

Electrocatalytic CO₂ Conversion to Oxalate by a Copper Complex

Raja Angamuthu,¹ Philip Byers,¹ Martin Lutz,² Anthony L. Spek,² Elisabeth Bouwman^{1*}

Global warming concern has dramatically increased interest in using CO₂ as a feedstock for preparation of value-added compounds, thereby helping to reduce its atmospheric concentration. Here, we describe a dinuclear copper(I) complex that is oxidized in air by CO₂ rather than O₂; the product is a tetranuclear copper(II) complex containing two bridging CO₂-derived oxalate groups. Treatment of the copper(II) oxalate complex in acetonitrile with a soluble lithium salt results in quantitative precipitation of lithium oxalate. The copper(II) complex can then be nearly quantitatively electrochemically reduced at a relatively accessible potential, regenerating the initial dinuclear copper(I) compound. Preliminary results demonstrate six turnovers (producing 12 equivalents of oxalate) during 7 hours of catalysis at an applied potential of -0.03 volts versus the normal hydrogen electrode.

Research toward carbon dioxide fixation enjoys much attention at present, as a result of the alarming reports that link global warming and its potentially devastating effects with the steadily increasing concentration of CO₂ in the atmosphere. Chemical activation of carbon dioxide could help to reduce its concentration in the atmosphere while at the same time exploiting it as a carbon feedstock for the production of useful organic compounds (1–5). Transition-metal complexes, especially of copper and zinc (6, 7), as well as simple salts such as lithium hydroxide monohydrate and soda-lime (mixture of sodium and calcium hydroxides) are well known for their assistance in the stoichiometric transformation of carbon dioxide to carbonate salts (8–17). Mixtures of glycol and amines (glycol-amine) as well as coordination complexes of polyamines have been reported to bind CO₂ reversibly through the formation of carbamates (8, 15, 17, 18). In contrast, reductive conversion of CO₂ into useful products of industrial significance such as formaldehyde, formic acid, methanol, or oxalic acid has proven more challenging to achieve selectively (19, 20).

The one-electron reduction of CO₂ into the CO₂^{•-} radical anion occurs at potentials as high as -1.97 V versus NHE (normal hydrogen electrode) in *N,N*-dimethylformamide, and the CO₂^{•-} may further react to form CO, carbonate, formate, or oxalate (19–21). Selective production of oxalate would be much preferred because dimethyl oxalate is a useful feedstock, for example, for the production of methyl glycolate. The assistance of transition-metal complexes appears mandatory to direct the reactivity of the CO₂^{•-} radical anion toward a specific product, in addition to optimizing electrochemical parameters such as current density. Moreover, the inner-sphere electron-transfer mechanisms that proceed with most

transition metal systems result in less-negative reduction potentials, which may improve overall thermodynamic favorability of the reduction, assuming there is an accessible way to liberate the product after the electron-transfer reaction (20). Reductive coupling of CO₂ to form the oxalate dianion has been accomplished by electrochemical methods, including outer-sphere electron transfer using mercury or lead electrodes and inner-sphere electron transfer using transition-metal complexes or anion radicals of aromatic hydrocarbons, esters, and nitriles as electrocatalysts (20–22). Mechanistic understanding of the metal-catalyzed reduction of CO₂ to C₂ or C₃ fragments is also highly relevant for an improved understanding of the natural photosynthetic transformation of atmospheric CO₂ to functionalized C₃ molecules (3-phosphoglycerate).

We herein report a copper complex, which spontaneously captures and reductively couples CO₂ from the air selectively, yielding an oxalate-

bridged copper(II) tetramer in acetonitrile solution. Moreover, we have found that this copper system can be used repeatedly as a catalyst for the reductive coupling of CO₂ to oxalate upon electrochemical reduction. The reduction of the copper(II) complex occurs at a readily accessible potential that is nearly 2 V less negative than that required for outer-sphere reduction of CO₂ to CO₂^{•-}.

The ligand HL [*N*-(2-mercaptopropyl)-*N,N*-bis(2-pyridylmethyl)amine] was designed for the synthesis of biomimetic models for nickel-containing superoxide dismutase. In addition to studies with nickel salts, reactions were performed with copper and zinc for comparison. Upon mixing of equimolar amounts of Cu(acac)₂ (Hacac is acetylacetonate), the ligand HL, and HBF₄ in acetonitrile at room temperature, we obtained a yellow-colored solution, in which as expected the thiolate-containing ligand was oxidized by the copper(II) ion. The solution was analyzed with positive-ion electrospray ionization mass spectroscopy (ESI-MS); a prominent signal at mass/charge (*m/z*) ratio of 335.91 showed an isotopic distribution envelope matching that calculated for the dinuclear copper(I) complex [1]²⁺ (Fig. 1) (23). This complex [1]²⁺ can also be synthesized by the reaction of the preoxidized disulfide ligand with two equivalents of [Cu(CH₃CN)₄]BF₄ in dry acetonitrile. This yellow-colored solution turned greenish-blue upon exposure to air; over the course of 3 days crystals formed, which we isolated in 72% yield and analyzed by x-ray diffraction. We observed a tetranuclear copper(II) structure [Cu^{II}₂(L-L)(μ-oxalato-κ⁴O¹,O²:O³,O⁴)₂(BF₄)₄] {2}(BF₄)₄, Fig. 1, with bridging oxalate anions that must originate from CO₂ in the air. A positive-ion ESI-MS spectrum acquired from the acetonitrile solution is consistent with this molecular struc-

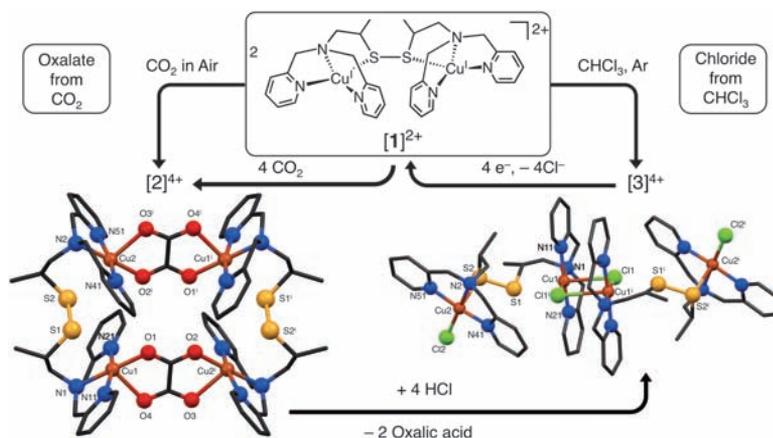


Fig. 1. Schematic overview of the formation and reactivity of the complexes [1]²⁺, [2]⁴⁺, and [3]⁴⁺. Cu, brown; N, blue; S, yellow; O, red; Cl, green; C, black. BF₄ anions, solvent molecules, and hydrogen atoms are omitted for clarity. Selected (average) bond lengths (Å) for [2]⁴⁺: Cu–O_{eq}, 1.963(2); Cu–O_{ax}, 2.283(2); Cu–N_{pyr}, 1.991(2); Cu–N_{amine}, 2.026(2); S1–S2, 2.0423(16); Cu1...S1, 2.9837(12); Cu2...S2, 2.9731(12); Cu1...Cu2, 5.3205(6); Cu1...Cu2ⁱ, 5.4295(6). Selected (average) bond lengths (Å) for [3]⁴⁺: Cu1–Cl1ⁱ, 2.2479(6); Cu2–Cl2, 2.2440(7); Cu1–Cl1, 2.8589(6); Cu–N_{pyr}, 1.984(1); Cu–N_{amine}, 2.052(2); S1–S2, 2.0388(11); Cu1...S1, 3.0036(9); Cu2–S2, 2.7343(7); Cu1...Cu1ⁱ, 3.5677(5); Cu1...Cu2, 6.1248(4). Symmetry operation *i*; 1 – *x*, 1 – *y*, 1 – *z*. Estimated standard deviations in the last digits are given in parentheses. Further details are provided in (23).

¹Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, Post Office Box 9502, 2300 RA Leiden, Netherlands.

²Bijvoet Center for Biomolecular Research, Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, Netherlands.

*To whom correspondence should be addressed. E-mail: bouwman@chem.leidenuniv.nl

ture, showing a prominent signal at m/z of 379.35 (figs. S9 and S10). We thus found that the initial Cu(I) complex is oxidized by CO_2 rather than O_2 . Indeed, purging carbon dioxide into a solution of complex $[1]^{2+}$ results in the formation of the tetranuclear oxalate-bridged complex $[2]^{4+}$, which was fully characterized by Fourier transform infrared spectroscopy (FT-IR), ESI-MS, and elemental analysis. That carbon dioxide is the origin of the oxalate dianion was proven with the use of $^{13}\text{C}\text{O}_2$; the resulting copper(II) complex showed a signal at m/z of 381.06 (fig. S11). The reaction of $[1]^{2+}$ in an O_2 atmosphere under strict exclusion of CO_2 resulted in a deep green solution containing a copper(II) compound with a molecular ion peak at $m/z = 361.16$ in positive ion ESI-MS that is consistent with the expected dihydroxo complex of molecular formula $[\text{Cu}^{\text{II}}(\text{L-L})\text{Cu}^{\text{II}}(\mu\text{-OH})_2(\text{H}_2\text{O})_2]^{2+}$ (fig. S12).

In the solid state, $[2]^{4+}$ consists of a cyclic centrosymmetric dimer of two dinuclear moieties bridged by two oxalato dianions (fig. S13). Each dinuclear moiety consists of two crystallographically independent copper(II) ions. The two copper(II) ions within the asymmetric unit bind to the same disulfide ligand and are separated by 5.3205 ± 0.0006 [$5.3205(6)$] Å. The copper ions are situated in square-pyramidal environments, with the three nitrogen donors of the meridionally coordinated dipicolylamine unit occupying three corners of the basal plane. One of the oxygens from the bridging oxalato dianion is situated at the fourth corner of the basal plane, with another oxygen from the same oxalato dianion occupying the apical position. However, for both copper ions one

of the disulfide sulfur atoms can be regarded as a sixth ligand at meaningful axial distances of 2.9837(12) and 2.9731(12) Å. (Further parameters are provided in table S1.)

In an attempt to crystallize the original complex $[1]^{2+}$, chloroform was let to diffuse into the initial reaction mixture containing the copper(I) complex in an argon atmosphere. Interestingly, this yielded the unexpected tetranuclear compound $[\text{ClCu}^{\text{II}}(\text{L-L})\text{Cu}^{\text{II}}(\mu\text{-Cl})_2(\text{BF}_4)_4]$ $\{[3](\text{BF}_4)_4$, Fig. 1} with bridging and terminal chloride anions that can only originate from chloroform (24). The solid-state structure of $[3]^{4+}$ was obtained by x-ray diffraction from a blue crystal of $[3](\text{BF}_4)_4$. The molecular structure of $[3]^{4+}$ is confirmed by a positive-ion ESI-MS spectrum of the compound acquired from acetonitrile solution, which shows a prominent signal at $m/z = 370.71$ (figs. S14 and S15). Complex $[3]^{4+}$ is a linear centrosymmetric dimer of two dinuclear moieties bridged by two chloride anions (figs. S16 and S17). The two copper(II) ions within the asymmetric unit are bound to the same disulfide ligand and are separated by 6.1248(4) Å. The copper ions in $[3]^{4+}$ are situated in pentacoordinate environments resembling those in complex $[2]^{4+}$; the thioether sulfur and the chloride donors replace the oxalato oxygen donors in $[2]^{4+}$.

Inspired by this finding, we explored whether complex $[2]^{4+}$ could be converted to this chloride complex $[3]^{4+}$ by treatment with HCl, in the process liberating the CO_2 -derived oxalic acid.

Addition of four equivalents of hydrochloric acid to an acetonitrile solution of $[2](\text{BF}_4)_4$ indeed leads to elimination of oxalic acid with concurrent

formation of $[3](\text{BF}_4)_4$ as confirmed by ESI-MS and elemental analysis. The electrochemical reduction of $[3](\text{BF}_4)_4$ occurs at the cathodic peak potential (E_{pc}) of +0.06 V versus NHE (fig. S18), producing a copper(I) complex that selectively produces complex $[2]^{4+}$ upon reaction with CO_2 . This result stimulated us to explore the possibility of using the copper/disulfide-ligand system as an electrocatalyst for the selective reduction of CO_2 .

To that end, we undertook electrochemical reduction of complex $[3]^{4+}$ by using controlled potential coulometry and monitored the process by using electronic absorption spectroscopy. The copper complex $[3](\text{BF}_4)_4$ (0.9 g, 0.5 mmol) was dissolved in 100 ml of 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile; the solution was then reduced at +0.03 V versus NHE. A current drop was observed after 195 C of charge was passed, the quantity expected for a one-electron reduction of each copper ion. The disappearance of the characteristic $d-d$ transition band (~ 670 nm) of $[3]^{4+}$ during electrolysis confirmed the formation of a copper(I) species (fig. S19). The resulting yellow-colored solution was shown by ESI-MS to contain the dinuclear copper(I) complex $[1]^{2+}$ (fig. S20). The cyclic voltammogram of this solution showed a reversible oxidation process at the anodic peak potential (E_{pa}) of +0.81 V versus NHE (fig. S21).

Bubbling carbon dioxide into this solution turned the color greenish-blue, indicating the formation of complex $[2]^{4+}$ as confirmed by ESI-MS analysis of the solution. The cyclic voltammogram of $[2]^{4+}$ produced in this reaction sequence was identical to that of the independently synthesized and isolated $[2]^{4+}$ and showed an irreversible reduction process at -0.03 V versus NHE (fig. S22). The bulk electrolysis experiment was then repeated under the same conditions but with use of lithium perchlorate as the supporting electrolyte in a CO_2 -saturated acetonitrile solution. These conditions resulted in the precipitation of lithium oxalate as the generated copper(I) complex spontaneously reacted with the CO_2 available in the solution to form oxalate (fig. S23). In order to quantify the selectivity of our electrocatalyst, we halted electrolysis after passing 195 C of charge (the charge expected for a one-electron reduction of each copper ion), purged the solution with CO_2 , and removed the lithium oxalate precipitate by filtration under an argon atmosphere. The 24-mg (0.24-mmol) yield of lithium oxalate [as confirmed by ESI-MS spectrometry, nuclear magnetic resonance (NMR), and FT-IR spectroscopy, figs. S24 and S25] corresponded to nearly quantitative current efficiency (96%) for formation of the desired product. The remaining blue-colored solution was shown to contain the dinuclear copper(II) complex $[(\text{CH}_3\text{CN})\text{Cu}^{\text{II}}(\text{L-L})\text{Cu}^{\text{II}}(\text{CH}_3\text{CN})]^{4+}$ $[4]^{4+}$ as characterized by ESI-MS spectrometry (fig. S26). We proceeded to saturate this solution with argon to remove the remaining CO_2 and then subjected it to a second electrolysis run; 185 C of charge was consumed before the current dropped, indicating regeneration of nearly 95% of the copper(I) complex.

Fig. 2. Formation of $[4]^{4+}$ from $[2]^{4+}$ or $[3]^{4+}$.

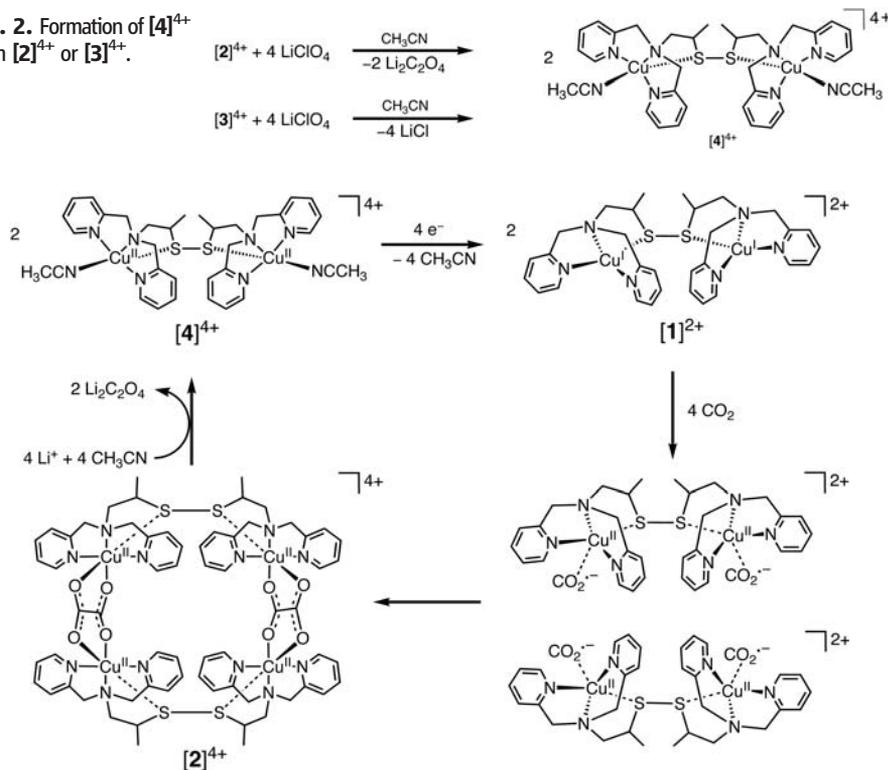


Fig. 3. Proposed electrocatalytic cycle for oxalate formation.

Both complexes $[2]^{4+}$ and $[3]^{4+}$ upon mixing with LiClO_4 in acetonitrile yield $[4]^{4+}$ as confirmed by ESI-MS spectrometry (Fig. 2 and figs. S27 and S28). Therefore, in another attempt to use the complex $[2]^{4+}$ as an electrocatalyst in this reaction, the electrochemical cell containing an acetonitrile solution of complex $[2]^{4+}$ and lithium perchlorate (as supporting electrolyte) was stirred to precipitate all the available oxalate. Then the solution was electrolyzed at -0.03 V versus NHE with continuous purging of CO_2 . The consumption of current continued linearly for more than 3.3 hours, consuming three equivalents of charge (12 electrons) per four copper ions, with concurrent crystallization of lithium oxalate. Thereafter, the rate of the reaction gradually decreased as the crystallized lithium oxalate started to cover the electrode surface, thereby hampering electron transfer (fig. S29). In total, the electrocatalysis could be extended for more than 7 hours, with consumption of 6 equivalents of charge (24 electrons) and generating 12 equivalents of oxalate per molecule of $[2]^{4+}$.

We have thus devised an electrocatalytic system based on a copper coordination compound that is able to activate and convert CO_2 selectively into oxalate at readily accessible potentials, in the simple but very effective catalytic cycle shown in Fig. 3. The finding that a copper(I) system is oxidized by CO_2 rather than O_2 implies that the selective binding of CO_2 to the copper(I) ions offers a low-energy pathway for the formation of the $\text{CO}_2^{\cdot-}$ radical anion. The copper(II) oxalate complex $[2]^{4+}$ is thermodynamically favored; the binding of CO_2 to the Cu(I) centers in $[1]^{2+}$ and the formation of oxalate appears to be highly selective and relatively rapid. Because

of the low solubility of lithium oxalate in acetonitrile, the release of the oxalate dianion from $[2]^{4+}$ in the presence of lithium perchlorate is instantaneous, generating the complex $[4]^{4+}$. Therefore, for the current system the electrocatalytic reduction of the copper(II) ion to copper(I) appears to be rate-limiting. The precipitation of the lithium oxalate formed during the reaction onto the electrode surface hampers efficient electron transfer. Tuning the redox potential of the copper complex by altering the ligand structure with a variety of substituents, immobilization of the complex onto the electrode surface, and improved methods for the removal of oxalate may result in improved efficiency of the catalytic system. We believe that our studies will instigate further development of coordination complexes for catalytic CO_2 sequestration, its selective conversion and use as fuels such as methanol or as feedstock in the synthesis of useful organic compounds.

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Supporting Online Material

www.sciencemag.org/cgi/content/full/327/5963/313/DC1
Materials and Methods
SOM Text
Figs. S1 to S30
Tables S1 and S2
References

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Ligand-Enabled Reactivity and Selectivity in a Synthetically Versatile Aryl C–H Olefination

Dong-Hui Wang, Keary M. Engle, Bing-Feng Shi, Jin-Quan Yu*

The Mizoroki-Heck reaction, which couples aryl halides with olefins, has been widely used to stitch together the carbogenic cores of numerous complex organic molecules. Given that the position-selective introduction of a halide onto an arene is not always straightforward, direct olefination of aryl carbon-hydrogen (C–H) bonds would obviate the inefficiencies associated with generating halide precursors or their equivalents. However, methods for carrying out such a reaction have suffered from narrow substrate scope and low positional selectivity. We report an operationally simple, atom-economical, carboxylate-directed Pd(II)-catalyzed C–H olefination reaction with phenylacetic acid and 3-phenylpropionic acid substrates, using oxygen at atmospheric pressure as the oxidant. The positional selectivity can be tuned by introducing amino acid derivatives as ligands. We demonstrate the versatility of the method through direct elaboration of commercial drug scaffolds and efficient syntheses of 2-tetralone and naphthoic acid natural product cores.

Unactivated carbon–hydrogen (C–H) bonds are among the simplest and most common structural motifs in naturally occurring organic molecules, and, as such, they are ideal

targets for chemical transformations. Although C–H bonds are generally unreactive, during the past several decades transition metal catalysis has emerged as an effective means of converting unac-

tivated C–H bonds into carbon–heteroatom and carbon–carbon (C–C) bonds (1–5). This technology has proven to be valuable in natural products synthesis, where several distinct C–H functionalization strategies have been exploited (6–12).

Traditionally, C–C bonds between aryl and olefinic fragments have been forged through the Pd-catalyzed Mizoroki-Heck reaction, which couples aryl halides or triflates with olefins (Fig. 1A). Considering the prominence of this transformation in organic synthesis (13), Pd-catalyzed olefination of aryl C–H bonds has the potential to emerge as a powerful platform for more direct access to carbogenic cores of complex molecules (Fig. 1, A and E), particularly in cases in which the position-selective introduction of a halide is problematic. However, the few pioneering examples of Pd-catalyzed C–H olefination in total synthesis to date are restricted to specific cases, generally including electron-rich heterocycles, such as indoles and pyrroles, and/or

Scripps Research Institute, 10550 North Torrey Pines Road, La Jolla, CA 92037, USA.

*To whom correspondence should be addressed. E-mail: yu200@scripps.edu