; Szilagy, R. K.; Fujisawa, K. *Inorg. Chem.* **2014**, 53, 8191. (d) Pokharel, U. R.; Fronczek, F. R.; Maverick, A. W. *Nat. Commun.* **2014**, 5, 5883.