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# Conversion of Carbon Dioxide to Oxalate by $\alpha$-Ketocarboxylatocopper(II) Complexes

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Ⓢ *Supporting Information*

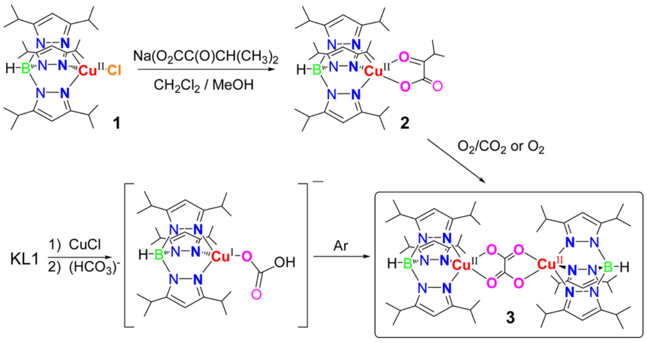
**ABSTRACT:** The $\alpha$-ketocarboxylatocopper(II) complex $[\{Cu(L1)\}\{O_2CC(O)CH(CH_3)_2\}]$ can be spontaneously converted into the binuclear oxalatocopper(II) complex $[\{Cu(L1)\}_2(\mu\text{-}C_2O_4)]$ upon exposure to $O_2/CO_2$ gas. $^{13}$C-labeling experiments revealed that oxalate ions partially incorporated $^{13}CO_2$ molecules. Furthermore, the bicarbonatocopper(I) complex $(NEt_4)[Cu(L1)\{O_2C(OH)\}]$ in an Ar atmosphere and the $\alpha$-ketocarboxylatocopper(I) complex $Na[Cu(L1)\{O_2CC(O)CH(CH_3)_2\}]$ in an $O_2$ atmosphere were also transformed spontaneously into the oxalato complex $[\{Cu(L1)\}_2(\mu\text{-}C_2O_4)]$.

Utilization of carbon dioxide ($CO_2$) is an important global challenge because of the significant and continued increase of the atmospheric $CO_2$ concentration. $CO_2$ has favorable properties as a chemical raw material because of its nontoxicity, abundance, and potential for being an economical raw material for C1 chemistry. Therefore, much effort has been focused on converting $CO_2$ to activated carbon sources in the past decades.[1] $CO_2$ is a kinetically and thermodynamically inert molecule; thus, it is difficult to chemically activate its short (1.16 Å) C═O bond. Because $CO_2$ has polar bonds, it can be considered as a weak, carbon-centered electrophile. This provides a means for activation via coordination to a metal center because of its Lewis base character. Following this principle, examples for transition-metal-catalyzed activation reactions were already reported.[1] Moreover, divalent metal hydroxido complexes with terminal or bridging ligands can yield carbonato metal complexes of cobalt(II),[2] nickel(II),[2b,3] copper(II),[2b,4] and zinc(II)[2,5] ions. In this reaction, $CO_2$ is transformed to carbonate ions ($CO_3^{2-}$) in an acid−base reaction without a change in the oxidation state. A more valuable, but also more challenging, activation strategy is the reductive activation of $CO_2$. The one-electron reduction to a $CO_2$ radical anion or a dioxidocarbonate radical ($CO_2^{\bullet -}$) is highly nonspontaneous with $E° = -1.97$ V at room temperature versus normal hydrogen electrode in *N*,*N*′-dimethylformamide, which is due to large reorganization energy between the linear molecule $CO_2$ and the bent radical anion $CO_2^{\bullet -}$.[6]

The range of oxidation potentials for the first-row transition-metal complexes is limited in converting $CO_2$ to $CO_2^{\bullet -}$. A few rare examples available for this chemistry include copper(I)[7] and iron(I)[8] complexes with N3S and P3 ligand environments, respectively. We devised another strategy by taking advantage of synergistic effects between a redox-noninnocent ligand[9] ($\alpha$-ketocarboxylate) and a redox-active metal center (copper). Earlier, we reported $\alpha$-ketocarboxylatoiron(II) complexes as structural and functional models for $\alpha$-keto acid dependent metalloenzymes.[10,11] Hereby, we focused on $\alpha$-ketocarboxylatocopper(II) and -copper(I) complexes with a hydrotris(3,5-diisopropyl-1-pyrazolyl)borate anion[12] (denoted as L1). These complexes yielded a binuclear oxalatocopper(II) complex utilizing atmospheric dioxygen ($O_2$), the keto group of the $\alpha$-ketocarboxylate ligand, and the solvent water in a spontaneous reaction. Tolman et al. previously reported the reaction of $\alpha$-ketocarboxylatocopper(I) complexes with $O_2$, obtaining hydroxylated ligands via high-valent, terminal oxo- or bis($\mu$-oxo)copper(III) intermediate.[13] To date, our work is the first example for the formation of a binuclear oxalatocopper(II) complex using a redox-noninnocent $\alpha$-ketocarboxylatocopper(II) complex, despite earlier reported attempts.[13,14] Our work differs in the composition and structure of the N-chelating ligand being N3 versus N2 or N4 coordination.[13,14] We present here initial mechanistic insights for the formation of an oxalate ion by $^{13}CO_2$-labeling experiments from $\alpha$-ketocarboxylatocopper complexes using Fourier transform infrared (FT-IR) and FT-Raman spectroscopic techniques and structural characterization by X-ray diffraction.

**Copper(II) Complexes.** The $\alpha$-ketocarboxylatocopper(II) complex $[\{Cu(L1)\}\{O_2CC(O)CH(CH_3)_2\}]$ (**2**) was synthesized by the reaction of $[Cu(L1)Cl]$ (**1**)[15] and sodium 3-methyl-2-oxobutyrate in Ar [see the Supporting Information (SI) and the top part of Scheme 1]. Complex **2** (Figure 1A) has a distorted square-pyramidal geometry and a characteristic IR band at 1692

Scheme 1



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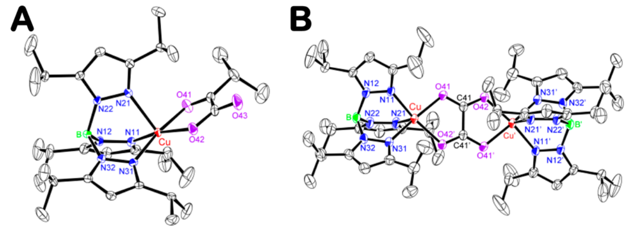


**Figure 1.** ORTEP plots for **2** (A) and **3** (B) showing 50% thermal ellipsoids and the atom-labeling scheme. Hydrogen atoms in **2** and **3** and a $CH_2Cl_2$ molecule in **2** are omitted for clarity. Symmetry code for **3**: $-x + 1, -y + 1, -z + 1$.

cm$^{-1}$ that was assigned to the carbonyl group of $\alpha$-ketocarboxylate. In air, the color of the solution of **2** was gradually changed from light green ($\lambda_{max}$, 727 nm) to light blue ($\lambda_{max}$, 703 nm). The IR stretching band of the ligand carbonyl group was red-shifted by 40 cm$^{-1}$ (1652 cm$^{-1}$; Figure S1 in the SI). X-ray structural analysis for the light-blue crystal confirmed the formation of a binuclear oxalatocopper(II) complex $[\{Cu(L1)\}_2(\mu\text{-}C_2O_4)]$ (**3**) with a bridged oxalate ion in $\eta^2:\eta^2$ manner, as shown in Figure 1B. The highest yield we were able to obtain for the oxalato complex **3** was 89%, with the average yield always being above 50%.

The formation of **3** was examined under various conditions, such as the presence of air, pure $O_2$, and $CO_2/O_2$ (1:1, v/v) gas mixture atmospheres (Figure S1 and Table S1 in the SI). No oxalate formation was detected when only $CO_2$ gas was used; however, the oxalate formed in air, $O_2$, or $CO_2/O_2$ (1:1, v/v). This can be rationalized by the critical role of $O_2$ in the activation of the $\alpha$-ketocarboxylato ligand. Partial incorporation of $CO_2$ from the atmosphere was confirmed by $^{13}CO_2$-labeling experiments. When a toluene solution of **2** was stirred for 3 days in $^{13}CO_2/O_2$ (1:1, v/v, 1 atm), a new IR band at 1607 cm$^{-1}$ appeared that was red-shifted by 49 cm$^{-1}$ relative to that of **3**. This peak can be assigned to the $^{13}C{=}O$ stretching mode (Figure S2 in the SI), which clearly indicates that $^{13}CO_2$ incorporation took place. It is important to note that these reactions occurred very slowly; thus, we were unable to obtain any reactive intermediates during the formation of the oxalato complex **3**. After 3 days of reaction time, the spectral changes in the IR indicated no formation of a carboxylate ion (Figure S3 in the SI). This chemistry is clearly different from that of the previously described $\alpha$-ketocarboxylatoiron(II) complexes.[10]

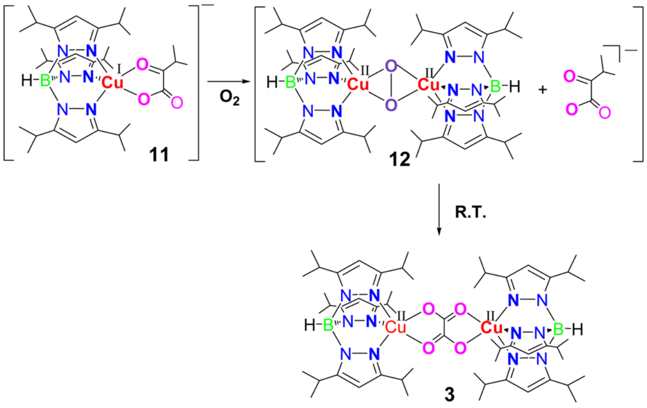
The phenyl-substituted $\alpha$-ketocarboxylatocopper(II) complex $[\{Cu(L1)\}\{O_2CC(O)C_6H_5\}]$ (**4**; Figure S4 in the SI) did not show any oxalate formation under the conditions described above. The starting complex **4** was recovered after the reaction. This was unexpected because, from the literature,[10] the activated $O_2$ species or peroxide intermediate can be readily generated by the $\alpha$-keto acid with an electron-withdrawing group. We conclude that the phenyl-substituted $\alpha$-ketocarboxylato complex lacks electronic structural features for generating the proposed $CO_2^{\bullet -}$ radical-anion intermediate. Given the observed reactivity of the alkyl-substituted $\alpha$-ketocarboxylato complex **2**, we propose that electron-donating substituents facilitate the activation of $O_2$ and decomposition of the $\alpha$-keto acid, yielding **3** under these reaction conditions.

The corresponding carboxylatocopper(II) complexes $[\{Cu(L1)\}(O_2CR)]$ [R = *i*Pr (**5**), Ph (**6**)] were also synthesized and reacted with $O_2$ and/or $CO_2$ under the same conditions (Figures S5 and S6 in the SI) without showing the formation of **3**. These observations indicate that the presence of an intact $\alpha$-ketocarboxylato ligand is essential for oxalate ion formation because of the ligand's role in $O_2$ activation and redox reactivity. Moreover, the same reactions using nickel(II) as the metal center were also explored given its relevance to nickel-containing carbon monoxide dehydrogenase and acetyl-CoA synthase.[16] However, no reductive activation of $CO_2$ by $\alpha$-ketocarboxylatonickel(II) complexes $[\{Ni(L1)\}(O_2CC(O)R)(H_2O)]$ [R = *i*Pr (**7**), Et (**8**)] was observed under the conditions described above. These results suggest that successful $CO_2$ incorporation into oxalate requires the presence of both a redox-active ligand and a metal center. Furthermore, we obtained the copper(II) complex $[\{Cu(L1)\}\{O_2CC(CH_3)_2(OH)\}]$ (**9**) in a dry air atmosphere from complex **2**. From **9**, no oxalato complex **3** was formed under any reaction conditions that we have considered. The given results suggest that the formation of **3** from **2** requires the presence of $O_2$ and trace amounts of water.

**Copper(I) Complexes.** To date, examples are rare for oxalate ion formation from atmospheric $CO_2$ using copper complexes.[7] In an earlier report, Peacock et al. discussed the formation of an oxalatocopper(II) complex using bicarbonate ion ($HCO_3^-$),[17] which was explained by internal electron transfer between *N*,*N*′,*N*″-1,4,7-triallyltriazacyclononanecopper(I) complex and bicarbonate ion. We attempted to make the bicarbonatocopper(I) complex $(Et_4N)[Cu(L1)\{O_2C(OH)\}]$ with our N3 ligand (KL1) from the reaction of $[Cu^I(L1)]$ with tetraethylammonium bicarbonate $[Et_4N(HCO_3)]$ in deoxygenated and dry acetone, dichloromethane, and methanol solvents. The color of the solution containing all starting materials gradually changed from colorless to light blue upon mixing. The IR spectrum of the reaction mixture after 24 h showed a strong characteristic band around 1650 cm$^{-1}$ and was assigned to the binuclear oxalatocopper(II) complex **3**. The oxalate anion is proposed to form by dimerization of the $CO_2^{\bullet -}$ radical anion (Scheme 1, bottom). However, this oxalate formation was also very slow; therefore, we could not obtain complex **3** as a pure product within 10 days of reaction time. A control reaction of the copper(II) complex **1**[15] with a bicarbonate anion was carried out, yielding the binuclear carbonatocopper(II) complex $[\{Cu(L1)\}_2(\mu\text{-}CO_3)]$ (**10**).[4b] We concluded that the formation of **3** starting from a bicarbonate ion requires the presence of copper(I) centers with electron transfer in the bicarbonatocopper(I) complex $(Et_4N)[Cu(L1)\{O_2C(OH)\}]$.

Similarly to copper(II) complexes, the reaction of $\alpha$-ketocarboxylatocopper(I) complex $Na[Cu(L1)\{O_2CC(O)CH(CH_3)_2\}]$ (**11**) was carried out in the presence of $O_2$. Complex **11** was synthesized by the reaction of $[Cu(L1)]$[12] with sodium 3-methyl-2-oxobutyrate. Under exposure to a pure $O_2$ atmosphere, the colorless solution was immediately changed to purple. The UV–vis absorption bands at 352 and 553 nm ($\lambda_{max}$ values) were assigned to the peroxidocopper(II) complex $[\{Cu(L1)\}_2(\mu\text{-}\eta^2:\eta^2\text{-}O_2)]$ (**12**; Scheme 2 and Figure S7 in the SI).[12] The solution was stirred for 24 h at room temperature, and **3** was obtained via a proposed $CO_2^{\bullet -}$ radical anion that is likely formed during the decomposition of $\alpha$-keto acid. On the other hand, in a pure $CO_2$ atmosphere, complex **3** was not formed, but rather the binuclear carbonatocopper(II) complex **10**[4b] was obtained (Scheme S1 in the SI). Thus, we propose that $O_2$ was reduced by copper(I) and consumed by the decomposition reaction of $\alpha$-ketocarboxylate. These observations also indicate that complex **12** clearly displays a chemistry different from that of any previously reported $\alpha$-ketocarboxylatocopper(I) complex.[12] In the given study, we propose the formation of the peroxidocopper(II) complex from the reaction of $[Cu(L1)]$

Scheme 2



with 3-methyl-2-oxobutyrate without the presence of any reactive high-valent oxocopper(III) intermediate. Furthermore, complex **3** can also be obtained from the reaction of the peroxidocopper(II) complex[12] with excess $\alpha$-ketocarboxylate in the form of sodium 3-methyl-2-oxobutyrate. Similarly to complex **2**, no oxalato complex **3** was obtained by the reaction of **12** with the phenyl-substituted excess $\alpha$-ketocarboxylate, sodium benzoylformate.

**Oxalate Release.** Because of the interest in $CO_2$ fixation and its conversion to organic compounds,[1] the release of an oxalate ion from **3** was also investigated, obtaining a colorless powder and blue crystals of $[\{Cu(L1)\}(\mu\text{-}OH)]_2$ (**13**). The former was identified to be sodium oxalate. From the $^{13}C$-labeling experiments, $^{13}CO_2$ was incorporated in sodium oxalate in 41% yield (Figure S8 in the SI).[18] These observations indicated the possibility for the scrambling of atmospheric $^{13}CO_2$ and $^{12}CO_2$ from $\alpha$-keto acid decomposition or from bicarbonate.

In conclusion, the first experimental evidence is reported for the formation of an oxalate ion owing to the presence of a redox-active Cu ion, an N3 ligand environment, and the noninnocent $\alpha$-keto acid ligand using air, pure $O_2$, and a $CO_2/O_2$ gas mixture (1:1). For the latter, the incorporation of atmospheric $CO_2$ was confirmed by $^{13}CO_2$ labeling. Unexpectedly, the electron-donating alkyl derivatives of $\alpha$-keto acids enabled this reaction via $O_2$ activation. The formation of the oxalate ion was facilitated by decomposition of the $\alpha$-ketocarboxylate ligands presumably to a $CO_2^{\bullet-}$ radical anion that remained bound for coupling, giving a side-on-coordinated oxalate ion. It is also notable that the copper(I) complex spontaneously converts bicarbonate to oxalate, which is only the second example using $Cu^{I}N3$ coordination in $CO_2$ redox chemistry. Theoretical studies are now underway for the molecular reaction mechanism of the formation of an oxalate ion.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Experimental details, spectroscopic data, ORTEP plots of complexes **4**−**6**, and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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